

# Chemical Principles

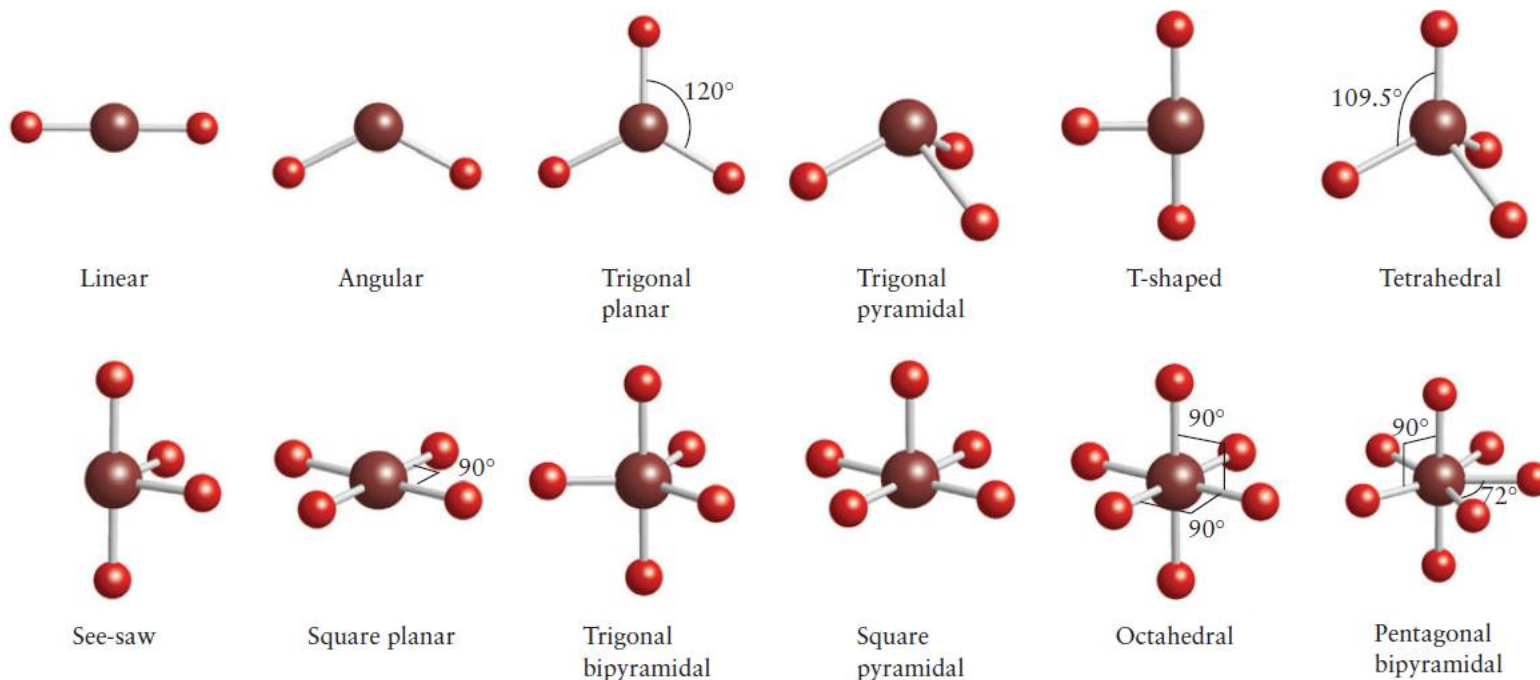
## **5. Molecular Theories**

# Three Theories

- VSEPR – extended Lewis theory, only consider electrostatic repulsions
- VB – considering overlaps of atomic orbitals, by Heitler, London, Slater and Pauling in 1920s'
- MO – more rigorous treatment of electrons, by Mulliken and Hund in late 1920s',

# Molecular Shapes

Possible structures and bond angles



Can we predict structures qualitatively only from the knowledge of valence electrons?

# VSEPR Theory

**VSEPR** - Valence Shell Electron Pair Repulsion Theory.

The molecular shapes are determined by minimizing the repulsion forces among the valence shell electron pairs VSEP.

Valence shell electrons are considered as electron regions which are:

- Bonding pair – electrons in covalence bond
- Nonbonding pair (lone pair) - electrons located on one atom

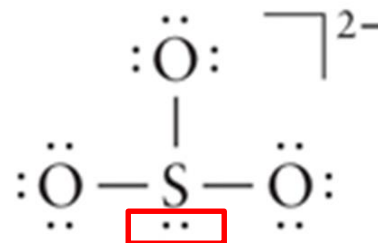
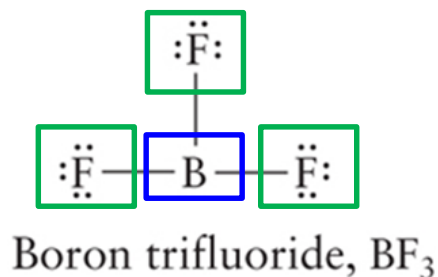
# VSEPR Theory

The generic formula "**A****X**<sub>n</sub>**E**<sub>m</sub>"

"**A**" represent a central atom,

"**X**" a bonded electron region

"**E**" a lone pair electron region



Given the number of VSEPs, it is straightforward to guess a structure in which the repulsions among VSEPs are minimized.

# How to Do It?

In Three Steps,

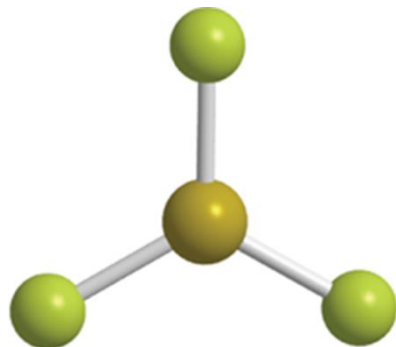
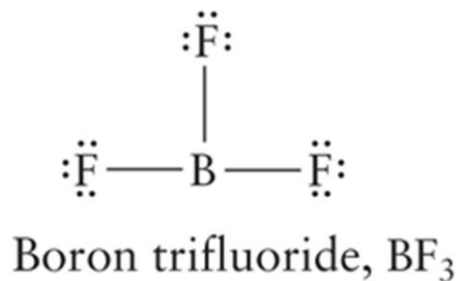
- Draw the Lewis structure of the molecule
- Count how many valence shell electron pairs (VSEPs) or electron regions need to be considered
- Determine the most favorable electron region shape and molecular shape.

# Simple VSEPR Models

Single Bond is the most basic Valence Shell Electron Pair (VSEP)

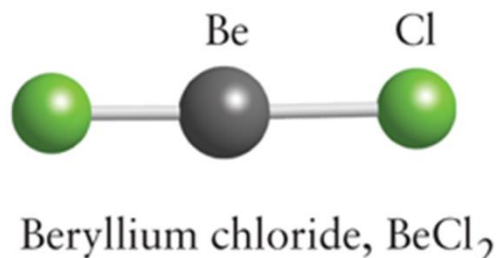
For example  $\text{BF}_3$

1. Draw the Lewis structure
2. Has **3** electron regions
3. The optimal shape of 3 electron regions is Trigonal planar

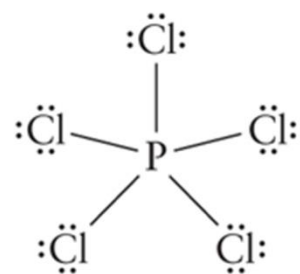
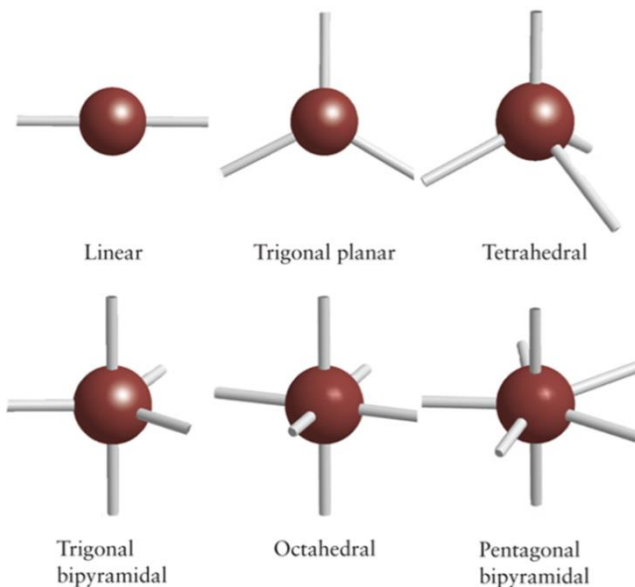


Boron trifluoride,  $\text{BF}_3$

# More Examples of Single Bond



$\text{BeCl}_2$  has 2 electron regions, therefore it has a **Linear** shape of electron regions.  
Bond Angles  $180^\circ$



Phosphorus pentachloride,  $\text{PCl}_5$

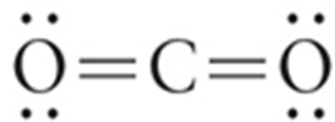
$\text{PF}_5$  has 5 electron regions, therefore it has a **Trigonal bipyramidal** shape of electron regions.

$90^\circ$  &  $120^\circ$

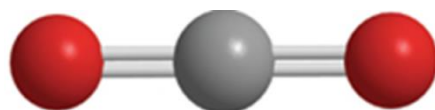


# The Multiple Bonds

Electron pairs in **multiple bonds** are treated the *same* as single bonds.

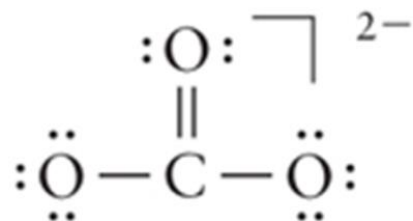


Carbon dioxide,  $\text{CO}_2$

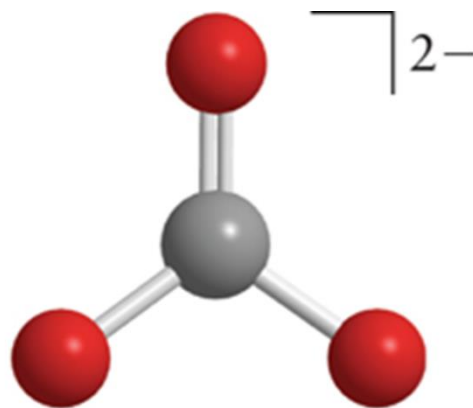


Carbon dioxide,  $\text{CO}_2$

$\text{CO}_2$  has 2 electron regions, therefore it has a **Linear** shape of electron regions.



Carbonate ion,  $\text{CO}_3^{2-}$

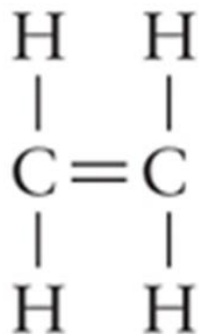


Carbonate ion,  $\text{CO}_3^{2-}$

$\text{CO}_3^{2-}$  has 3 electron regions, therefore it has a **Trigonal Planar** shape of electron regions.

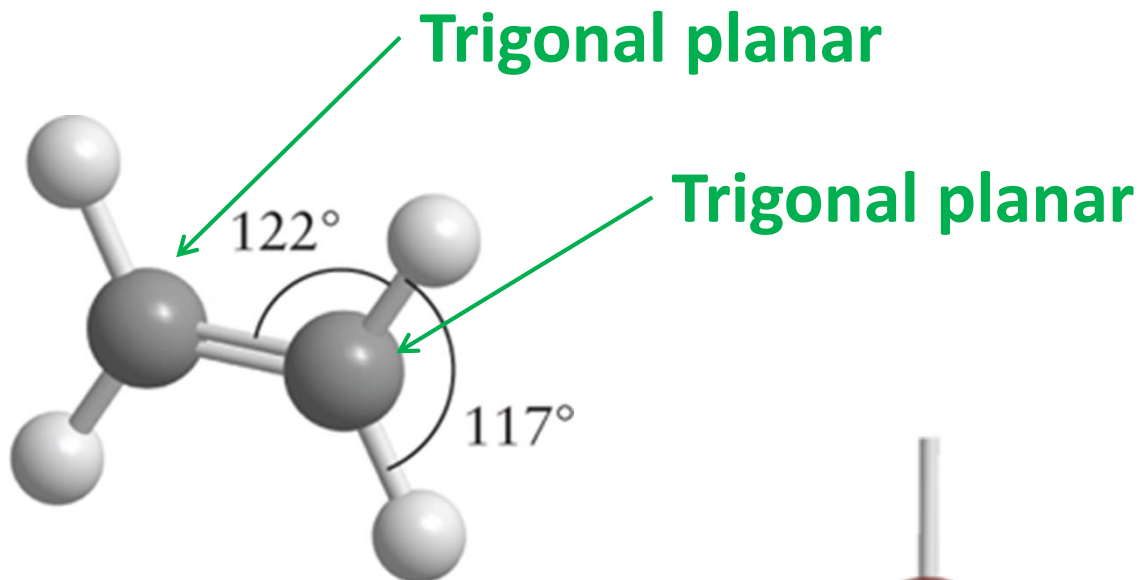
## More Complex Molecule

When there is more than one central atom, we consider the bonding about each atom independently.



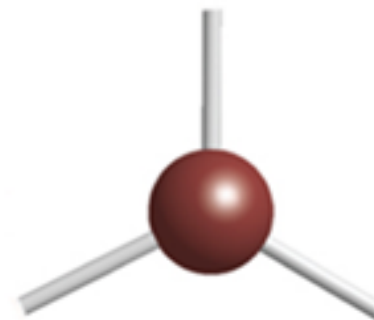
Ethene,  $\text{C}_2\text{H}_4$

Lewis Diagram



Ethene,  $\text{C}_2\text{H}_4$

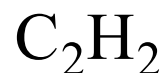
VSEPR 3D shape



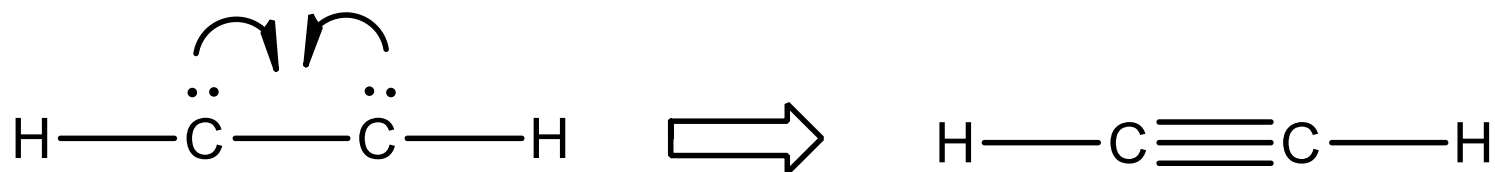
Trigonal planar

# Triple Bonds

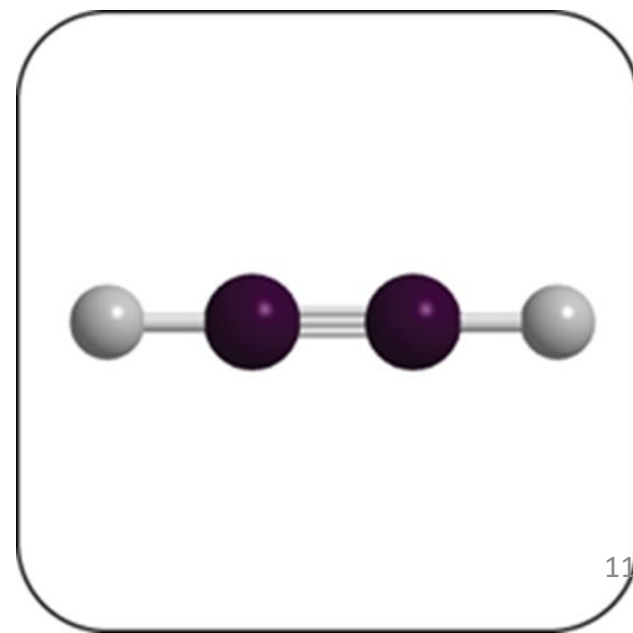
Shape for the ethyne (acetylene) molecule,



Valence electrons:  $2(4) + 2(1) = 10$



Each "central" atom has two electron regions, therefore, linear for each center atom.

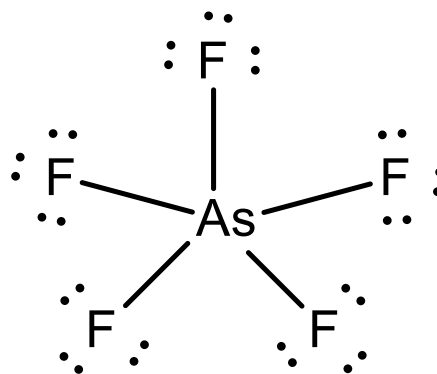


Predict the electron-pair shape and bond angles for arsenic pentafluoride,  $\text{AsF}_5$ .

- A. Trigonal planar,  $120^\circ$
- B. Tetrahedral,  $109.5^\circ$
- C. Trigonal bipyramidal,  $90^\circ$  and  $120^\circ$
- D. Octahedral,  $90^\circ$



Valence electrons:  $1(5) + 5(7) = 40$



Predict the electron pair shape and bond angles for arsenic pentafluoride,  $\text{AsF}_5$ .

A. Trigonal planar,  $120^\circ$

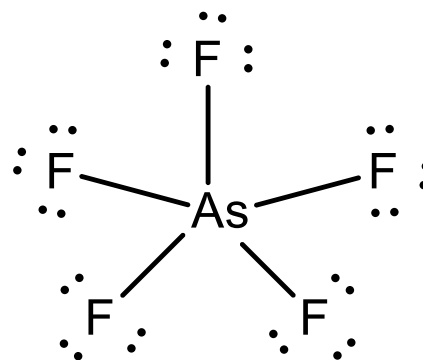
B. Tetrahedral,  $109.5^\circ$

C. Trigonal bipyramidal,  $90^\circ$  and  $120^\circ$

D. Octahedral,  $90^\circ$



Valence electrons:  $1(5) + 5(7) = 40$



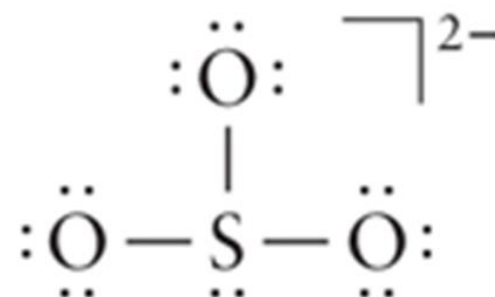
# Lone-pair is treated as one VSEP

Sulfite,  $\text{SO}_3^{2-}$ , which has one lone pair, is an example of an  **$\text{AX}_3\text{E}$**  species.

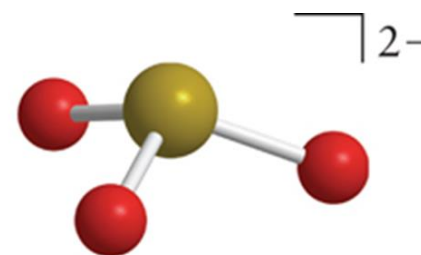
It has 4 electron regions (VSEPs)

The optimal shape for electron regions is **Tetrahedral**

The molecular shape only considers positions of atoms - **Trigonal pyramidal**



Tetrahedral

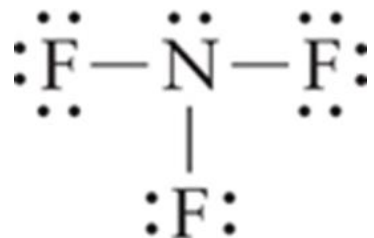


Trigonal pyramidal

# Lone-pair is treated as one VSEP



Draw the Lewis structure.

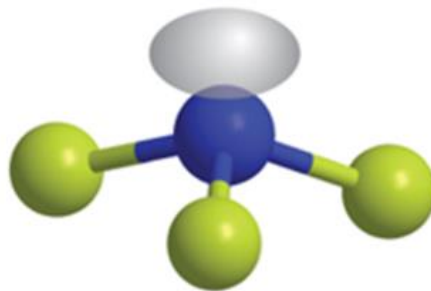


Count the bonds and lone pairs on the central atom.  
Draw the 3D shape. Assign the electron arrangement.



Tetrahedral

Identify the shape considering only atoms.



Trigonal pyramidal

# More Details on Molecular Shapes

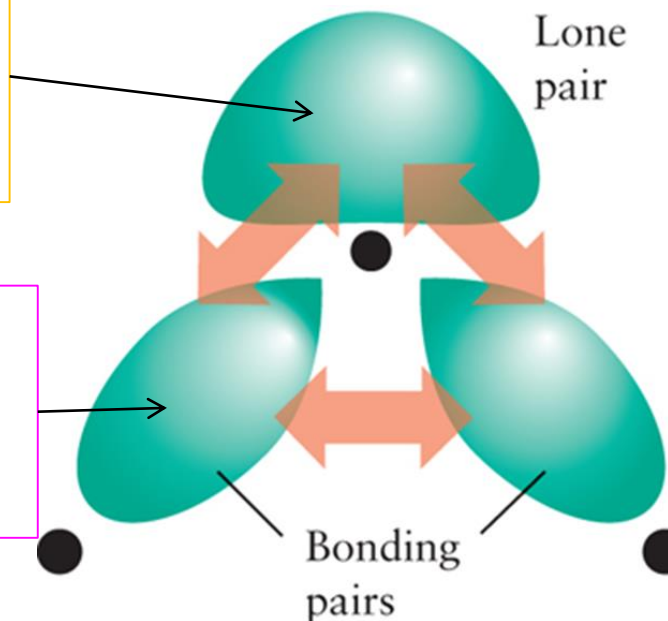
Lone pair is closer to nuclei, which pushes bonding atoms, causes smaller bond angles than expected.

**Lone pairs**

occupy a larger area.

**Bonding pairs**

occupy a smaller area.



**Lone pairs** are not

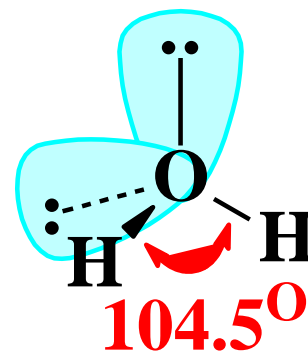
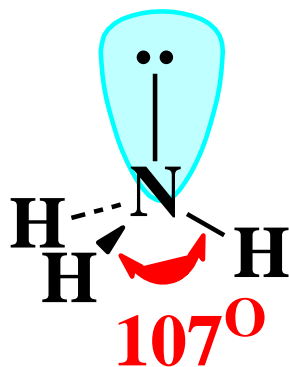
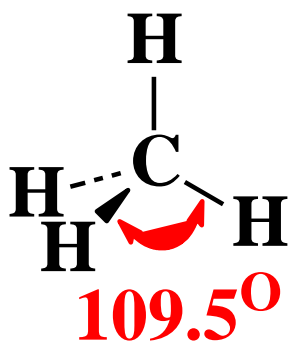
localized so they spread over a **larger volume**.

**Bonding pair** are more **pinned-down**, localized between two positively charged nuclei.



## More Details on Molecular Shapes

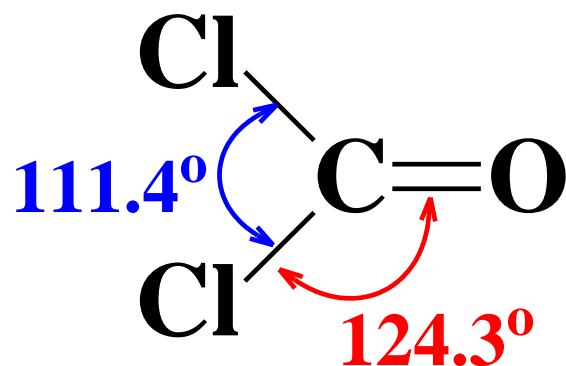
By experiment, the H-X-H bond angle decreases on moving from C to N to O:



Since electrons in a bond are attracted by two nuclei, they do not repel as much as the lone pairs. Therefore, the bond angle decreases as the number of lone pairs increase.

### The Effect of Multiple Bonds

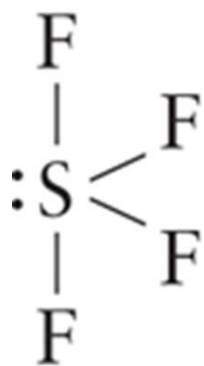
Similarly, electrons in multiple bonds repel more than electrons in single bonds.



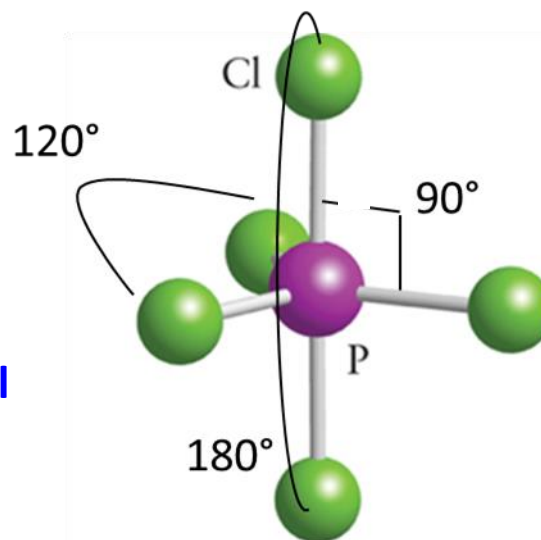
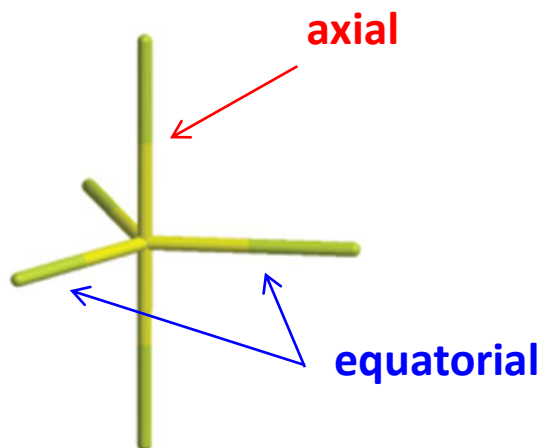
# Where should be the Lone Pair?

The fact that lone pair is closer to nucleus has an impact to where is its optimal position.

- $\text{SF}_4$ ,  $\text{AX}_4\text{E}$ , has a trigonal bipyramidal shape for electron regions
- Two different positions can accommodate the lone pair: **axial** and **equatorial**

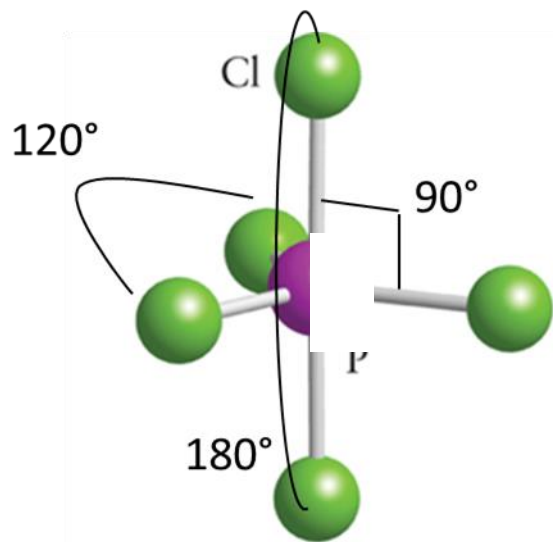


?



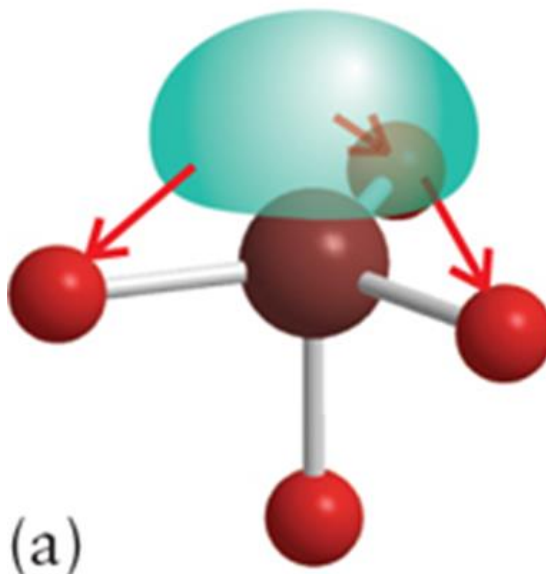
# Where should be the Lone Pair?

Large angle means less repulsion – the lone pair occupies the equatorial position

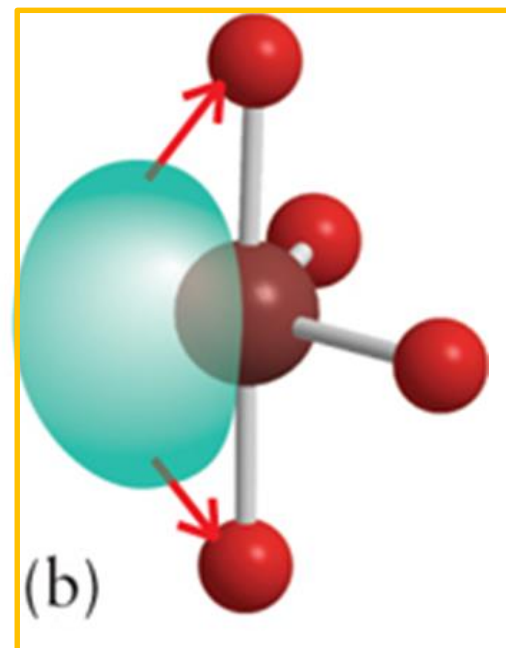


trigonal bipyramidal

3 neighbors at  $90^\circ$



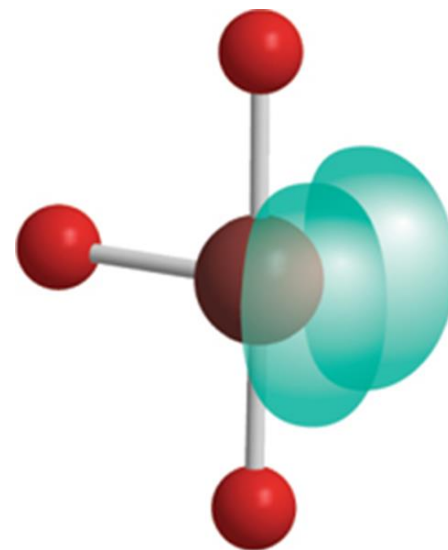
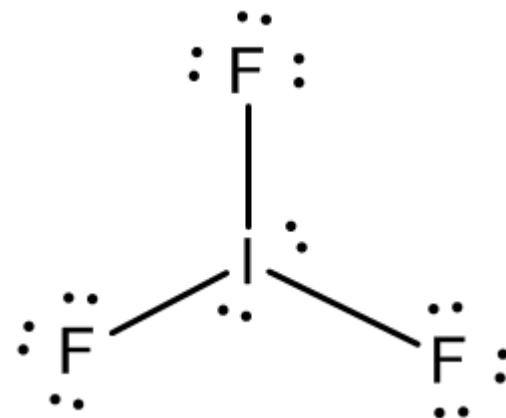
2 neighbors at  $90^\circ$



**See-Saw**

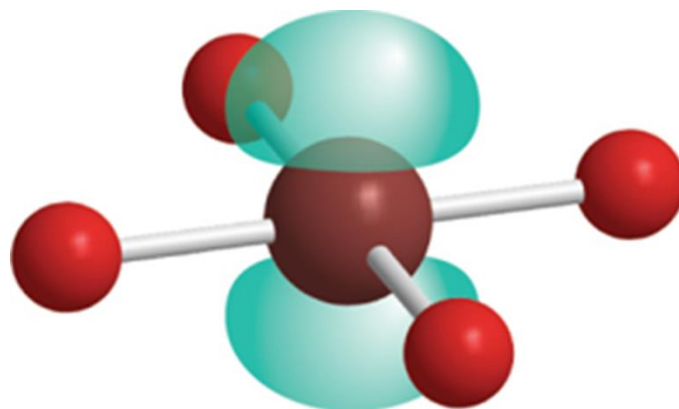
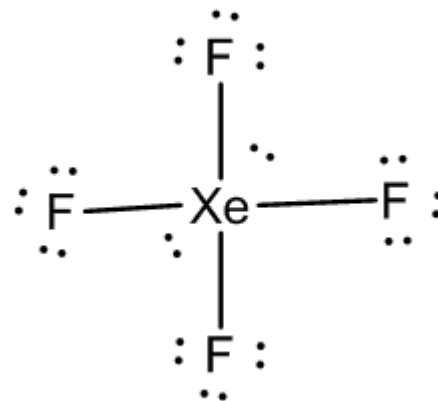
## Another example - $\text{IF}_3$

1. Lewis structure
2. There are 5 electron regions ( $\text{AX}_3\text{E}_2$  type), which takes trigonal bipyramidal shape
3. The lone pairs are accommodated at the equatorial positions. The molecule has the “T” shape.



Determine the (1) VSEPR electron arrangement, (2) VSEPR formula, and (3) VSEPR molecular shape name for  $\text{XeF}_4$

- A. Tetrahedral,  $\text{AX}_4$ , tetrahedral
- B. Octahedral,  $\text{AX}_4\text{E}_2$ , octahedral
- C. Octahedral,  $\text{AX}_4\text{E}_2$ , "T"
- D. Octahedral,  $\text{AX}_4\text{E}_2$ , square planar

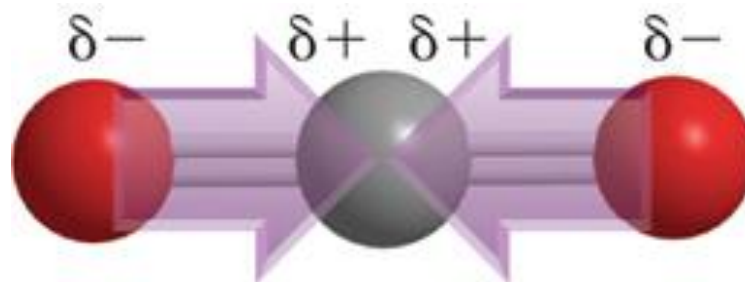


## A consequence of molecular shape – polar or nonpolar

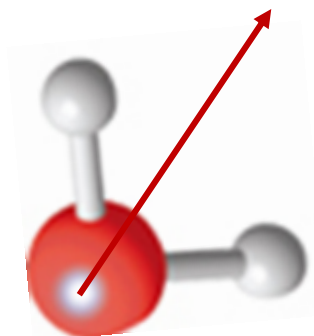
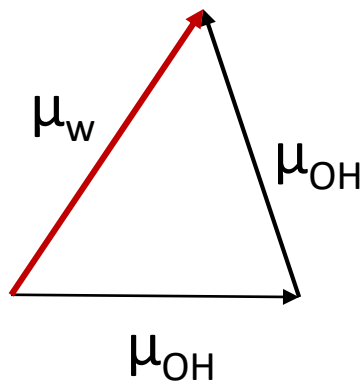
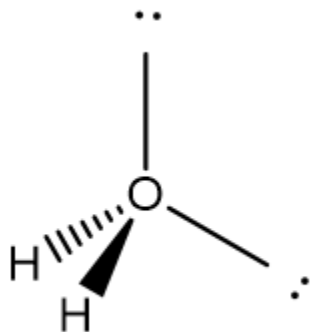
- Chemical bond may be polarized, as represented by a **vector** of electric dipole moment,

$$\mu = qr$$

- The **vector addition rule** applies.
- For example,  $\text{CO}_2$  has two opposing dipole moments, the total dipole is zero, it is a **nonpolar** molecule.



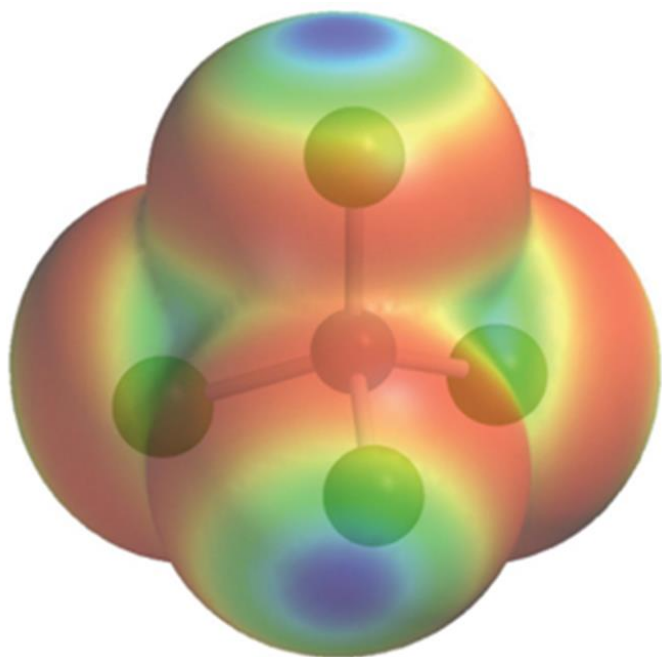
# Water is a polar molecule



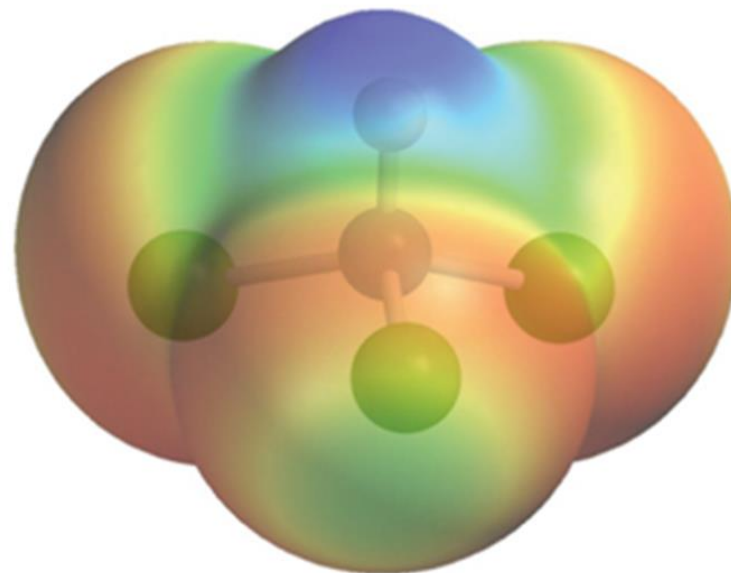
- Both bonds are polar, 1.5D
- Because of the angle (104.5), the net dipole is 1.837 D
- Water is a **polar** molecule.



## More examples



$\text{CCl}_4$  is nonpolar due to symmetry

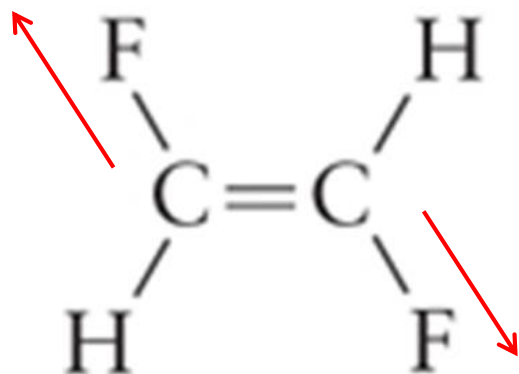


$\text{CHCl}_3$  is polar because of the symmetry is broken

# More examples

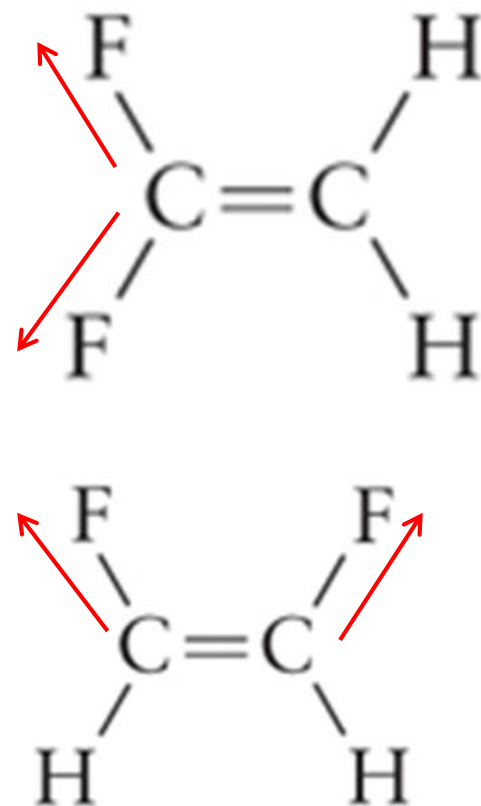
Double or triple bonds fix atoms into a position.

Opposing dipoles



**Symmetric dipole** = Non-polar

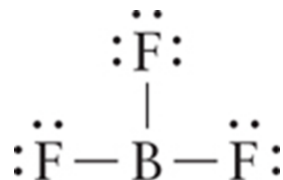
directional dipoles



**Asymmetric dipole** = Polar

Predicting the polar character of a molecule for (a) a boron trifluoride molecule,  $\text{BF}_3$ , and (b) an ozone molecule  $\text{O}_3$ .

(1) Draw the Lewis structure.



(2) Assign the electron arrangement



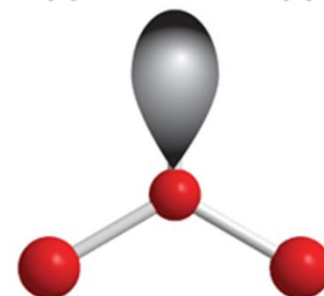
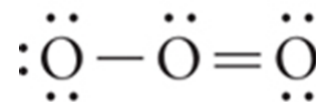
Trigonal planar

(3) Identify the VSEPR formula.

$\text{AX}_3$

(4) Name the molecular shape.

Trigonal planar

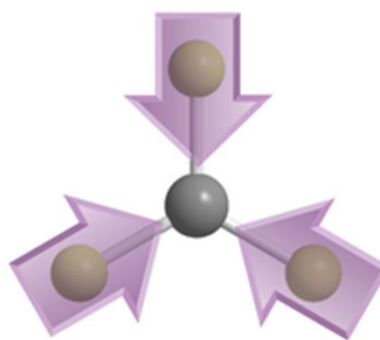


Trigonal planar

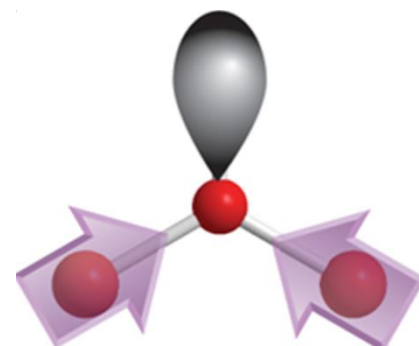
$\text{AX}_2\text{E}$

Angular or Bent

(5) Identify the polarity.



Symmetric dipole nonpolar



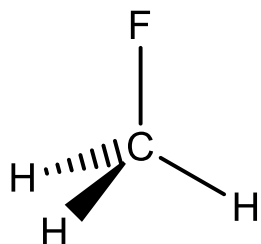
asymmetric dipole polar

Exercise - Predict shapes and molecular dipoles of following molecules

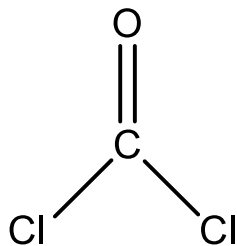
- A.  $\text{CH}_3\text{F}$
- B.  $\text{COCl}_2$
- C.  $\text{XeF}_4$
- D.  $\text{BrF}_3$

Predict shapes and molecular dipoles of following molecules

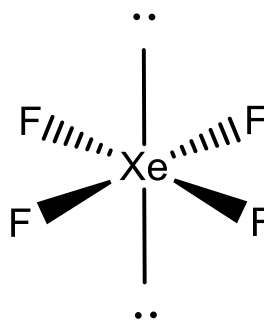
- A.  $\text{CH}_3\text{F}$
- B.  $\text{COCl}_2$
- C.  $\text{XeF}_4$
- D.  $\text{BrF}_3$



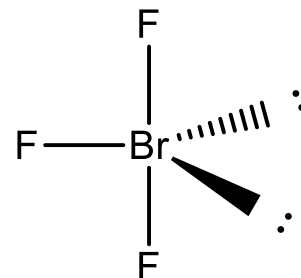
A.



B.

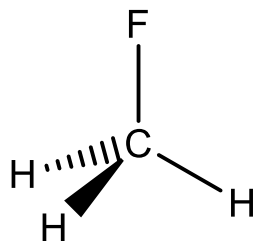


C.

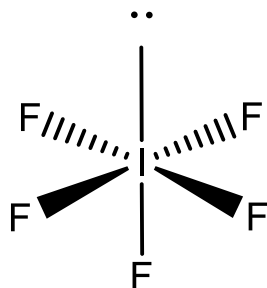


D.

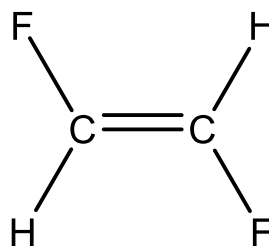
Which of the following has a symmetrical dipole?



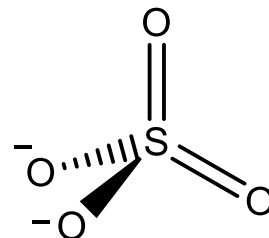
A.



B.



C.



D.

# Valence Bond Theory

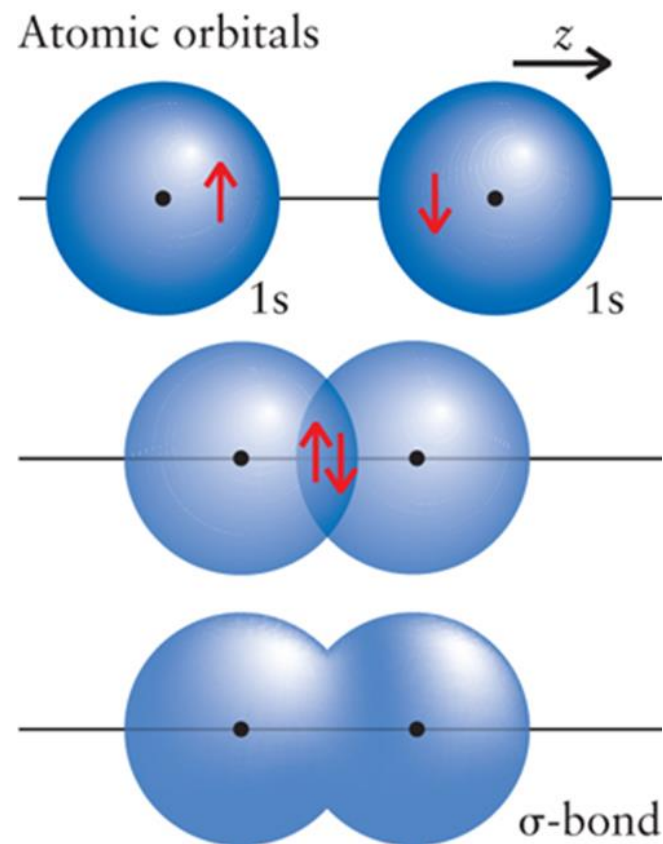
A quantum mechanical description of the distribution of electrons in bonds that goes beyond Lewis's theory and the VSEPR model.

We shall concentrate on **the most essential and qualitative** concepts:

- A chemical bond forms when two **valence** orbitals of atoms overlap, and each of the overlapping orbitals has one (**unpaired**) electron.
- The result is an electron cloud (orbital) **between** the two nuclei, which connect the two atoms together. The bond orbital has two electrons in anti-parallel spins.

# The $\sigma$ -bond between two s-orbitals

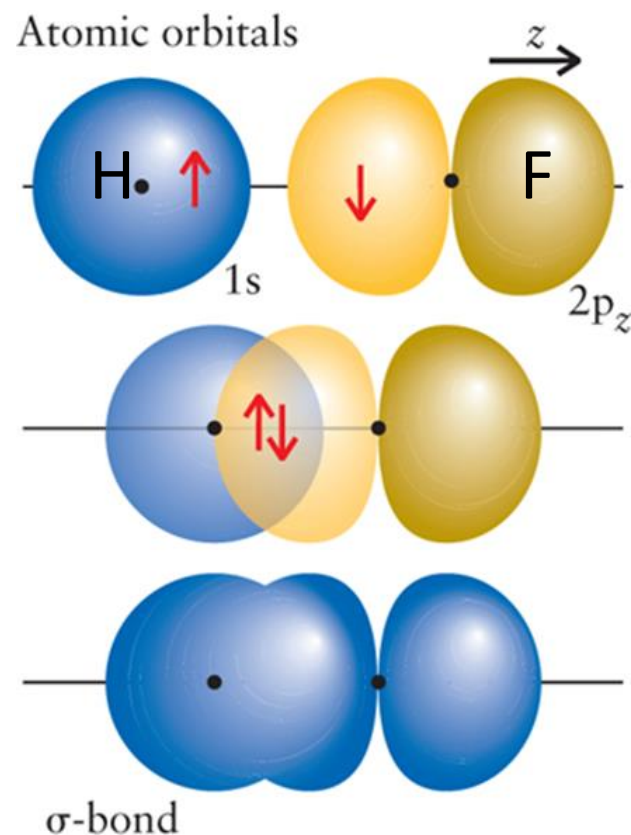
- A hydrogen atom has one electron in its 1s-orbital.
- As two H atoms come together, their 1s-electrons pair (denoted  $\uparrow\downarrow$ ) begin to overlap.
- The result is an electron cloud between the nuclei, it is called a " $\sigma$ -bond" .





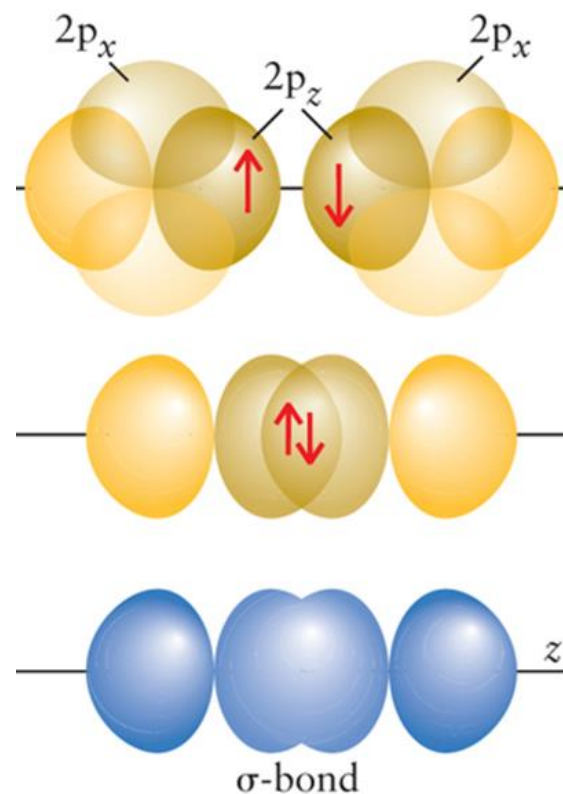
# The $\sigma$ -bond between s and p orbitals

- F has an unpaired valence electron atom in its  $2p_z$ -orbital. Hydrogen has an unpaired electron in its  $1s$ -orbital.
- The orbitals overlap and merge into a electron cloud that spreads over both atoms
- It is also called  $\sigma$ -bond.
- $\sigma$ -bond is symmetric about the axis connecting two atoms

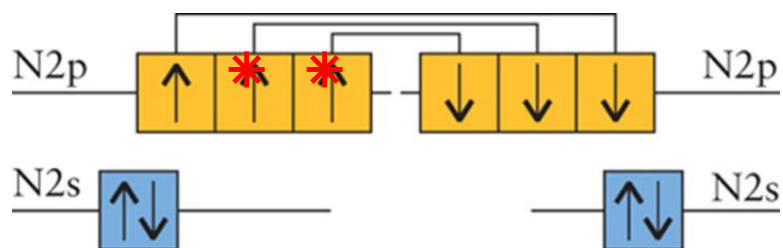


# The $\sigma$ -bond between two p-orbitals (e.g. $N_2$ )

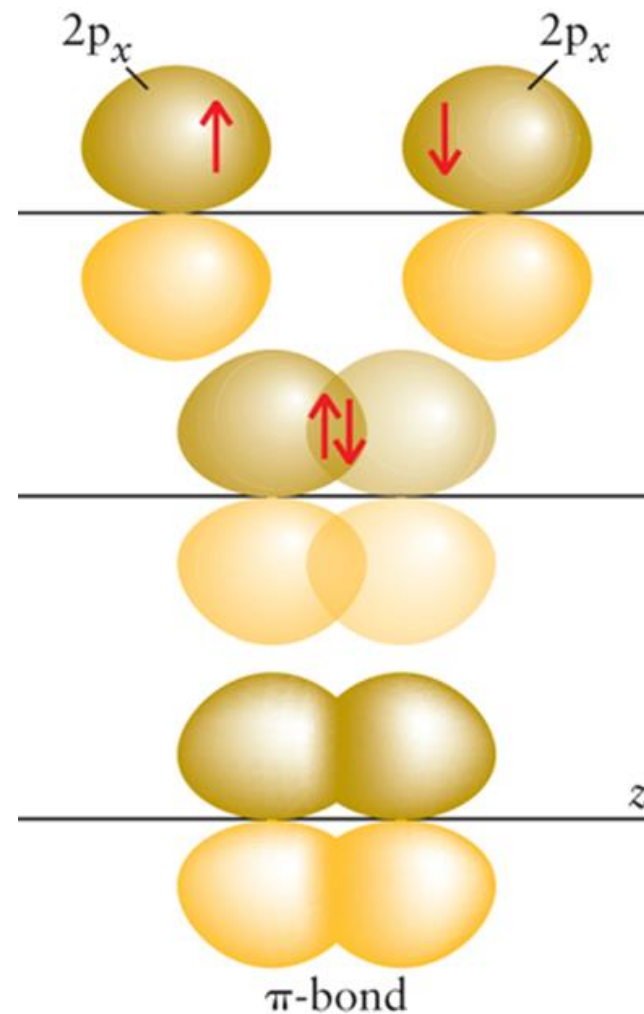
- Each 2p orbital has one unpaired valence electron
- Two p-orbitals along the interatomic axis overlap
- The overlap forms a  $\sigma$ -bond, accommodating two electrons, with axial symmetric.

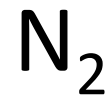
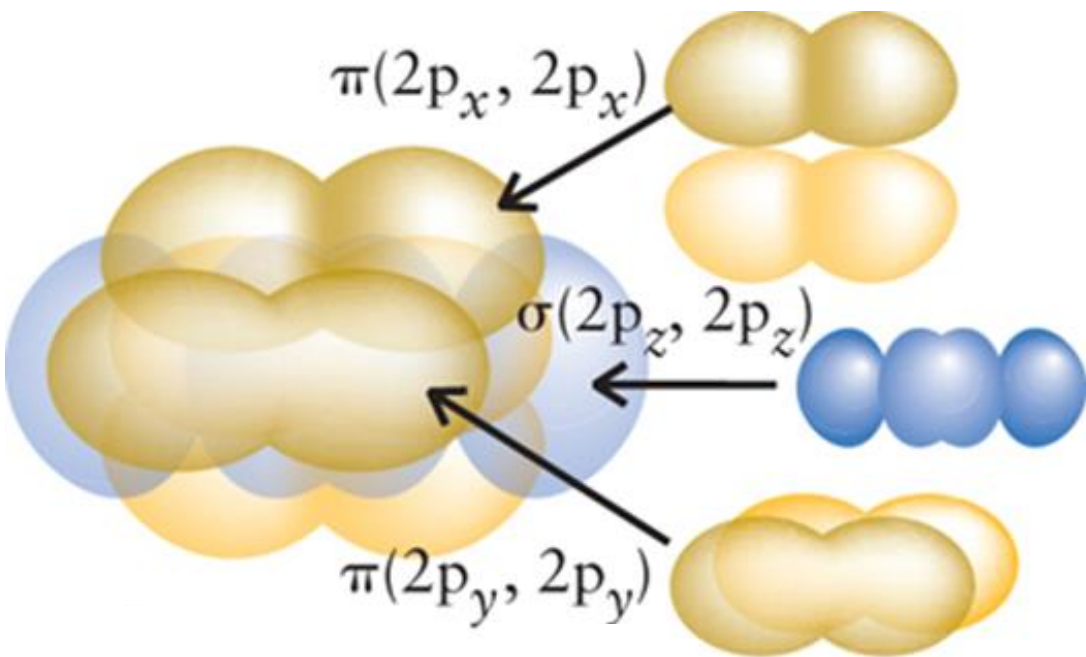


# Valence-Bond Theory : $\pi$ -bond of $N_2$

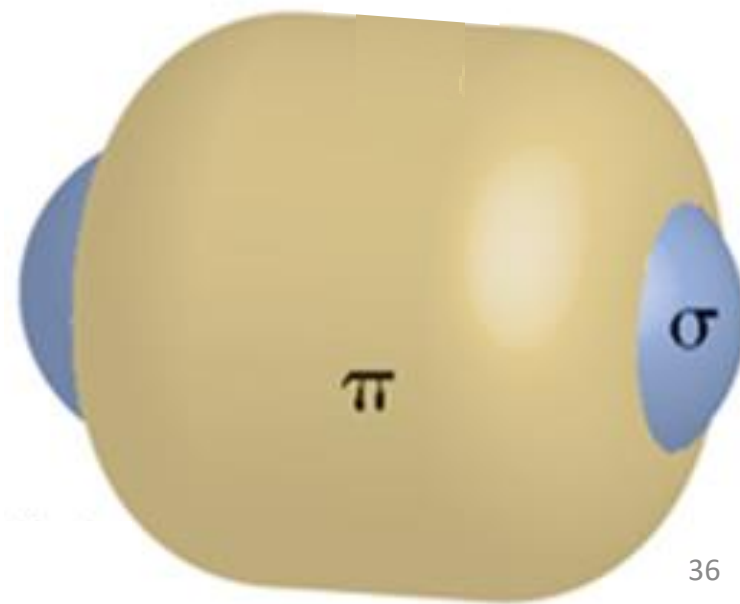


- The other two  $2p$ -orbitals ( $2p_x$  and  $2p_y$ ) are perpendicular to the internuclear axis.
- These  $p$ -orbitals can overlap in a **side-by-side** arrangement.
- The result is symmetric about the nodal plane, called a “ **$\pi$ -bond**”.





Two  $\pi$ -bond merge forming a long doughnut-shaped cloud surrounding the  $\sigma$ -bond cloud, resembling a **cylindrical hot dog**.

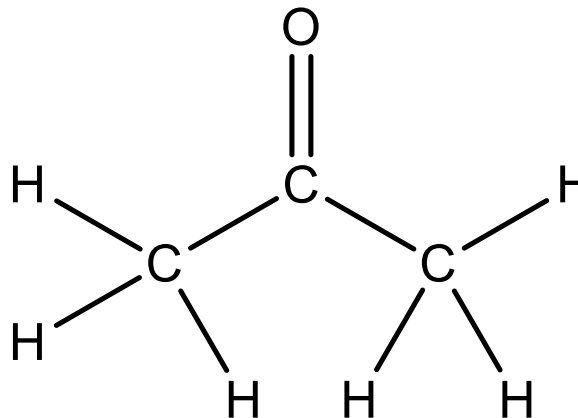


# The valence bond theory in simple cases

- Single bond must be a  $\sigma$ -bond.
- Double bond includes a  $\sigma$ -bond and a  $\pi$ -bond
- Triple bond includes one  $\sigma$ -bond and two  $\pi$ -bonds
- The head-to-head overlaps more than the side-by-side does, so  $\sigma$ -bond is stronger than  $\pi$ -bond.  
(recall the non-additive bond energies of a triple bond)

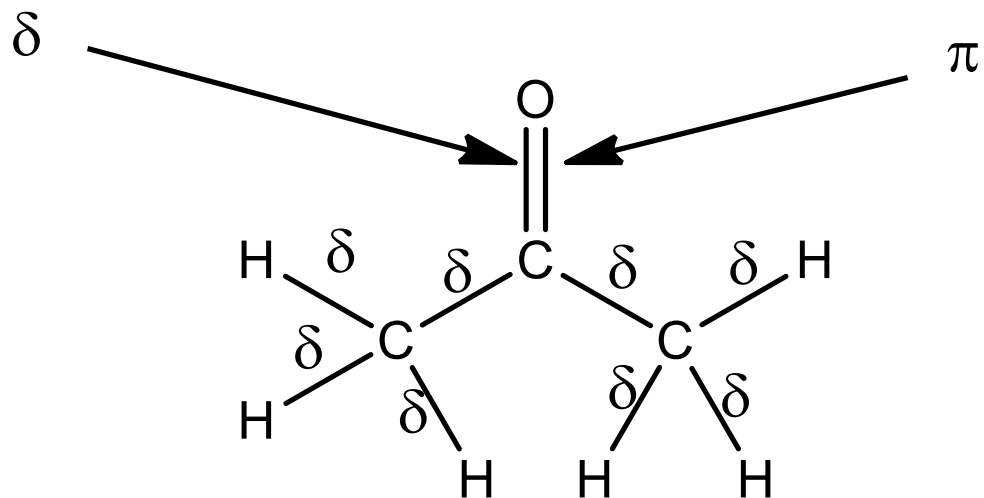
How many sigma ( $\sigma$ ) bonds and pi ( $\pi$ ) bonds are there in acetone?

- A. Eight  $\sigma$  and one  $\pi$
- B. Six  $\sigma$  and one  $\pi$
- C. Nine  $\sigma$  and one  $\pi$
- D. One  $\sigma$  and nine  $\pi$



How many sigma ( $\sigma$ ) bonds and pi ( $\pi$ ) bonds are there in acetone?

- A. Eight  $\sigma$  and one  $\pi$
- B. Six  $\sigma$  and one  $\pi$
- C. Nine  $\sigma$  and one  $\pi$
- D. One  $\sigma$  and nine  $\pi$



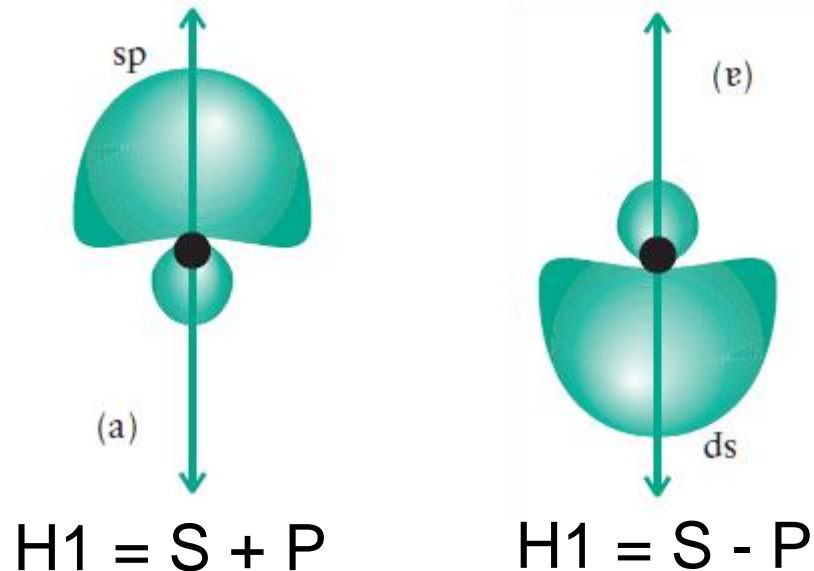
# Hybrid Orbitals

- The valence orbitals can be “**prepared**” to satisfy the condition (unpaired electron, in right symmetry) of bonding.
- For example,  $\text{BeF}_2$  molecule:
  - the F-Be-F bond angle is  $180^\circ$  according to VSEPR theory.
  - F has one unpaired 2p electron, but Be has the  $1s^2 2s^2$  electron configuration - no unpaired electron available for bonding.
  - If one electron from the 2s orbital is promoted to 2p orbital, there are two unpaired electrons,  $1s^2 2s^1 2p^1$
  - Allow the 2s and 2p orbitals to be mixed or form a hybrid orbital – the **sp hybrid orbital**, each has one unpaired electron, can form two  $\sigma$ -bonds



# SP Hybrid Orbitals

- Mathematically, a linear combination of 2s and 2p orbital (wave functions) does the job:



- Each of the hybrid orbitals can overlap with the p orbital of F.
- Although the hybridization costs energy, the overlap reduces the total energy, the molecule is stabilized.

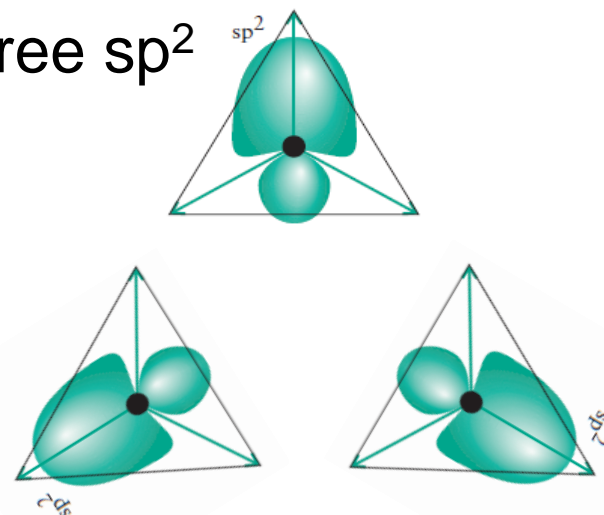
# SP<sup>2</sup> Hybrid Orbitals

- The concept can be extended.
- In BF<sub>3</sub>, three bonds are identical
  - B electron configuration 2s<sup>2</sup>2p<sub>x</sub><sup>1</sup> is changed to 2s<sup>1</sup>2p<sub>x</sub><sup>1</sup>2p<sub>y</sub><sup>1</sup>
  - The three orbitals recombined to three sp<sup>2</sup> hybrid orbitals in a **trigonal** plane.

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

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

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



- Each has one electron, overlapping with a 2p orbital of F to form a chemical bond

# SP<sup>3</sup> Hybrid Orbitals

A carbon atom has sp<sup>3</sup> hybridization

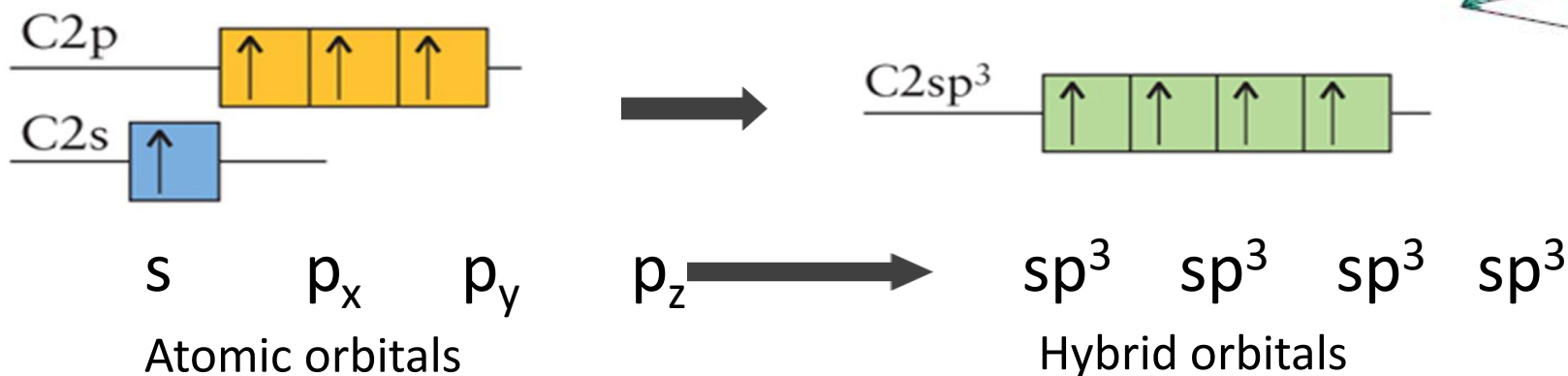
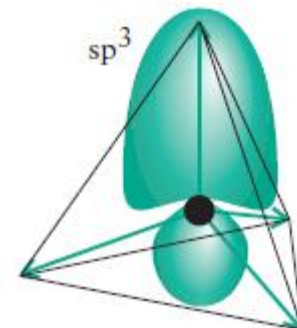
The linear **combinations** of the four original atomic orbitals:

$$h_1 = s + p_x + p_y + p_z$$

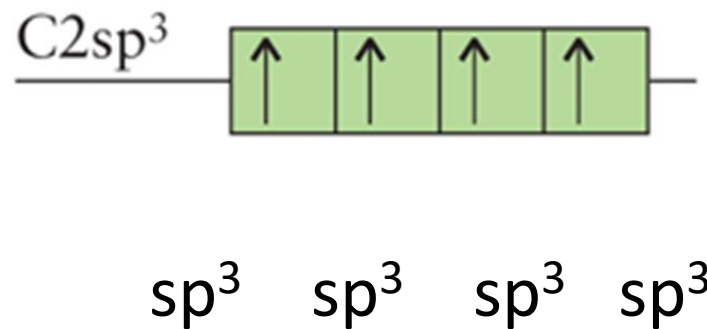
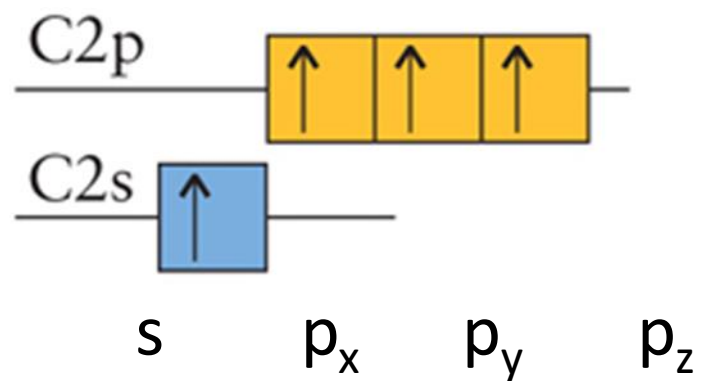
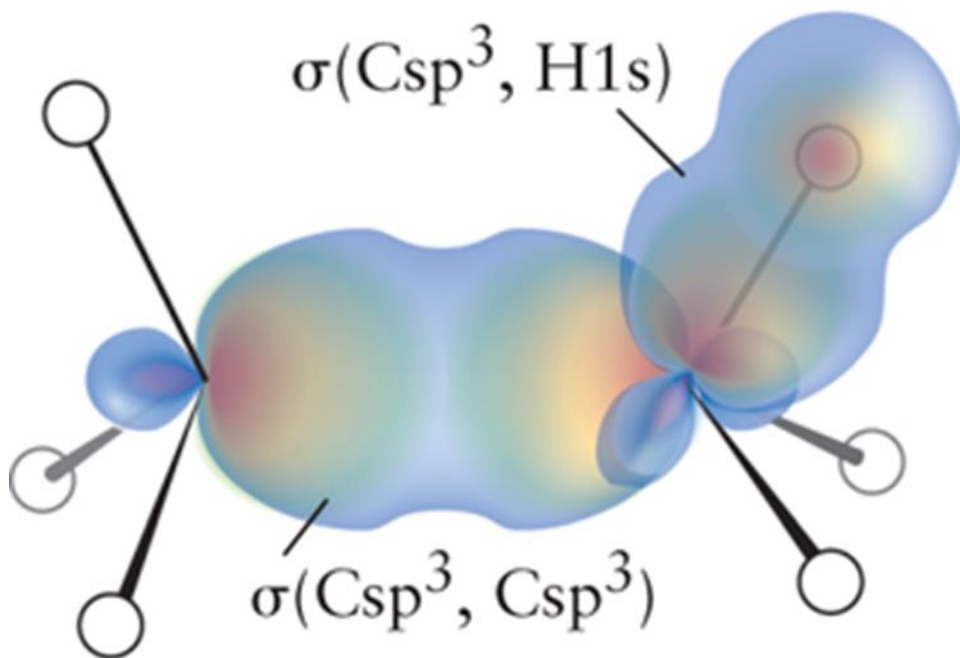
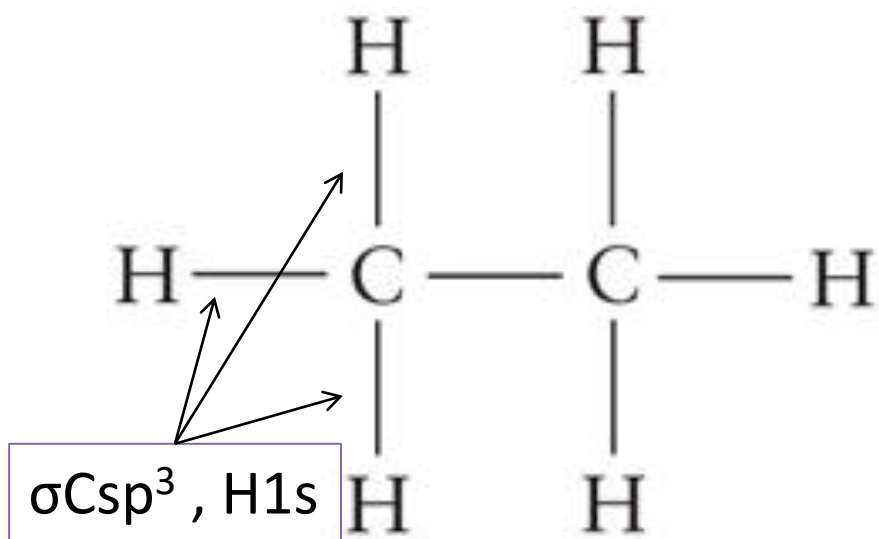
$$h_2 = s - p_x - p_y + p_z$$

$$h_3 = s - p_x + p_y - p_z$$

$$h_4 = s + p_x - p_y - p_z$$



The 4 hybrid bonds are the same, but in 4 orientations of tetrahedral.

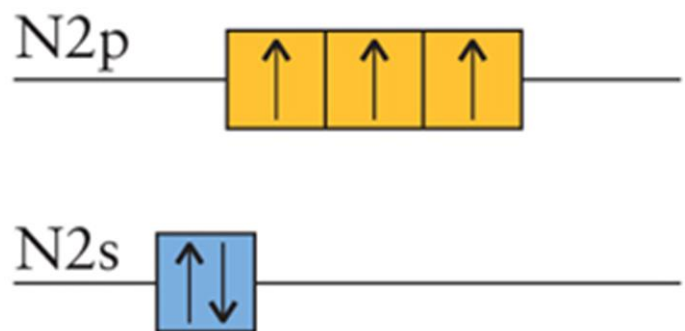
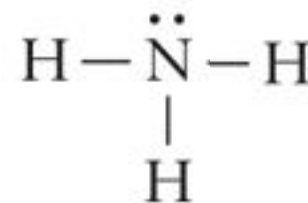


Atomic orbitals

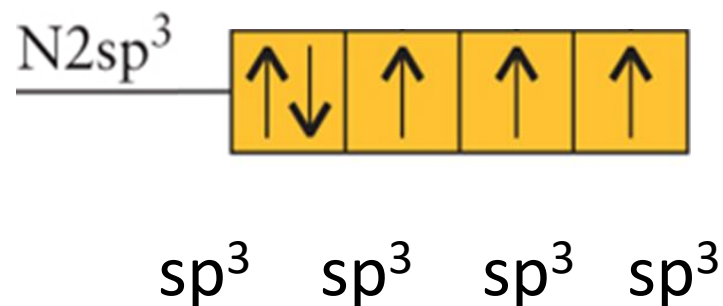
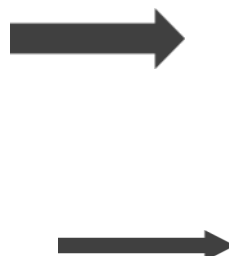
Hybrid orbitals

# SP<sup>3</sup> Hybrid Orbitals of NH<sub>3</sub>

- What are the hybridization bonds of NH<sub>3</sub>?
- We know from VSEPR theory that it has four valence electron pairs (VEPs) in pyramidal.
- Must be sp<sup>3</sup> hybridization.
- One sp<sup>3</sup> is nonbonding, it is a lone-pair.



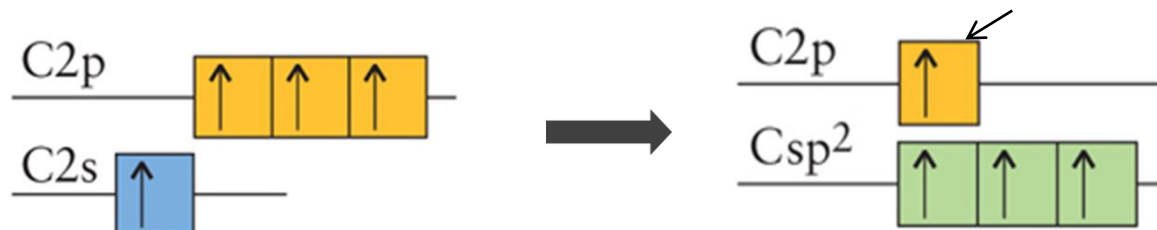
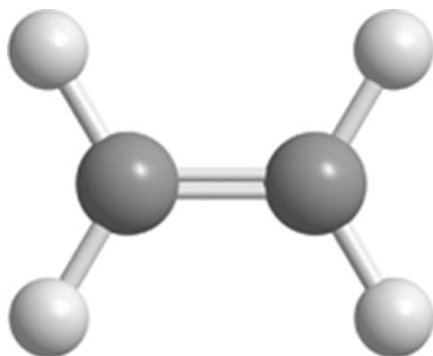
Atomic orbitals



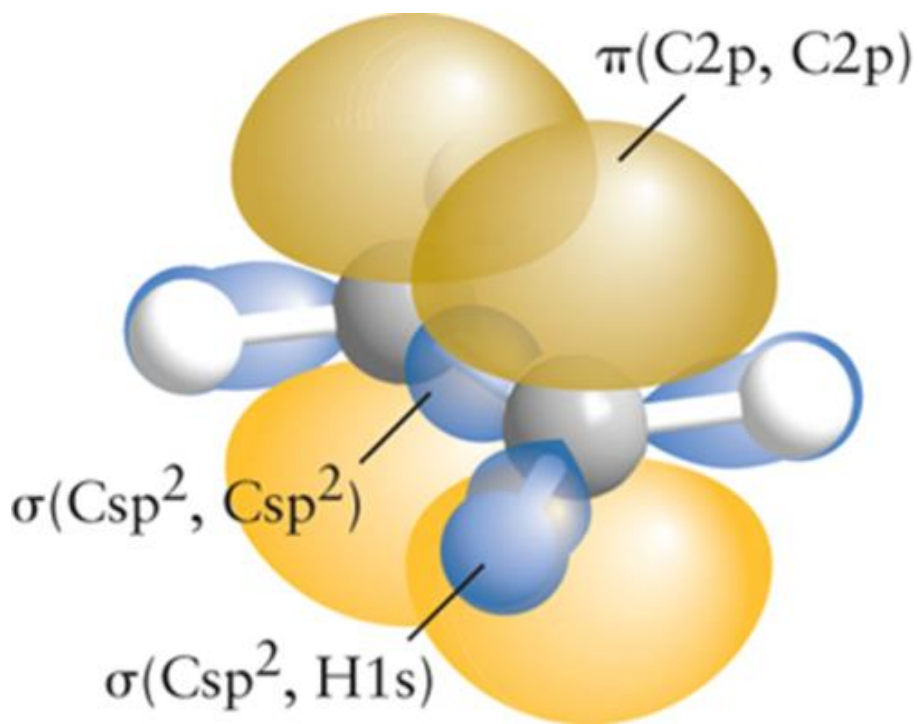
Hybrid orbitals

# Hybridization must predict structure correctly

- The hybridization is a theory to explain observations.
- The best hybridization must predict the correct structure.
- For example, ethylene ( $\text{C}_2\text{H}_4$ ) is planar, which means:
  - Each carbon center is triangular planar.
  - The hybridization of carbon atom must be  $\text{SP}^2$ .
  - One remaining p-orbital is used for the side-by-side  $\pi$ -bond.



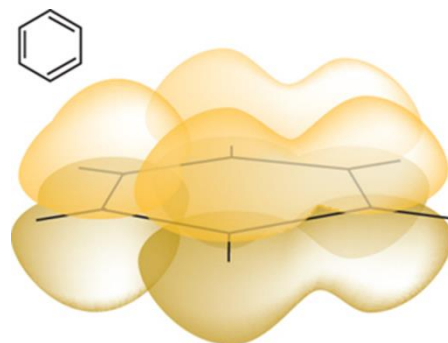
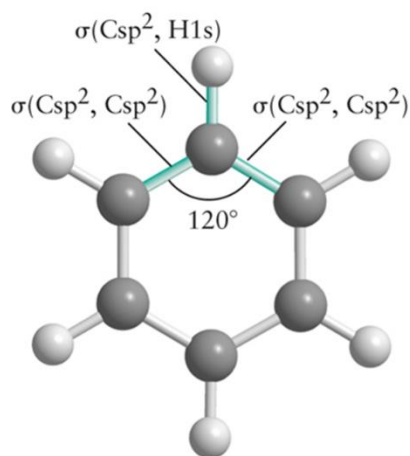
# Double bond



- Double bond prevents a molecule from rotating around the bond.
- The  $\sigma$ -bond is axial symmetric, free rotation.
- The  $\pi$ -bond must be broken in order to rotate.

# Benzene

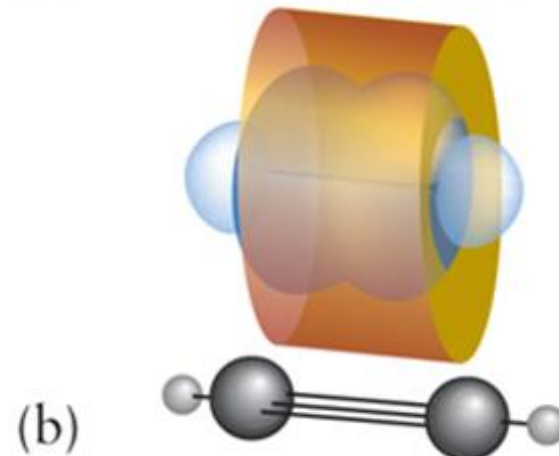
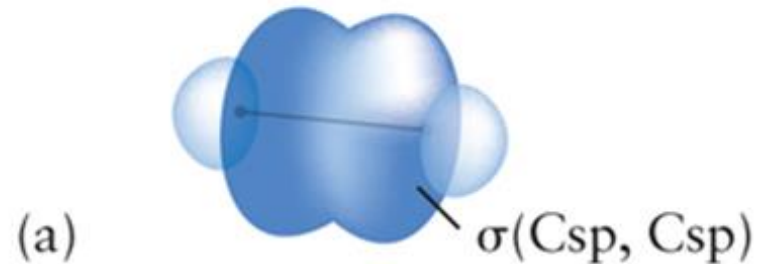
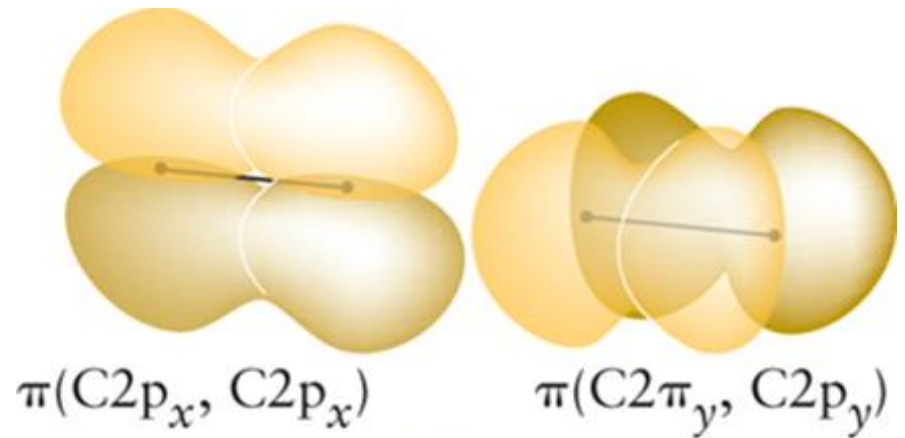
- Benzene is planar, each carbon center is triangular planar
- The carbon must be  $SP^2$  hybridization, forming three  $\sigma$ -bonds.
- The remaining p-orbital forming a  $\pi$ -bond with adjacent atom.
- There are three such  $\pi$ -bonds from 6 atom p-orbitals.





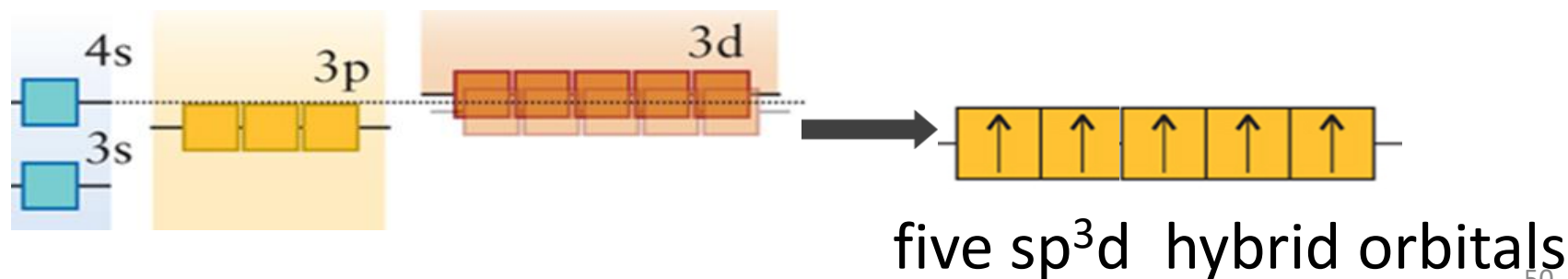
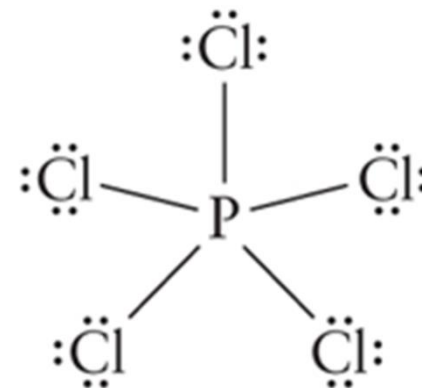
# Triple Bond

- Ethyne HC-CH (acetylene) is linear, the carbon must be  $sp$  hybridization.
- Each carbon has two remaining  $p$ -orbitals, each forms a  $\pi$ -bond.
- The two  $\pi$  orbitals form a cylindrical symmetry.



# Extended Valence – Bipyramidal VEP

- At period 3 and above, d-orbitals may be involved in hybridization.
- $\text{PCl}_5$  is trigonal bi-pyramidal, it has five identical bonds.
- P is  $[\text{Ne}]3s^23p^3$ , there are only 3 unpaired electrons. To have 5 identical bond, we need 5 unpaired electron orbital.
- The hybrids are made by one s-, three p-orbitals and one d-orbital:  $sp^3d$



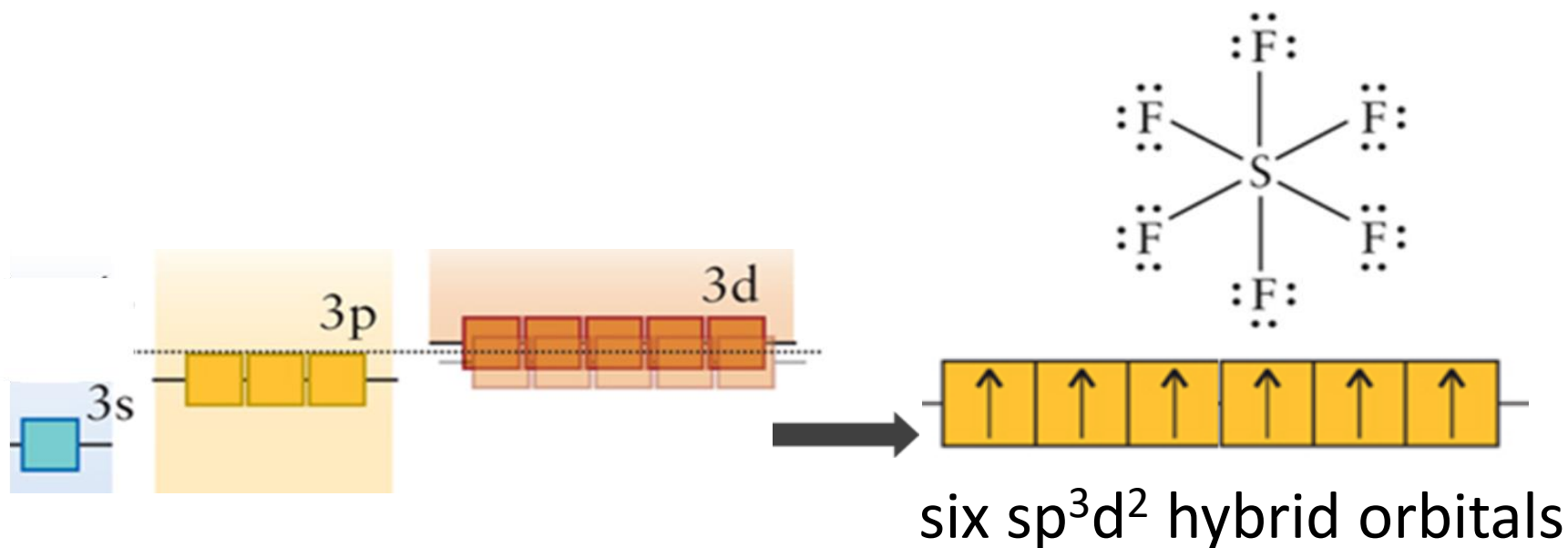
# Extended Valence – Octahedral VEPs

To make six VEPs, uses one s-, three p-orbitals and two d-orbitals.

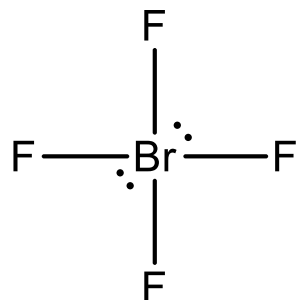
For example, SF<sub>6</sub> has six identical bonds

Sulfur is [Ne]3s<sup>2</sup>3p<sup>4</sup>, only 2 unpaired electrons

Six hybrids are made by: sp<sup>3</sup>d<sup>2</sup>



Assign a hybridization scheme for bromine in  $\text{BrF}_4^-$ .

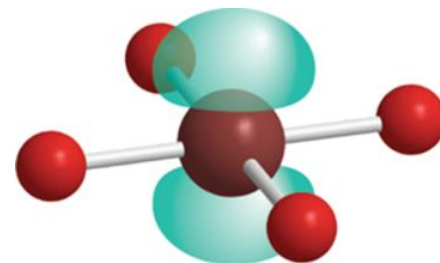
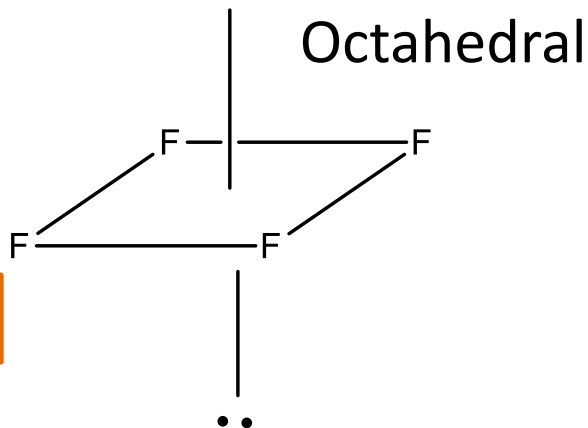


A.  $sp^2$

B.  $sp^3$

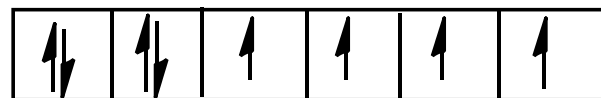
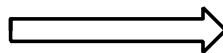
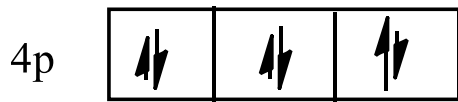
C.  $sp^3d$

D.  $sp^3d^2$



Square planar

Number of atomic orbitals to be hybridized is 6.



6  $sp^3d^2$  hybrid orbitals

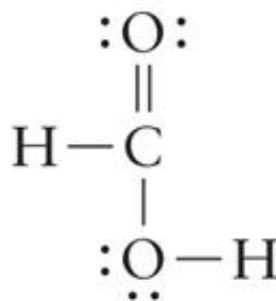
Add the  $e^-$  to the  $\text{Br}^-$  due to formal charge.

## Multiple Bonds are rare for period 3 and above

- Atoms of the Period 2 elements C, N, and O readily form double bonds because of the side-by-side  $\pi$ -bond.
- However, double bonds are rarely found between atoms of elements in Period 3 and later periods
- The atoms are so *large* and the *bond lengths are so great* that it is difficult for effective side-by-side overlap.

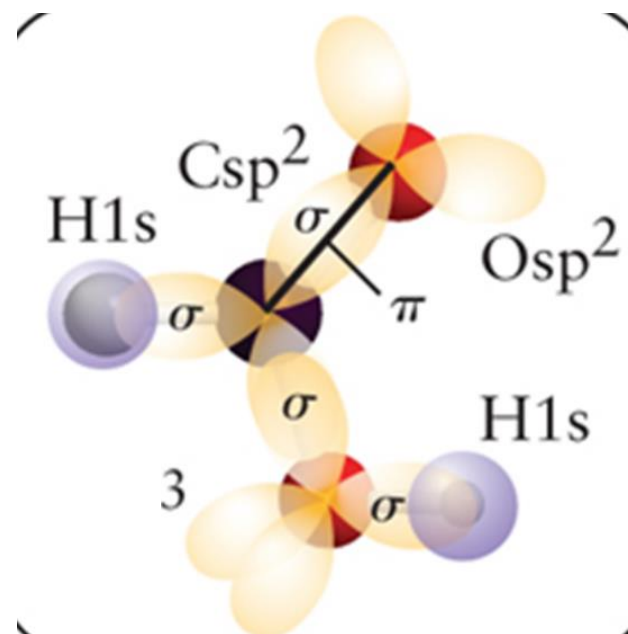
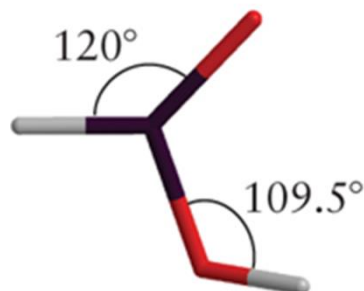
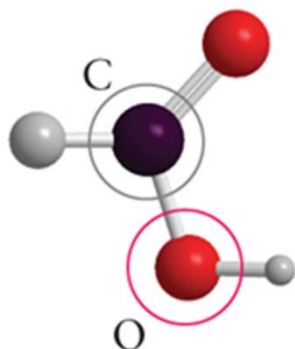
For a formic acid molecule,  $\text{HCOOH}$ , predict its structure using VSEPR theory, describe the chemical bonds in terms of  $\sigma$ - and  $\pi$ -bonds hybrid orbitals using the valence bond theory.

Draw the Lewis structure.

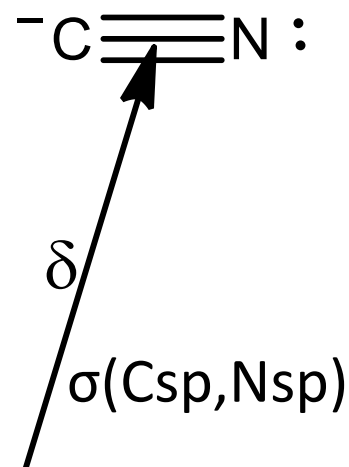
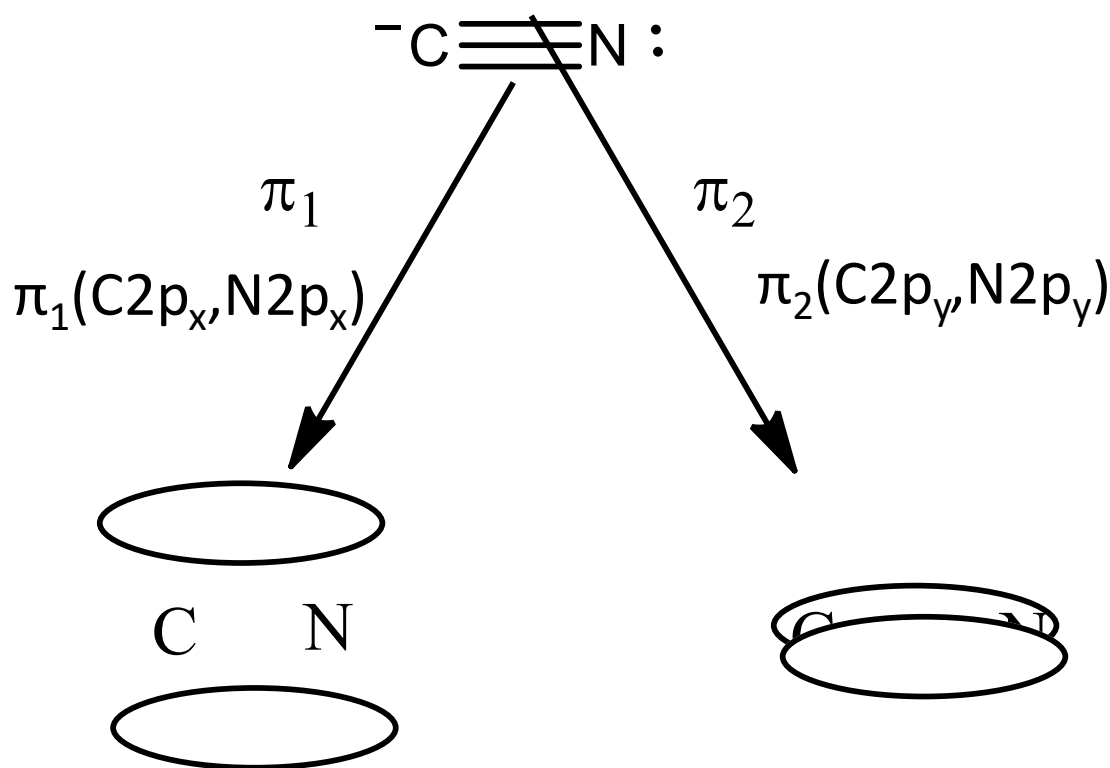


hybridization  
and bond types

VSEPR



What are the hybridization orbitals and chemical bond types of  $\text{CN}^-$  anion?



A linear geometry, with  $180^\circ$  bond angles

# Molecular Orbital Theory



# Molecular Orbital Theory

- **VSEPR** theory is qualitative, inspired by physical intuition. **Valence-bond** theory explained chemical bonds in terms of overlap
- Both are easy to understand, but cannot explain some properties of molecule. such as paramagnetic properties of  $O_2$  and bonding of electron deficient molecule such as  $B_2H_6$
- **Molecular orbital theory**, based on quantum mechanics and introduced in the late 1920s by Mulliken and Hund, has proved to be **the most successful theory** of the chemical bonds. It is much more general and powerful

# Molecular Orbitals – Overview

- Both VSEPR theory and Valence bond theory are based on localized orbitals – the orbital is either a chemical bond between two atoms, or a lone pair on an atom, and each orbital is occupied by a pair of electrons.
- MO theory treats all electrons as delocalized. The electrons occupy molecular orbitals, which may spread over entire molecule.
- MO theory is directly derived from the quantum theory of atoms. Many concepts, such as quantum number, wave function and nodes, energy levels, degeneracy, Pauli exclusion principle, Aufbau principle, etc. hold.
- It is easy to calculate (by computer), and it is not limited to organic molecules for which localized bonds are common.

# Molecular Orbital and Atomic Orbital

1. Molecular orbitals ( $\psi_j$ ) can be made by linear combination of atomic orbitals ( $\varphi_i$ ):

$$\psi_j = \sum_{i=1}^N c_{ij} \varphi_i \quad j = 1, 2, 3 \dots N$$

2. The number of MOs equals the number of AOs. The valence shell AOs are mostly used.
3. The expansion coefficient ( $c_{ij}$ ) indicates the contribution of i-th AO to the j-th MO.

# Molecular Orbital and Atomic Orbital

4. By solving the Schrödinger equations:

$$\hat{H}\psi_j = E_j\psi_j \quad j = 1, 2, 3 \dots N$$

the combination coefficients ( $c_{ij}$ ) and energies ( $E_j$ ) are obtained.

5. AOs that are symmetry matched, geographically close and energy level comparable contribute to the MOs.

6. The MO wave functions can be classified as bonding, nonbonding and anti-bonding three types

# Illustration of MOs by H<sub>2</sub>

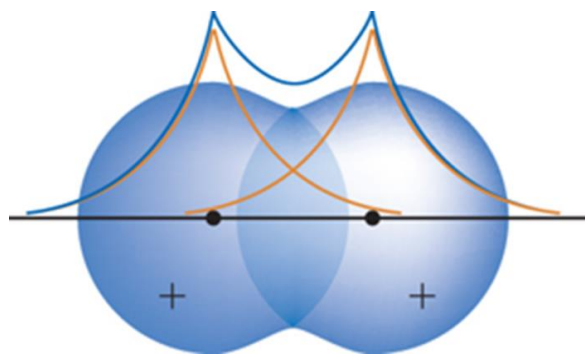
The MOs is built from the valence (1s) AO of atom A and B:

$$\psi_j = c_{1j}\varphi_{1s}(A) + c_{2j}\varphi_{1s}(B), \quad j = 1, 2$$

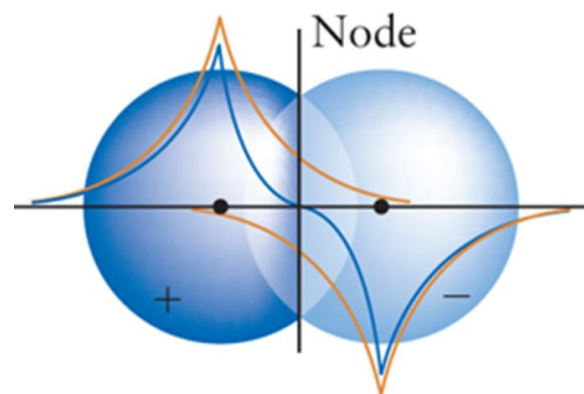
By solving the Schrödinger equation, we have the solution MOs (ignore normalization):

$$\psi_1 = \varphi_{1s}(A) + \varphi_{1s}(B),$$

$$\psi_2^* = \varphi_{1s}(A) - \varphi_{1s}(B)$$



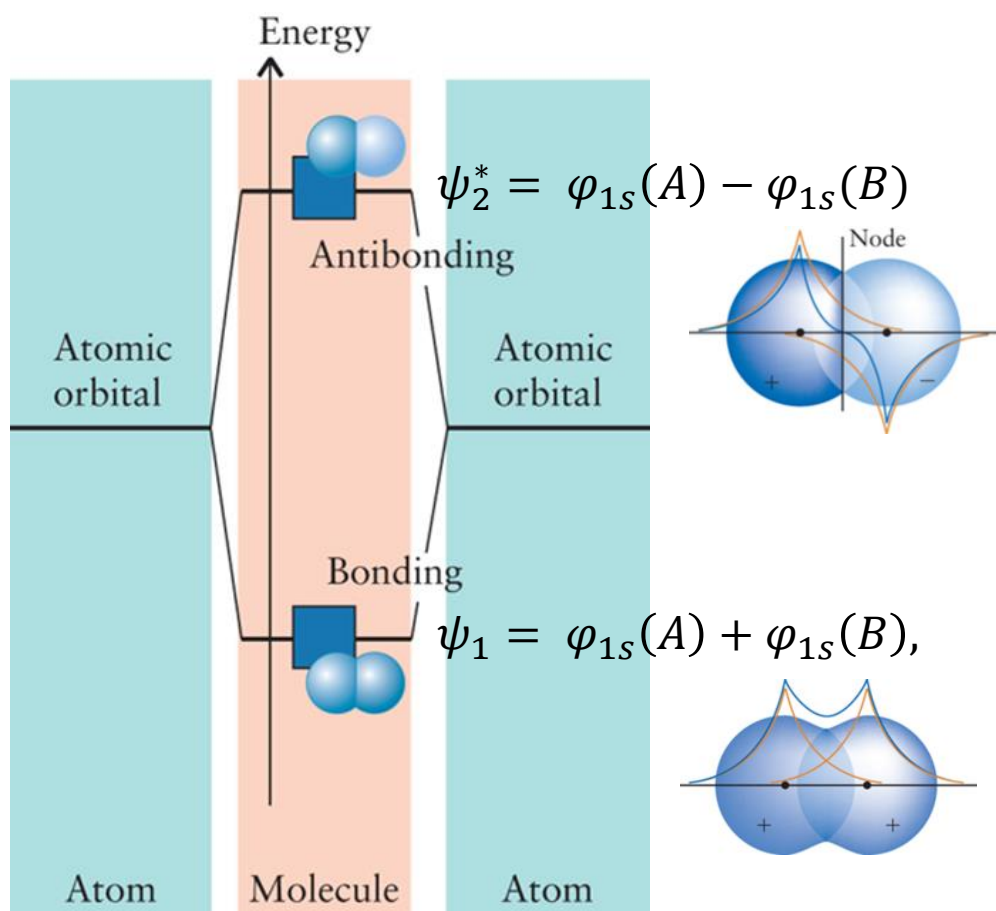
constructive interference  
**bonding**



deconstructive interference  
**antibonding**

# Illustration of MOs by H<sub>2</sub>

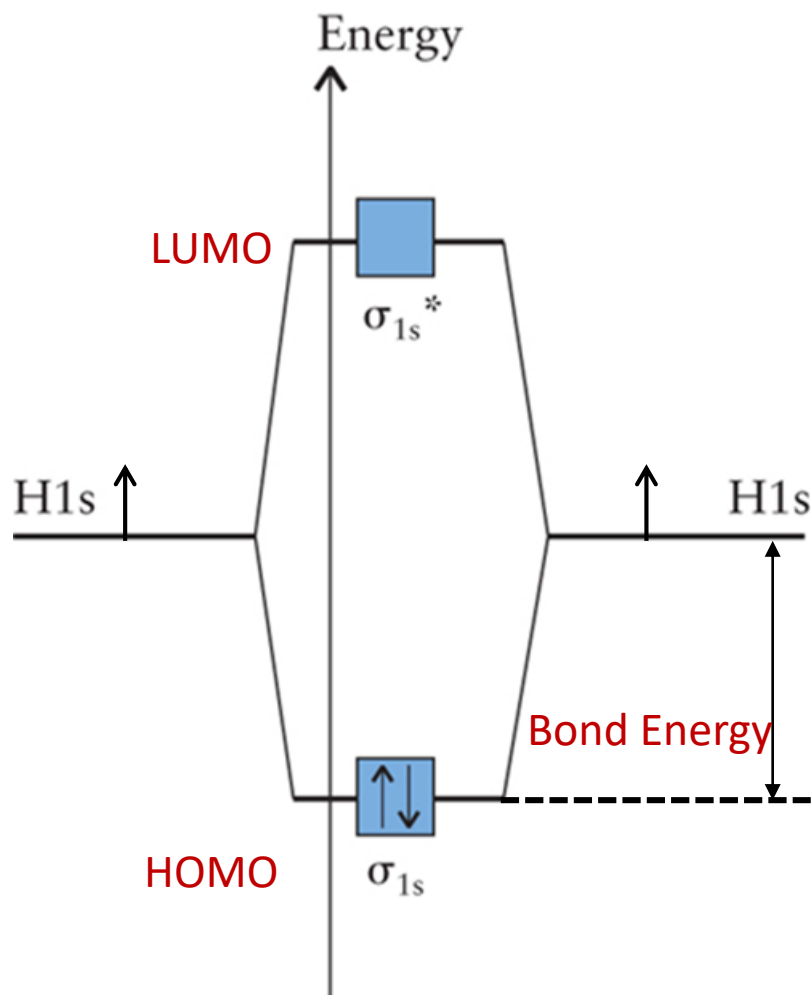
The Energy Diagram - relative energies of the original atomic orbitals and the bonding ( $\psi$ ) and antibonding ( $\psi^*$ ) molecular orbitals.



MO with node is higher in energy than AOs, give rise to **antibonding** MO. It is denoted as  $\sigma_{1s}^*$

MO without node is lower in energy than the AOs. indicate a **bonding** MO, denoted as  $\sigma_{1s}$

# Illustration of MOs by H<sub>2</sub>

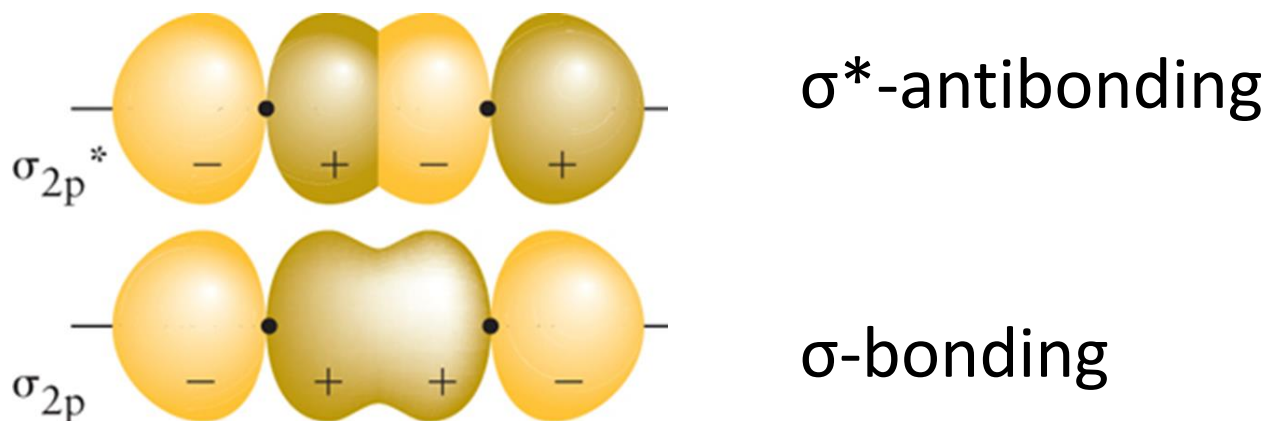


- Both electrons occupy the bonding  $\sigma_{1s}$  orbital with antiparallel spins (Aufbau and Pauli principles).
- The **bond energy** is the energy difference between AO energy and  $\sigma_{1s}$  orbital energy.
- The highest occupied molecular orbital is called **HOMO**; lowest unoccupied molecular orbital is called **LUMO**

**We know what the bond looks like, how the electrons are distributed and what the bond energy is!**

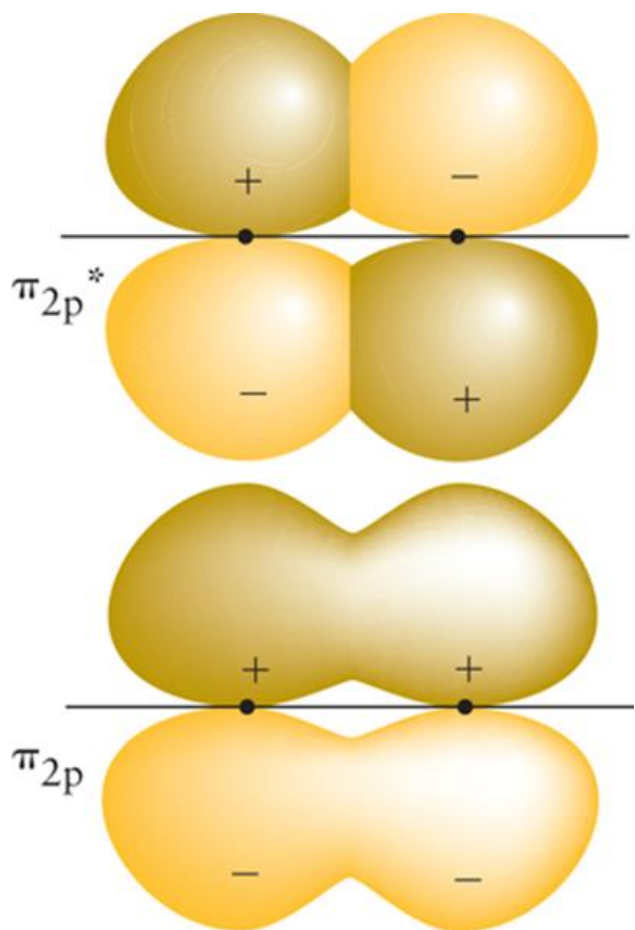
## MOs made from p-orbitals: $\sigma$ -bonds

- If the two 2p-orbitals are directed toward each other along the inter-nuclear axis (**symmetry matched**), they will combine to form two  $\sigma$  type MOs.
- One without node is lower in energy than the two p-AOs, is bonding  $\sigma$  orbital.
- Another with a nodal plane, is higher in energy than that of 2 p-AOs, is antibonding  $\sigma^*$  orbital.





## MOs made from p-orbitals: $\pi$ -bonds



Combination of two **perpendicular** p-orbitals (symmetry matched) forms the side by side bonding and antibonding  $\pi$ -orbitals.

Bonding – no node, energy is lower than that of the two p orbitals

Anti-bonding – there is a nodal plane, energy is higher than the two p-orbitals.

# Diatomic Molecules

Molecular orbitals (MO) can be built from symmetry matched valence-shell atomic orbitals (AO).

Place electrons using a building-up principles:

- Aufbau principle: Electrons start from the lowest-energy MO;
- Pauli exclusion principle: each MO can accommodate up to two electrons, and spin-paired if together;
- Hund's rule: If more than one molecular orbital of the same energy exists, electrons enter them singly and adopt parallel spins.

# Bond Order

The bond order can be defined from the occupancy of MOs:

$$\text{BO} = \frac{1}{2} (N_b - N_{ab})$$

$N_b$  - number bonding electrons

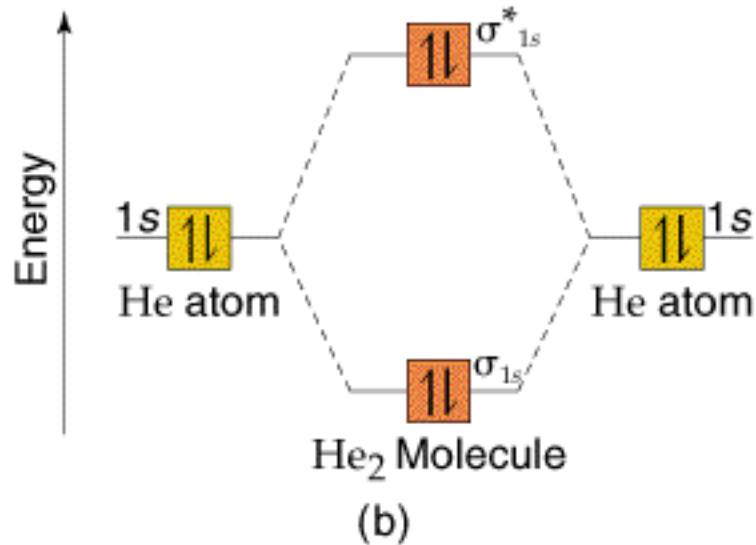
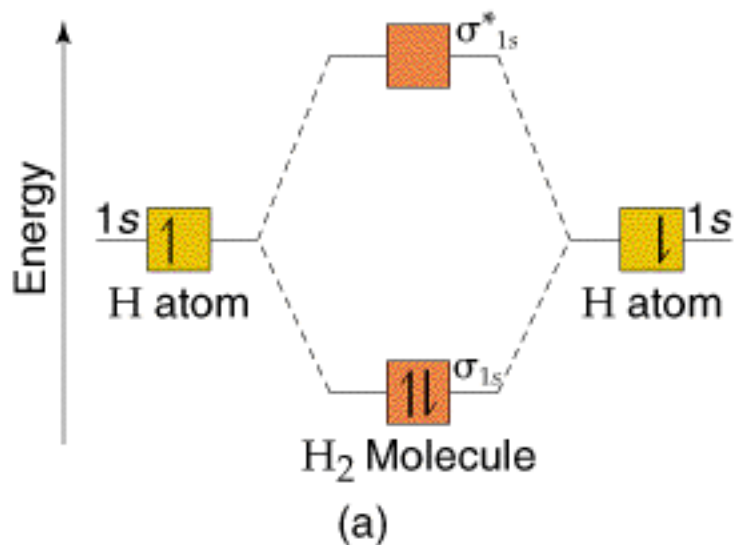
$N_{ab}$  - number of antibonding electrons.

- Bond order = 0 for nonbond.
- Bond order = 1 for single bond.
- Bond order = 2 for double bond.
- Bond order = 3 for triple bond.

# Molecular Orbitals for H<sub>2</sub> and He<sub>2</sub>

H<sub>2</sub> has two bonding electrons. BO=1

He<sub>2</sub> has two bonding electrons and two anti-bonding electrons. BO=0



# Molecular Orbitals for $\text{Li}_2$ and $\text{Be}_2$

AO:

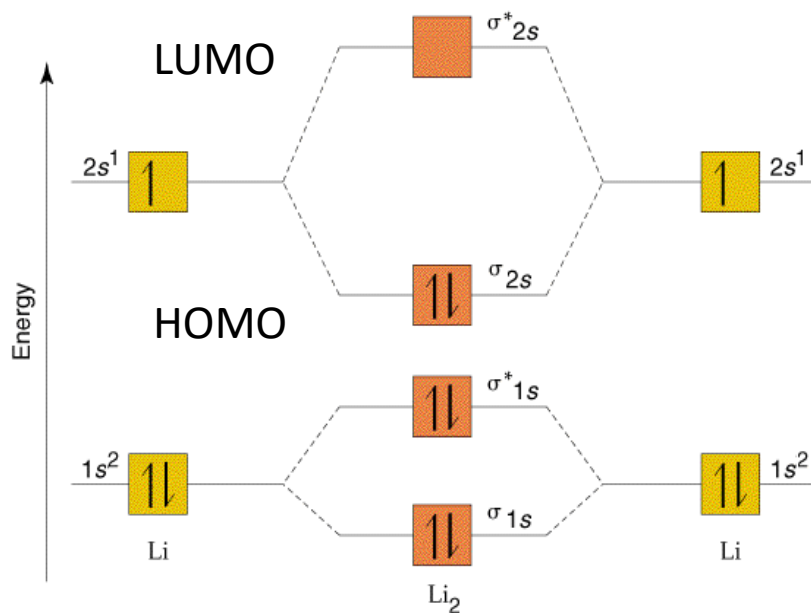
Li -  $[\text{He}]2s^1$

Be -  $[\text{He}]2s^2$

MOs:

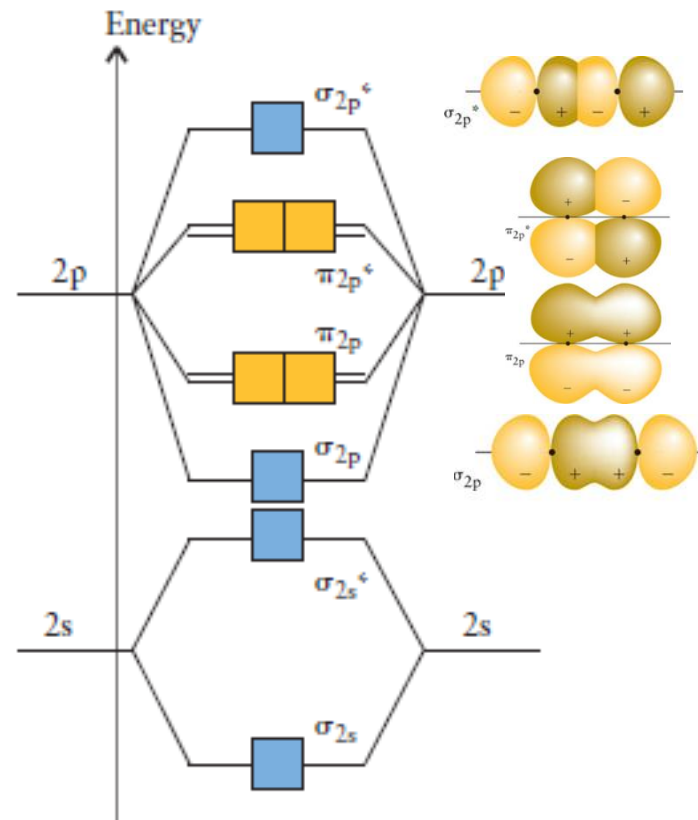
$\text{Li}_2$  has 4 bonding electrons,  
2 anti-bonding electrons,  
 $\text{BO}=1$

$\text{Be}_2$  has 4 bonding electrons  
and 4 anti-bonding electrons.  
 $\text{BO}=0$



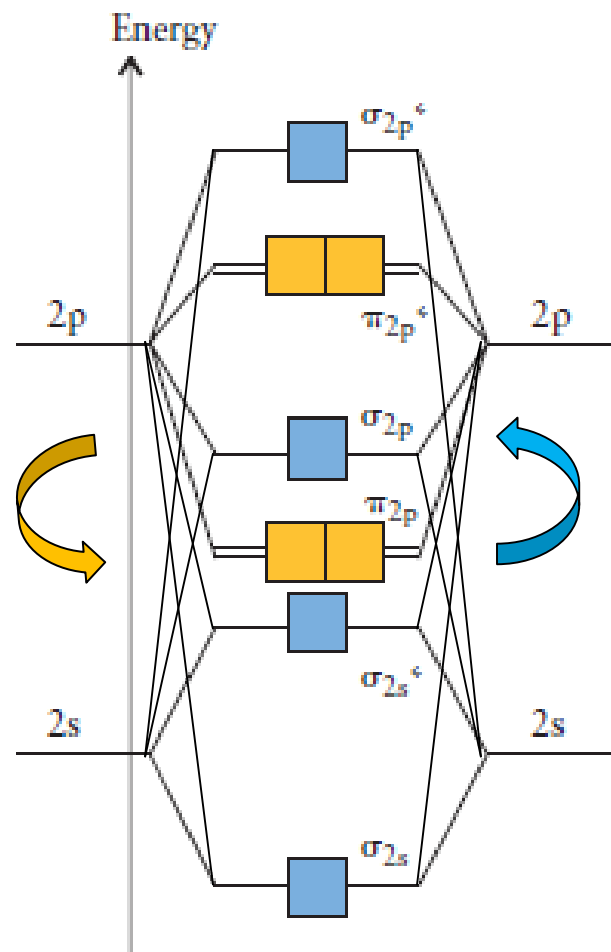
# Second-Row Diatomic Molecules – O<sub>2</sub> and F<sub>2</sub>

- For electron “rich” atoms, O<sub>2</sub>, F<sub>2</sub>, due to the **shielding** effect, the energy difference between 2s and 2p orbitals is large.
- Because the energy difference between 2s and 2p is large, the combination between 2s and 2p orbitals is too weak to count, the energy levels are “normal”
- Since the head-to-head overlap is large, the  $\sigma_{2p}$  orbital is more stable than the  $\pi$ -orbitals as bonding orbitals. The antibonding is reversed proportionally.



# Second-Row Diatomic Molecules – B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>

- For electron poor molecules B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>. Because the energy difference between 2s and 2p is small, 2s and 2p orbitals can be mixed in forming the MO orbitals.
- The combination of four symmetry matched orbitals (two s and two p) forms 4  $\sigma$  type MO orbitals.
- The energy levels are changed so that both  $\sigma_{2p}$  and  $\sigma_{2p}^*$  are pushed higher. **This leads to  $\sigma_{2p}$  is higher than  $\pi_{2p}$** , but  $\sigma_{2p}^*$  is still higher than  $\pi_{2p}^*$ .



# Second-Row Diatomic Molecules

	Large 2s-2p interaction			Small 2s-2p interaction		
	B <sub>2</sub>	C <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	F <sub>2</sub>	Ne <sub>2</sub>
$\sigma_{2p}^*$	<div>□</div>	<div>□</div>	<div>□</div>	<div>□</div>	<div>□</div>	<div>↑↓</div>
$\pi_{2p}^*$	<div>□ □</div>	<div>□ □</div>	<div>□ □</div>	<div>↑ ↑</div>	<div>↑↓ ↑↓</div>	<div>↑↓ ↑↓</div>
$\sigma_{2p}$	<div>□</div>	<div>□</div>	<div>↑↓</div>	<div>↑↓ ↑↓</div>	<div>↑↓ ↑↓</div>	<div>↑↓ ↑↓</div>
$\pi_{2p}$	<div>↑ ↑</div>	<div>↑↓ ↑↓</div>	<div>↑↓ ↑↓</div>	<div>□</div>	<div>□</div>	<div>↑↓</div>
$\sigma_{2s}^*$	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>
$\sigma_{2s}$	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>	<div>↑↓</div>
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	□
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	□
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	□

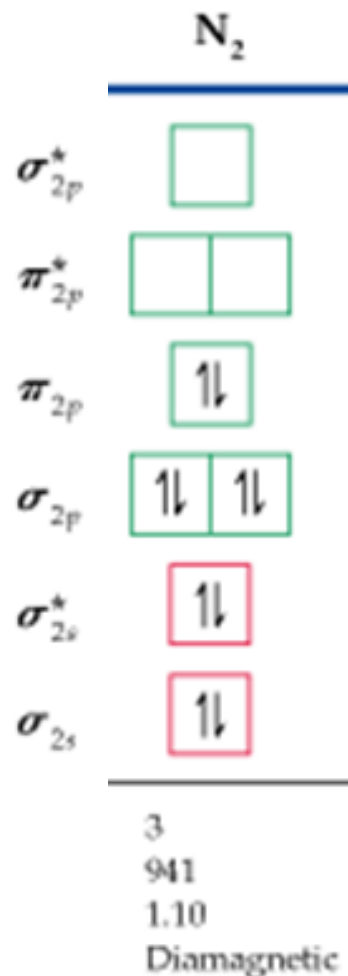
**Bond Order** and **Bond Lengths** are obtained, we will discuss some of them.

**Bond enthalpy** can be considered as bond energy for now, we will explain what is enthalpy.

**Paramagnetic** – respond to magnetic field, has unpaired electrons; **diamagnetic** – does not respond to magnetic field, all electrons are paired.



# Diatomic Molecule N<sub>2</sub>

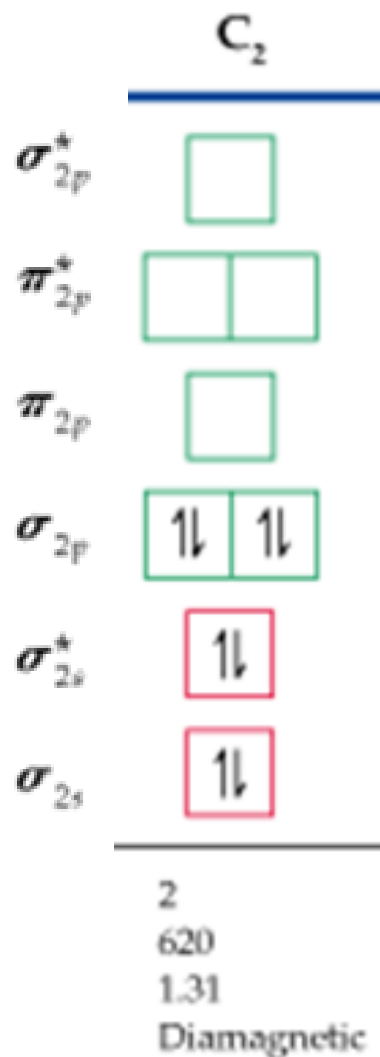


The Lewis symbol is:  
:N≡N:

MO theory:

- ✓ BO=3, agree with Lewis and VB
- ✓ The three bonds are two  $\pi$  bonds and one  $\sigma$  bonds, agree with VB theory.
- ✓ The lone-pairs are actually from 2s orbitals that form nonbonding orbitals.

# Diatomic Molecule C<sub>2</sub>



The Lewis symbol (octet) is: **C≡C**

Cannot explain the bond strength and bond length

MO theory:

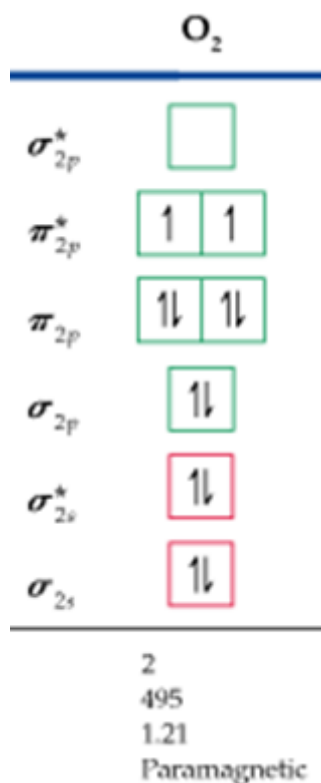
- ✓ BO=2
- ✓ The two bonds are two  $\pi$  bonds only.  
There is no  $\sigma$  bond
- ✓ The lone-pairs are formed by 2s orbitals
- ✓ So a proper Lewis symbol (non-octet) should be:



# Diatomic Molecule O<sub>2</sub>

Lewis symbol:  $\ddot{\text{O}}=\ddot{\text{O}}$

All electrons are paired. However, oxygen is a paramagnetic



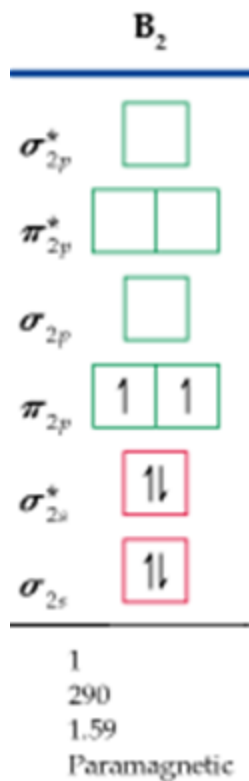
MO Theory:

- ✓ BO=2
- ✓ The two bonds are one normal  $\sigma$  bond, two  $\pi$ -bonding and one  $\pi$ -antibonding.
- ✓ The lone-pairs are formed by 2s orbitals as well.
- ✓ There are unpaired electrons – paramagnetic.



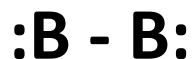
# Diatomic Molecule B<sub>2</sub>

Lewis symbol is an exception anyway.



MO Theory:

- ✓ BO=1
- ✓ However, the bond is special, it is two  $\pi$ -bonding orbitals each occupied by one electron.
- ✓ The lone-pairs are formed by 2s orbitals as well.
- ✓ There are unpaired electrons – paramagnetic.
- ✓ So a proper Lewis symbol (non-octet) should be:

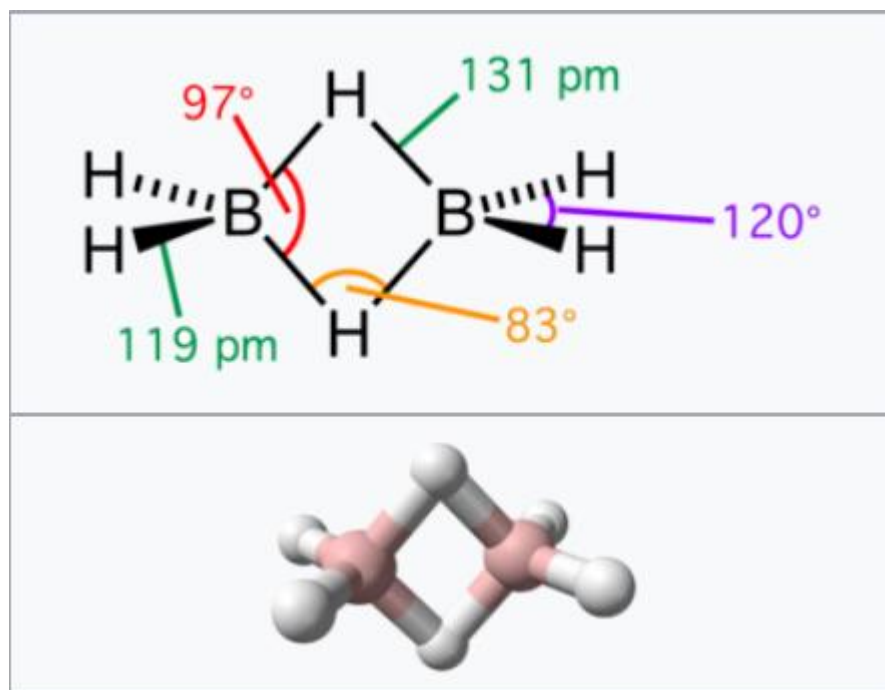


# Diborane $B_2H_6$

Lewis's theory fails to account for the compound **diborane**,  $B_2H_6$ .

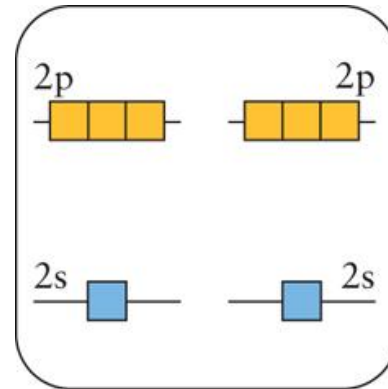
The problem is that diborane has only **12** valence electrons.

MO theory predicts the **bridge hydrogen** structure.

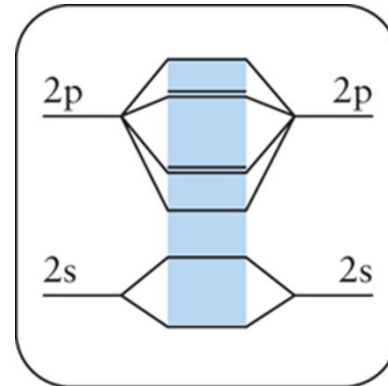


Self-test 4.10B Suggest a configuration for the  $\text{O}_2^+$  ion and state its bond order.

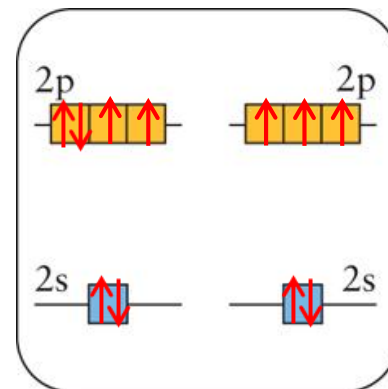
Identify the valence atomic orbitals.



Construct the molecular orbital energy level diagram.

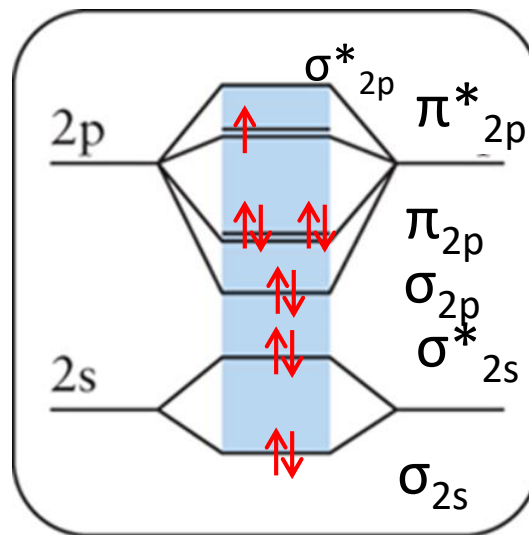


Count the valence electrons.



$$\text{O}_2^+: 6 + 6 - 1 = 11$$

Construct the electron configuration.



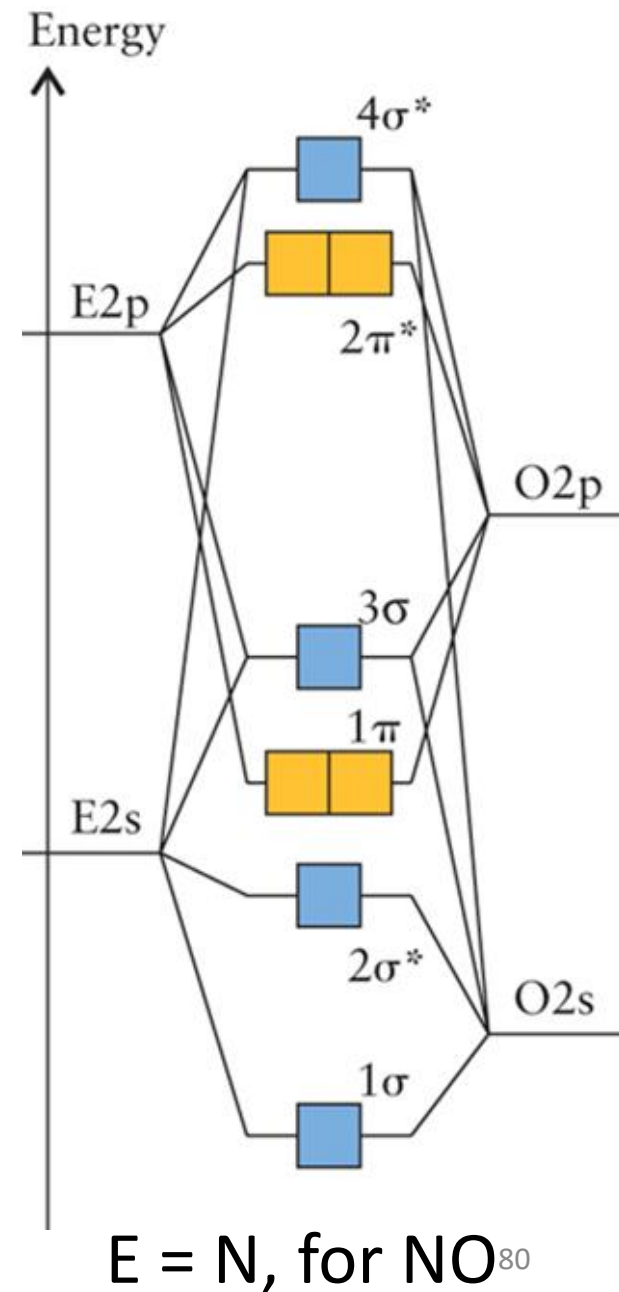
Determine the bond order

$$\text{The bond order for } O_2^+ = \frac{1}{2} (8 - 3) = 2.5$$

Paramagnetic, at least one MO has an unpaired electron.

# Bonding in Heteronuclear Diatomic Molecules

- The bond in a heteronuclear diatomic molecule has unequal sharing of AOs:
$$\psi = c_A\varphi_A + c_B\varphi_B$$
- The more electronegative element has lower energy, it's AO dominating the MO.
- The names of MOs are different as it is not clear how the MO is made.
- The s-p interaction applies, so  $3\sigma$  is higher than  $1\pi$ .



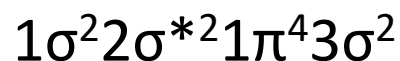


Self-test 4.11B Write the configuration of the ground state of the cyanide ion,  $\text{CN}^-$ , assuming that its molecular orbital energy-level diagram is the same as that for NO.

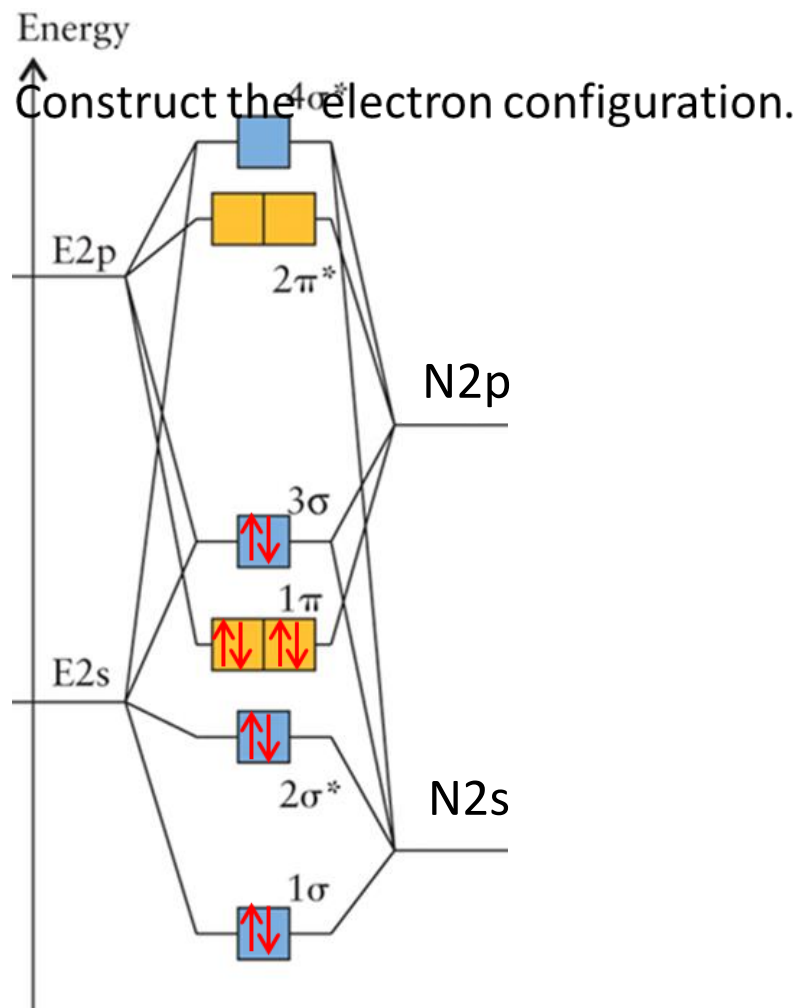
- Count the valence electrons:

$$\text{CN}^- : 4 + 5 + 1 = 10$$

- The configuration is



- The  $\text{BO} = 3$
- It is diamagnetic

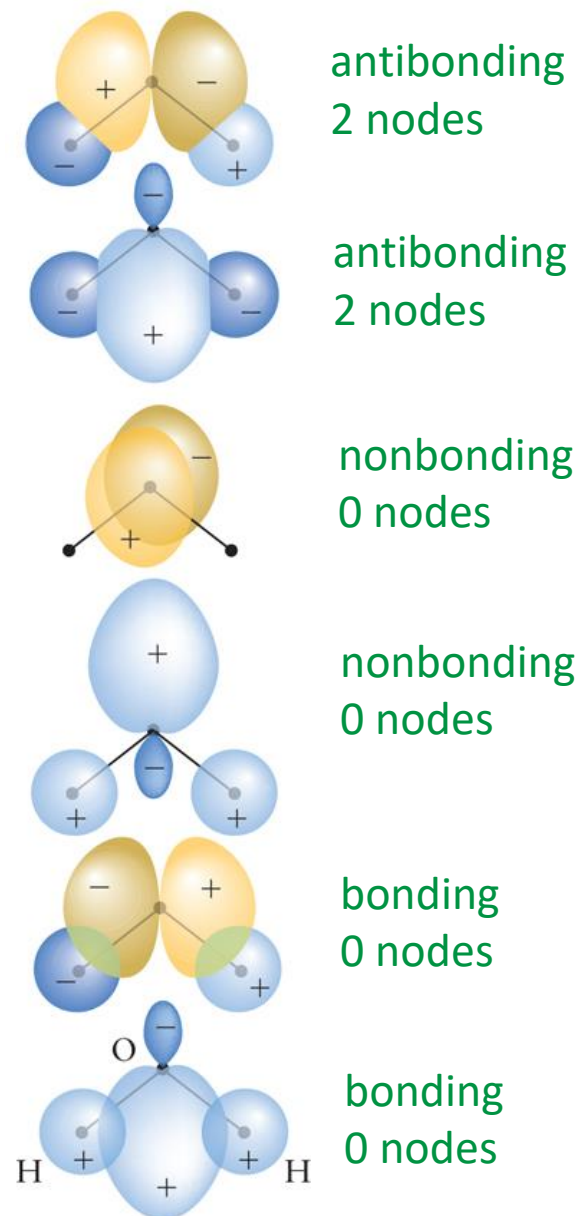


# Bonding in Polyatomic Molecule : Water

Water has 6 valence AOs (one  $2s$ , three  $2p$  from oxygen and two  $1s$  from hydrogen), 8 valence electrons.

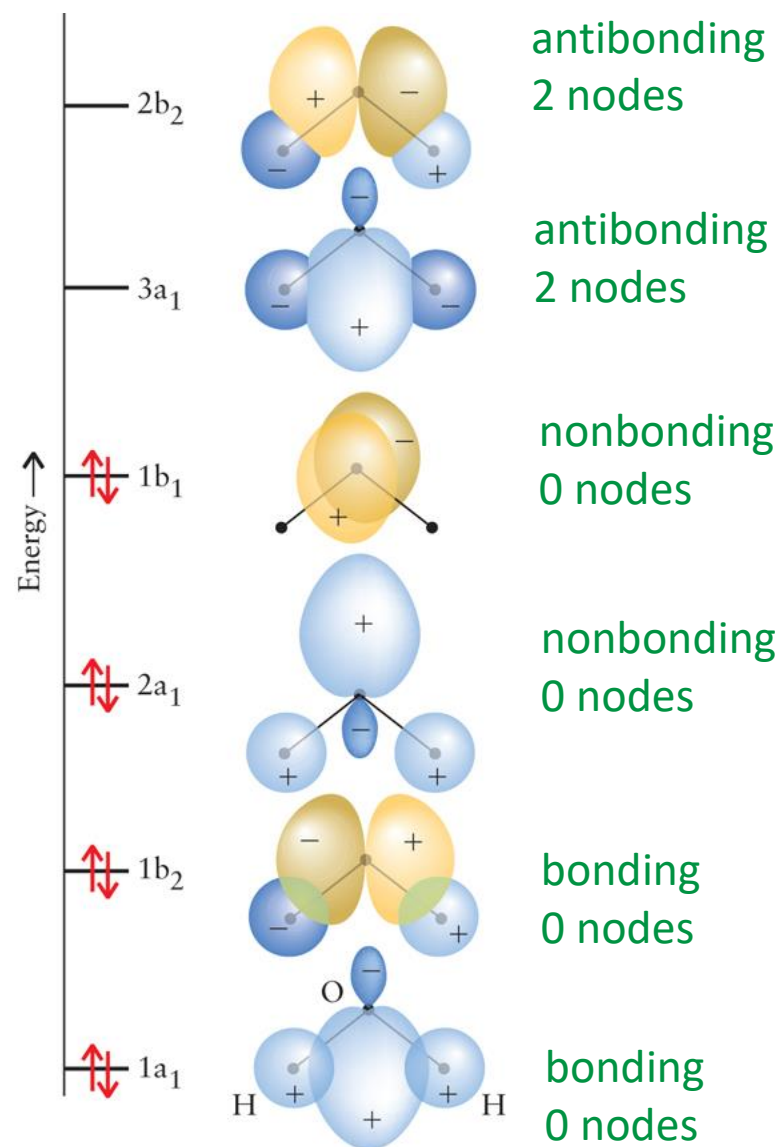
Combination of these 6 AOs makes 6 Mos.:

- Two **bonding** orbitals having no node on the bonds.
- Two **nonbonding** orbitals having no interaction along the bonds
- Two **antibonding** orbitals having nodes on the bonds.



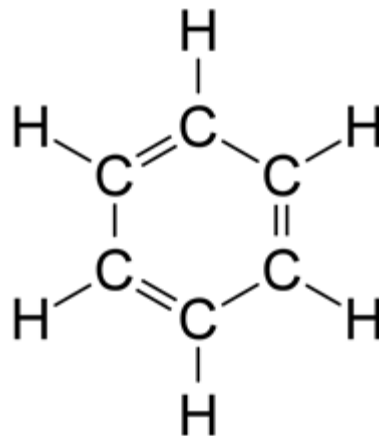
# Bonding in Polyatomic Molecule : Water

- The occupied orbitals show:
  - 2 bonding orbitals are two OH bonds
  - 2 nonbonding orbitals are 2 lone-pairs
- The picture is **consistent** with Valence Bond theory.
- However, the bonds are **not localized**, electrons are distributed in space to hold the atoms together. – which is **contrast** to the VB theory,

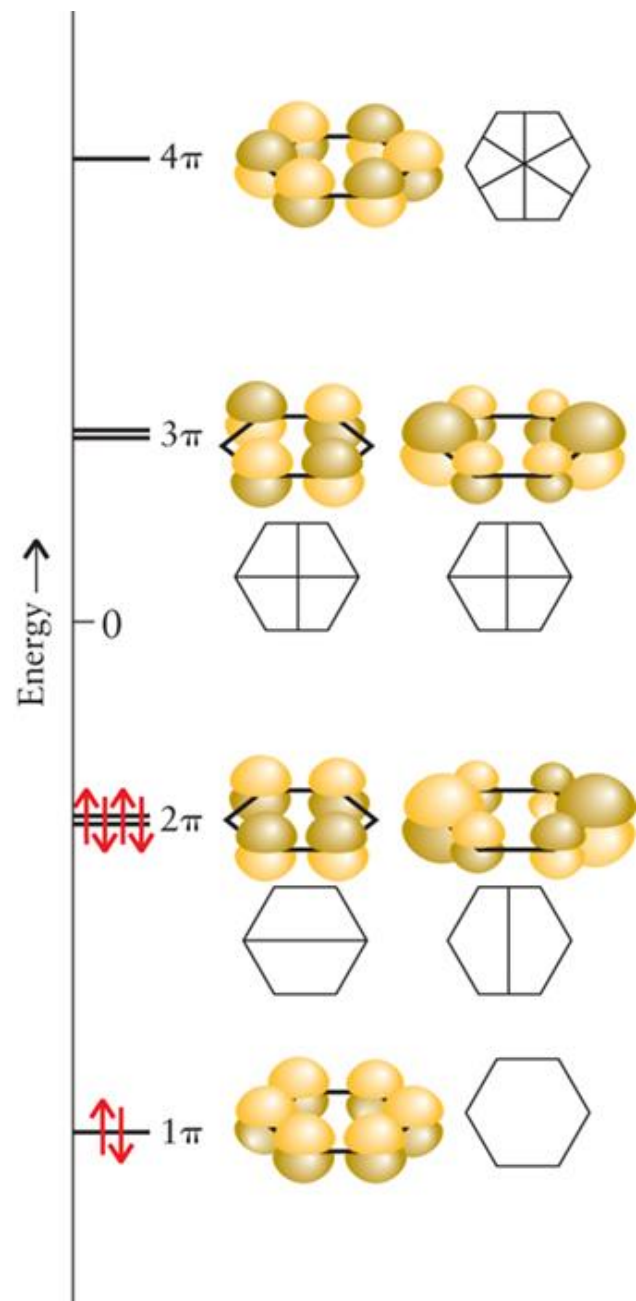


# Bonding in Polyatomic Molecule : Benzene

- C : 4 valence AOs, H : 1 valence AO, there are  $6 \times 4 + 6 = 30$  valence AOs, making 30 MOs.
- There are 30 electrons, 15 MOs are occupied, 15 MOs are unoccupied.
- The occupied 15 MOs are: 6 C-C bonds, 6 C-H bonds, and 3  $\pi$  bonds.



# $\pi$ - Bonding in Benzene



The six  $\pi$  MOs are combinations of six  $2p_z$  orbitals perpendicular to the molecular plane.

- One has no node, the lowest in energy, bonding.
- Two having one nodal plane are the second lowest in energy, degenerated, bonding.
- Next two having two nodal planes are even higher in energy, anti-bonding.
- One having 3 nodal planes are the highest orbital, anti-bonding

Six electrons occupy the lower three orbitals.  $BO=3$ .

6 atoms lined up in a row, each has one electron. What are the wave functions that are required to describe the 6 electrons?

- 6 MOs from 6 AOs
- Each MO has accommodate two electrons
- The lowest energy MO, has no node, the second lowest has one, and the third has two node, and so on.
- This is similar to the 1-D **Particle in Box** Model.
- First three are occupied.