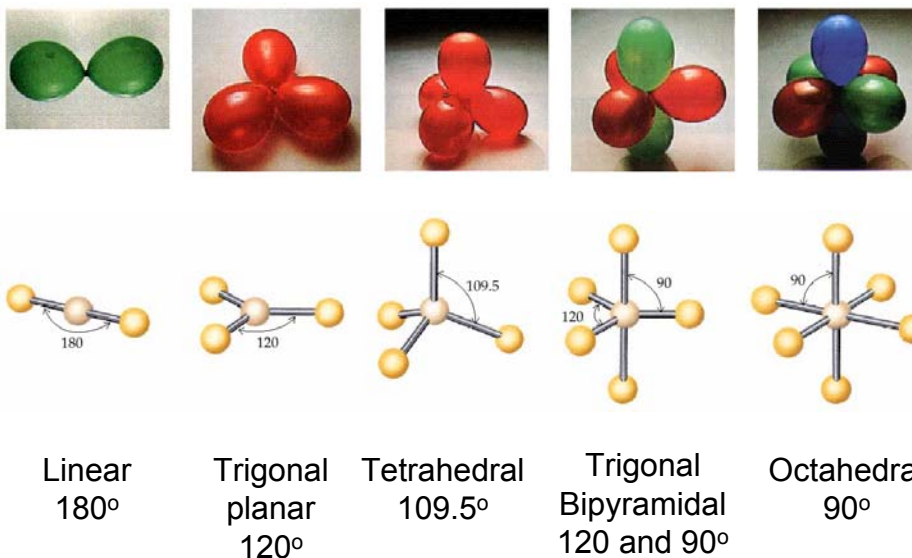


Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals

Chapter 10

Electron Pair Geometries in VSEPR Theory

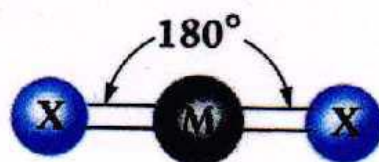


Electron Pair Geometry

Molecular Geometry



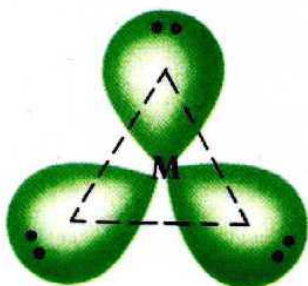
linear



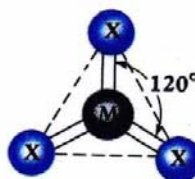
Linear
(AB₂)

Electron Pair Geometry

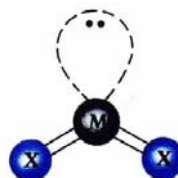
Molecular Geometry



Trigonal planar



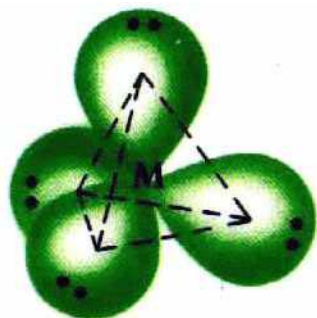
Trigonal planar
(AB₃)



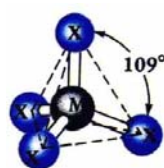
Bent
(AB₂E)

Electron Pair Geometry

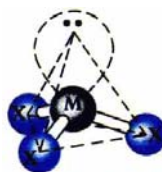
Molecular Geometry



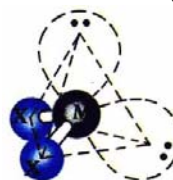
Tetrahedral



Tetrahedral
(AB₄)



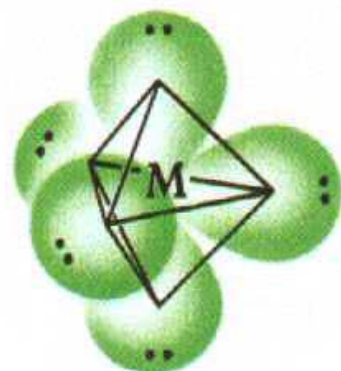
Pyramidal
(AB₃E)



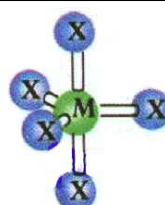
Bent
(AB₂E₂)

Electron Pair Geometry

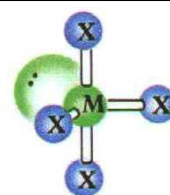
Molecular Geometry



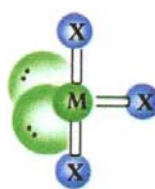
Trigonal Bipyramidal



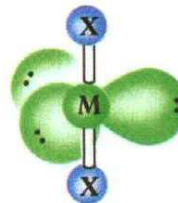
Trigonal
Bipyramidal
(AB₅)



Unsymmetrical
Tetrahedron
(AB₄E)



T-shaped
(AB₃E₂)



Linear
(AB₂E₃)

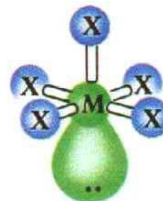
Electron Pair Geometry Molecular Geometry



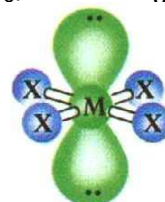
Octahedral



Octahedral
(AB₆)

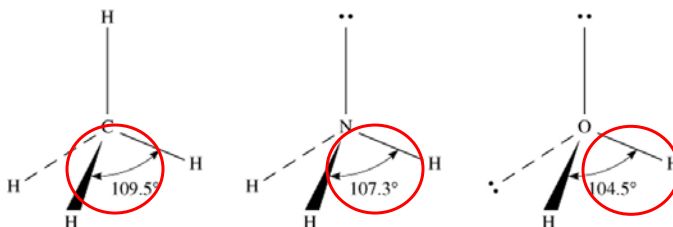
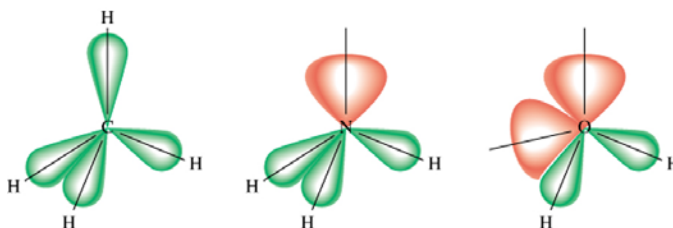


Square
pyramidal
(AB₅E)



Square planar
(AB₄E₂)

Lone Pairs Distort Bond Angles



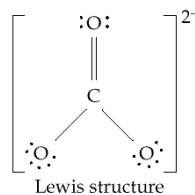
bonding-pair vs. bonding pair repulsion < lone-pair vs. bonding pair repulsion < lone-pair vs. lone pair repulsion

Applying VSEPR Theory

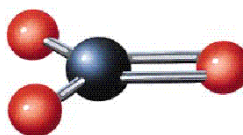
1. Determine the Lewis structure
2. Determine the number of electron pairs (or clouds) around the CENTRAL ATOM – multiple bonds count as ONE CLOUD (see next slide).
3. Find out the appropriate VSEPR geometry for the specified number of electron pairs, both bonding and lone pairs.
4. Use the positions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

Multiple Bonds and Molecular Geometry

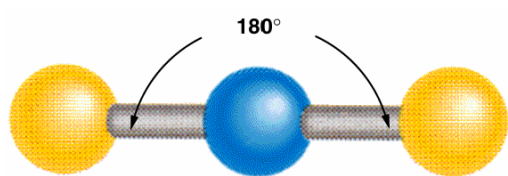
Multiple bonds count as one -



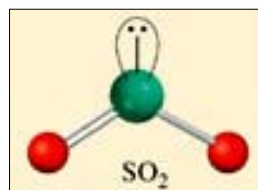
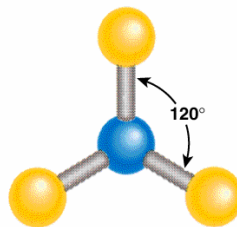
e.g. 4 bonding pairs around C, but trigonal planar instead of tetrahedral.



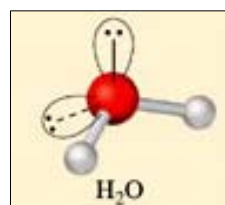
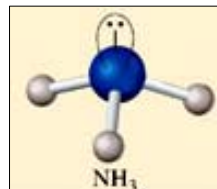
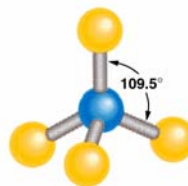
LINEAR - AB₂ e.g. BeCl₂



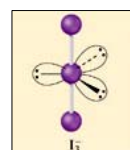
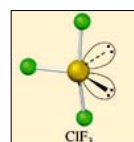
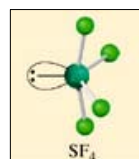
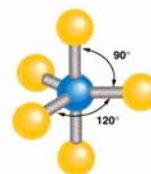
TRIGONAL PLANAR - BF₃ (AB₃)
- SO₂ (AB₂E)



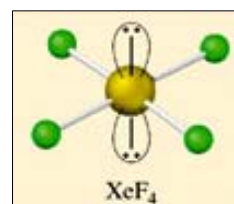
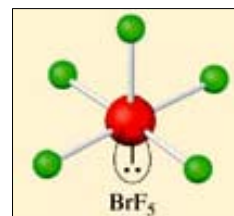
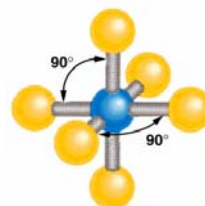
TETRAHEDRAL - CH_4 (AB_4)
 - NH_3 (AB_3E)
 - H_2O (AB_2E_2)



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

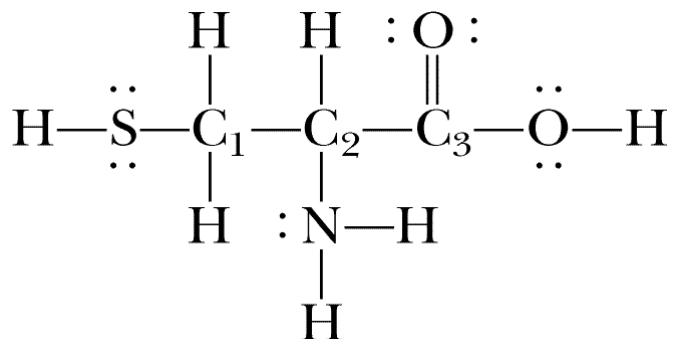


OCTAHEDRAL - SF_6 (AB_6)
 - BrF_5 (AB_5E)
 - XeF_4 (AB_4E_2)



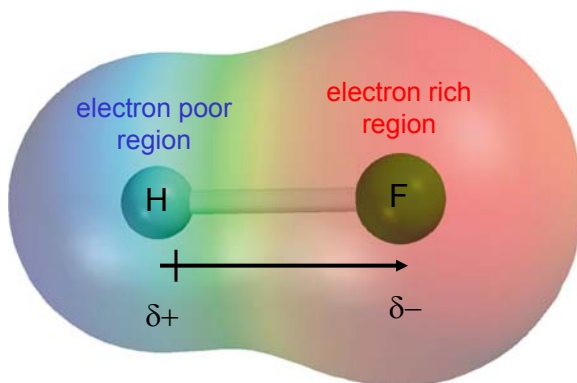
Example 10.1 Use the VSEPR model to predict the geometry of the following molecules and ions: (a) AsH_3 , (b) OF_2 , (c) AlCl_4^- , (d) I_3^- , (e) C_2H_4

Molecular Geometries of Molecules with more than 1 Central Atom

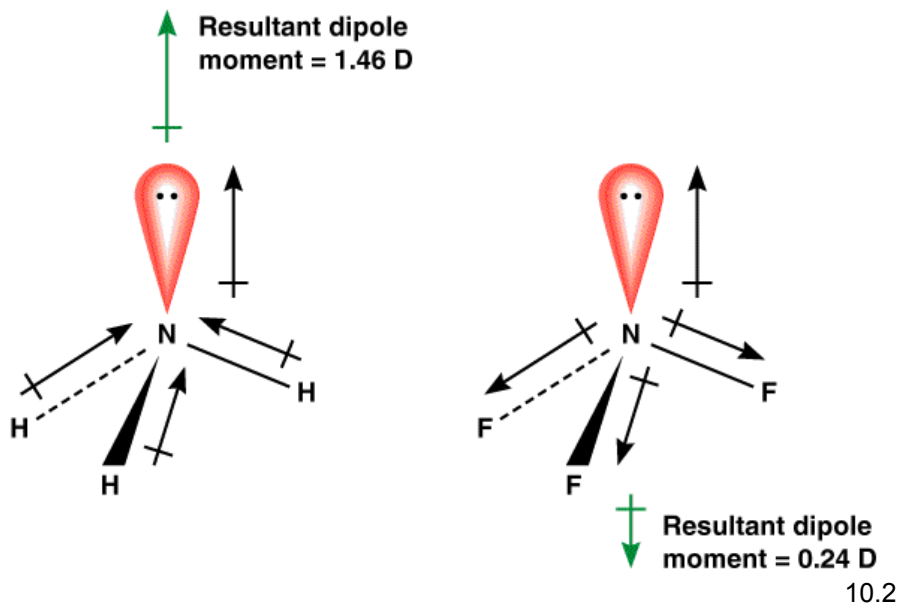


cysteine

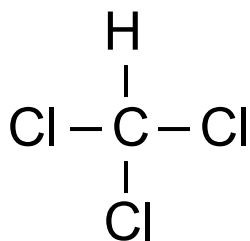
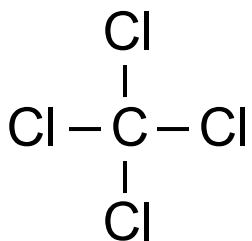
Dipole Moments and Polar Molecules



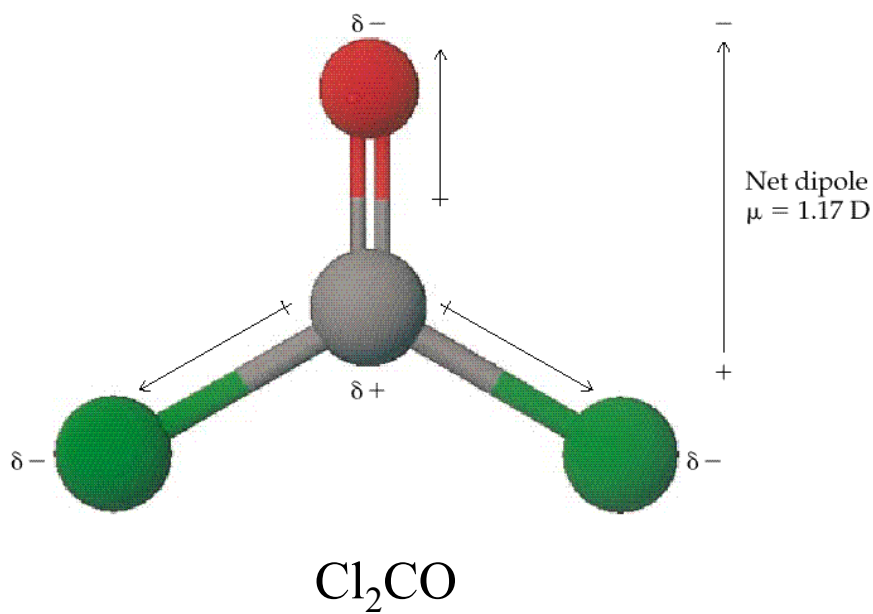
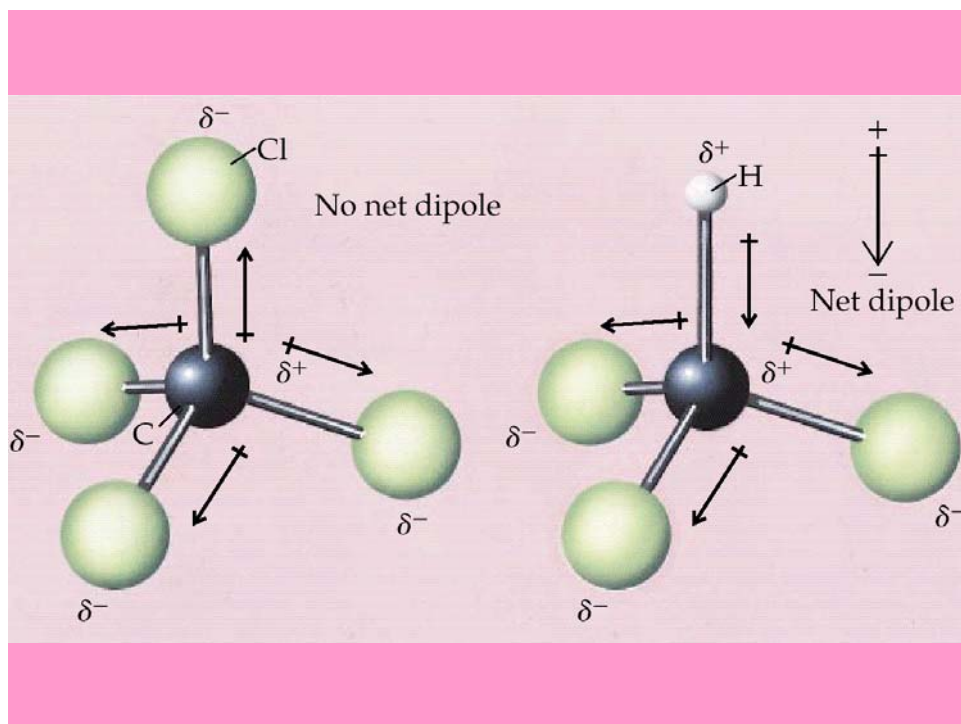
Bond Moments and Resultant Dipole Moments

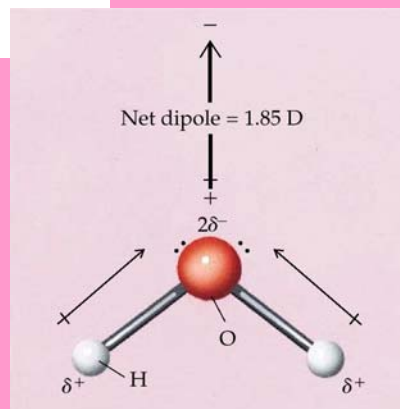
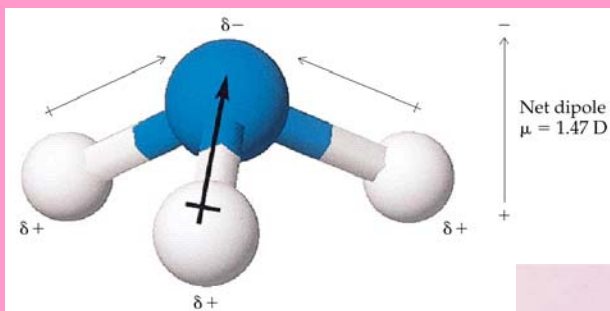


CCl4 vs CHCl3

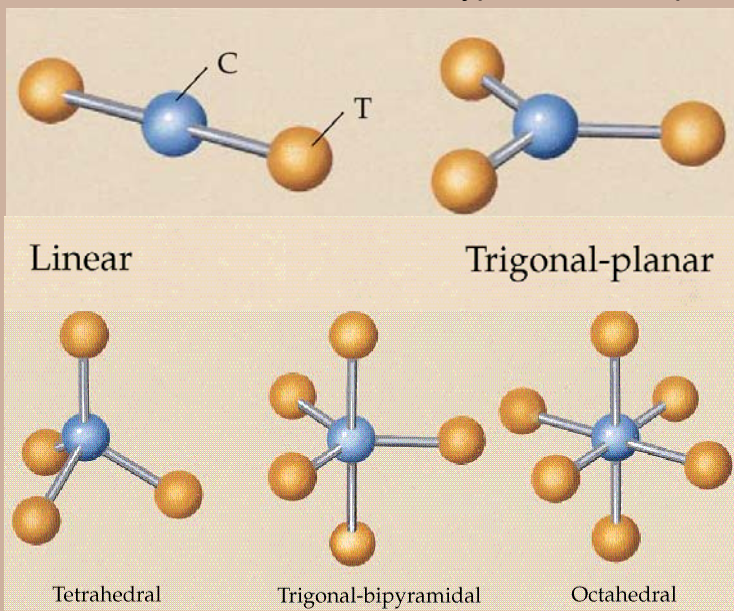


Which molecule is polar? You must look at the geometry to decide.



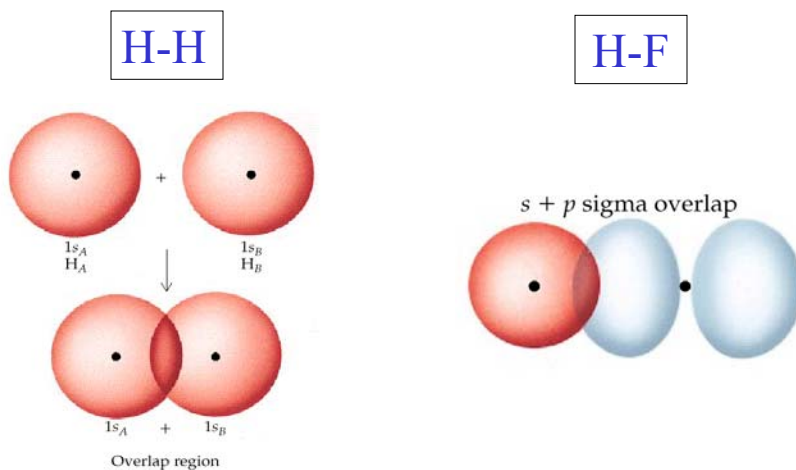


These types of molecules, where C = central atom and T = terminal atoms of the same type, are never polar.



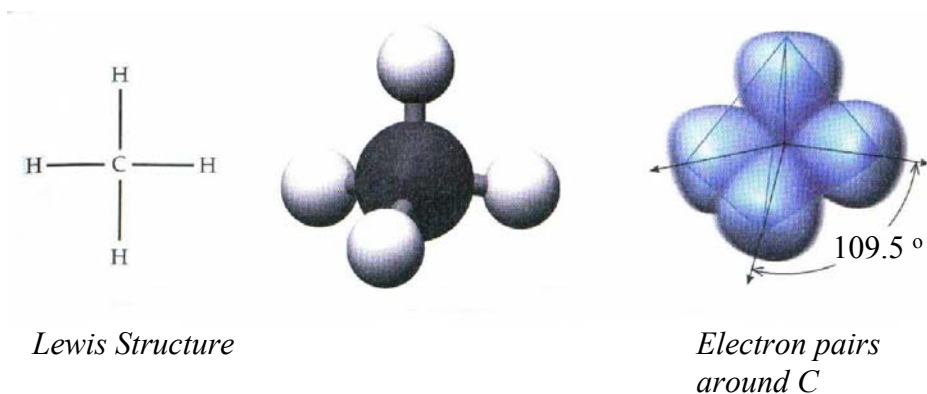
Valence Bond Theory (hybrid orbitals)

The Orbital Overlap Model of Bonding

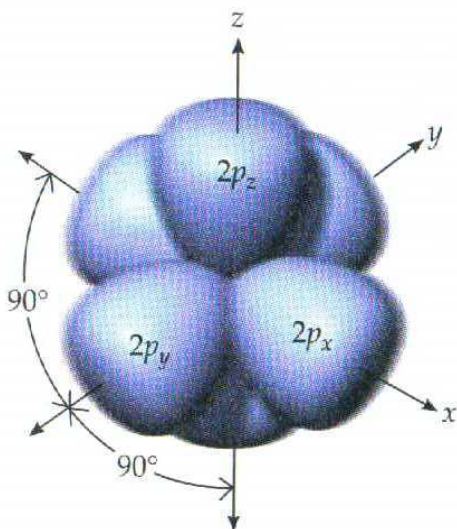


End to end overlap = sigma (σ) bond

Predicted Bonding and VSEPR Geometry for CH₄



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 CH₄, we need 4 hybrid orbitals, so 4 atomic orbitals are required as follows: (s + p + p + p) = sp³

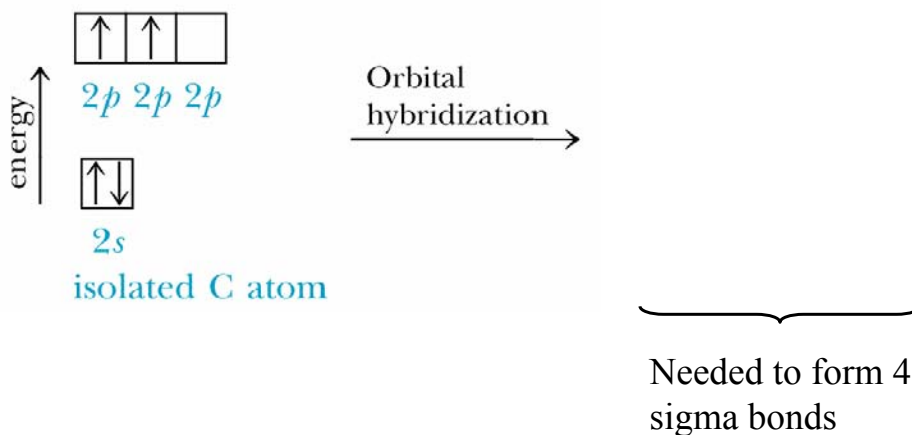


Fig. 10.7

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

Formation of sp³ Hybrid Orbitals

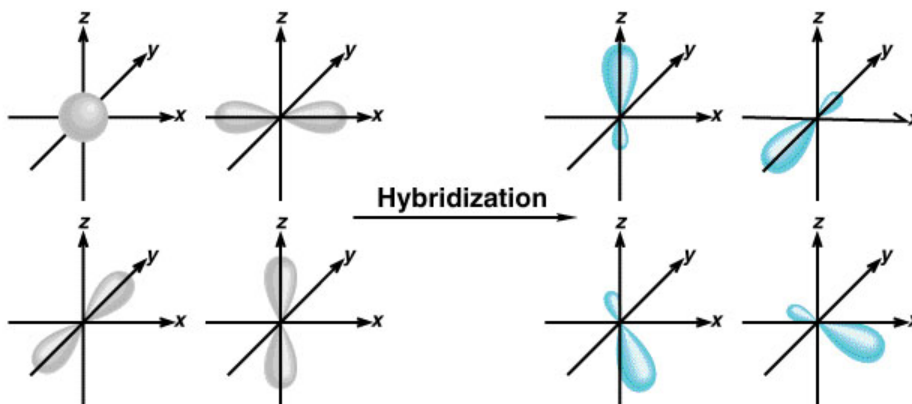
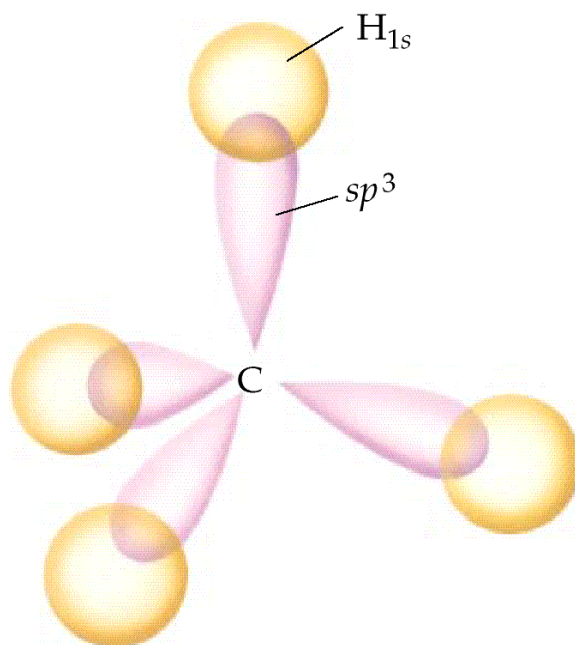
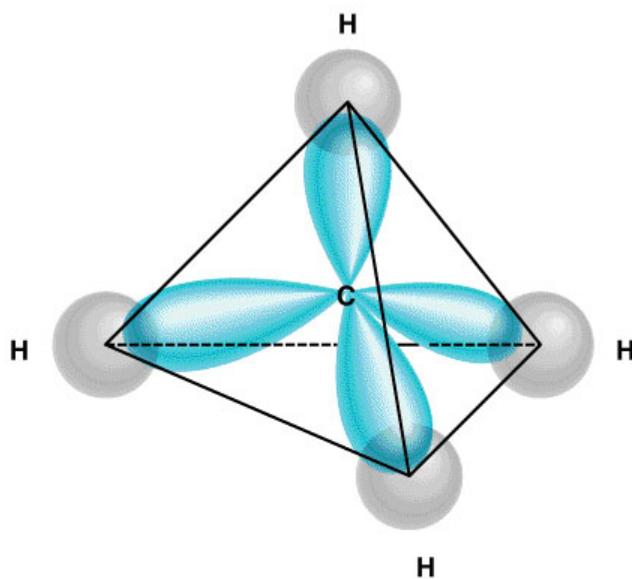


Fig. 10.8

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

Formation of Covalent Bonds

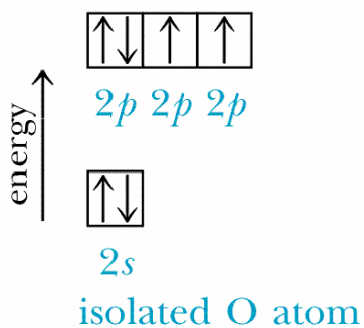


Hybridization Rules

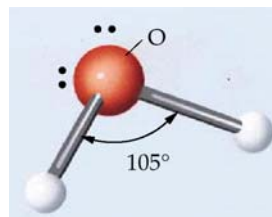
(will be upgraded as we proceed)

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

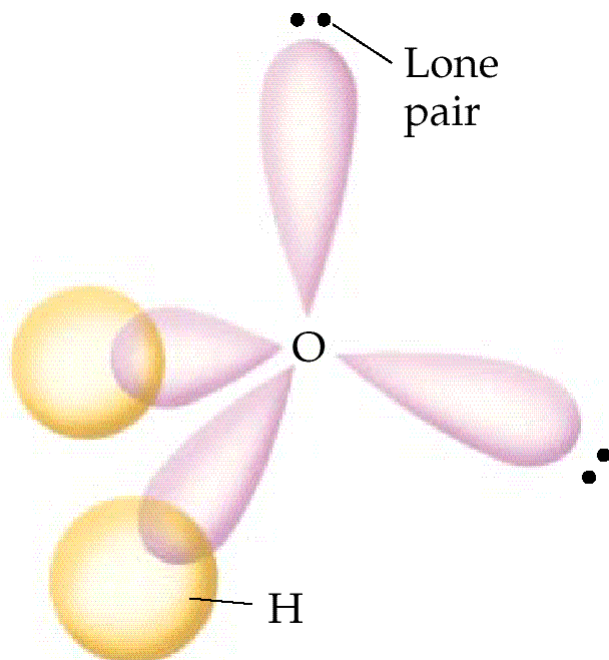
sp^3 hybridization for H_2O



Orbital
hybridization →

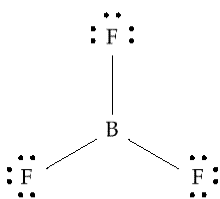


Needed to form 2
sigma bonds and
2 lone pairs

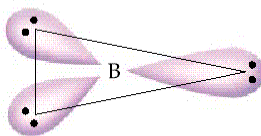


sp² Hybridization

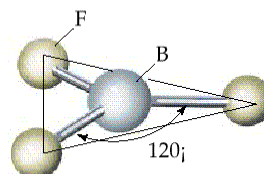
BF₃ - trigonal planar according to VSEPR Theory
(incomplete octet exception)



Lewis dot structure

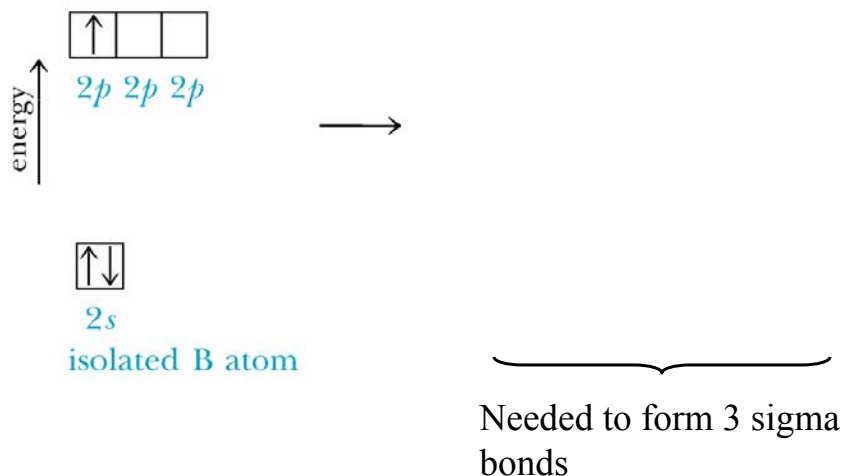


Electron-pair geometry



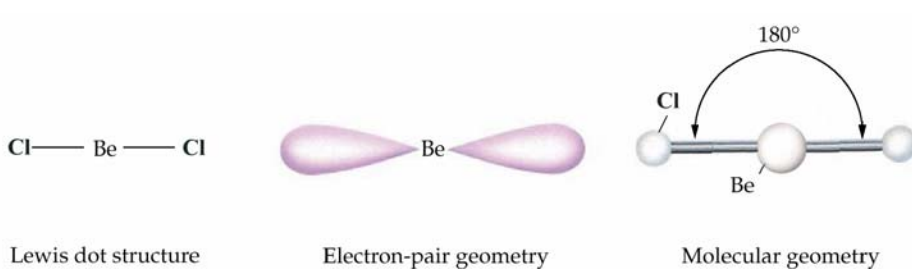
Molecular geometry

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

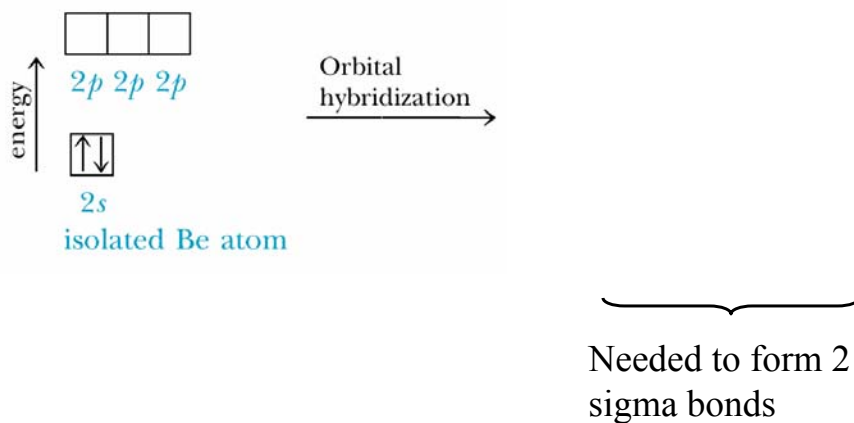


sp Hybridization

BeCl_2 - linear according to VSEPR Theory



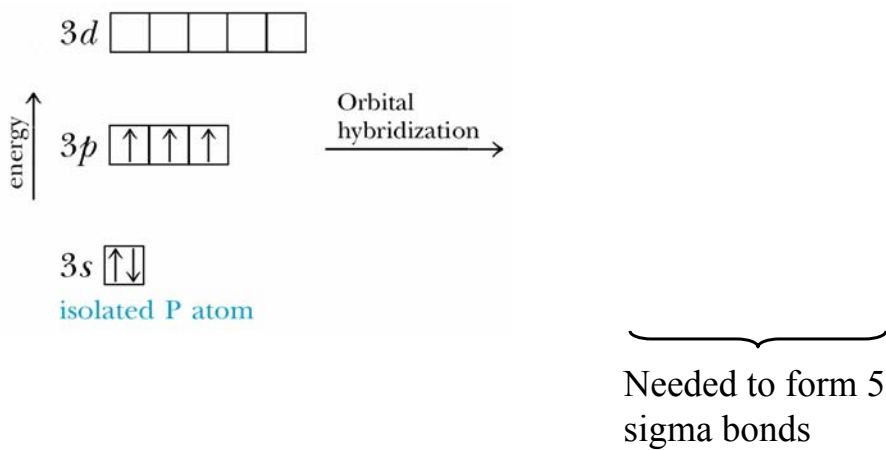
For BeCl_2 , we need 2 hybrid orbitals, so 2 atomic orbitals are required as follows: $(s + p) = sp$



sp³d Hybridization

Ex 10.4 Describe the hybridization state of phosphorus in PBr_5

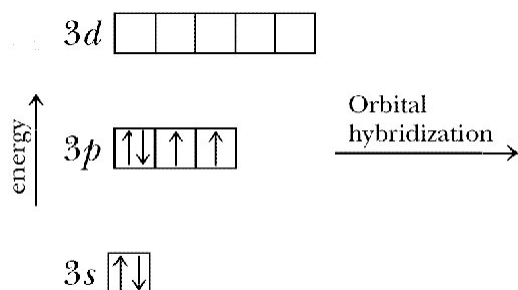
For PBr_5 , we need 5 hybrid orbitals, so 5 atomic orbitals are required as follows: $(s + p + p + p + d) = sp^3d$



sp^3d^2 Hybridization

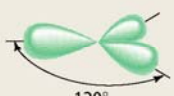
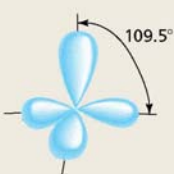
e.g. SF_6

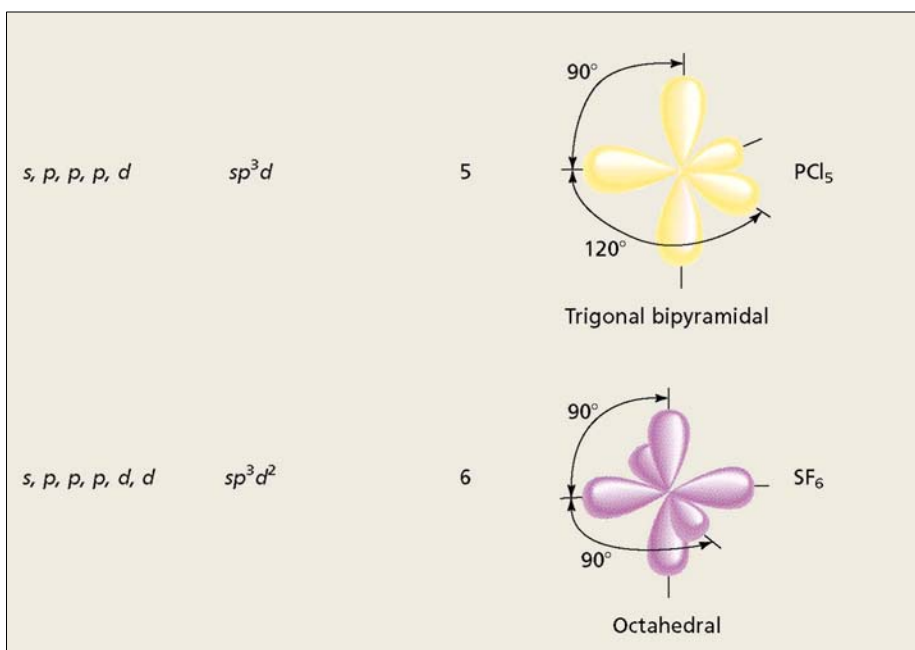
For SF₆, we need 6 hybrid orbitals, so 6 atomic orbitals are required as follows: (s + p + p + p + d + d) = sp³d²



Isolated S atom

Needed to form 6 sigma bonds

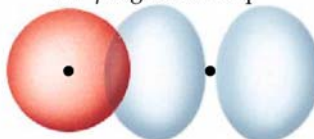
Table 10.4 Important Hybrid Orbitals and Their Shapes				
Pure Atomic Orbitals of the Central Atom	Hybridization of the Central Atom	Number of Hybrid Orbitals	Shape of Hybrid Orbitals	Examples
s, p	sp	2	 180° Linear	BeCl ₂
s, p, p	sp^2	3	 120° Planar	BF ₃
s, p, p, p	sp^3	4	 109.5° Tetrahedral	CH ₄ , NH ₄ ⁺



Multiple Bonds

Sigma (σ) bonds = end-to-end overlap

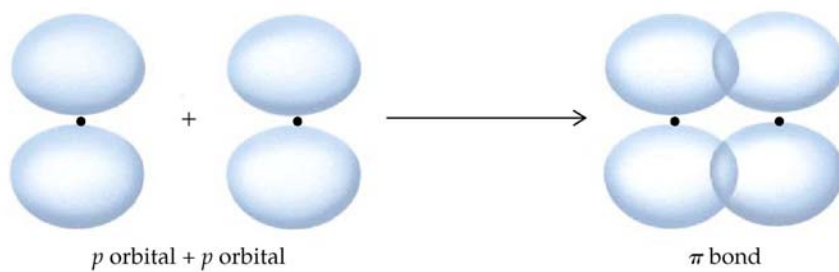
(a) $s + p$ sigma overlap



(b) $p + p$ sigma overlap



Pi (π) bond = side-by-side overlap



C - C 1 σ bond

C = C 1 σ bond
 1 π bond

C $\equiv$ C 1 σ bond
 2 π bonds

Hybridization Rules

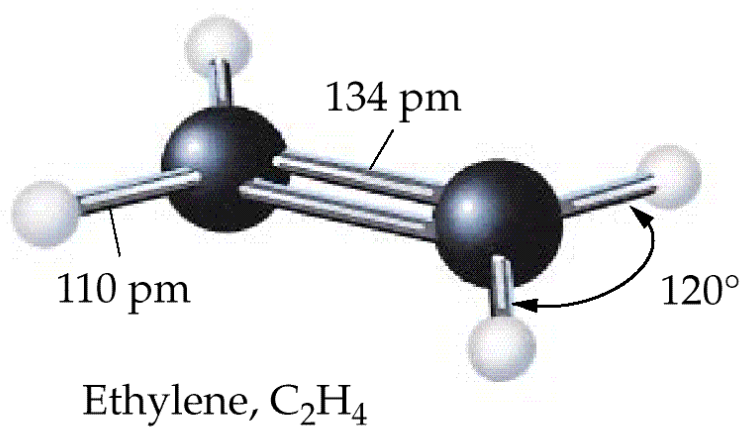
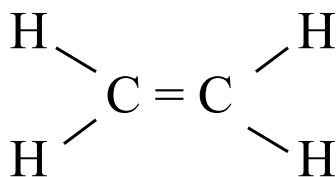
(upgraded – more will be added)

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

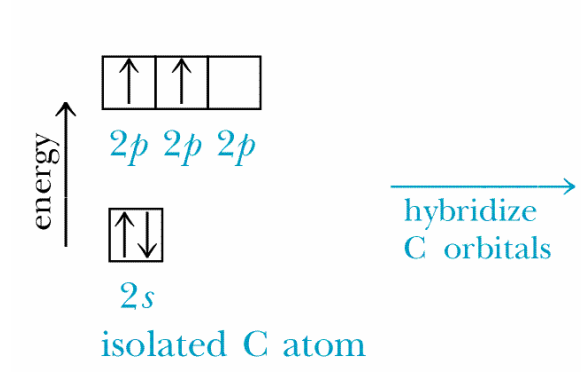
DOUBLE BONDS: Ethylene, CH_2CH_2

Lewis Structure:

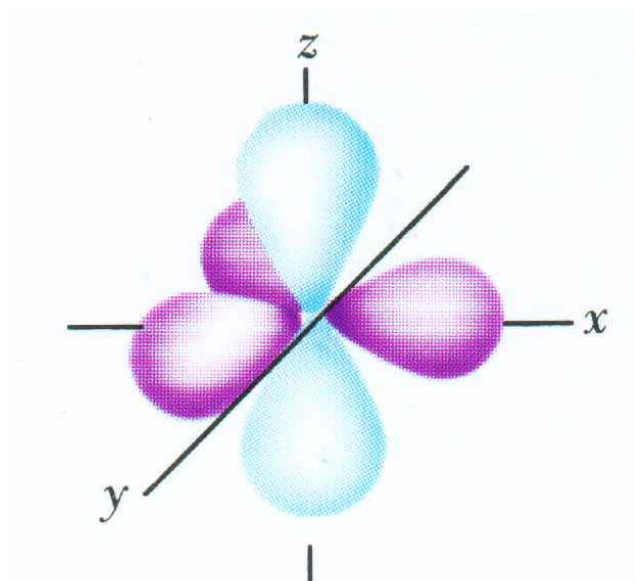
Apply VSEPR Theory and Determine Hybridization



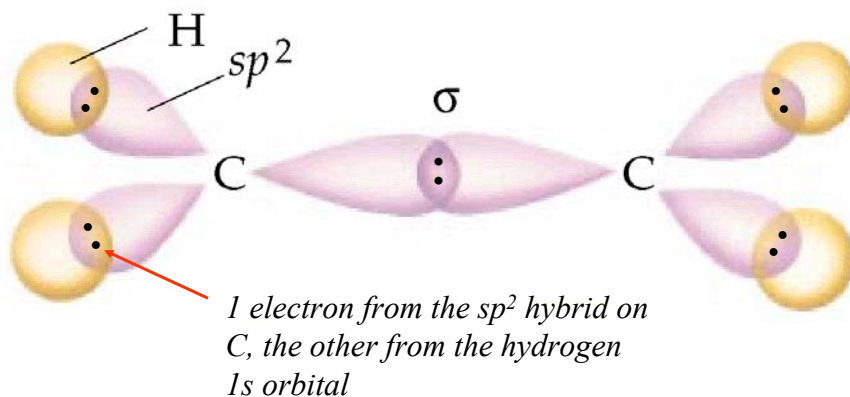
sp^2 hybridization on each C atom -



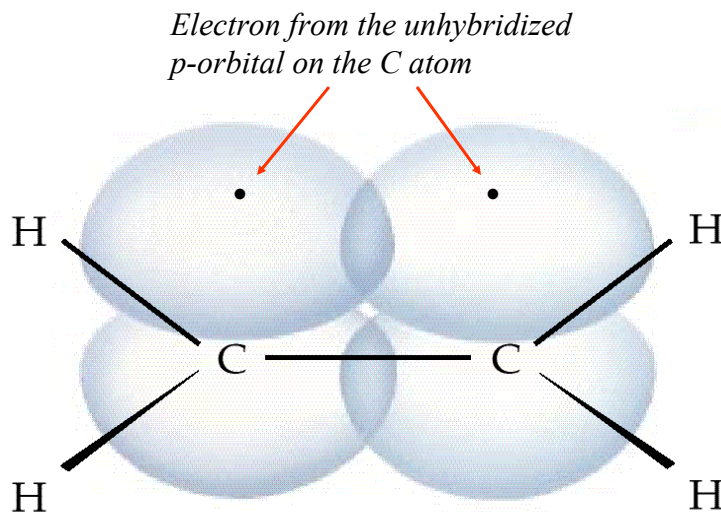
sp^2 hybrids and unhybridized p-orbital



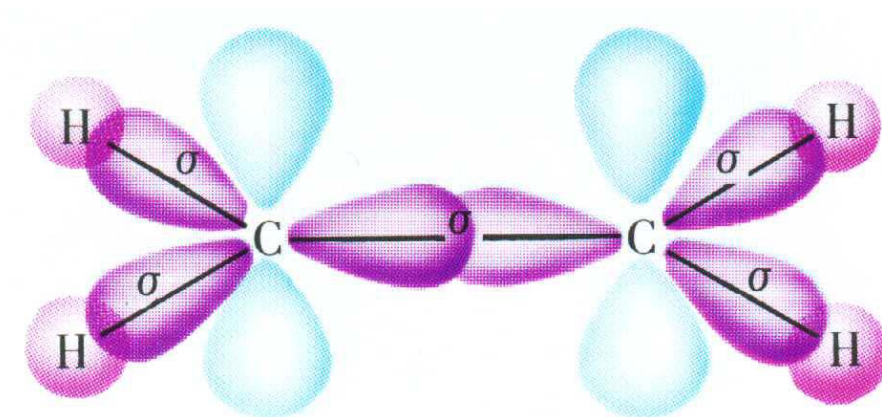
σ bond = end-to-end overlap of the sp^2 hybridized orbitals



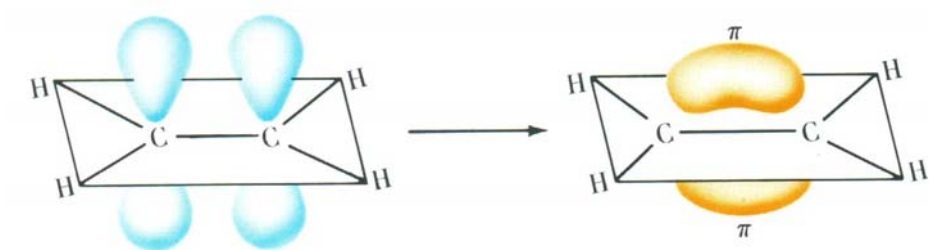
π bond = side-by-side overlap of the unhybridized p -orbitals



Sigma (σ) Bonding in Ethylene



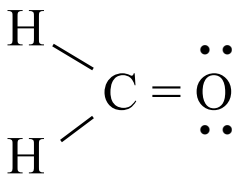
Pi (π) Bonding in Ethylene

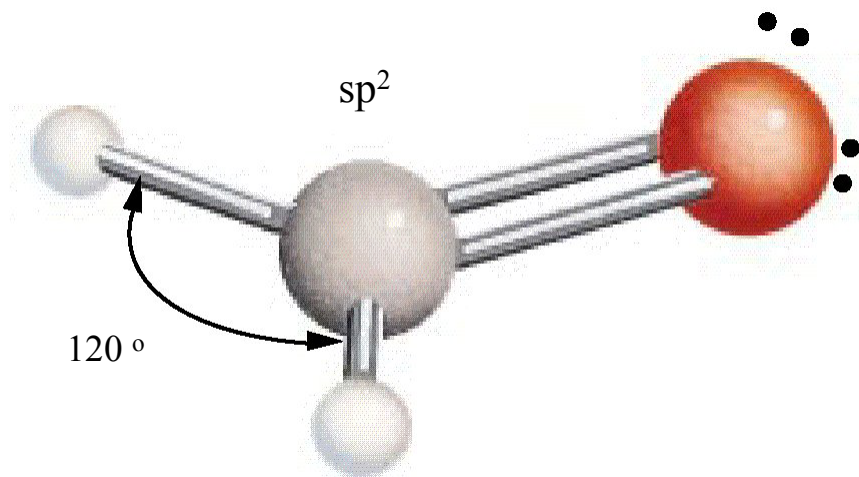


DOUBLE BONDS: Formaldehyde, CH₂O

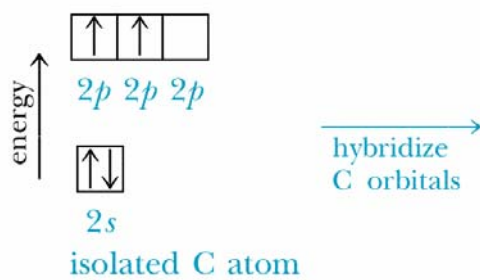
Lewis Structure:

Apply VSEPR Theory and Determine Hybridization

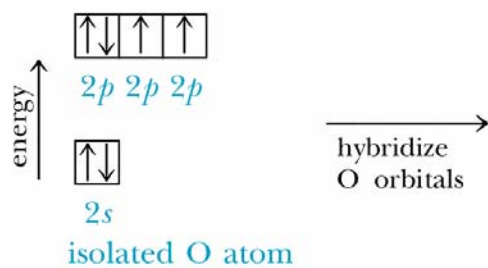




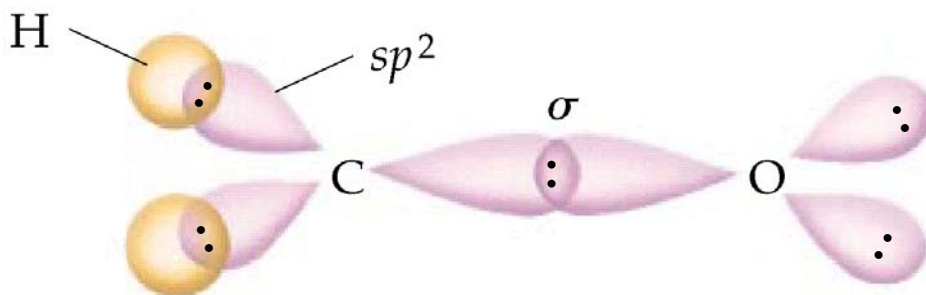
sp^2 hybridization on C -



sp^2 hybridization on O -

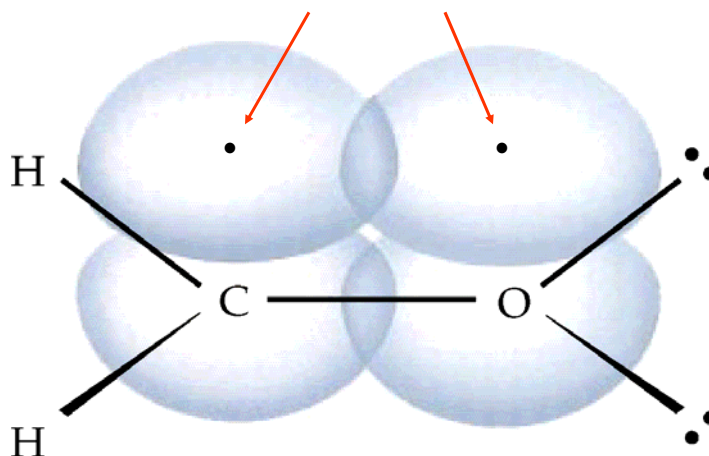


Sigma (σ) Bonding in Formaldehyde



Pi (π) Bonding in Formaldehyde

*Electron from the unhybridized
p-orbitals*



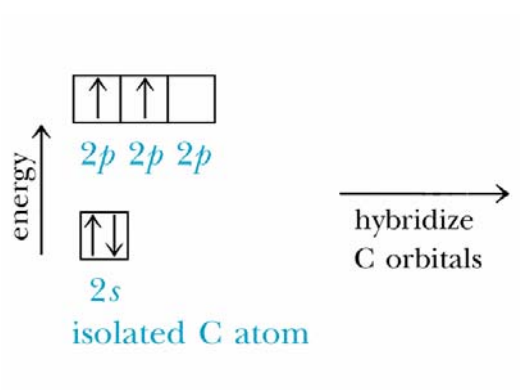
TRIPLE BONDS: Acetylene, C_2H_2

Lewis Structure:

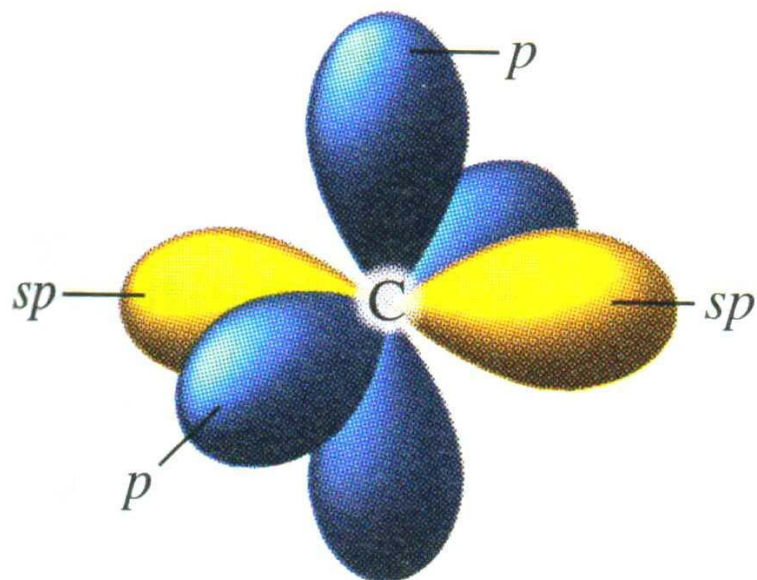
Apply VSEPR Theory and Determine Hybridization



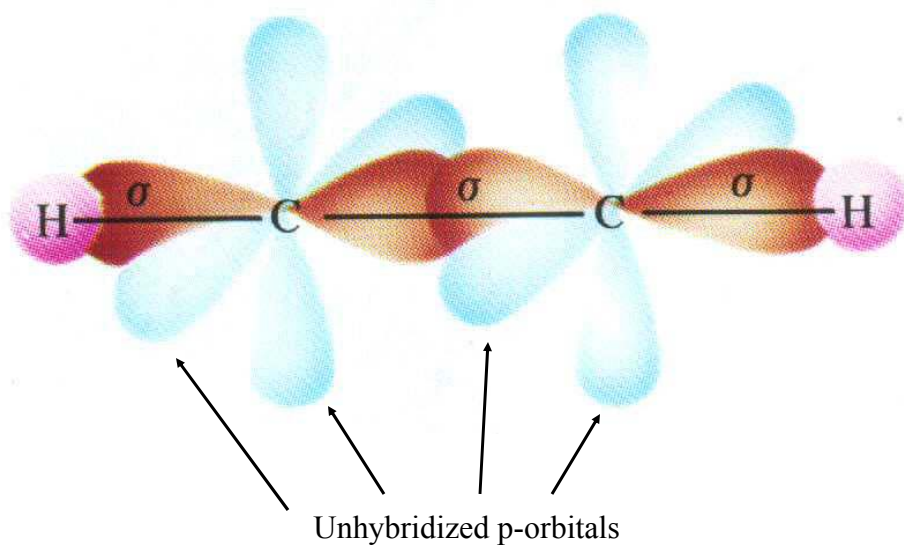
sp hybridization on each C atom -



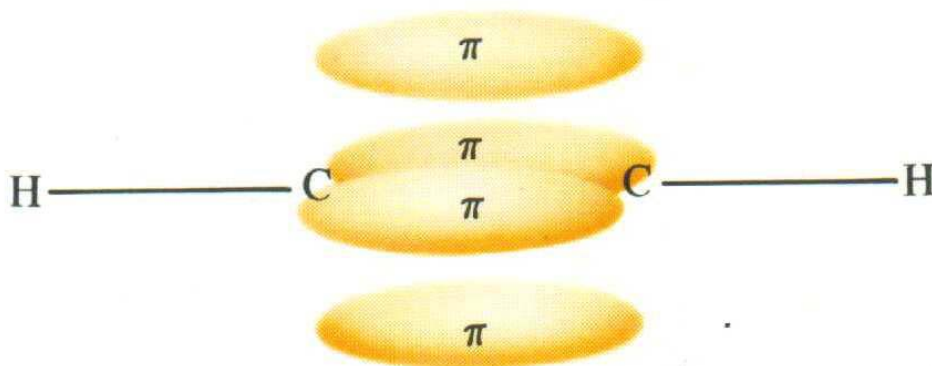
sp hybrids and unhybridized p-orbitals



Sigma (σ) Bonding in Acetylene



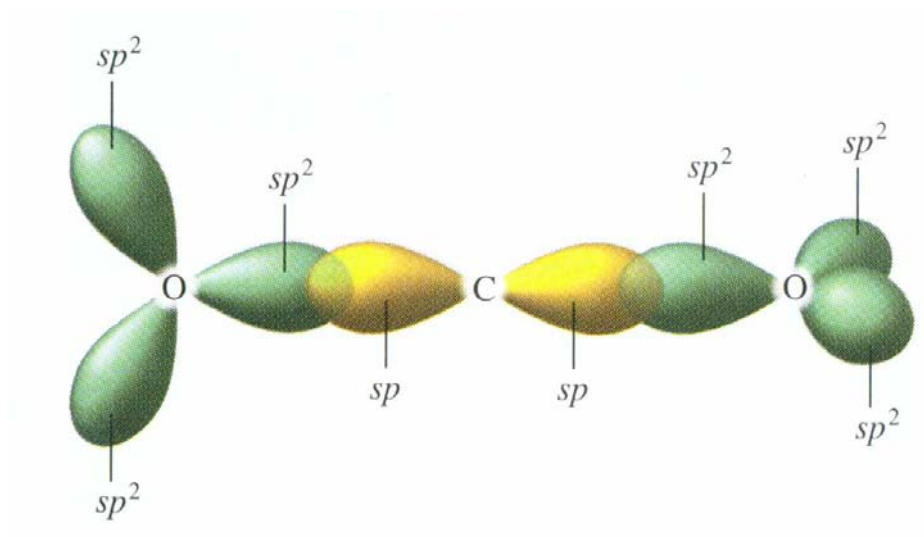
Pi (π) Bonding in Acetylene



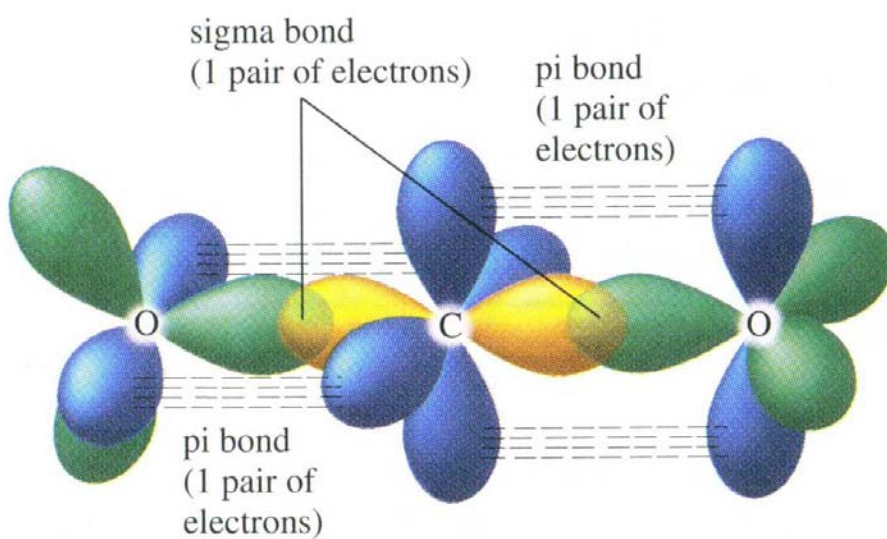
Explain the Bonding Using Valence Bond Theory



Sigma Bonding in CO₂



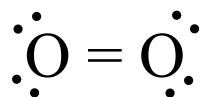
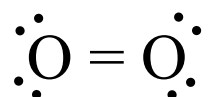
Pi Bonding in CO₂



VSEPR Theory - electron pair repulsions influence molecular shape

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

Applied to O₂ - $2(6) = 12$ valence electrons or 6 pairs



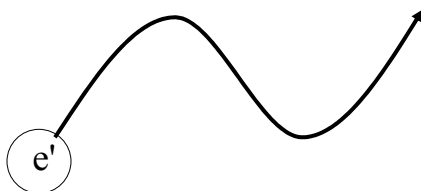
This prediction is **WRONG!** Since all of the electrons are paired up, the molecule should be diamagnetic, but experiments prove that it is **PARAMAGNETIC!**

An additional refinement in bonding theory is necessary =

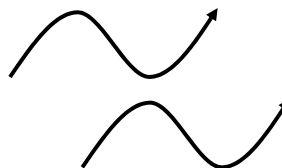
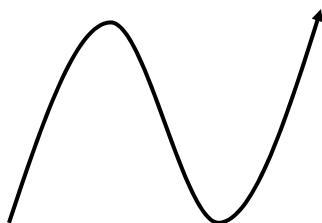
Molecular Orbital Theory

Molecular Orbitals - Preliminary Ideas

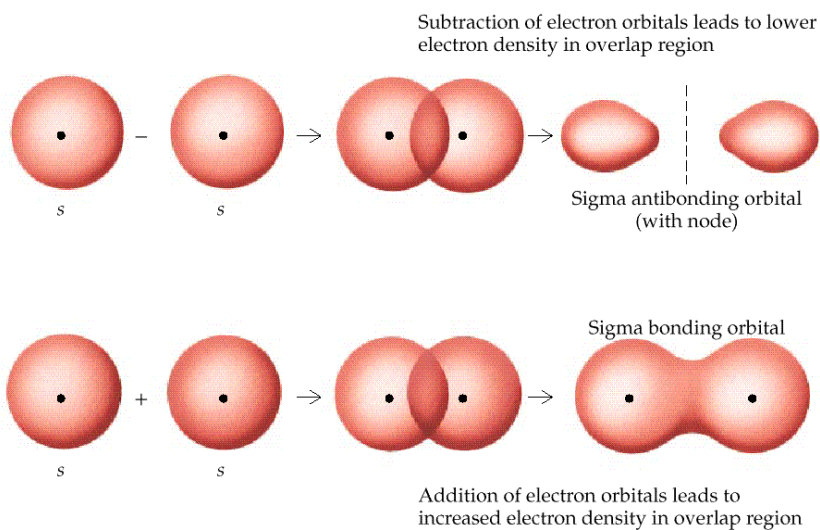
Don't forget that electrons behave like WAVES, and there are WAVE FUNCTIONS (ψ) that describe the electron position in space = ATOMIC ORBITALS (ψ^2)



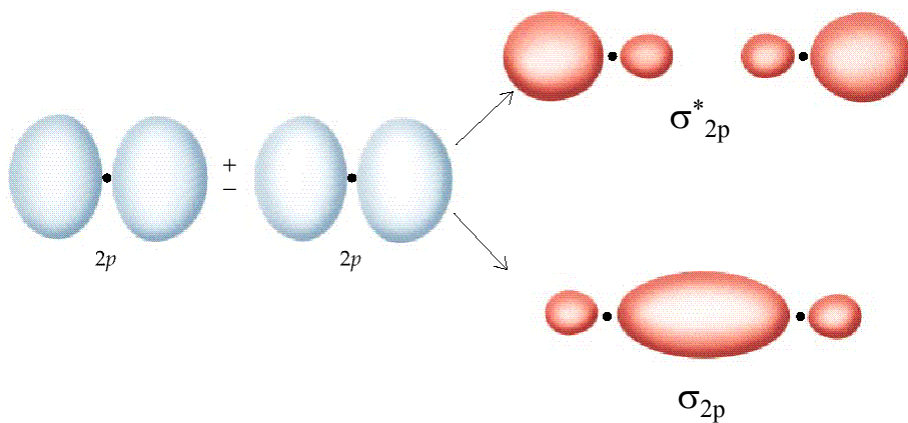
Waves (electrons) can interfere with each other, either **CONSTRUCTIVELY** or **DESTRUCTIVELY**



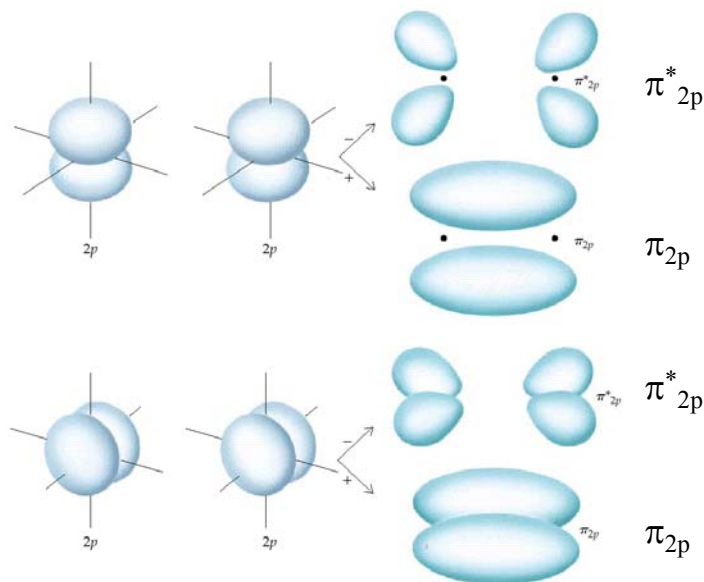
Molecular Orbitals - destructive and constructive interference of atomic orbitals



Sigma bond formation involving p-orbitals



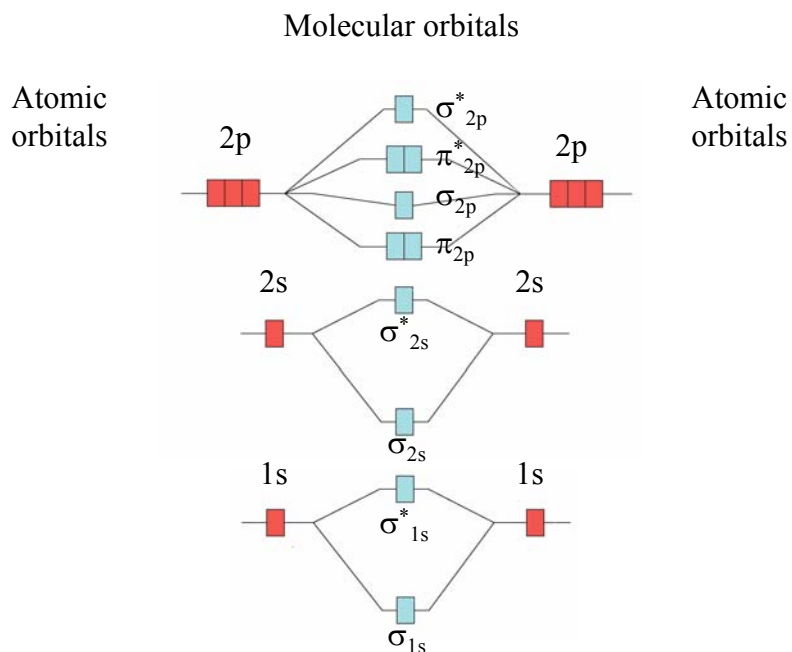
Pi bond formation involving p-orbitals



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



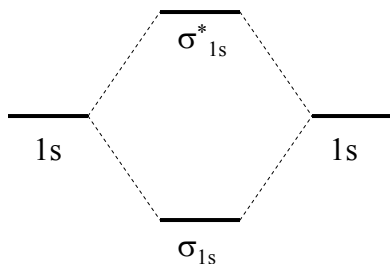
Molecular Orbital Electron Configurations

e.g. O_2

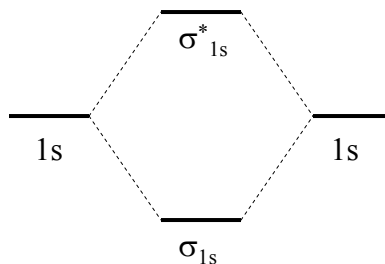
Bond Order

$$\text{Order} = \frac{1}{2} [\# \text{ electrons bonding MO's} - \# \text{ electrons antibonding MO's}]$$

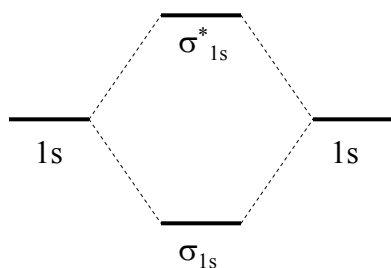
1. The greater the bond order, the more stable the molecule
2. A high bond order means higher bond energies and shorter bond lengths.
3. Fractional bond orders are possible



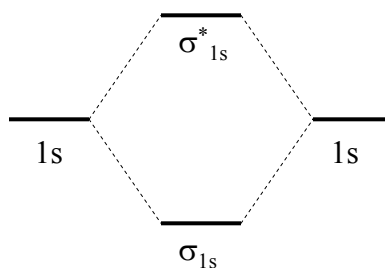
Bond order =



Bond order =



Bond order =



Bond order =

Homonuclear Diatomic Molecules of Second Row Elements

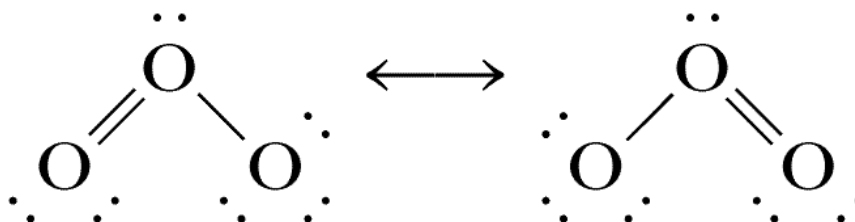
(the inner MO's formed from overlap of the 1s orbitals aren't shown)

	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

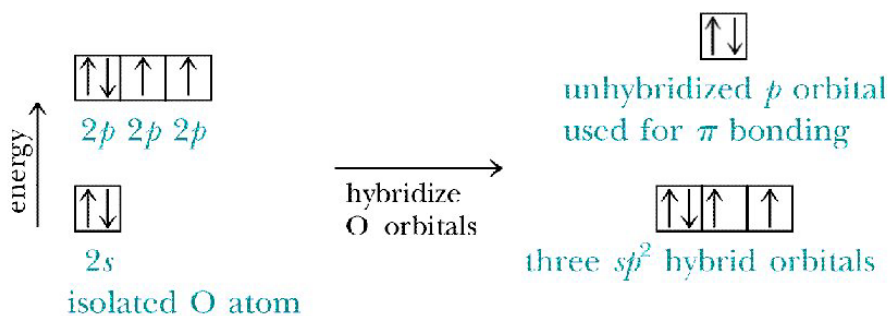
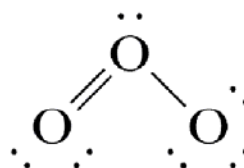
Resonance and MO Theory

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

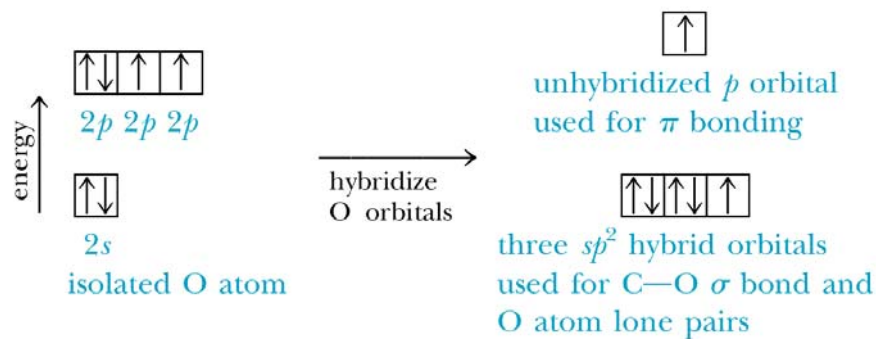
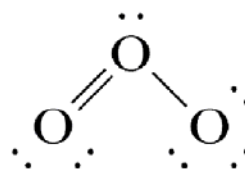
Lewis structure: $3(6) = 18$ or 9 pairs



sp^2 hybridization of the central oxygen -

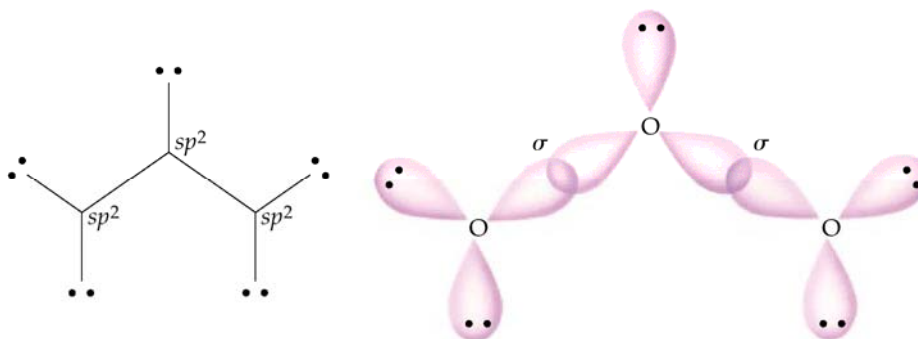


sp^2 hybridization of the terminal oxygens -



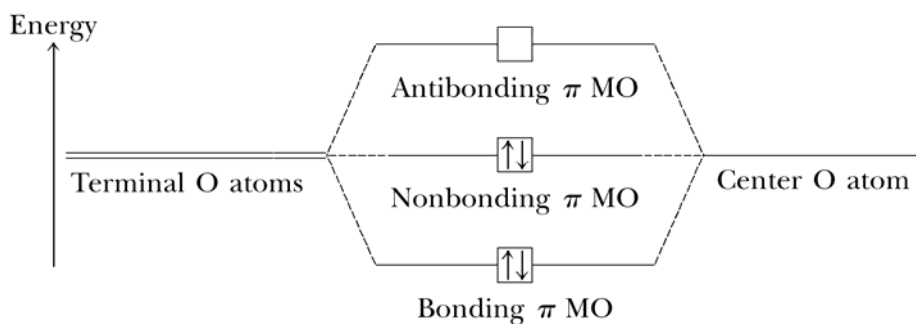
Sigma Bonding in O_3

Explain using Valence Bond Theory

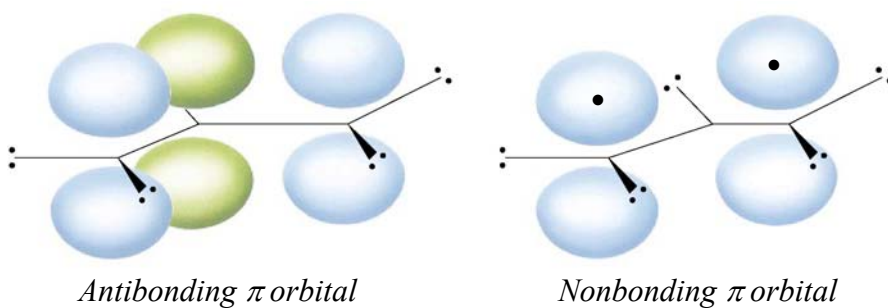


Pi Bonding in O₃

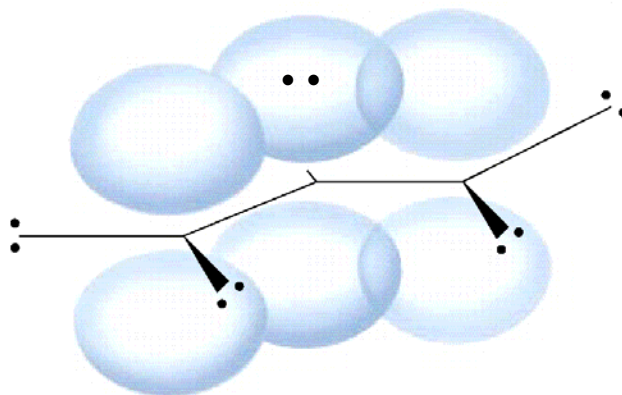
Combine 3 p-orbitals = 3 molecular orbitals



Pi Bonding in O₃

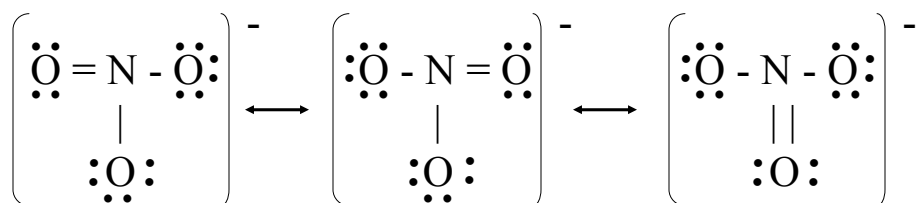


Electrons in the bonding MO are free to move
along the length of the molecule = delocalization

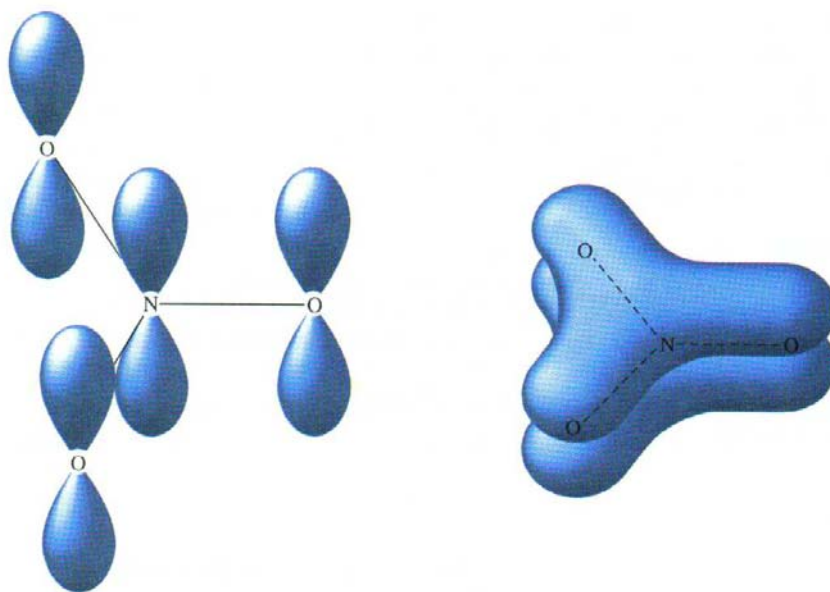


Bonding π orbital

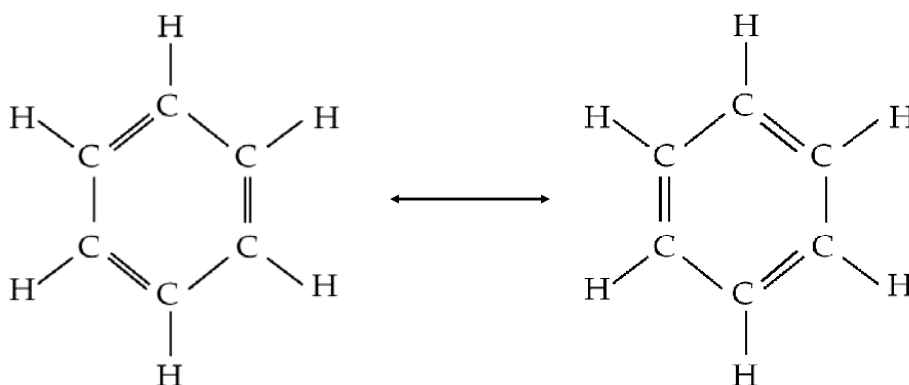
Another example - NO_3^-



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



Benzene - C₆H₆



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

