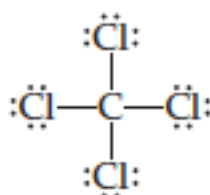


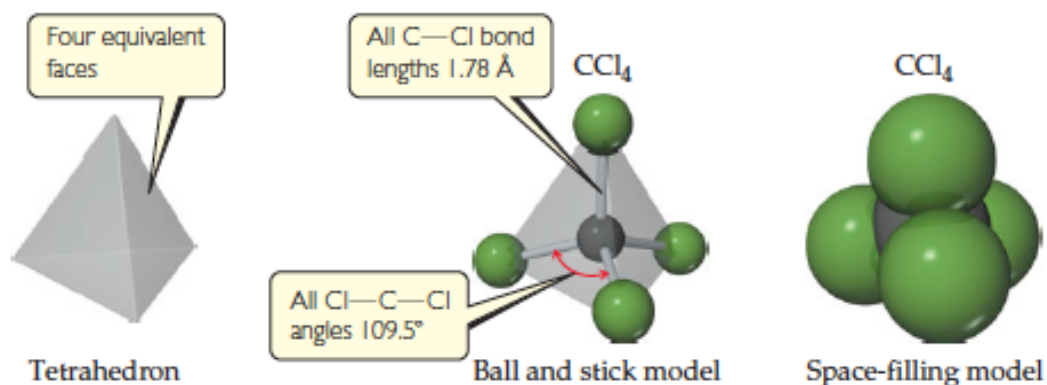
## Valence Shell Electron Pair Repulsion (VSEPR)

### 9.1 Molecular Shapes

The Lewis structure is drawn with the atoms all in the same plane. Lewis structures, however, do not indicate the shapes of molecules; they simply show the number and types of bonds.



The shape of a molecule is determined by its bond angles, the angles made by the lines joining the nuclei of the atoms in the molecule.



In order to predict the molecular shape, we assume that the valence electrons repel each other. Therefore, the molecule adopts the three-dimensional geometry that maximizes repulsion. We call this model the **Valence Shell Electron Pair Repulsion (VSEPR)** model.

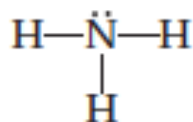
### 9.2 The VSEPR Model.

A covalent bond forms between two atoms when a pair of electrons occupies the space between the atoms. This is a bonding pair of electrons. Such a region is an electron domain.

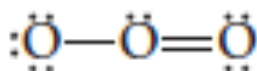
A nonbonding pair or lone pair of electrons defines an electron domain located principally on one atom.

In general, each nonbonding pair, single bond, or multiple bond produces a single electron domain around the central atom in a molecule.

Example  $\text{NH}_3$  has three bonding pairs and one lone pair (four electron domains)



$\text{O}_3$  has three electron domains around the central oxygen atom (a single bond, a double bond, and a nonbonding pair of electrons):



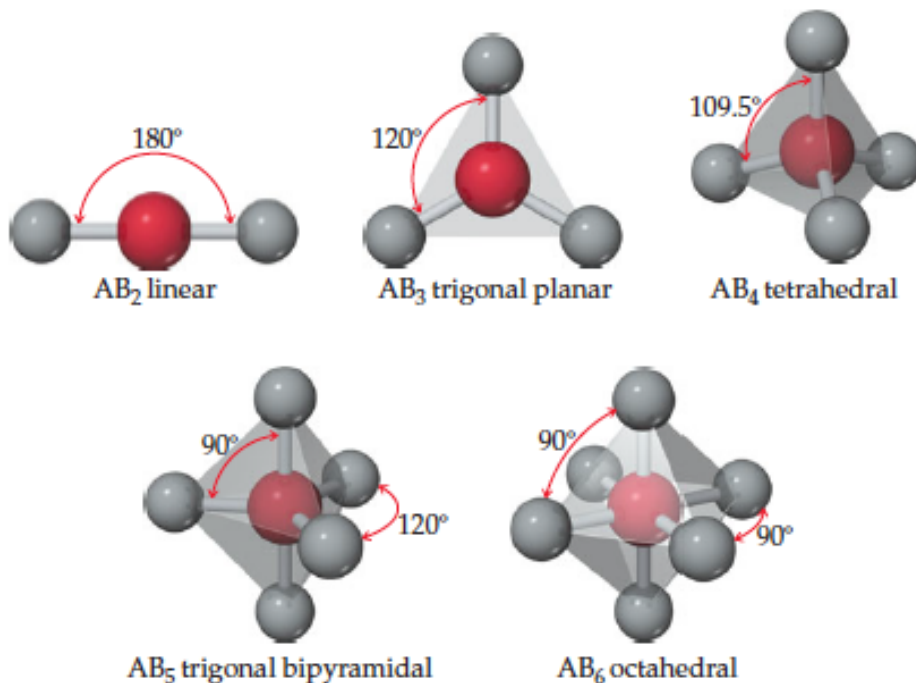
VSEPR predicts the the best arrangement of electrons is the one that maximizes the repulsion among them.

The arrangement of electron domain about the central atom of an  $\text{AB}_n$  molecule is its electron-domain geometry. The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them.

There are five different electron-domain geometries:

Linear (two electron domains), trigonal planar (three electron domains), tetrahedral (four domains), trigonal bipyramidal (five domains) and octahedral (six domains).

**Shapes allowing maximum distances between atoms in  $\text{AB}_n$  molecules.**

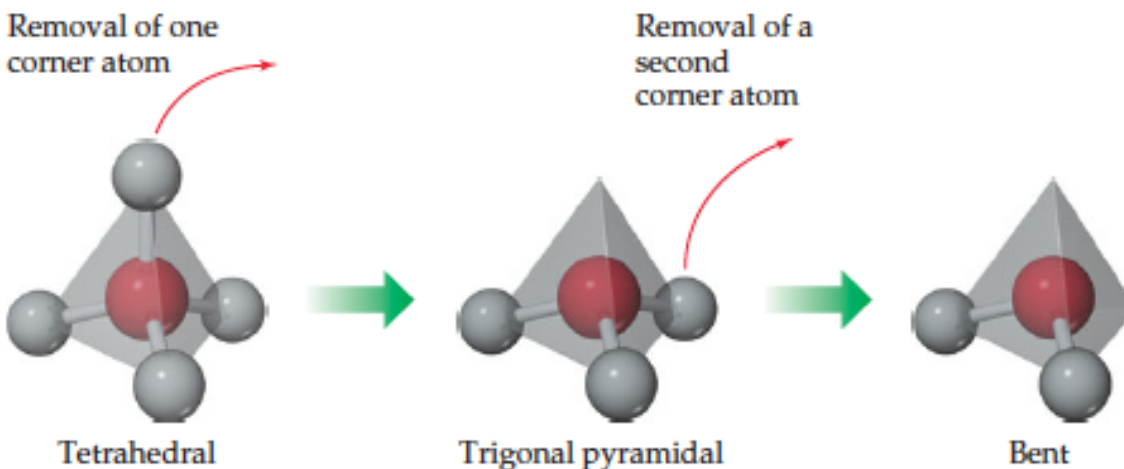


The molecular geometry is the arrangement of the atoms in space. To determine the shape of the molecule, we distinguish between lone pairs and bonding pairs.

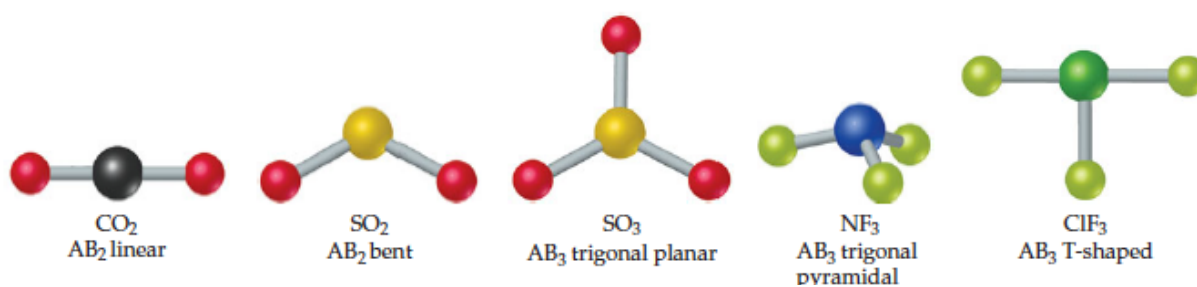
1- We use the electron domain geometry to help us predict the molecular geometry.

2- Determine the three-dimensional structure of the molecule. We ignore lone pairs in the molecular geometry.

### Derivatives of the tetrahedral molecular shape.

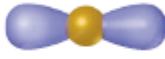


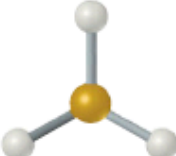
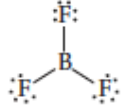
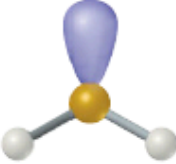
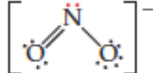

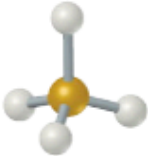
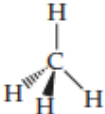
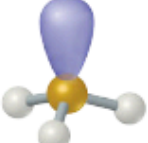
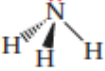




### Shapes of AB<sub>2</sub> and AB<sub>3</sub> molecules.

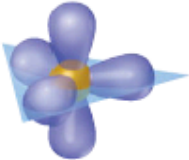
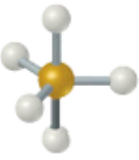
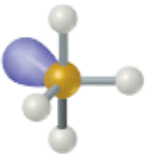



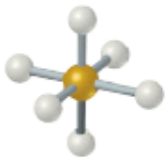

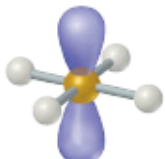


We will encounter 11 basic molecular shapes.

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

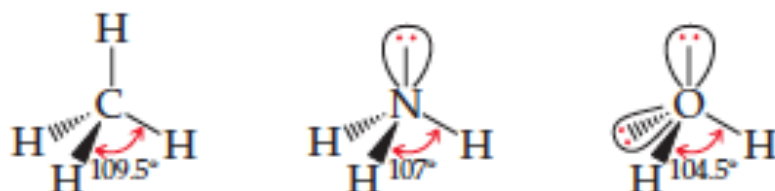
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
3	 Trigonal planar	3	0	 Trigonal planar	
		2	1	 Bent	
4	 Tetrahedral	4	0	 Tetrahedral	
		3	1	 Trigonal pyramidal	
		2	2	 Bent	

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

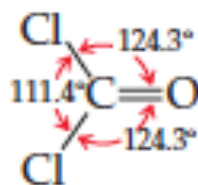
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	$\text{PCl}_5$
		4	1	 Seesaw	$\text{SF}_4$
		3	2	 T-shaped	$\text{ClF}_3$
		2	3	 Linear	$\text{XeF}_2$
6	 Octahedral	6	0	 Octahedral	$\text{SF}_6$
		5	1	 Square pyramidal	$\text{BrF}_5$
		4	2	 Square planar	$\text{XeF}_4$

### 9.3 Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

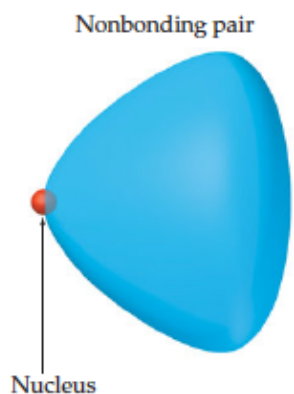
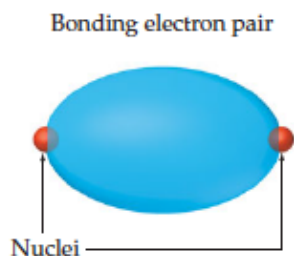
Electron domains for nonbonding electron pairs exert greater repulsive forces on adjacent electron domains and tend to compress bond angles.



Electron domains for multiple bonds exert a greater repulsive force on adjacent electron domains than do electron domains for single bonds.

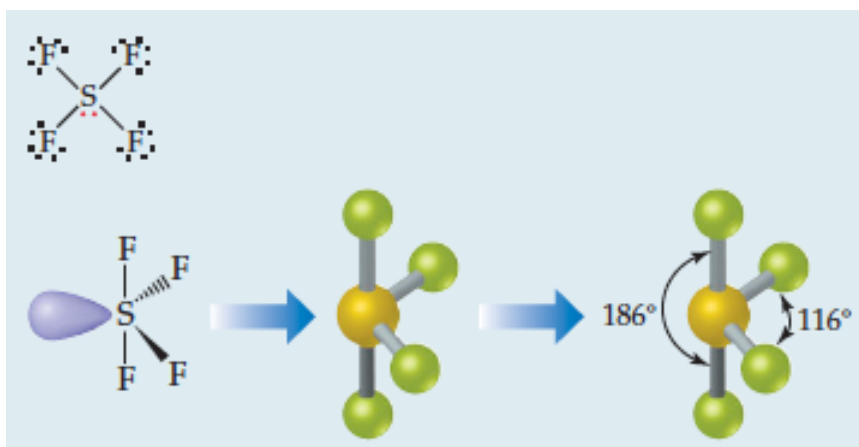


Relative volumes occupied by bonding and nonbonding electron domains.

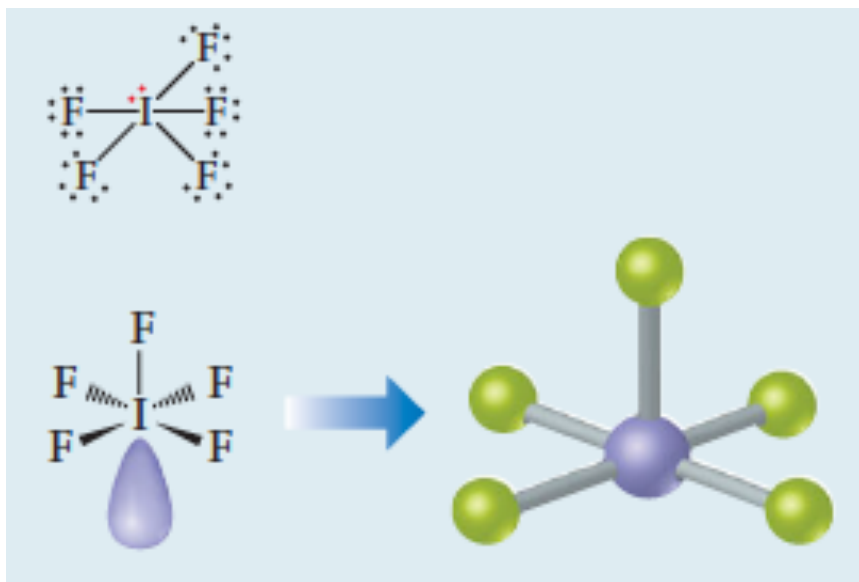


Example: Use the VSEPR model to predict the molecular geometry of (a) SF<sub>4</sub>, (b) IF<sub>5</sub>.

a) Lewis structure and seesaw shaped



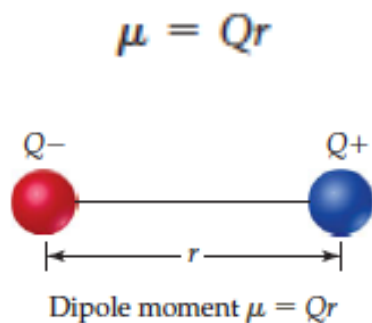
b) Lewis structure and square pyramidal.



## 9.4 : MOLECULAR SHAPE AND MOLECULAR POLARITY

Polar molecules interact with electric fields.

Whenever two electrical charges of equal magnitude but opposite sign are separated by a distance, a dipole is established. The quantitative measure of the magnitude of a dipole is called its dipole moment. If two equal and opposite charges  $Q^+$  and  $Q^-$  are separated by a distance  $r$ , the magnitude of the dipole moment is the product of  $Q$  and  $r$  :



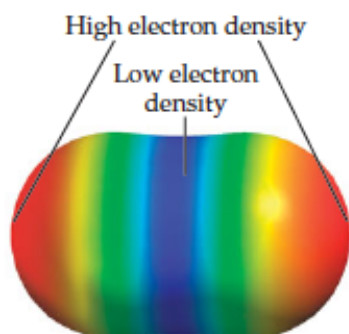
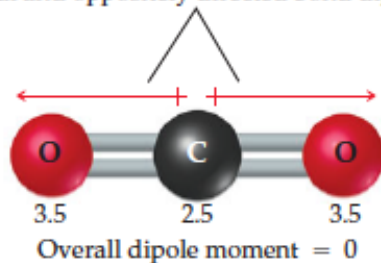
Bond polarity is a measure of how equally the electrons in a bond are shared between the two atoms of the bond. As the difference in electronegativity between the two atoms increases, so does the bond polarity. The dipole moment of a diatomic molecule is a measure of the amount of charge separation in the molecule.

For a molecule consisting of more than two atoms, the dipole moment depends on both the polarities of the individual bonds and the geometry of the molecule. For each bond in the molecule, we consider the bond dipole, which is the dipole moment due only to the two atoms in that bond. Because both bond dipole and dipole moments are vector quantities, the orientation of these individual dipole moments determines whether the molecule has an overall dipole moment.

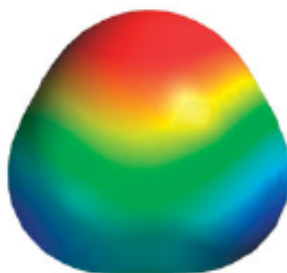
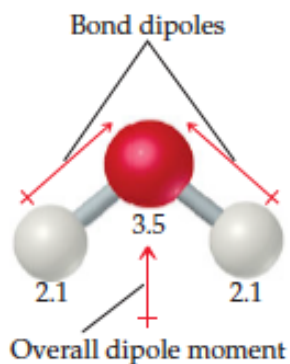


**Example:** CO<sub>2</sub> a nonpolar molecule. The numbers are electronegativity values for these two atoms.

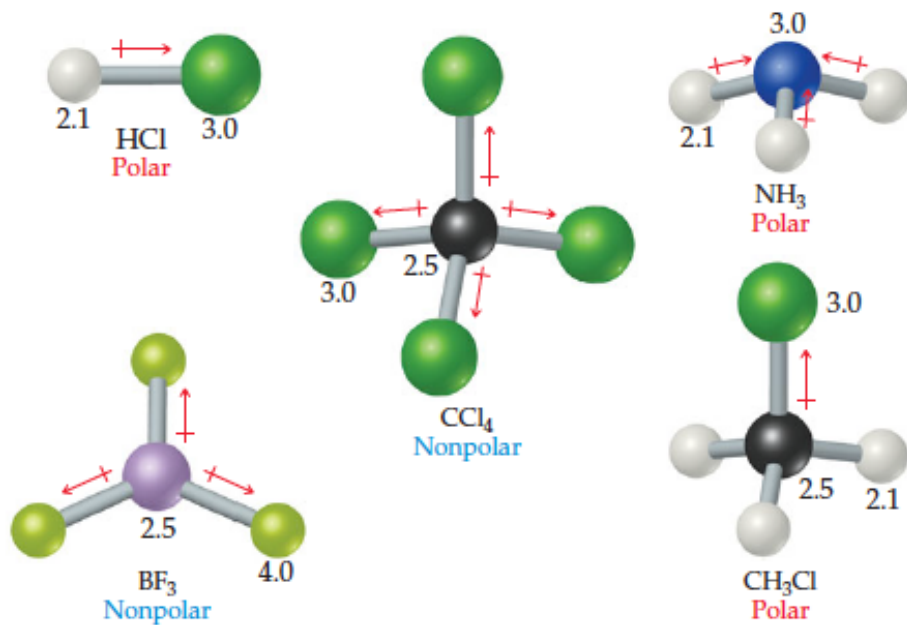
Equal and oppositely directed bond dipoles



H<sub>2</sub>O, a polar molecule. The numbers are electronegativity values.



Polar and nonpolar molecules containing polar bonds. The numbers are electronegativity values.



## 9.5: COVALENT BONDING AND ORBITAL OVERLAP

A covalent bond forms when the orbitals of two atoms overlap

The shared region of space between the orbitals is called the orbital overlap.

There are two electrons (usually one from each atom) of opposite spin in the orbital overlap.

As the two nuclei approach each other, their atomic orbitals overlap.

As the amount of overlap increases, the energy of interaction decreases.

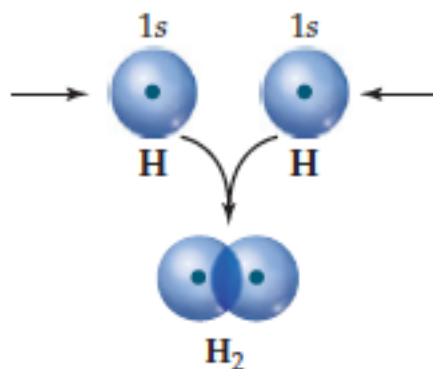
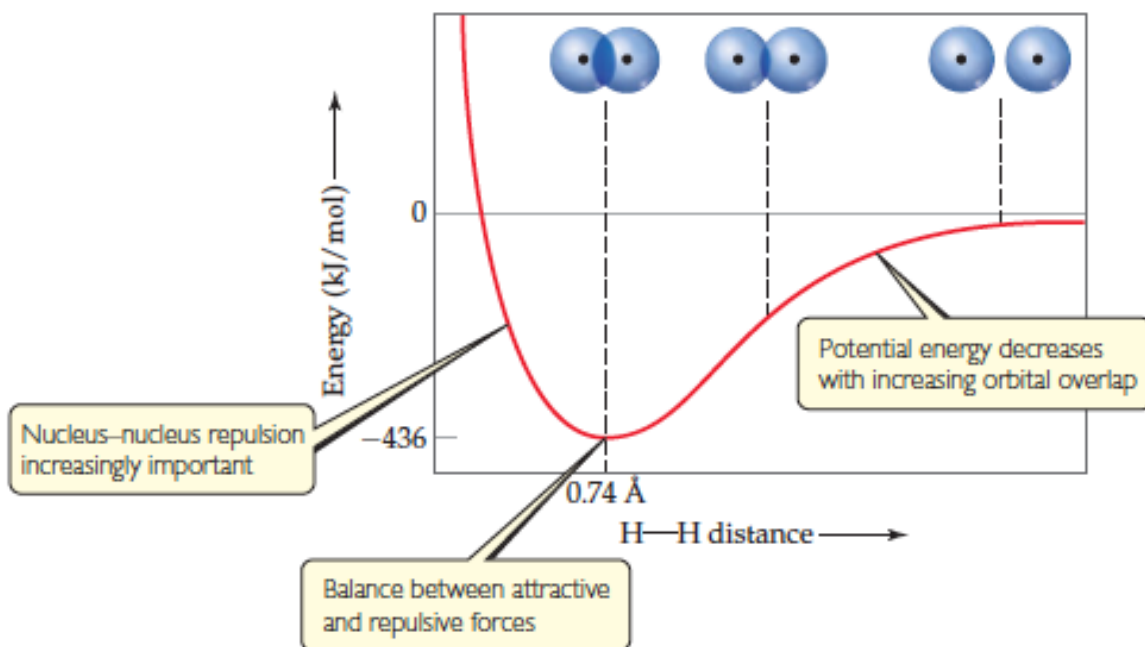
At some distance the minimum energy is reached.

The minimum energy corresponds to the bonding distance (or bond length).

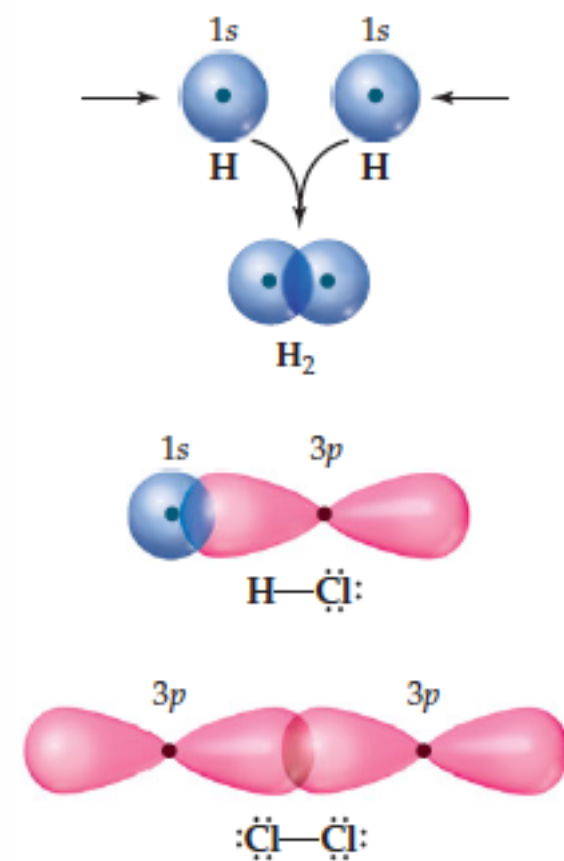
As two atoms get closer, the nuclei begin to repel and the energy increases.

At the bonding distance, the attractive forces between nuclei and electrons just balance the repulsive forces (nucleus-nucleus, electron-electron).

Covalent bonds in  $H_2$ . Formation of the  $H_2$  molecule as atomic orbitals overlap.

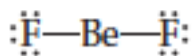


Covalent bonds in  $\text{H}_2$ ,  $\text{HCl}$ , and  $\text{Cl}_2$  result from overlap of atomic orbitals.

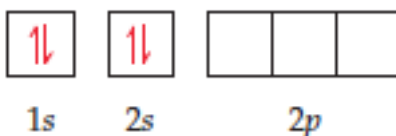


## 9.6: Hybrid Orbitals.

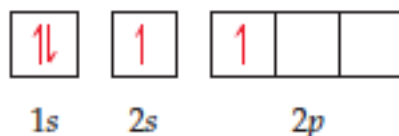
Consider the  $\text{BeF}_2$  molecule, which has the Lewis structure



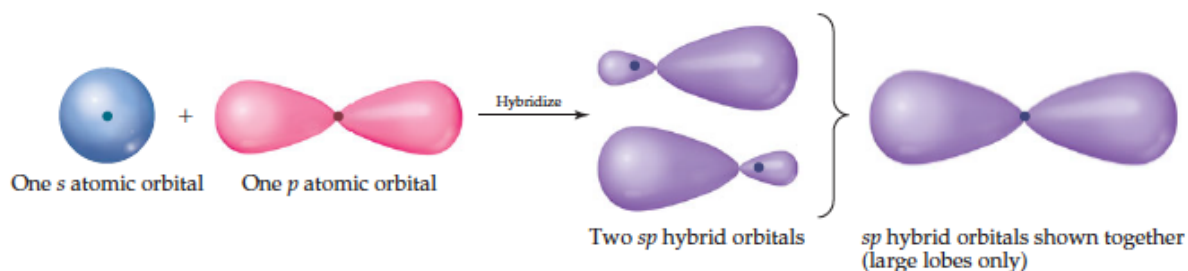
Be has the a  $1S^2, 2S^2$  electron configurations. F has a  $(1S^2, 2S^2, 2P^5)$  electron configuration. There is no unpaired electron available for bonding. The orbital diagram for a ground-state Be atom is:



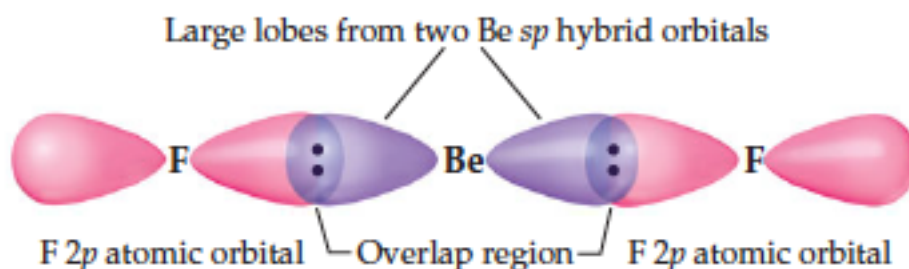
We can solve the problem by allowing by “promoting” one of the 2s electrons to a 2p orbital: The 2S and 2P orbital on Be to mix or form two new **hybrid orbitals** ( a process called **hybridization**)



Because we have hybridized one s and one p orbital, we call each hybrid an sp hybrid orbital. According to the valence-bond model, a linear arrangement of electron domains implies sp hybridization. The two lobes of the sp orbitals are  $180^\circ$  apart.



The electrons in the  $sp$  hybrid orbitals form shared electron bonds with the two fluorine orbitals.

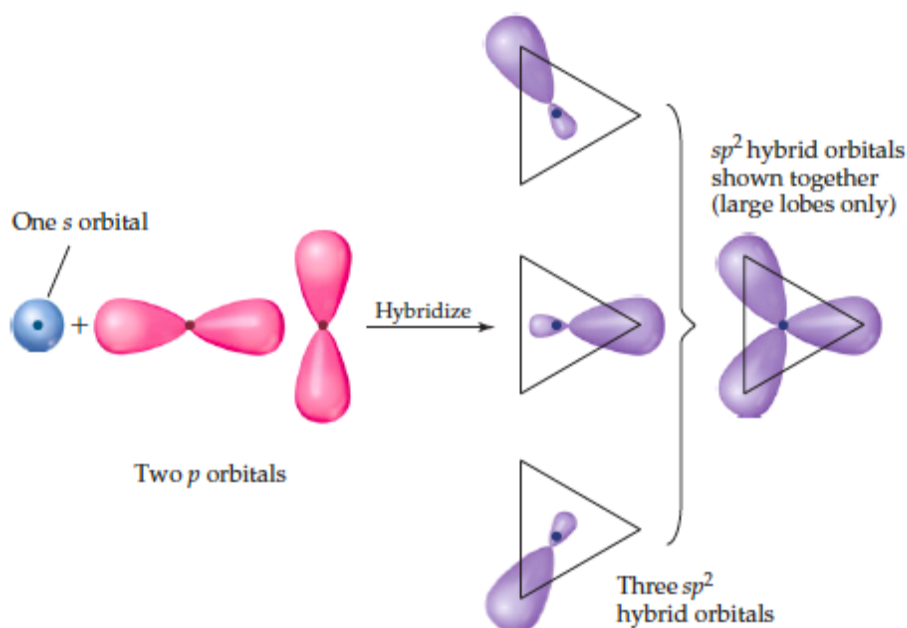


### 9.7: $sp^2$ and $sp^3$ hybrid orbitals.

Important: When we mix  $n$  atomic orbitals, we must get  $n$  hybrid orbitals.

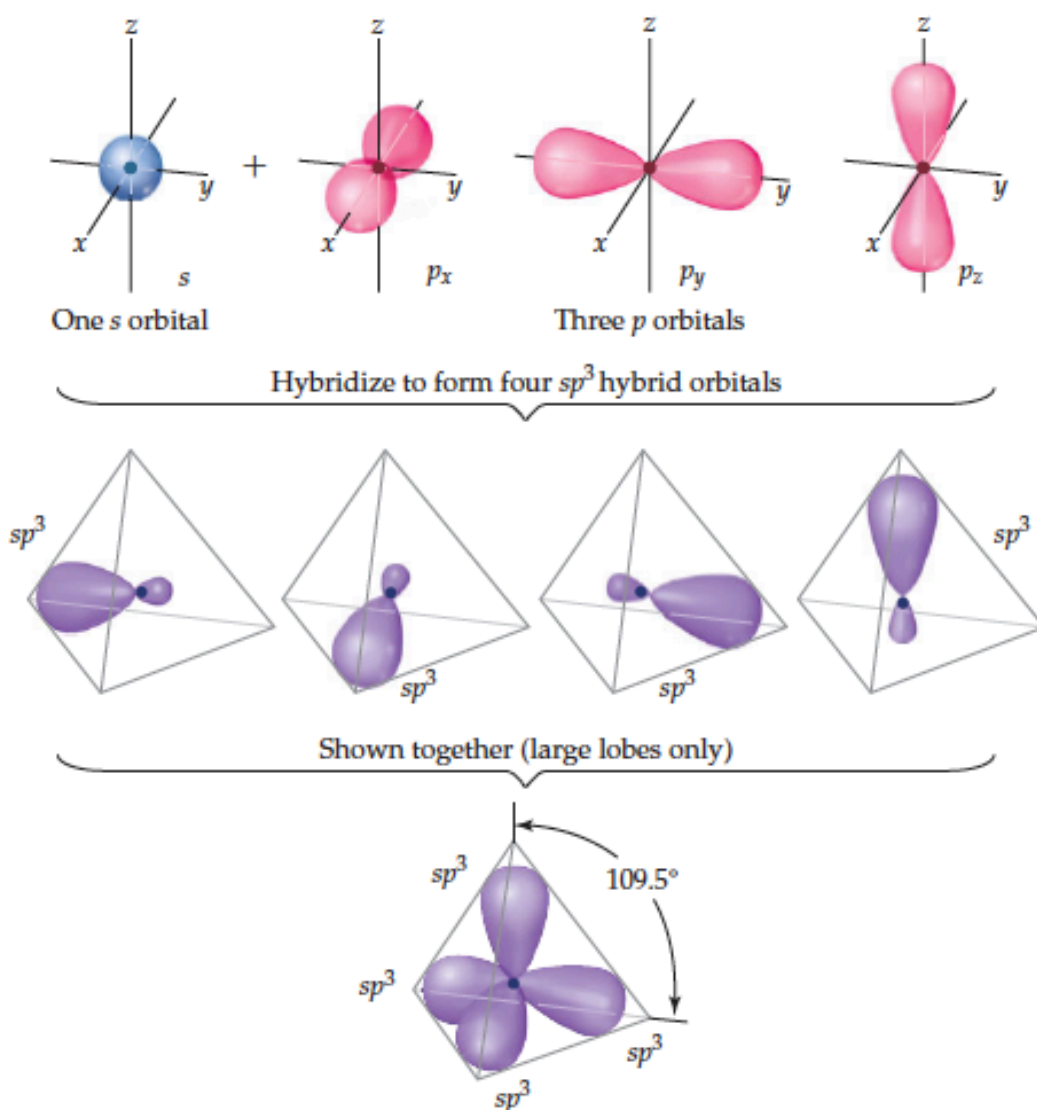
Three  $sp^2$  hybrid orbitals are formed from hybridization of one  $s$  and two  $p$  orbitals. An unfilled  $2p$  atomic orbital remains unhybridized. The three  $sp^2$  hybrid orbitals lie in the same plane,  $120^\circ$  apart from one another. Molecules with trigonal planar electron-pair geometry have  $sp^2$  orbitals on the central atom.

Example : The 3  $sp^2$  hybrid orbitals are used to make three equivalent bonds with the three fluorine atoms, leading to the trigonal-planar molecular geometry of  $BF_3$ .



Four  $sp^3$  hybrid orbitals are formed from hybridization of one  $s$  and three  $p$  orbitals. Therefore, there are four large lobes. Each lobe points toward the vertex of a tetrahedron. The angle between the lobes is  $109.5^\circ$ . Molecules with tetrahedral electron-pair geometry have  $sp^3$  orbitals on the central atom.

### Example $CH_4$

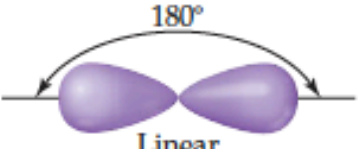
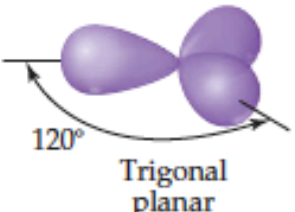
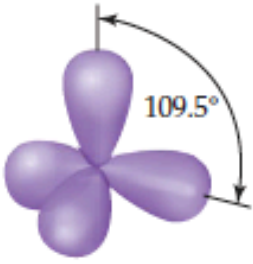


**Summary:** We need to know the electron-domain geometry before we can assign hybridization.

The following steps allow us to describe the hybrid orbitals used by an atom in bonding:

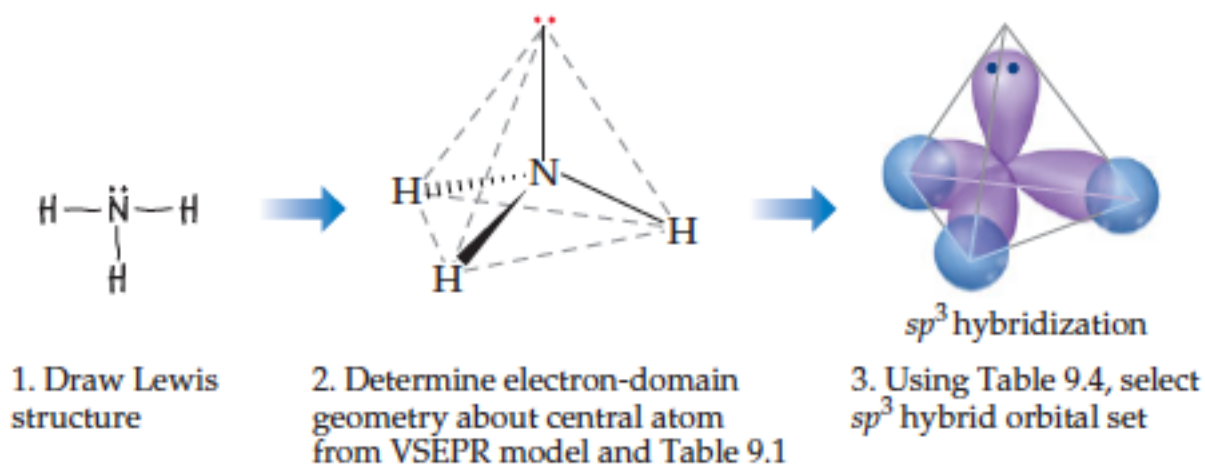
1. Draw the Lewis structure for the molecule or ion.
2. Use the VSEPR model to determine the electron-domain geometry around the central atom.
3. Specify the hybrid orbitals needed to accommodate the electron pairs based on their geometric arrangement (Table 9.4 below)

**TABLE 9.4 • Geometric Arrangements Characteristic of Hybrid Orbital Sets**

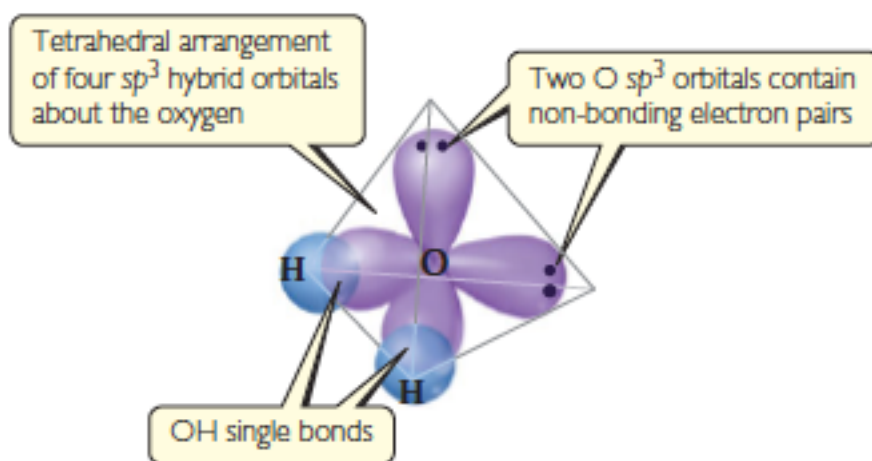
Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
$s, p$	Two $sp$	 <p>Linear</p>	$\text{BeF}_2, \text{HgCl}_2$
$s, p, p$	Three $sp^2$	 <p>Trigonal planar</p>	$\text{BF}_3, \text{SO}_3$
$s, p, p, p$	Four $sp^3$	 <p>Tetrahedral</p>	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$



### Example NH<sub>3</sub>



### Example H<sub>2</sub>O



## Multiple Bonds

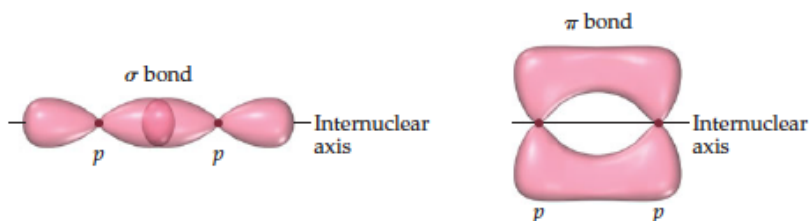
Covalent bonds in which the electron density lies along the line connecting the atoms (the internuclear axis) are called sigma bonds.

Sigma bonds: electron density lies on the axis between the nuclei.

All single bonds are sigma bonds.

### Multiple bonds.

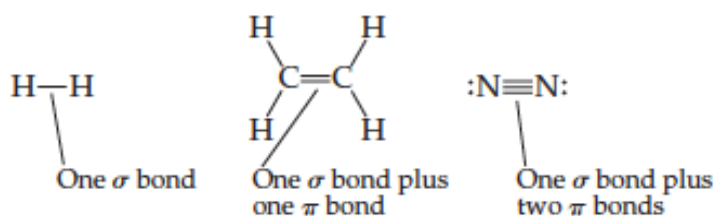
Pi bonds: electron density lies above and below the plane of the nuclei



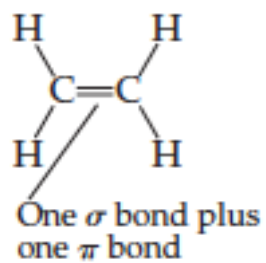
A double bond consists of one sigma bond and one pi bond.

A triple bond consists of one sigma bond and two pi bonds.

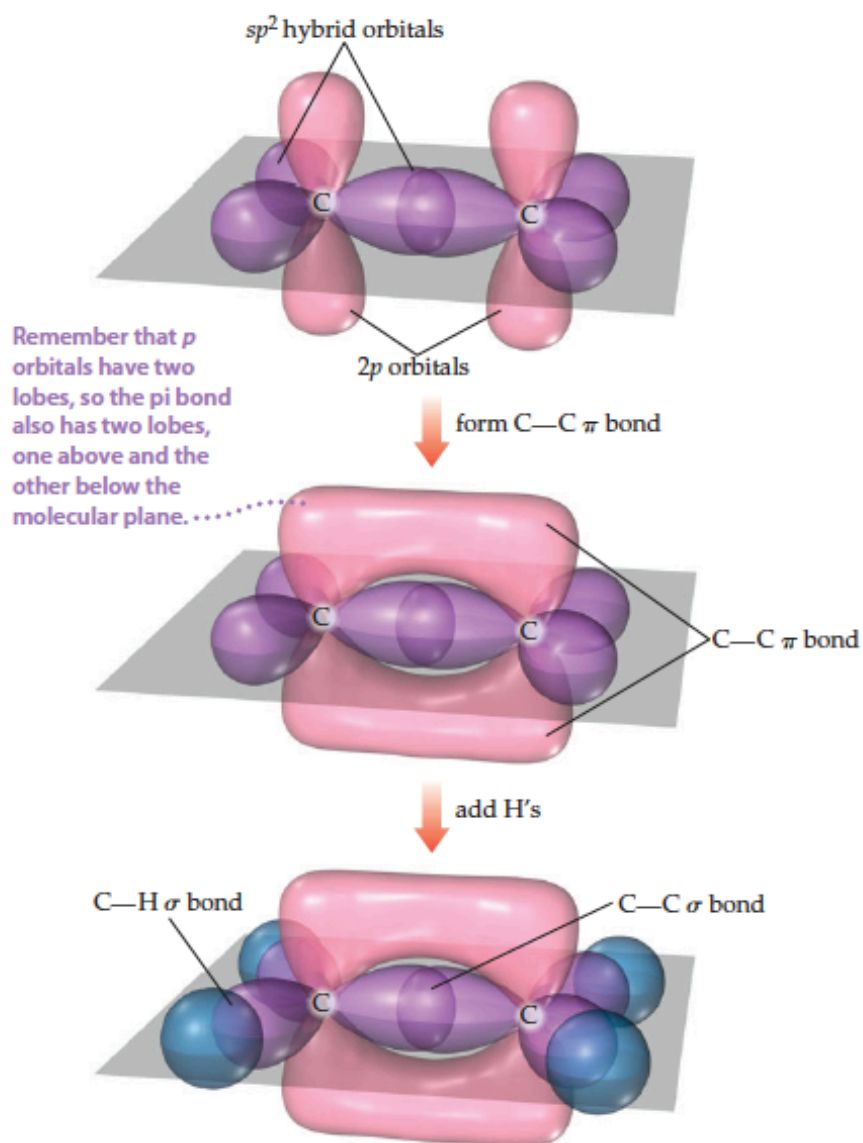
Often, the p orbitals involved in the pi bonding come from unhybridized orbitals.



Example: Ethylene  $C_2H_4$



Both C atoms are  $sp^2$  hybridized. Both C comes with trigonal planar electron pair and molecular geometry



### Example C<sub>2</sub>H<sub>2</sub>



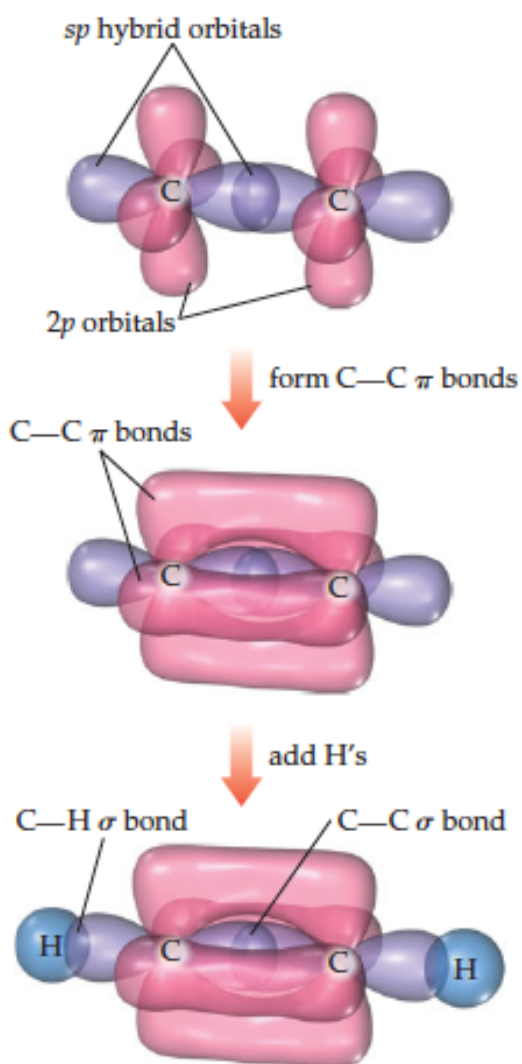
The electron-domain geometry of each C is linear.

Therefore, C atoms are SP hybridized.

The sp hybrid orbitals form the C-C and C-H sigma bonds.

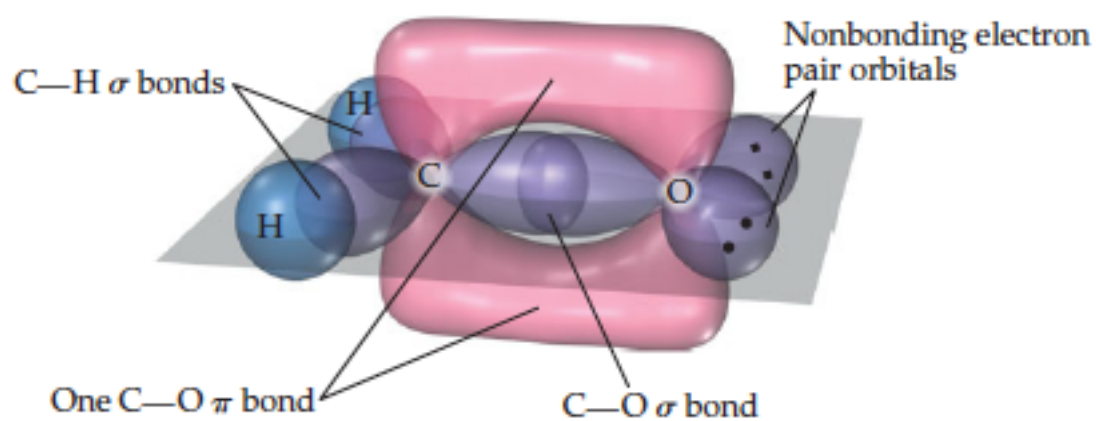
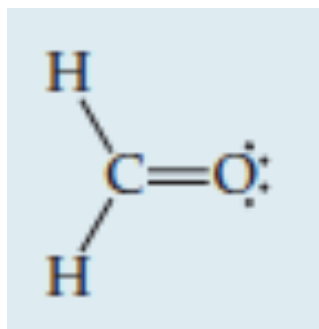
There are two unhybridized p orbitals on each C atom.

Both unhybridized p orbitals form the two pi bonds. One pi bond is above and below the plane of the nuclei. The other pi orbital is in front and behind the plane of the nuclei.



When a triple bond forms (e.g. N<sub>2</sub>) one pi bond is always above and below and the other is in front and behind the plane of the nuclei.

Example:  $\text{H}_2\text{CO}$



## 9.8 : Resonance Structures, Delocalization, and pi Bonding

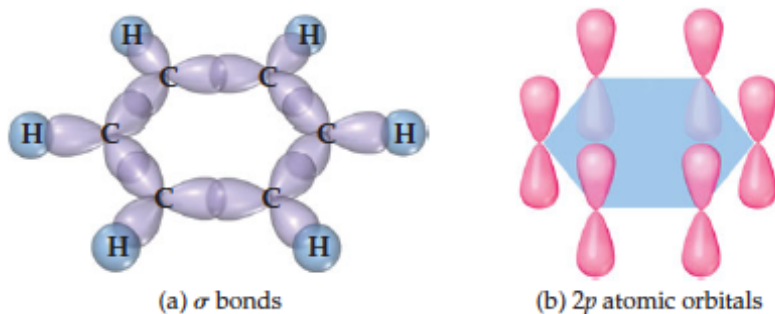
### Delocalized pi bonding

So far all the bonds we have discussed are localized between two nuclei.

In the case of benzene ( $C_6H_6$ ):



Each C atom is  $sp^2$  hybridized there are six C-C sigma bonds and six C-H bonds formed from the  $sp^2$  hybrid orbitals. There is only one unhybridized P orbital on each carbon atom, resulting in six unhybridized carbon P orbitals in a ring.



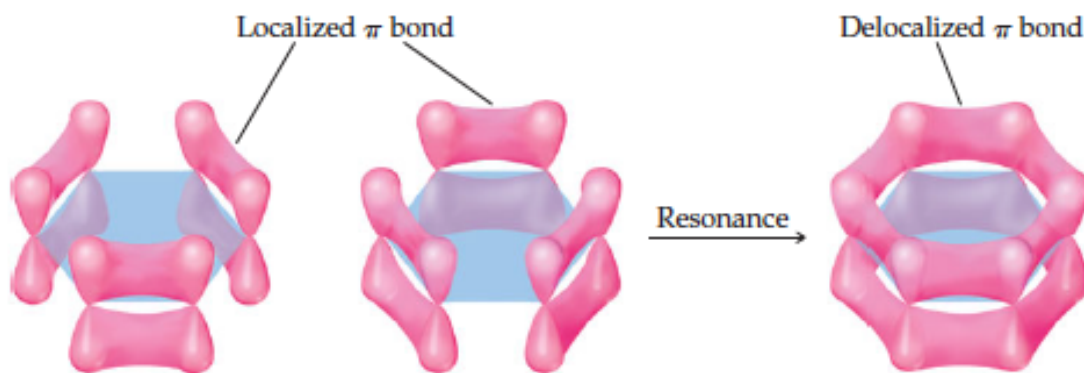
In benzene there are two positions for the three Pi bonds localized between the carbon atoms or delocalized over the entire ring (i.e the pi electrons are shared by all six carbon atoms).

Experimentally, all C-C bond are the same length in benzene.

Therefore, all C-C ends are of the same type ( single bonds are longer than double bonds)

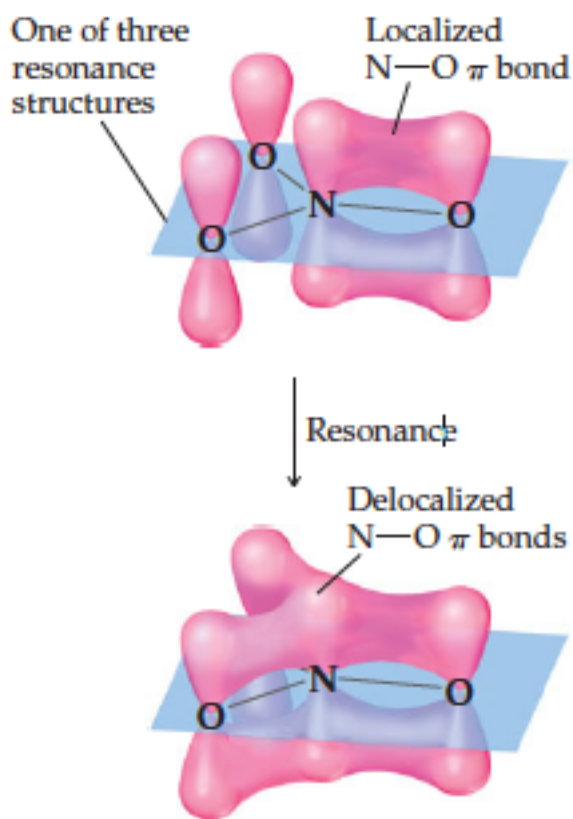
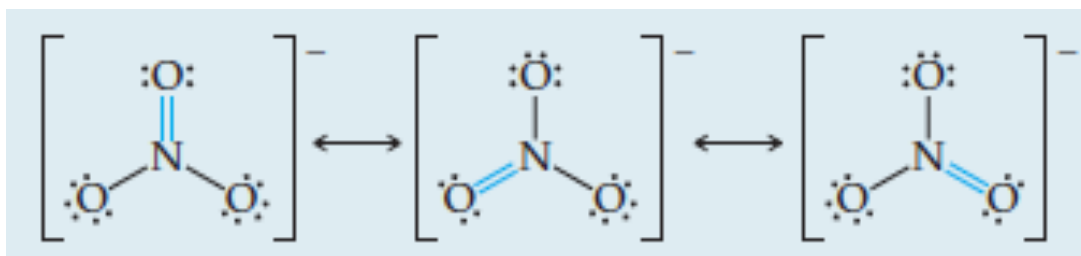
Delocalization of the electrons in its bonds gives benzene a special stability.

Delocalization of bonds is also responsible for the color of many organic molecules.



### Localized and delocalized pi bonds in $\text{NO}_3^-$

$\text{NO}_3^-$  has three resonance structures. In each structure, the electron-domain geometry at nitrogen is trigonal planar, which implies  $sp^2$  hybridization of the N atom. The  $sp^2$  hybrid orbitals are used to construct the three sigma bonds present in each resonance structure. The unhybridized 2p orbital on the N atom can be used to make bonds.



## General Conclusion

Every pair of bonded atoms shares one or more pairs of electrons.

Two electrons shared between atoms on the same axis as the nuclei are sigma bonds.

sigma bonds are always localized in the region between two bonded atoms.

If two atoms share more than one pair of electrons, the additional pair form pi bonds.

When resonance structures are possible, delocalization is also possible.