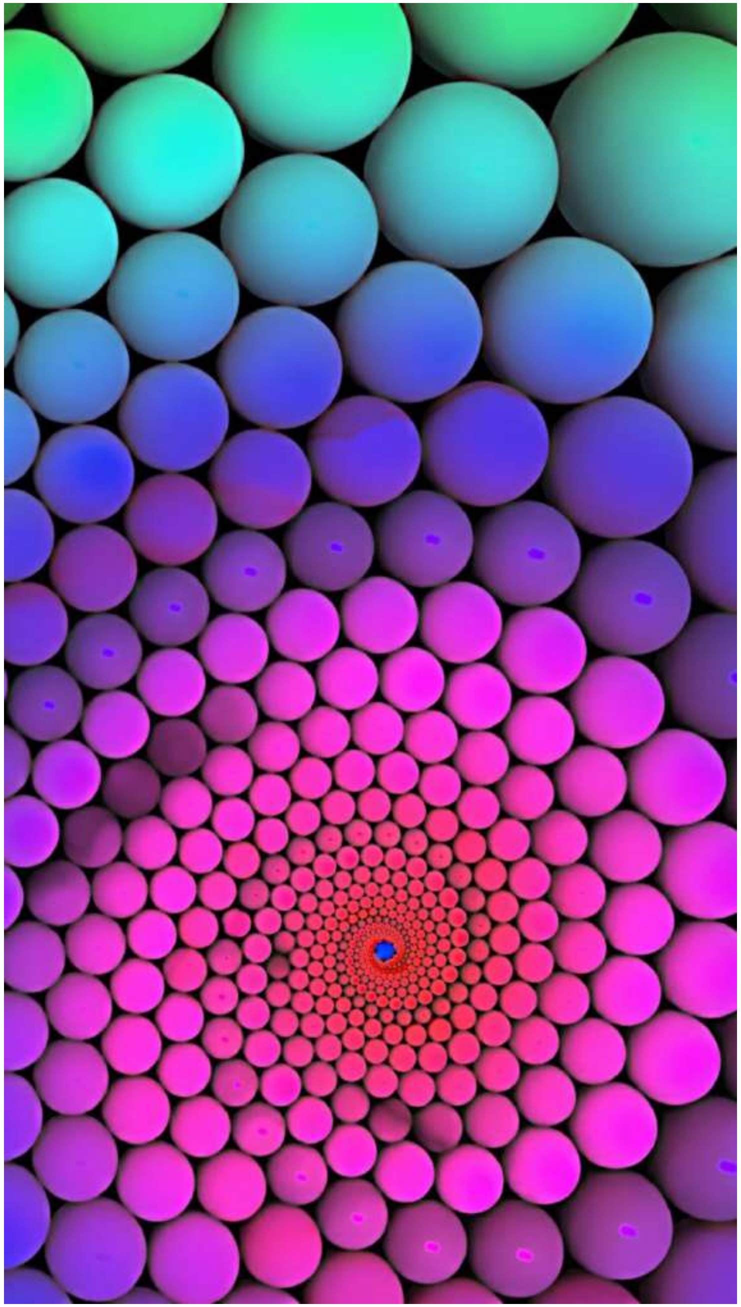
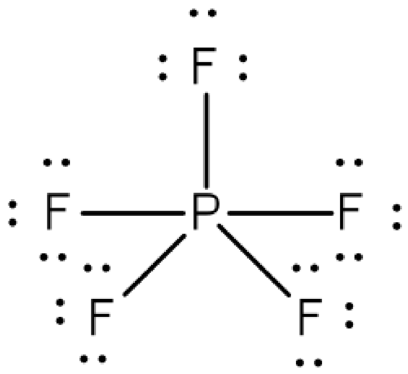
Chapter 9: Molecular Geometry and Bonding Theories

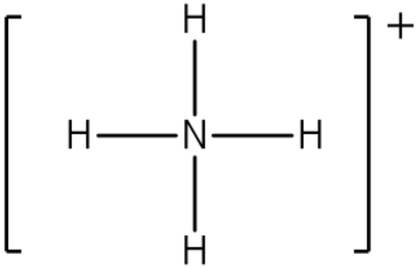
Jennie L. Borders

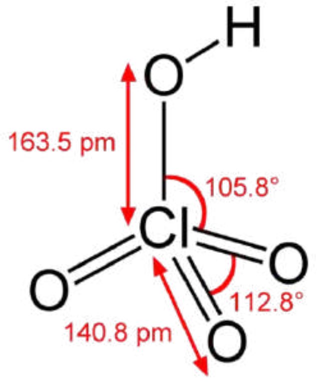


Section 9.1 – Molecular Shapes

- Lewis do not indicate the shapes of molecules; they simply show the number and types of bonds between atoms.
- The overall 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.



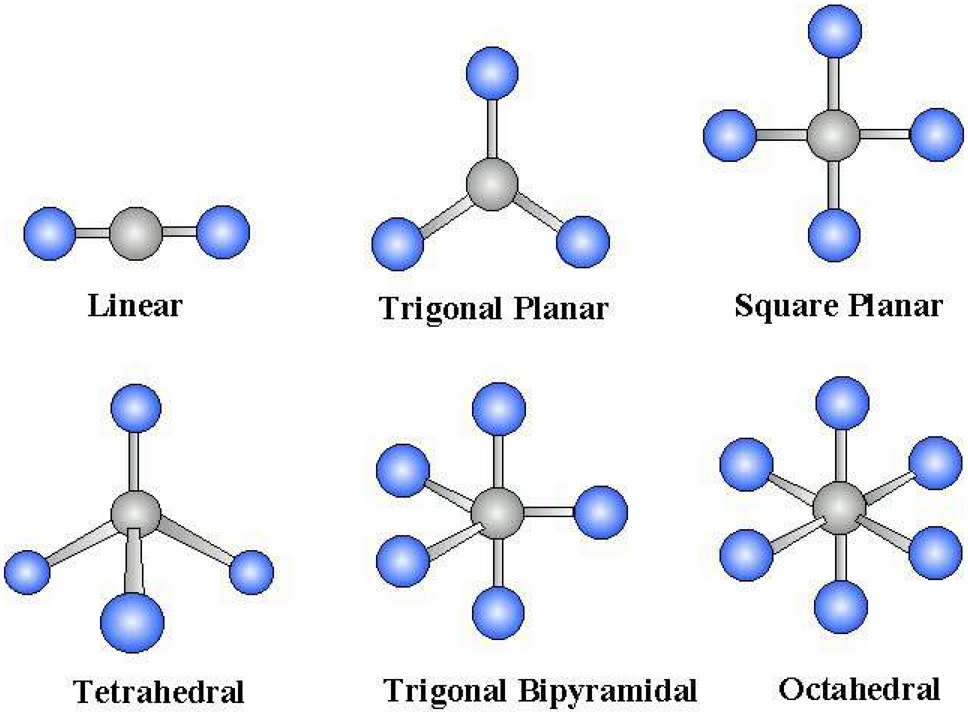




Molecular Shapes

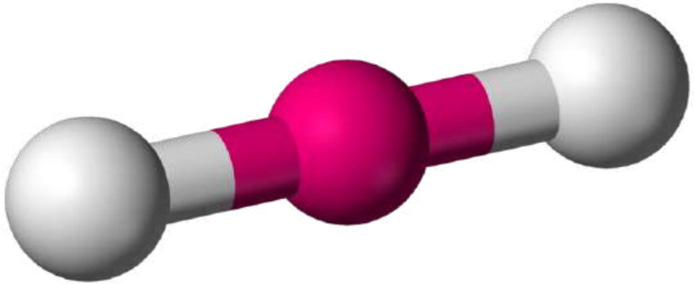
- The shape of any particular AB_n molecule can usually be derived from one of five basic geometric structures.
- A = the central atom
- B = the bonded atoms
- n = the number of

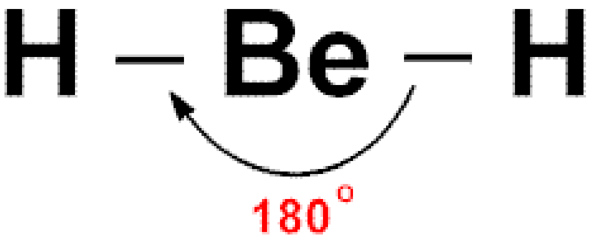
  bonded atoms

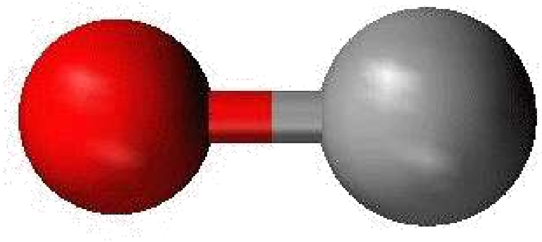


Molecular Shapes

- An AB or AB_2 molecule has a linear shape with 180° bond angles.

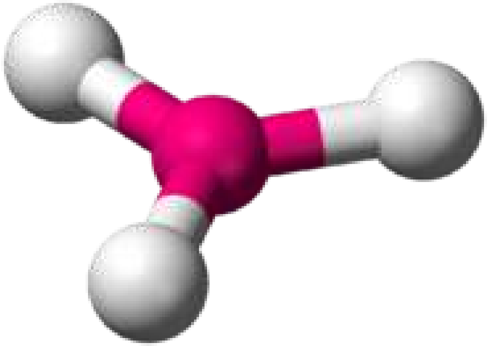


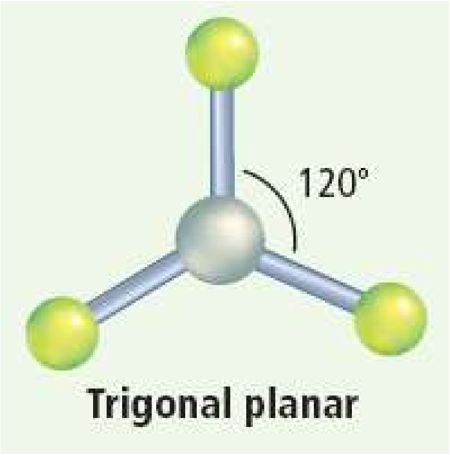


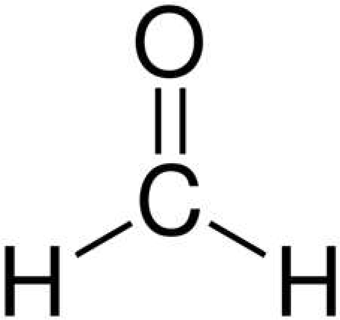


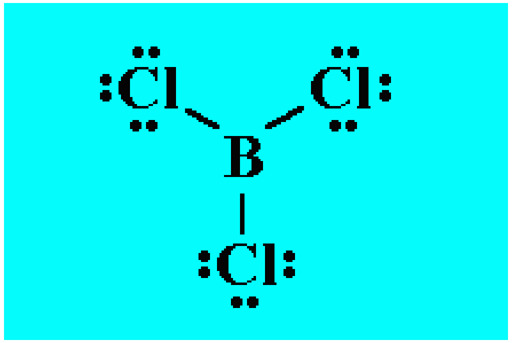
Molecular Shapes

- An AB_3 molecule has a trigonal planar shape with 120^{o} bond angles.



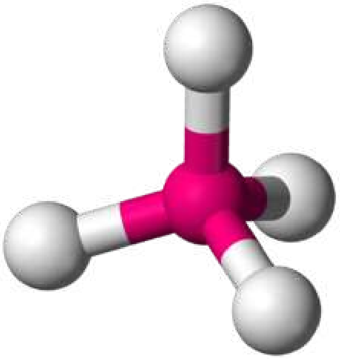


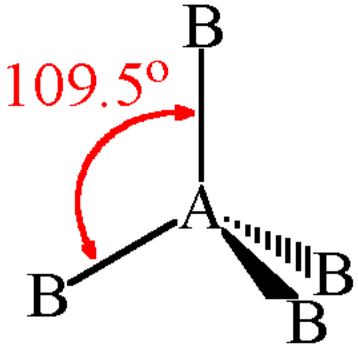


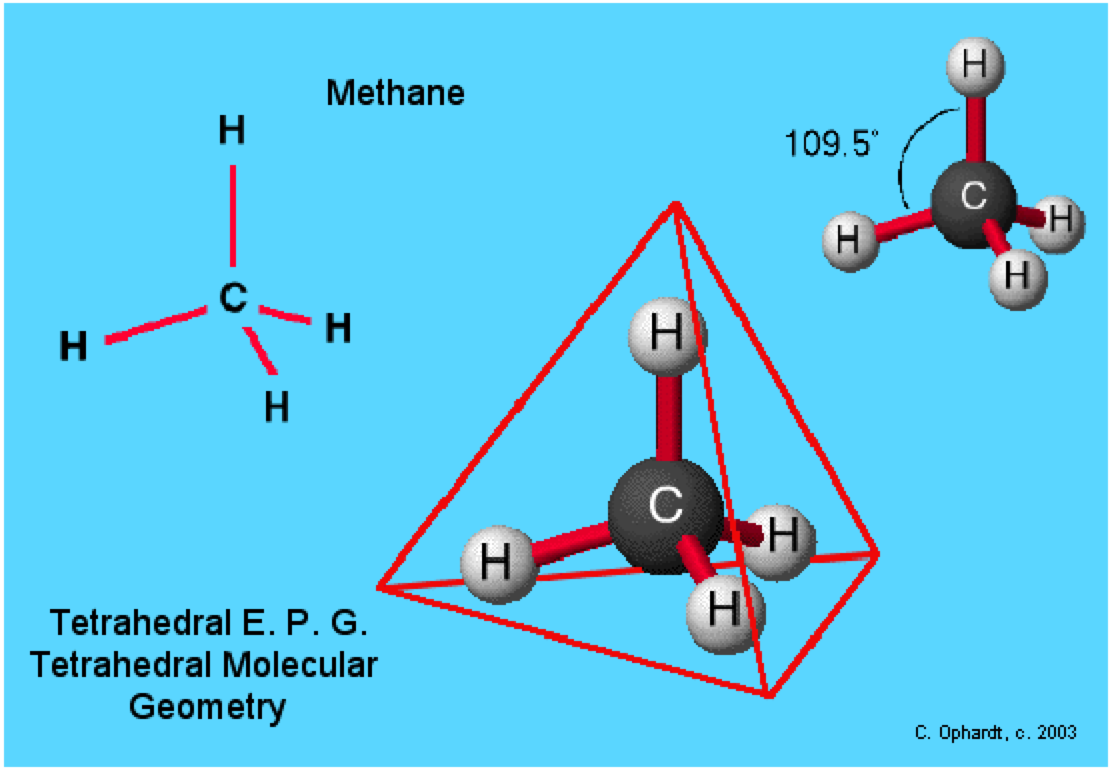


Molecular Shapes

- An AB_4 molecule has a tetrahedral shape with 109.5° bond angles.



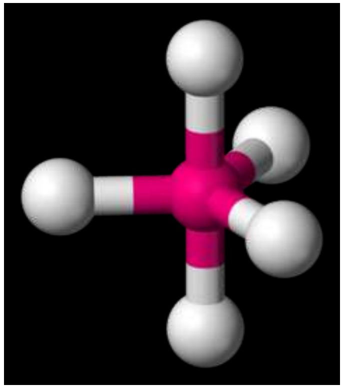


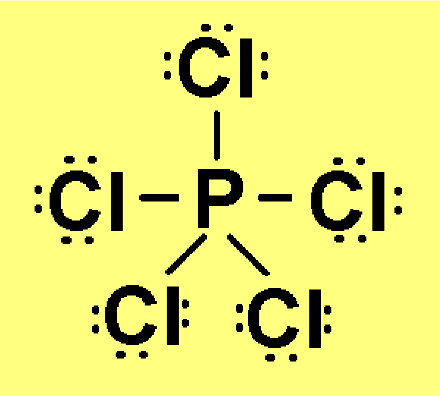


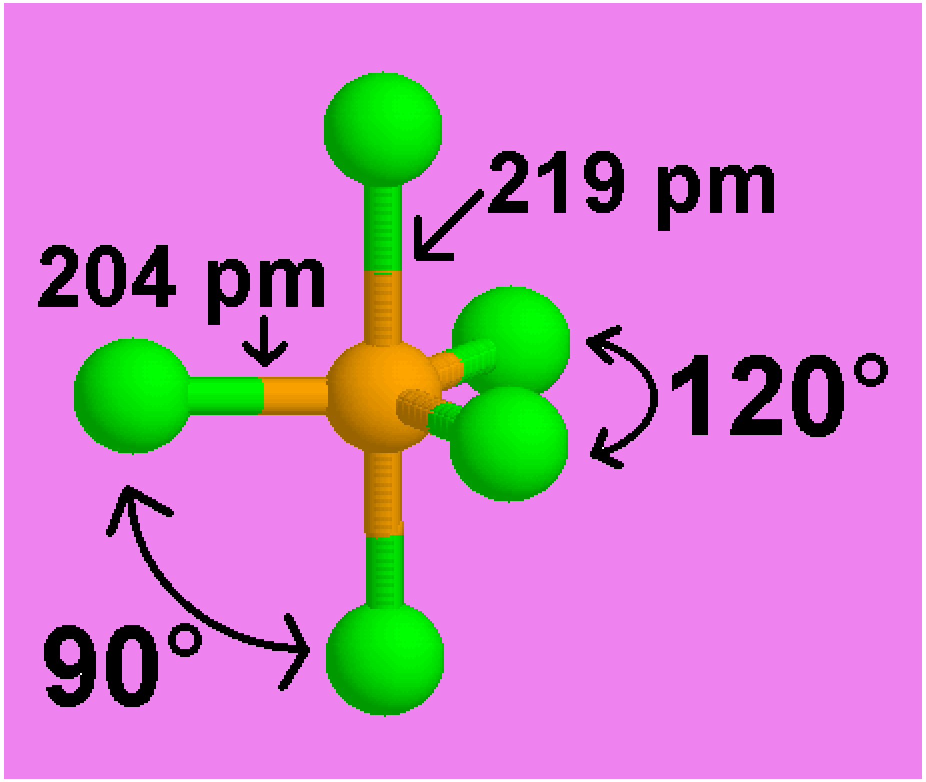
C. Ophardt, c. 2003

Molecular Shapes

- An AB_5 molecule has a trigonal bipyramidal shape with 90º and 120º bond angles.

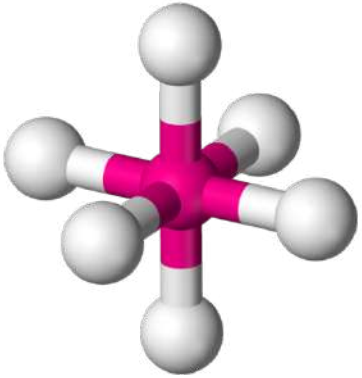


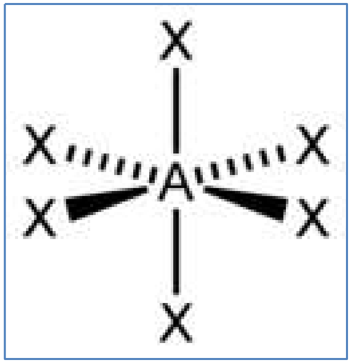


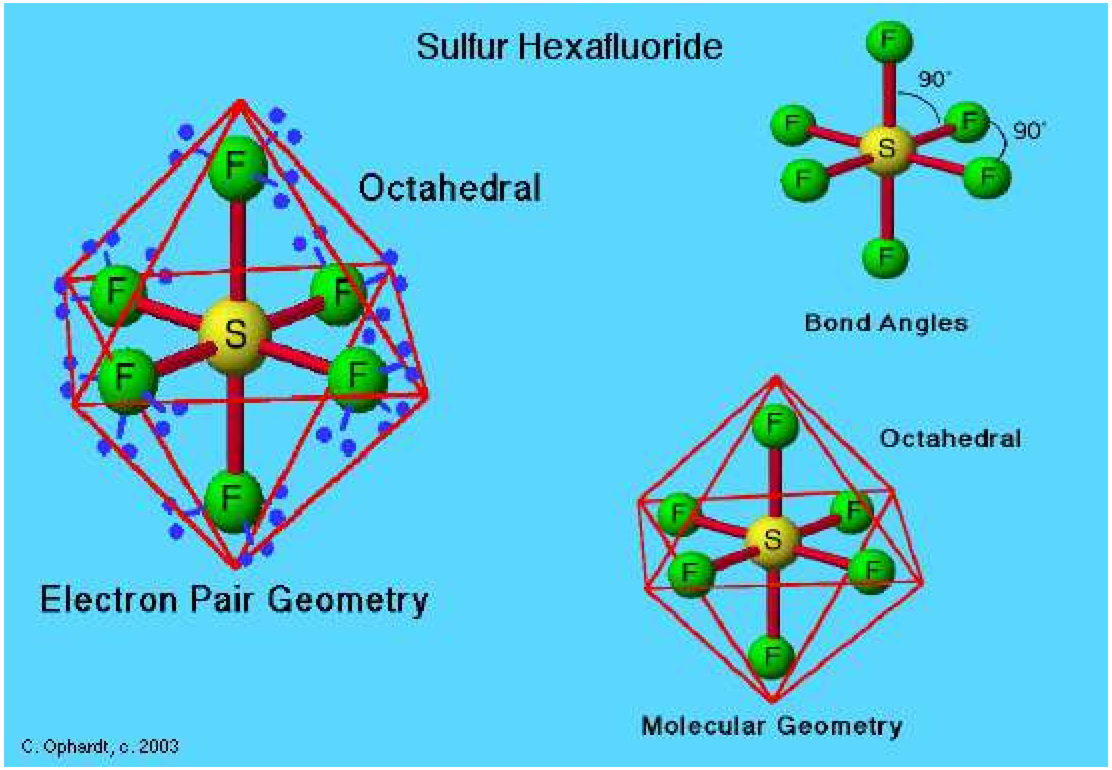


Molecular Shapes

- An AB_6 molecule has an octahedral shape with 90^o bond angles.



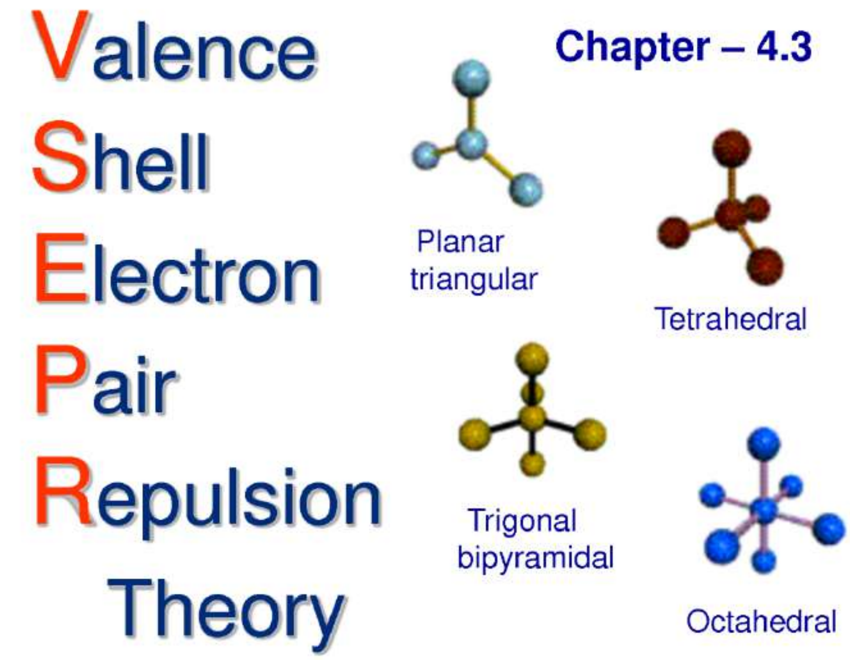




C. Ophardt, c. 2003

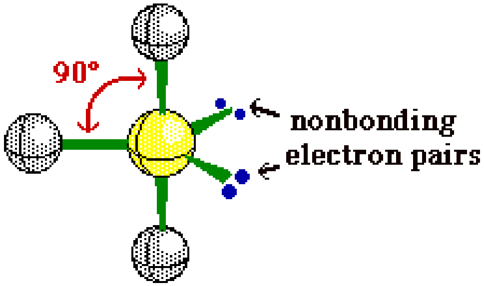
Section 9.2 – The VSEPR Model

- The valence shell electron pair repulsion (VSEPR) model can be used to predict the shape of a molecule based on the fact that electrons repel one another



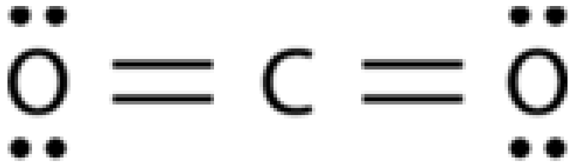
Bonding vs. Nonbonding

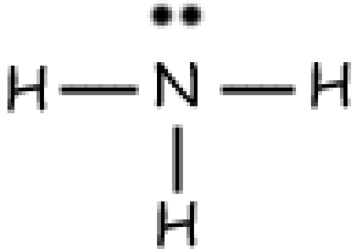
- A bonding pair of electrons are located between the nuclei of the two atoms that are bonded together.
- A nonbonding pair (lone pair) of electrons are located on one atom.
- Both pairs represent and electron domain which is a region in which electrons are likely to be found.

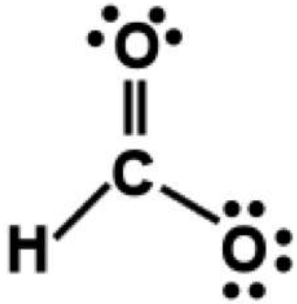


Multiple Bonds

- Double and triple bonds only represent one electron domain.





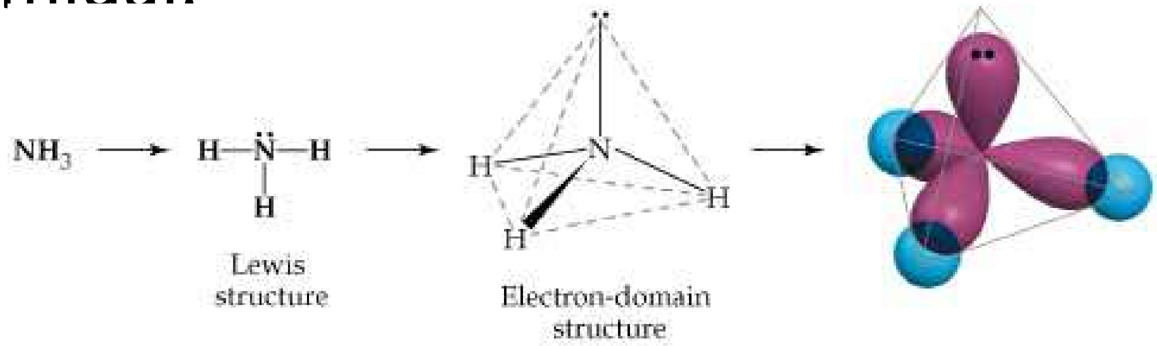


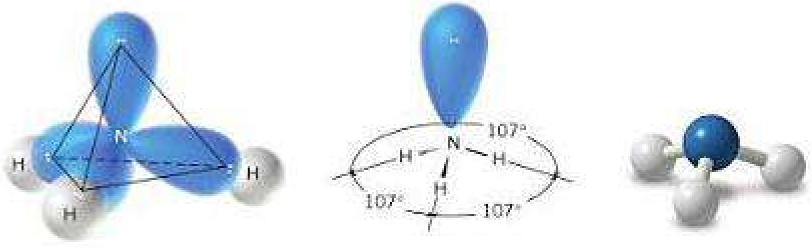
VSEPR Model

- The best arrangement of electron domains is the one that minimizes the repulsions among the electrons.
- The arrangement of electrons about the central atom of an AB_n molecule or ion is called its electron-domain geometry.
- The molecular geometry is the arrangement of only the atoms in a molecule or ion – nonbonding pairs are excluded from the shape.

Electron Domain vs. Molecular

- The electron domain geometry for NH_3 is tetrahedral, but the molecular geometry is trigonal pyramidal.



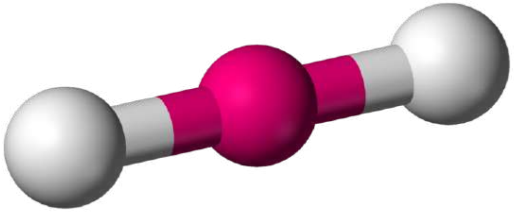


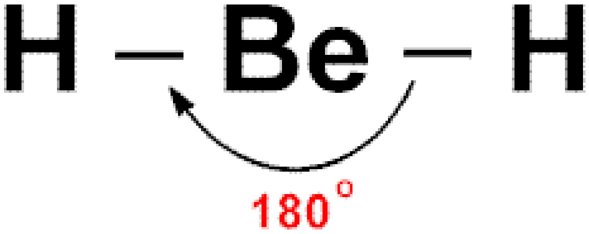
Molecular geometry of NH_3

VSEPR Model

- Possible shapes for AB_2:

Bonding	Nonbonding	Shape
2	0	linear

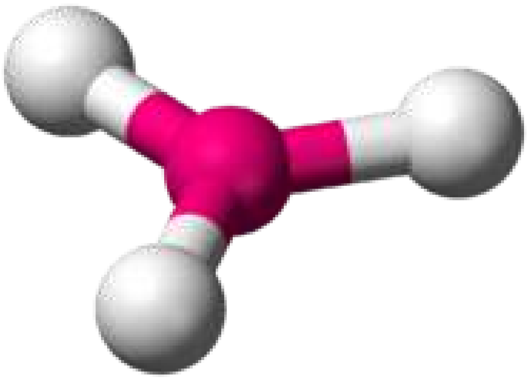


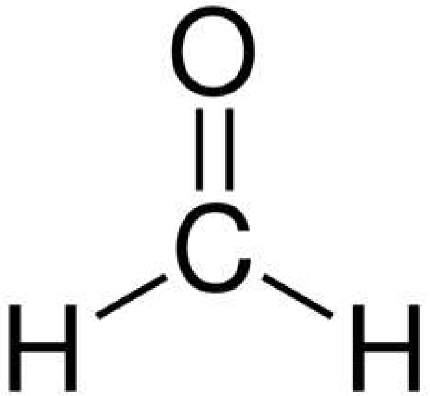


VSEPR Model

- Possible shapes for AB_3:

Bonding	Nonbonding	Shape
3	0	trigonal planar

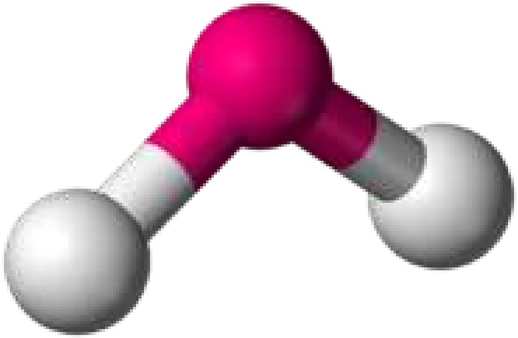


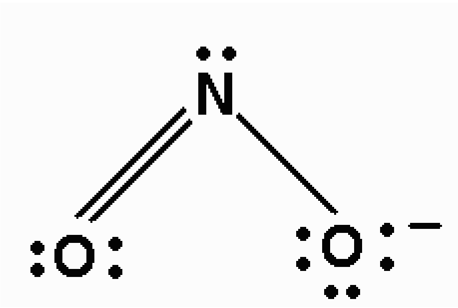


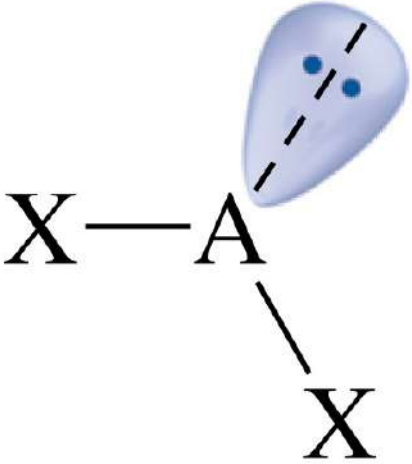
VSEPR Model

- Possible shapes for AB_3:

Bonding	Nonbonding	Shape
2	1	bent



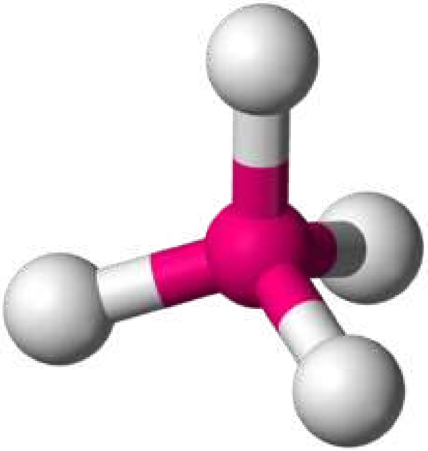


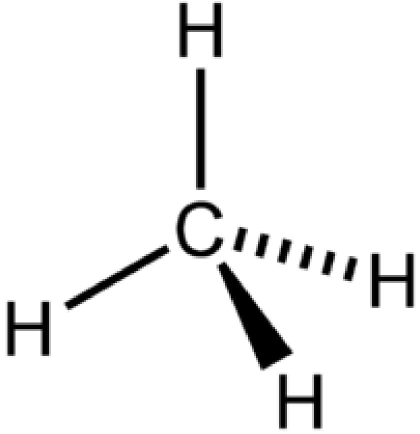


VSEPR Model

- Possible shapes for AB_4:

Bonding	Nonbonding	Shape
4	0	tetrahedral

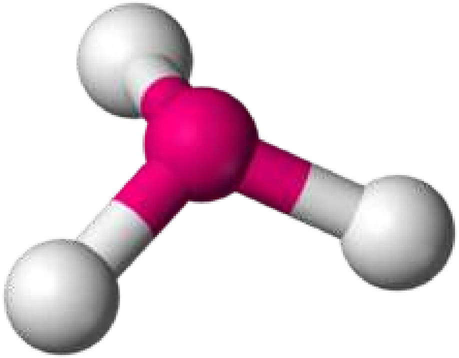


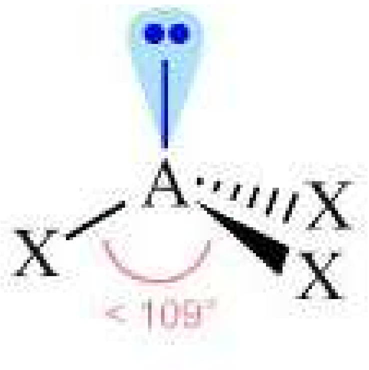


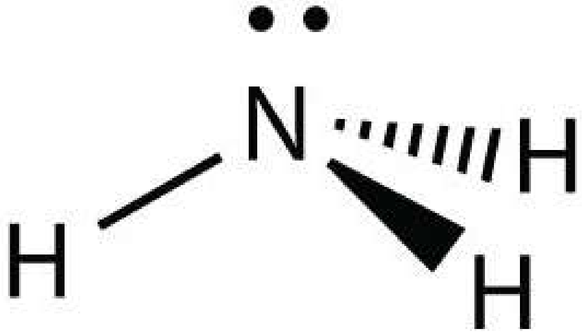
VSEPR Model

- Possible shapes for AB_4:

Bonding	Nonbonding	Shape
3	1	trigonal pyramidal



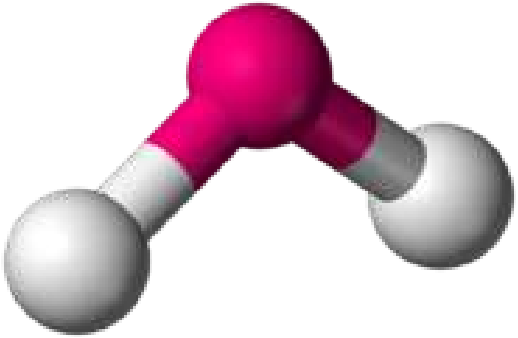


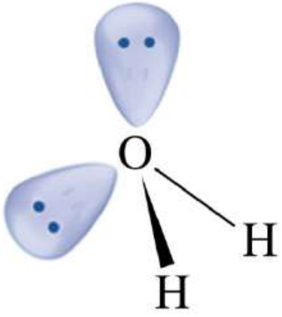


VSEPR Model

- Possible shapes for AB_4:

Bonding	Nonbonding	Shape
2	2	bent





VSEPR notation: AX_2E_2

Sample Exercise 9.1

- Use the VSEPR model to predict the molecular geometry of
  a. O_3

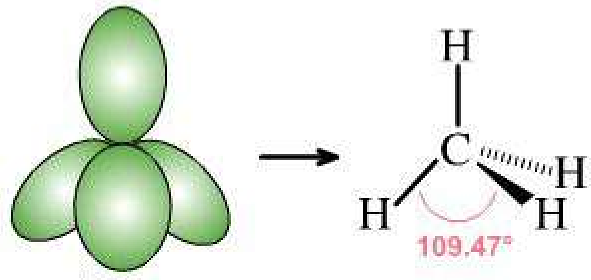
  b. $SnCl_3^-$

Practice Exercise

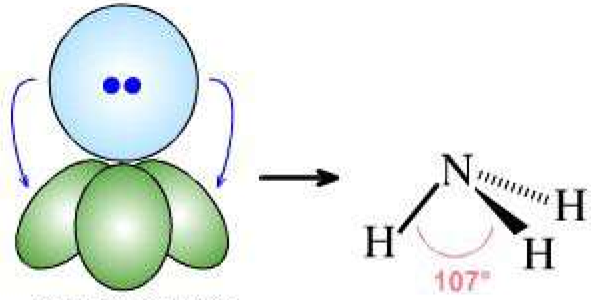
- Predict the electron-domain geometry and the molecular geometry for
    a. $SeCl_2$
    b. CO_3^{2-}

Bond Angles

- Because a nonbonding pair experiences less nuclear attraction than bonding pairs, its electron domain is more spread out.
- As a result, the electron domains for nonbonding electron pairs exert greater repulsive forces on adjacent electron domains and tend to compress the bond angles.



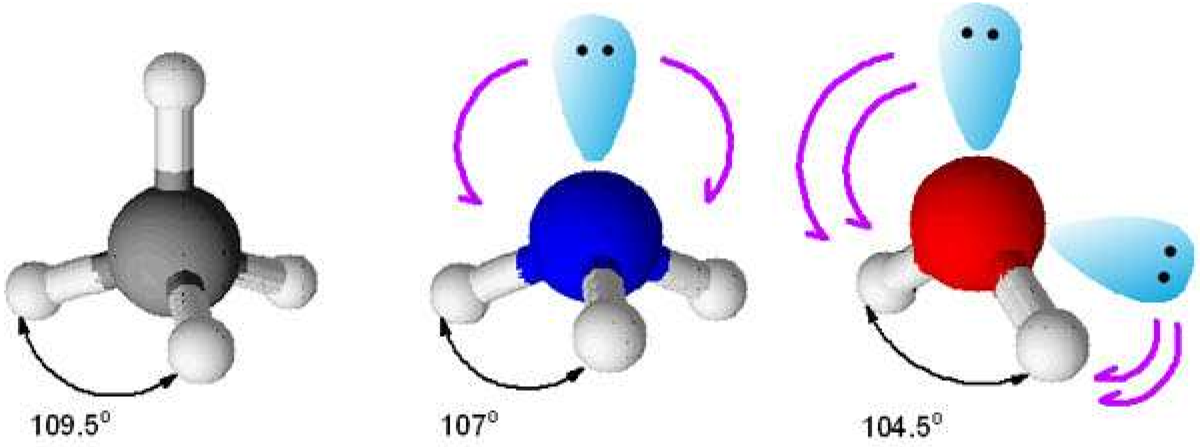
4 balloons



3 + 1 big balloons

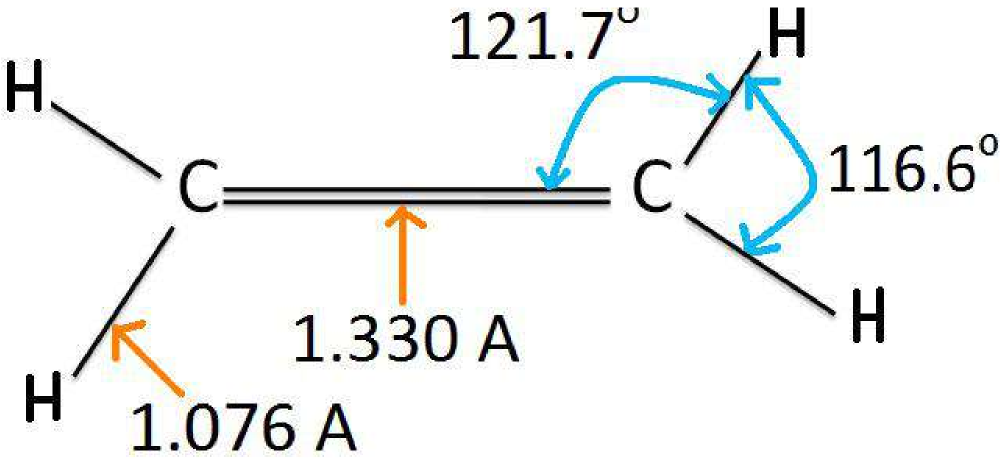
Bond Angles

- Notice the difference in the bond angles of CH_4, NH_3, and H_2O, all of which have a tetrahedral electron domain geometry.



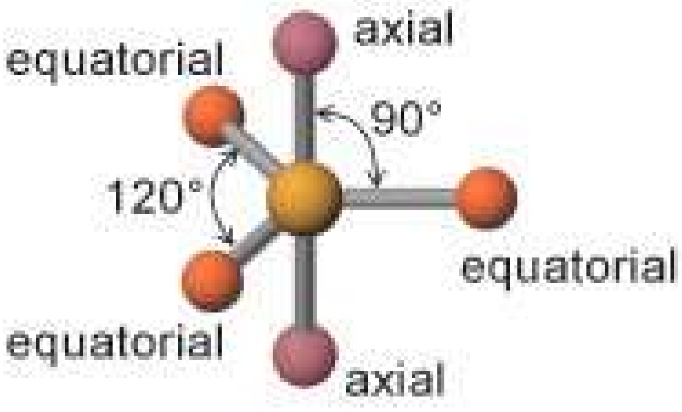
Bond Angles

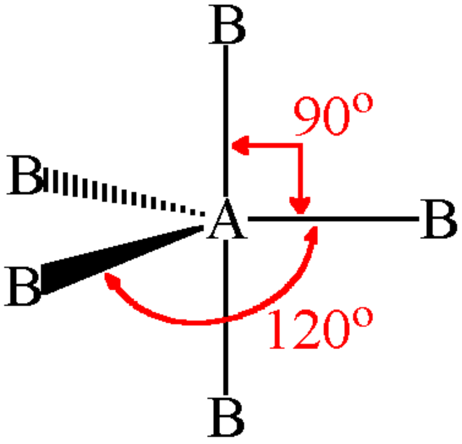
- Multiple bonds contain a higher electron density so they also represent larger electron domains.



Expanded Octet Molecules

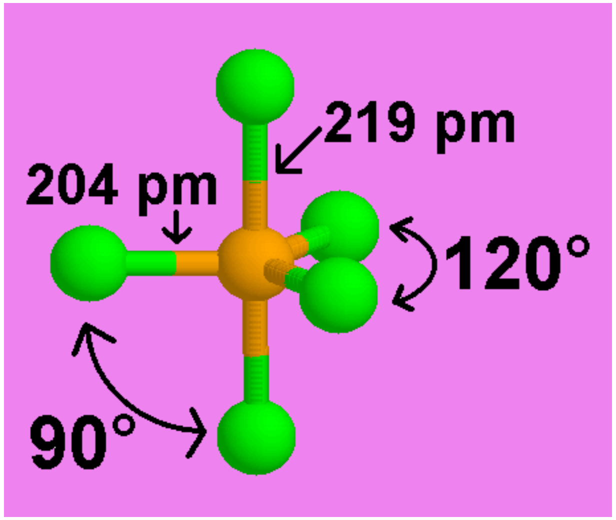
- When a central atom has 5 electron domains, then the shape is trigonal bipyramidal.
- There are two different positions on this molecule: axial and equatorial. The axial position is at a 90^{o} angle to its neighbors. The equatorial position is at 120^{o} or 90^{o} angles to its neighbors.

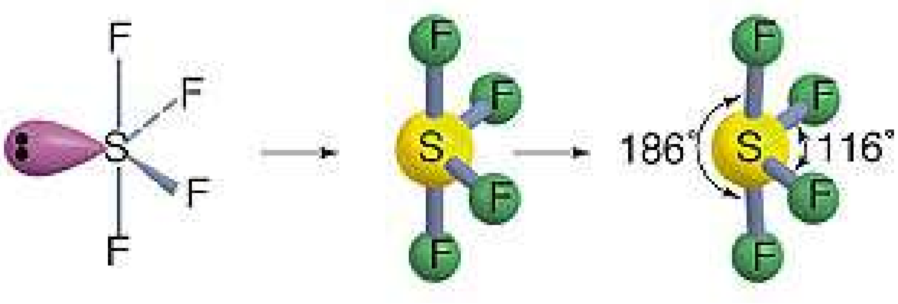




Axial vs. Equatorial

- The equatorial position experiences less repulsion, so nonbonding pairs will always occupy the equatorial positions.

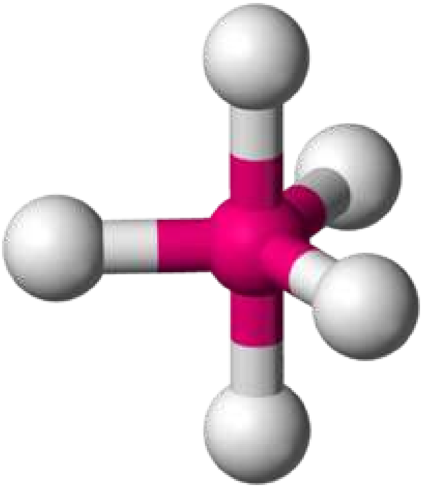


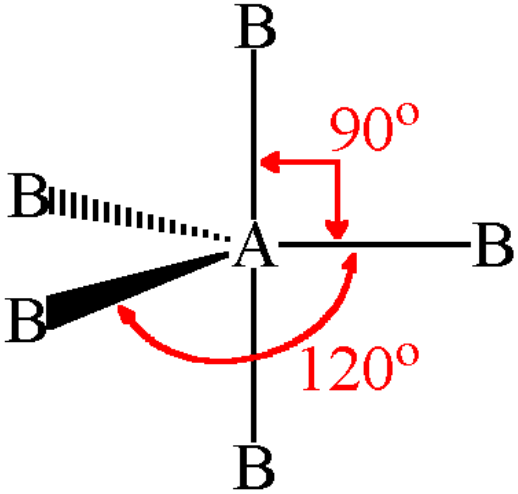


VSEPR Model

- Possible shapes for AB_5:

Bonding	Nonbonding	Shape
5	0	trigonal bipyramidal

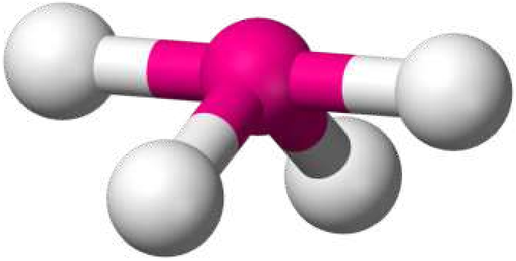


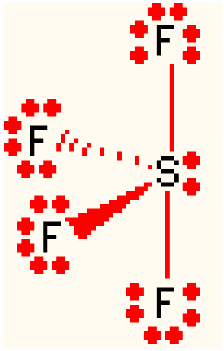


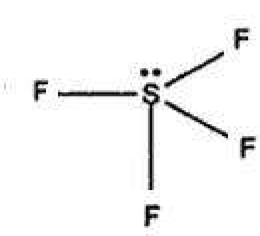
VSEPR Model

- Possible shapes for AB_5:

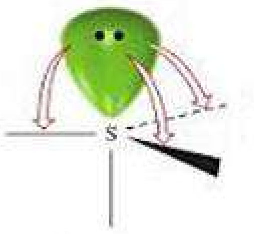
Bonding	Nonbonding	Shape
4	1	seesaw

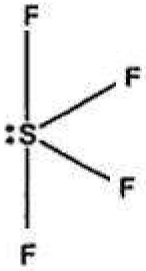




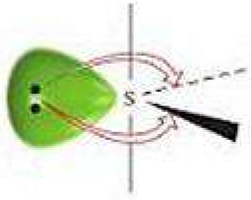


Lone pair in axial position





Lone pair in equatorial position

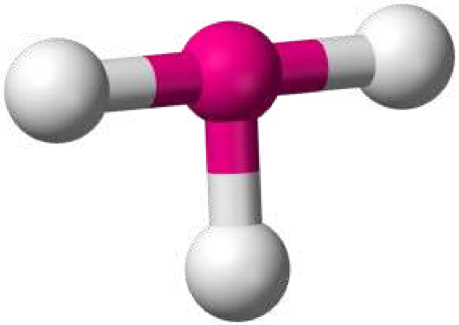


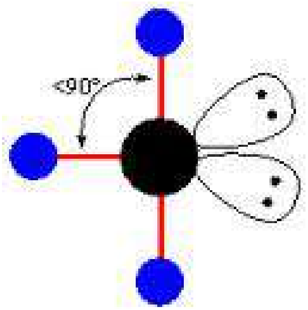
(Preffered arrangement)

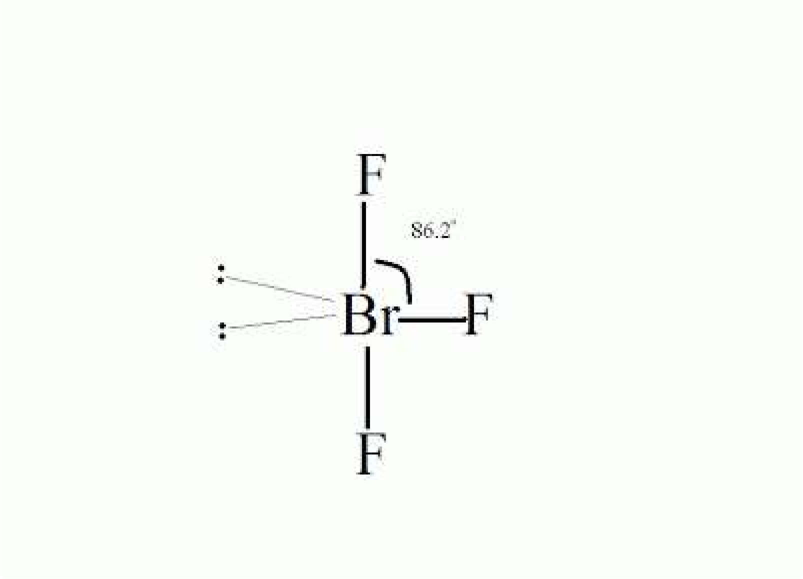
VSEPR Model

- Possible shapes for AB_5:

Bonding	Nonbonding	Shape
3	2	T-shaped



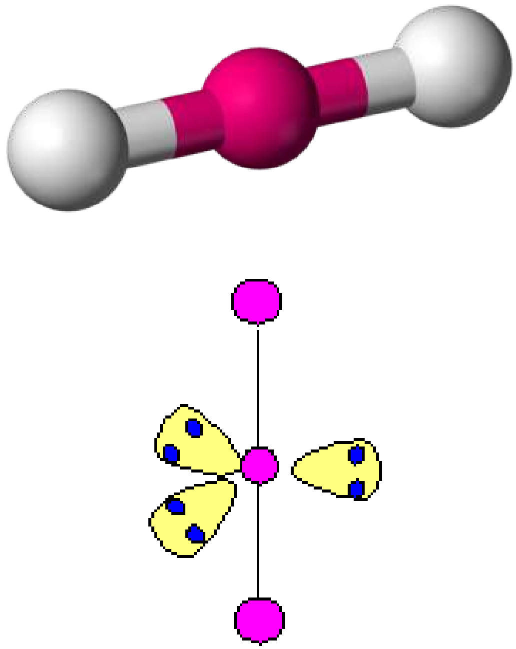


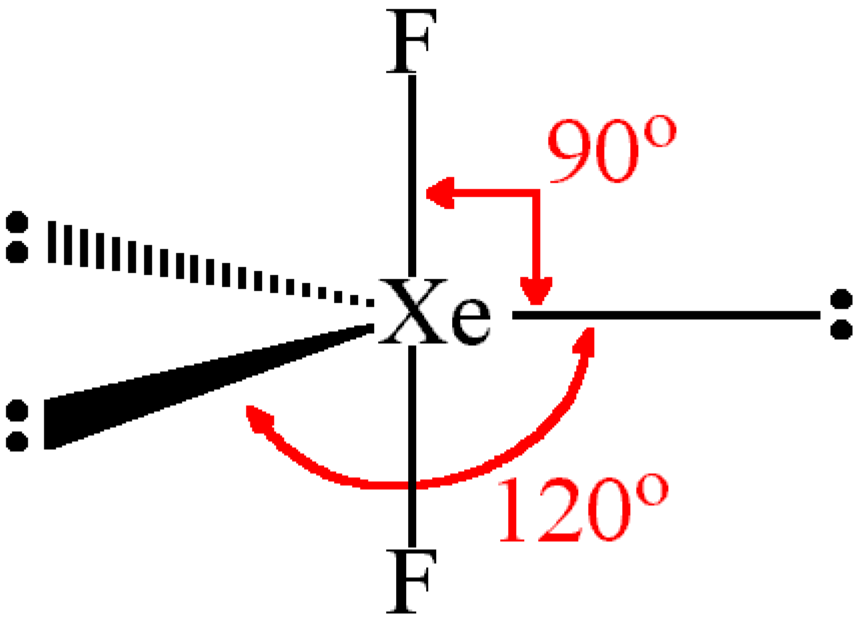


VSEPR Model

- Possible shapes for AB_5:

Bonding	Nonbonding	Shape
2	3	linear

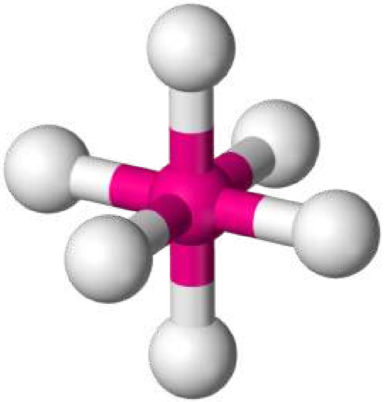


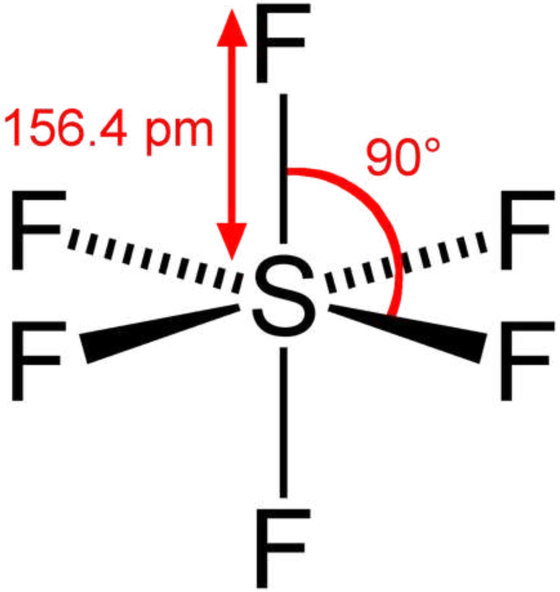


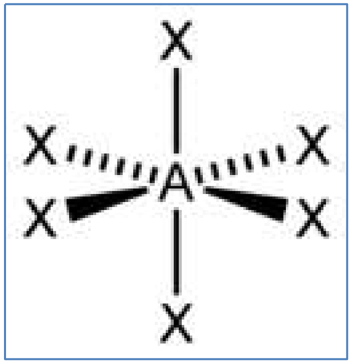
VSEPR Model

- Possible shapes for AB_6:

Bonding	Nonbonding	Shape
6	0	octahedral



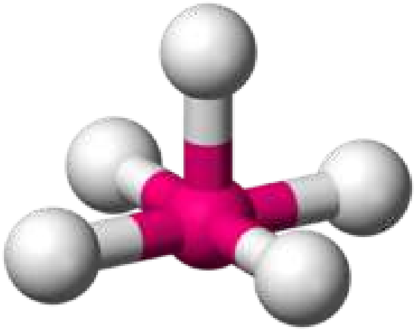


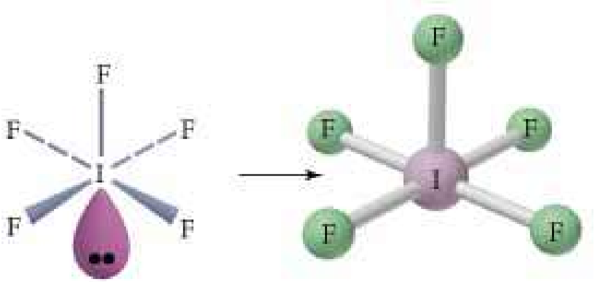


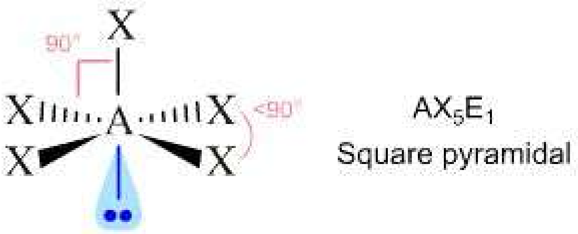
VSEPR Model

- Possible shapes for AB_6:

Bonding	Nonbonding	Shape
5	1	square pyramidal



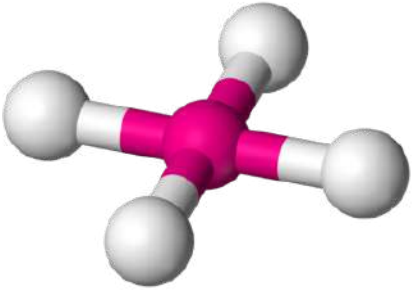


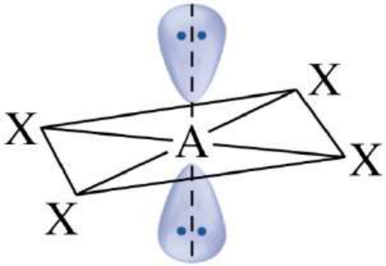


VSEPR Model

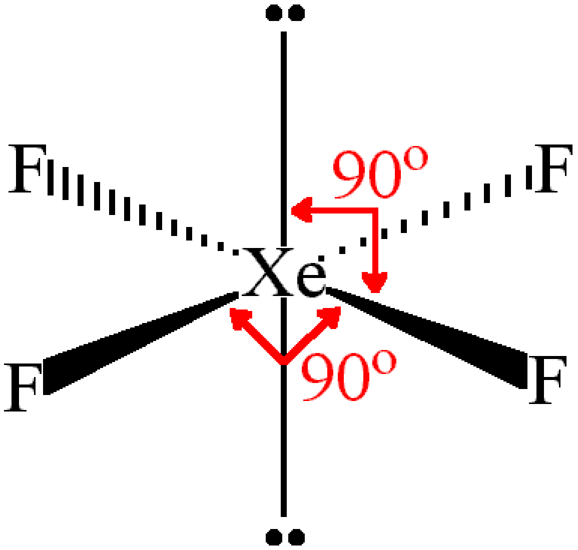
- Possible shapes for AB_6:

Bonding	Nonbonding	Shape
4	2	square planar





Square planar



Sample Exercise 9.2

- Use the VSEPR model to predict the molecular geometry of

  a. SF_4

  b. IF_5

Sample Exercise

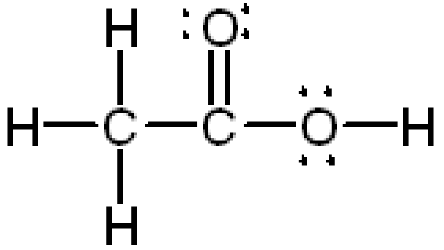
- Predict the electron-domain geometry and molecular geometry of

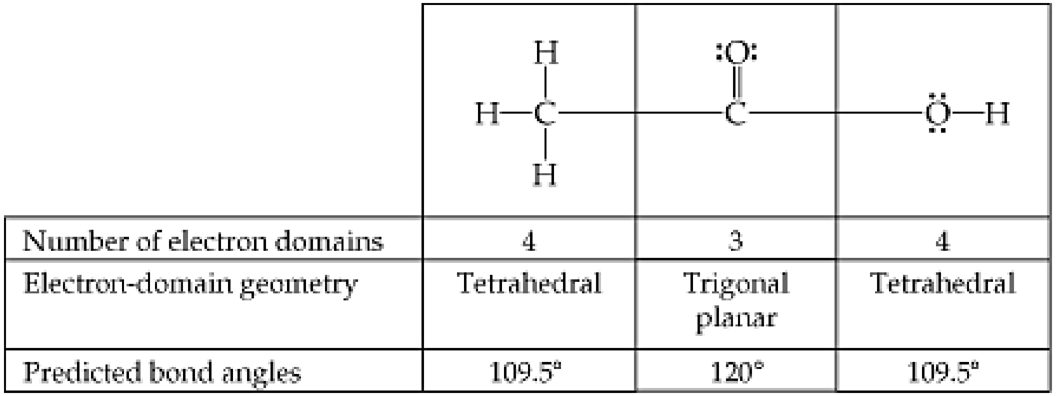
    a. ClF_3

    b. ICl_4^-

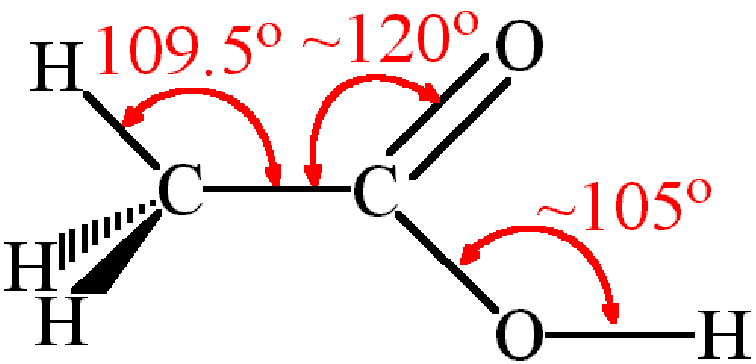
Shapes of Large Molecules

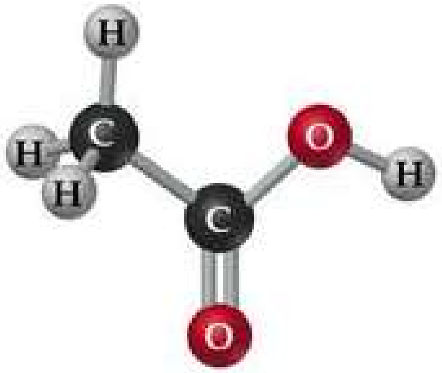
- Larger molecules can be broken into sections to see the shapes involved.





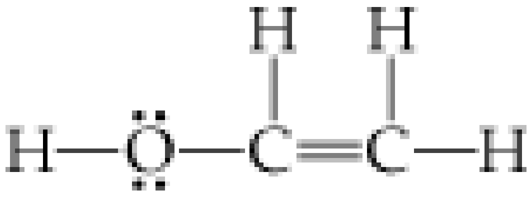
Number of electron domains	4	3	4
Electron-domain geometry	Tetrahedral	Trigonal planar	Tetrahedral
Predicted bond angles	109.5°	120°	109.5°





Sample Exercise 9.3

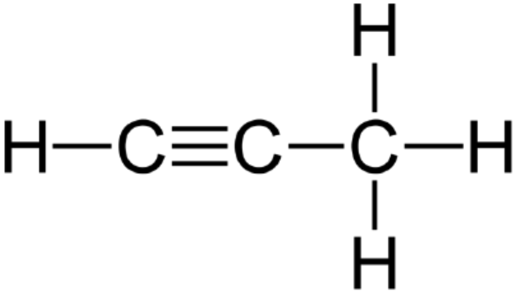
- Eyedrops used for dry eyes usually contain the water-soluble polymer called poly(vinylalcohol), which is based on the unstable organic molecule called vinyl alcohol:



Predict the approximate values for the H – O – C and the O – C – C bond angles.

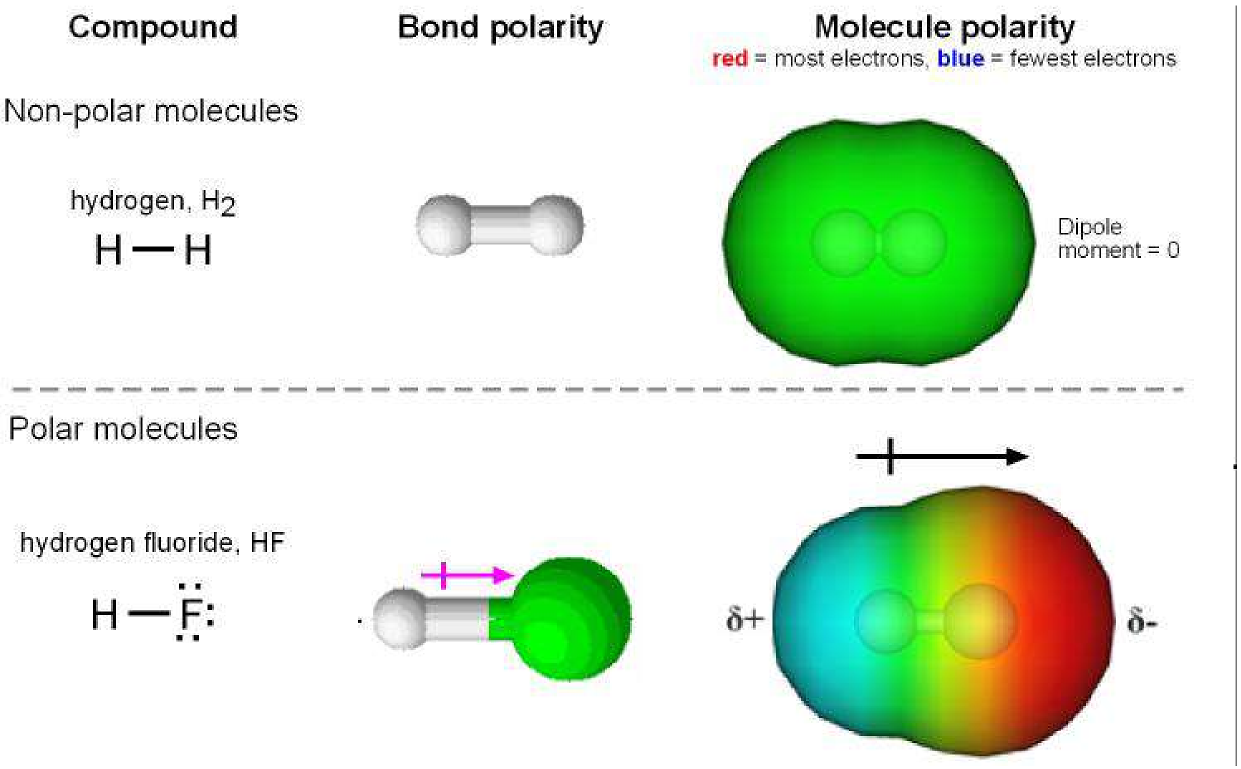
Sample Exercise

- Predict the H – C – H ad C – C – C bond angles in the following molecule, called propyne:



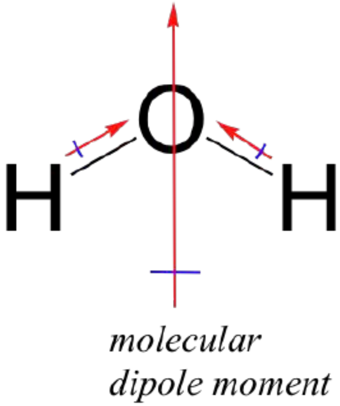
Section 9.3 – Molecular Shape and Molecular Polarity

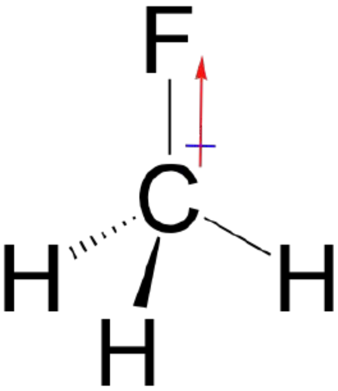
- Remember that bond polarity is a measure of how equally the electrons in a bond are shared between the two atoms of the bond.

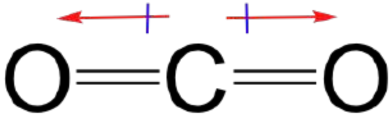


Bond Polarity

- For a molecule that consists of more than two atoms, the dipole moment depends on both the polarities of the individual bonds and the geometry of the molecule.
- Bond dipoles and dipole moments are vector quantities – magnitude and direction.

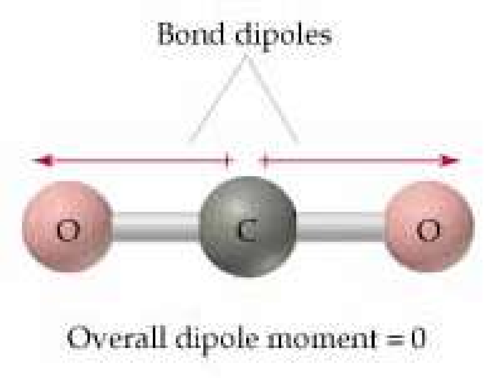






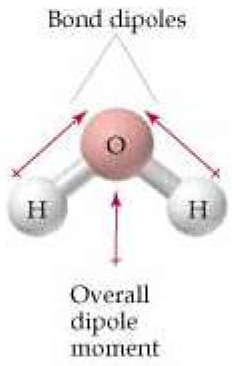
Polarity

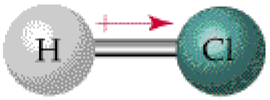
- The overall dipole moment is the vector sum of its bond dipoles.
- If the dipoles are of equal magnitude but in opposite directions, then they cancel out making the molecule nonpolar.



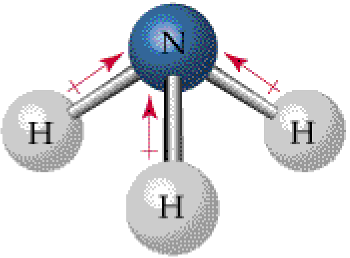
Polarity

- If the dipoles do not cancel out, then the molecule is polar. Be sure to consider shape before deciding polarity.

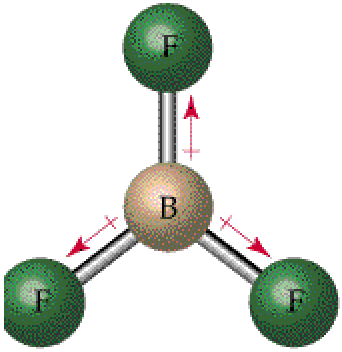




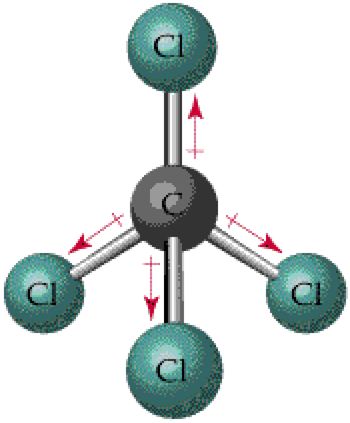
Polar



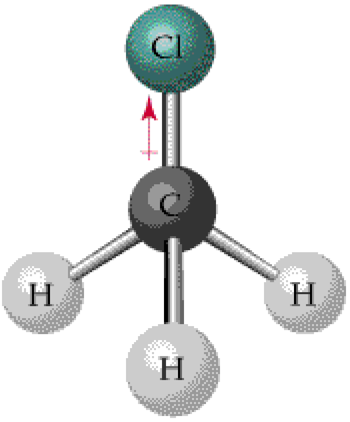
Polar



Nonpolar



Nonpolar



Polar

Sample Exercise 9.4

- Predict whether the following molecules are polar or nonpolar:

a. BrCl

b. SO_2

c. SF_6

Practice Exercise

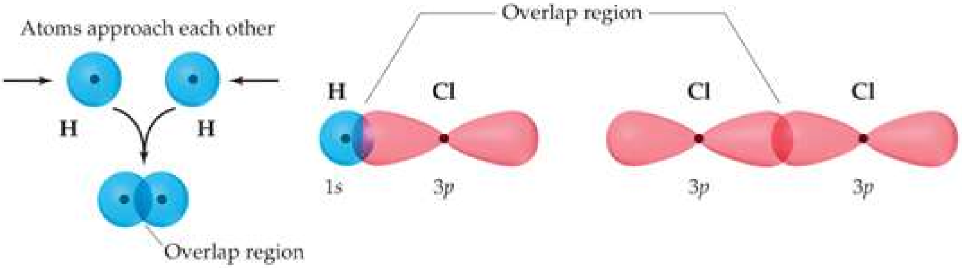
- Determine whether the following molecules are polar or nonpolar:

  a. NF_3

  b. BCl_3

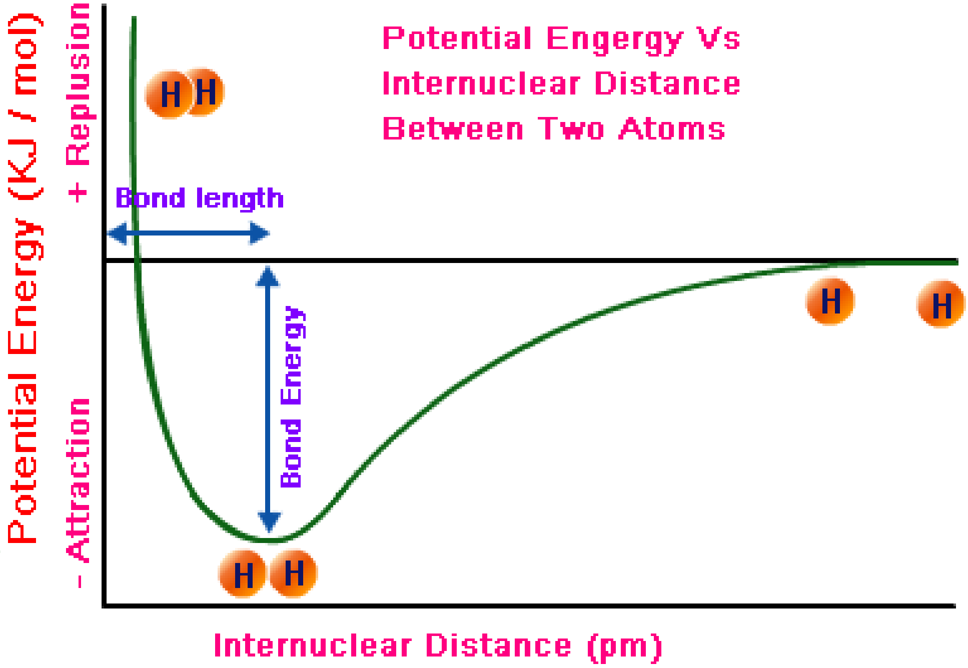
Section 9.4 – Covalent Bonding and Orbital Overlap

- In the Lewis theory, covalent bonding occurs when atoms share electrons.
- In the valence-bond theory, we visualize the buildup of electron density between two nuclei as occurring when the orbitals of the atoms overlap.
- The overlap of the orbitals allows two electrons of opposite spin to share the common space between the nuclei, forming a covalent bond.



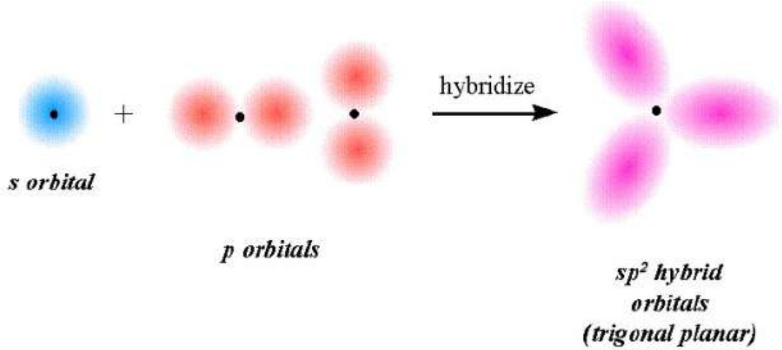
Bond Length

- The bond length of a covalent bond corresponds to the minimum of the potential energy curve.



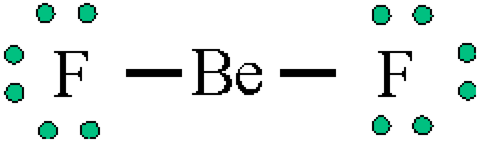
Section 9.5 – Hybrid Orbitals

- To explain geometries, we assume that the atomic orbitals on an atom mix to form new orbitals called hybrid orbitals.
- The process of mixing atomic orbitals is called hybridization.
- The number of hybrid orbitals must equal the number of atomic orbitals.



sp Hybrid Orbitals

- BeF$_2$



- F = ↑↓ ↑↓ ↑↓ ↑↓ ↑
  1s 2s 2p

- This shows that F can bond by filling its 2p sublevel.

- Be = ↑↓ ↑↓ ___ ___ ___
- 1s 2s 2p

sp Hybrid Orbitals

- Since Be has no unpaired electrons, it should not form bonds, so one of the electrons is “promoted” to a 2p orbital.

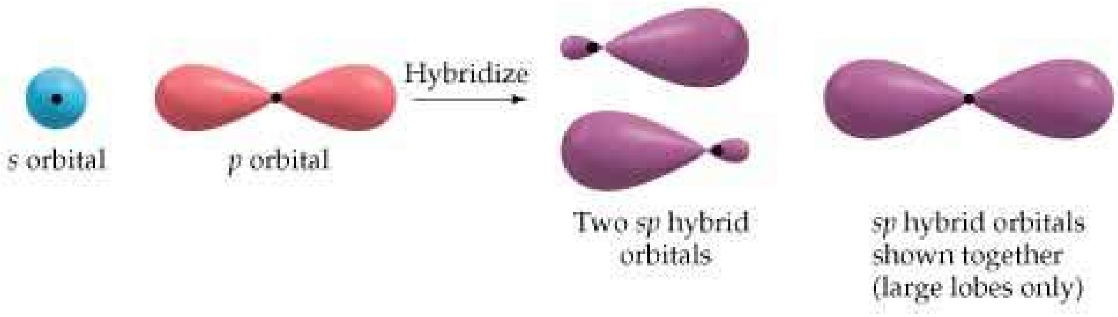
- Be = ↑↓ ↑ ↑ ___ ___

  1s 2s 2p

- However, this arrangement would not make the two Be – F bonds equal because one would involve and s orbital and one would involve a p orbital.

sp Hybrid Orbitals

- We can form 2 hybrid sp orbitals which have 2 lobes like a p orbital, but 1 lobe is much larger than the other.



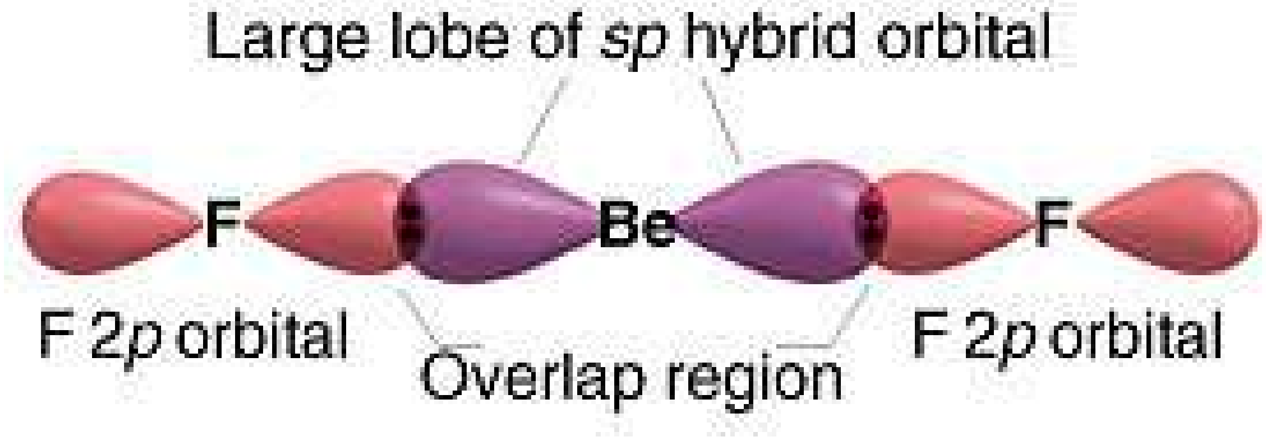
- Be = $\underline{\uparrow\downarrow}$ $\underline{\uparrow\ \ }$ $\underline{\uparrow\ \ }$ ___ ___

  1s sp 2p

- The remaining 2p orbitals remain the same.

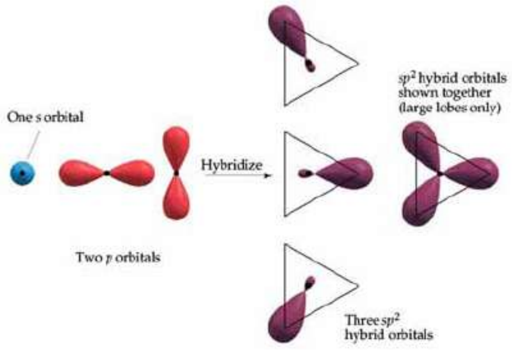
sp Hybrid Orbital

- The hybrid orbitals and bonding in BeF_2 would look like the following diagrams.



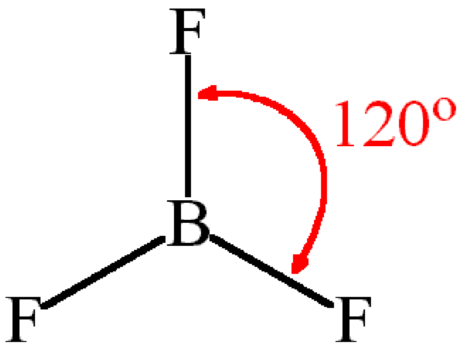
Hybrid Orbitals

- Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals.
- Each of the hybrid orbitals is equivalent to the others but points in a different direction.
- Thus mixing one 2s and one 2p orbital yields two equivalent sp hybrid orbitals that point in opposite directions



sp^2 Hybrid Orbitals

- BF_3



- F = ↑↓ ↑↓ ↑↓ ↑↓ ↑
  1s 2s 2p

- This shows that F can bond by filling its 2p sublevel.

- B = ↑↓ ↑↓ ↑ ___ ___
  1s 2s 2p

sp^2 Hybrid Orbitals

- Since B has one unpaired electron, it should only form one bond, so one of the electrons is "promoted" to a 2p orbital to allow for 3 bonds.

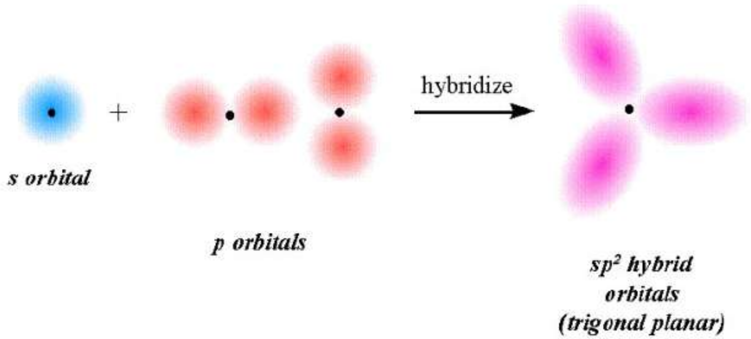
- B = ↑↓ ↑ ↑ ↑ ___

1s	2s	2p		
↑↓	↑	↑	↑	

- However, this arrangement would not make the three B – F bonds equal because one would involve and s orbital and two would involve p orbitals.

sp^2 Hybrid Orbitals

- We can form 3 hybrid sp^2 orbitals which have 2 lobes like a p orbital, but 1 lobe is much larger than the other.



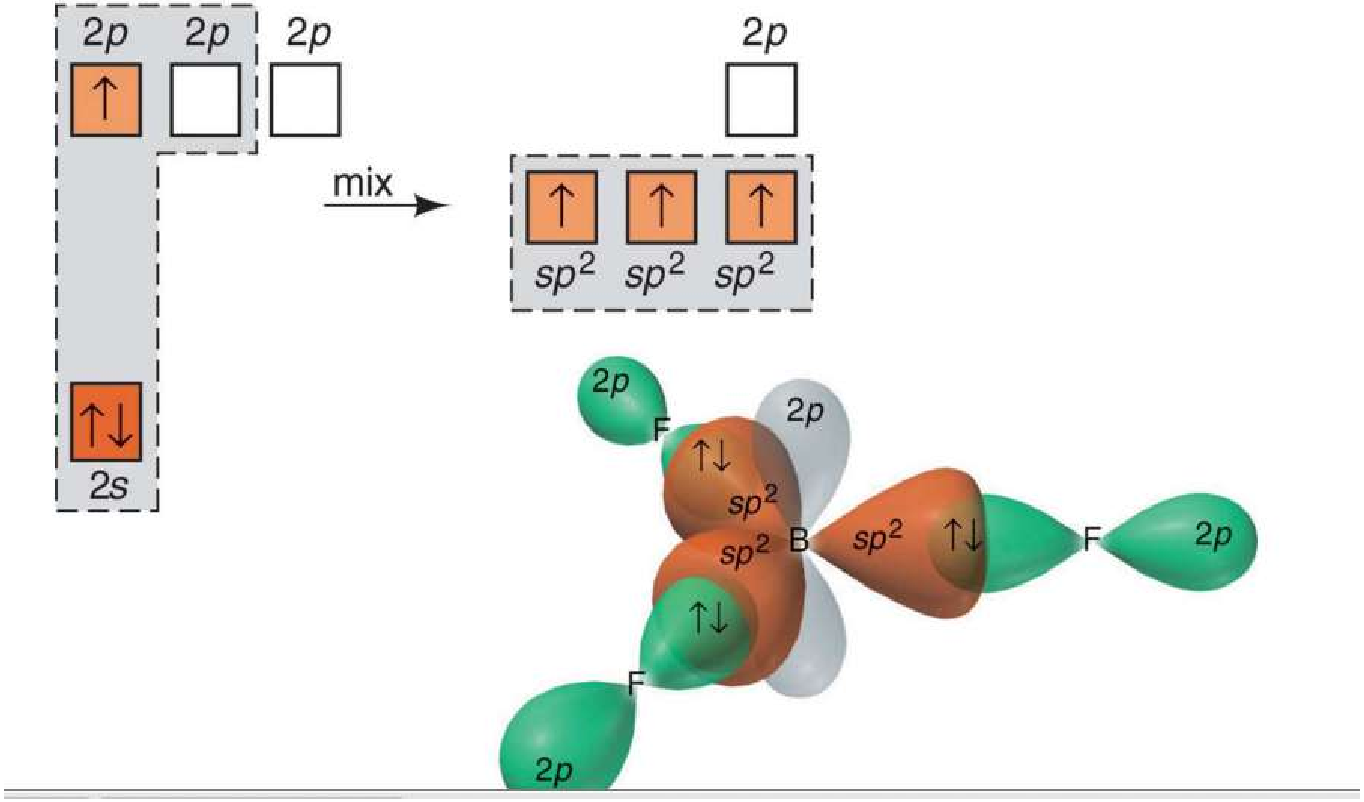
- B = ↑↓ ↑ ↑ ↑ ___

  1s sp^2 2p

- The remaining 2p orbital remains the same.

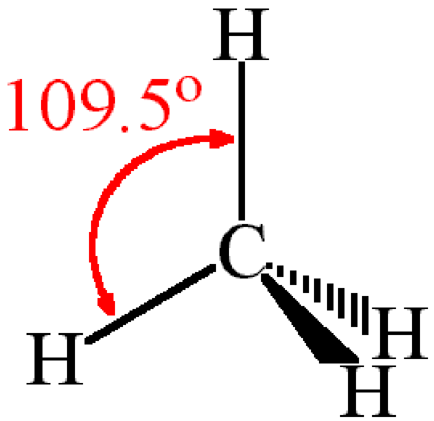
sp^2 Hybrid Orbitals

- The hybrid orbitals and bonding in BF_3 would look like the following diagrams.



sp^3 Hybrid Orbitals

- CH_4



- H = ↑
  1s
- This shows that H can bond by filling its 1s sublevel.
- C = ↑↓ ↑↓ ↑ ↑ ___
  1s 2s 2p

sp^3 Hybrid Orbitals

- Since C has two unpaired electrons, it should only form two bonds, so one of the electrons is “promoted” to a 2p orbital to allow for 4 bonds.

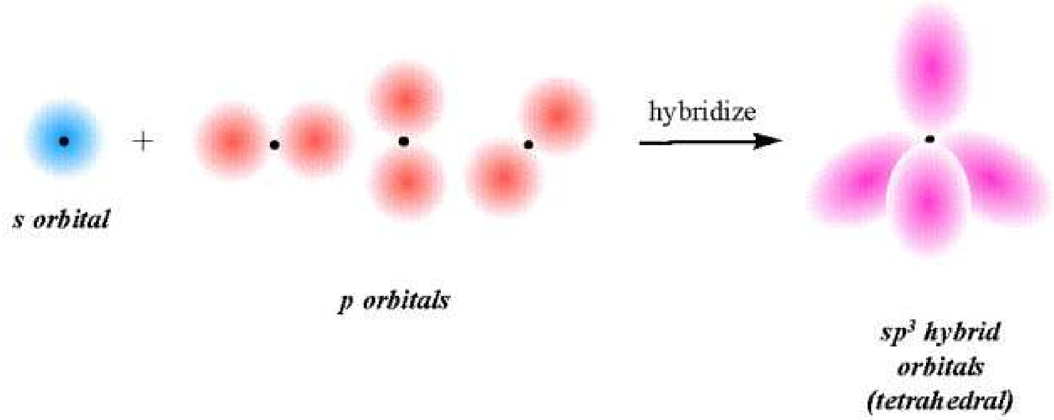
- C = ↑↓ ↑ ↑ ↑ ↑

  1s 2s 2p

- However, this arrangement would not make the four C – H bonds equal because one would involve and s orbital and three would involve p orbitals.

sp^3 Hybrid Orbitals

- We can form 4 hybrid sp^3 orbitals which have 2 lobes like a p orbital, but 1 lobe is much larger than the other.

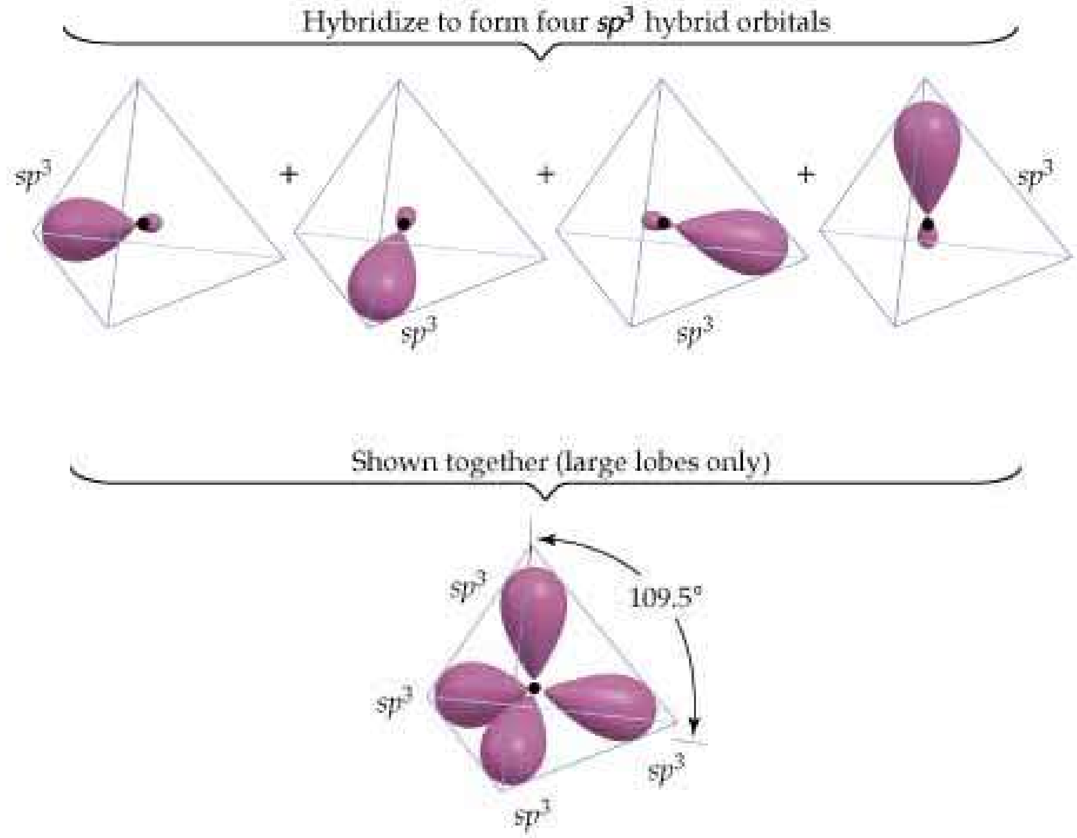


- C = $\underset{1s}{\underline{\uparrow\downarrow}}\quad\underline{\uparrow}\;\;\underline{\uparrow}\;\;\underline{\uparrow}\;\;\underline{\uparrow}$

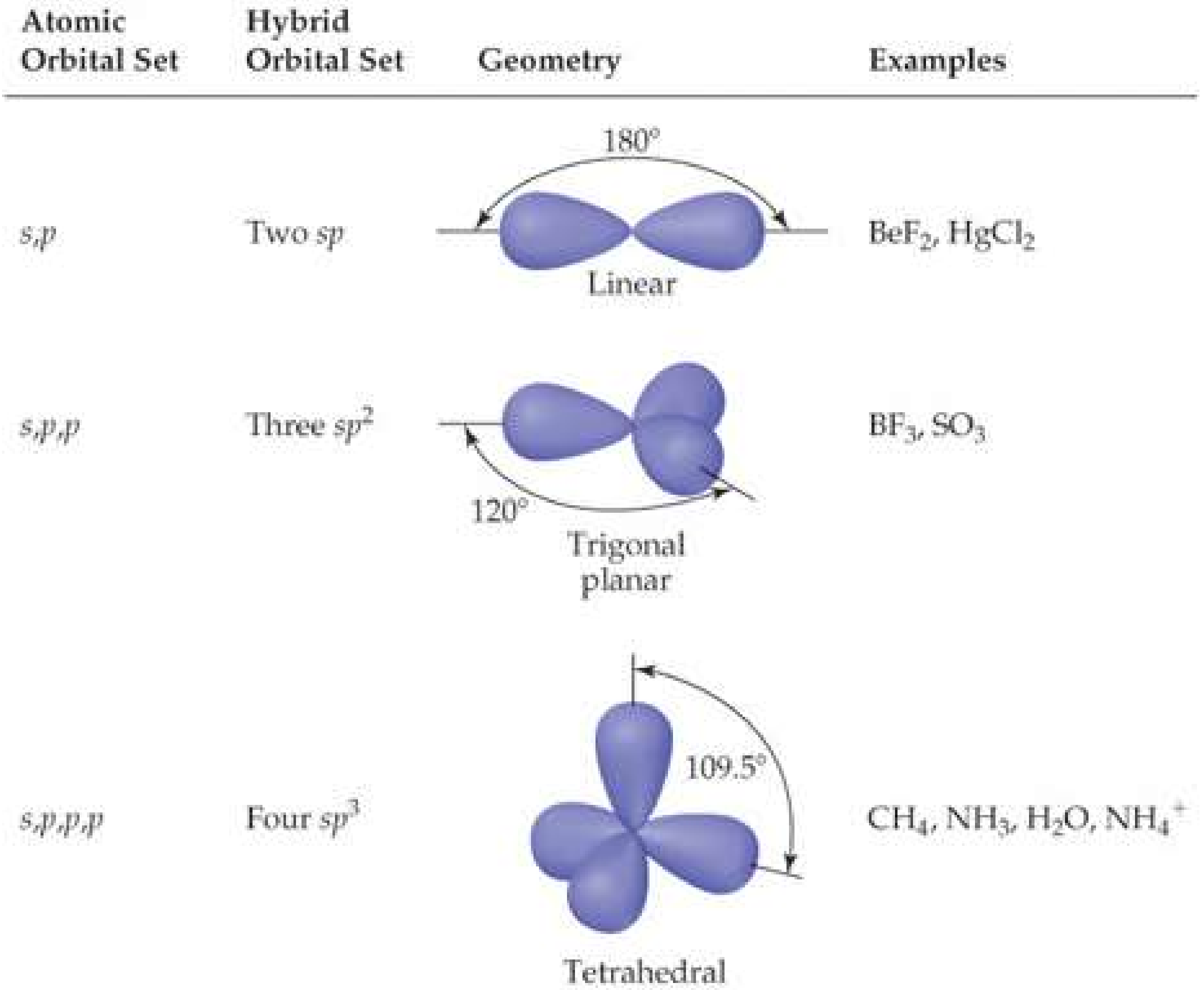
  1s $\qquad\qquad$ sp^3

sp^3 Hybrid Orbitals

- The hybrid orbitals and bonding in CH_4 would look like the following diagrams.



Hybrid Orbital Chart



Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,*p*	Two *sp*	180° Linear	BeF_2, $HgCl_2$
s,*p*,*p*	Three sp^2	120° Trigonal planar	BF_3, SO_3
s,*p*,*p*,*p*	Four sp^3	109.5° Tetrahedral	CH_4, NH_3, H_2O, NH_4^+

Sample Exercise 9.5

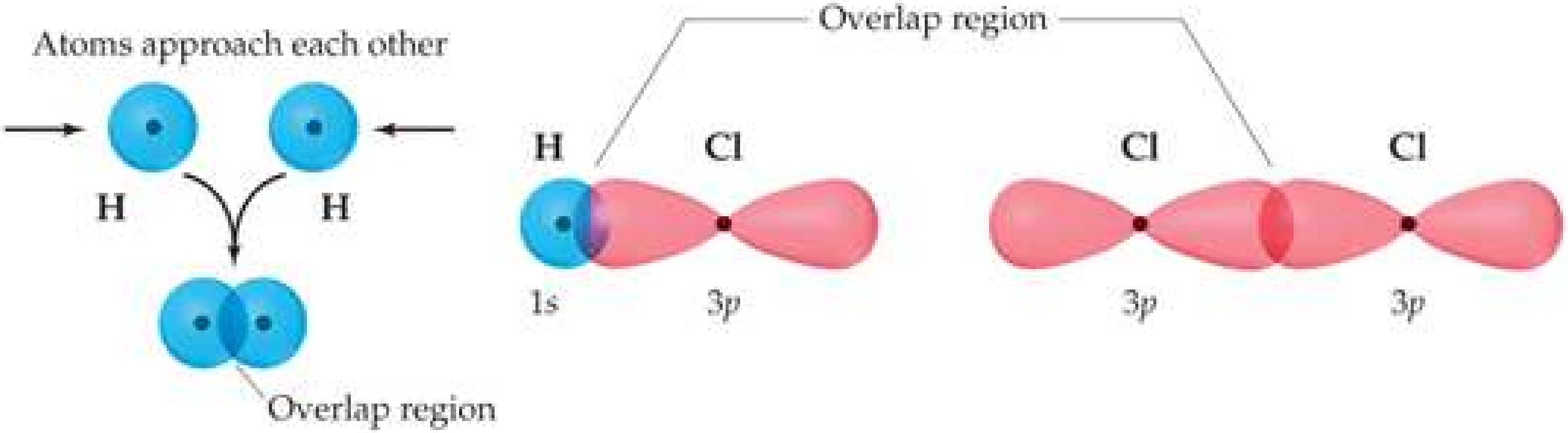
- Indicate the hybridization of orbitals employed by the central atom in NH_2^-.

Practice Exercise

- Predict the electron-domain geometry and the hybridization of the central atom in SO_3^{2-}.

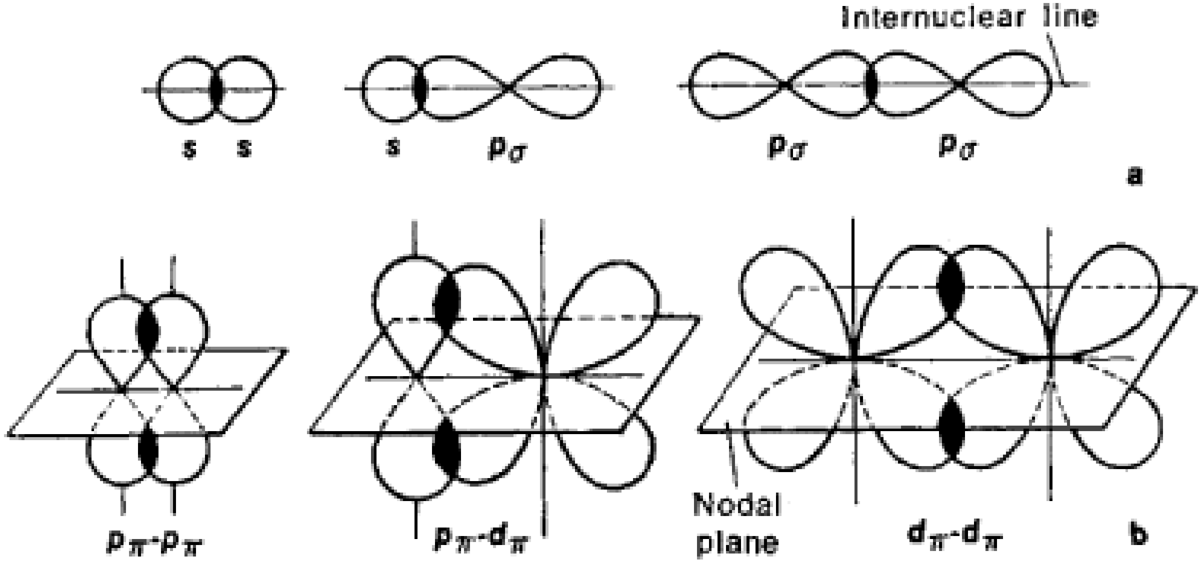
Section 9.6 – Multiple Bonds

- A sigma (σ) bond is a bond that occurs when a line that passes through the two nuclei of the bonded atoms also passes through the middle of the orbital overlap.



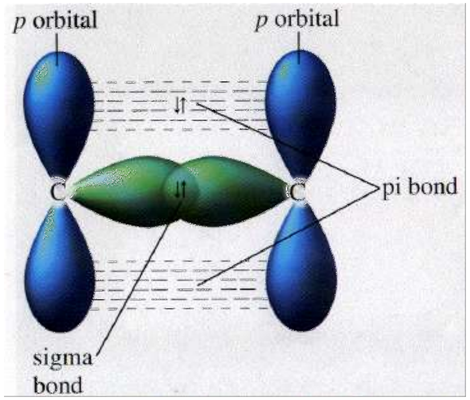
Multiple Bonds

- A pi (π) bond is a bond that occurs when the overlap of the orbitals is perpendicular to the internuclear axis.
- In a pi bond the overlap occurs above and below the internuclear axis.



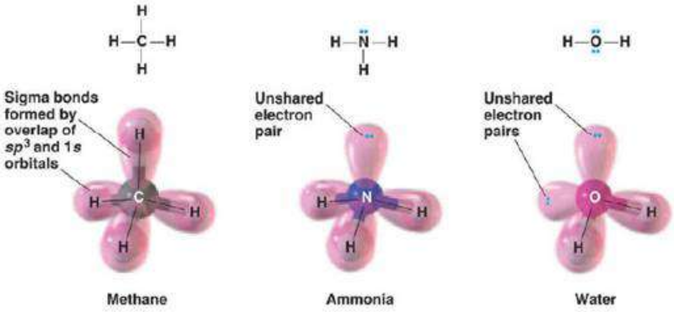
Pi vs. Sigma

- Unlike a sigma bond, in a pi bond there is no probability of finding the electron on the internuclear axis.
- Since the p orbitals in a pi bond overlap sideways rather than directly facing each other, the total overlap in a pi bond tends to be less than in a sigma bond. This means that pi bonds tend to be weaker than sigma bonds.

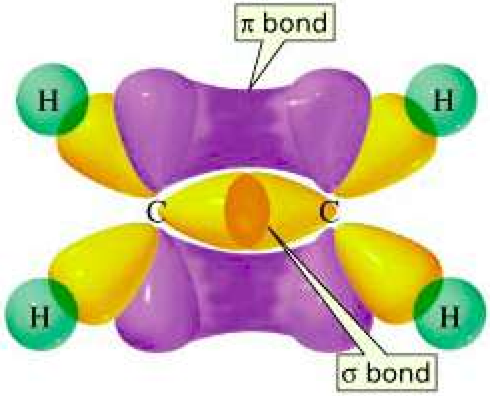


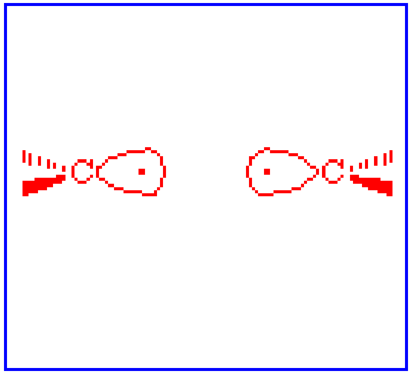
Type of Bond

- Single bonds are sigma bonds.



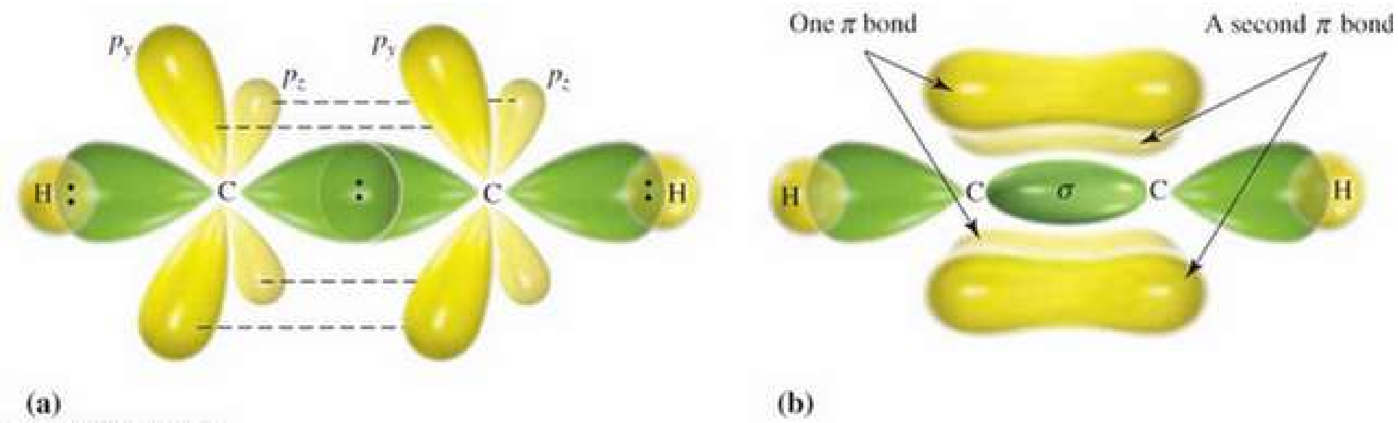
- A double bond consists of 1 sigma bond and 1 pi bond.





Type of Bond

- A triple bond consists of 1 sigma bond and 2 pi bonds.



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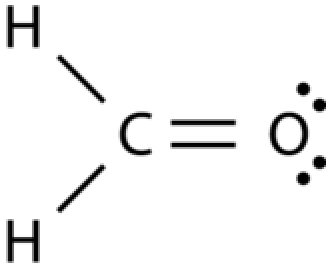
- Since pi bonds occur using unhybridized p orbitals, it can only occur with sp and sp^2 hybridization.

Sample Exercise 9.6

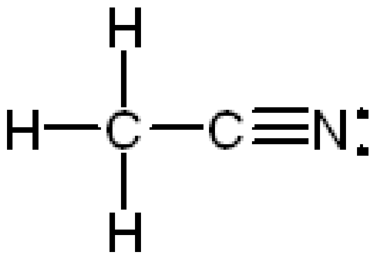
- Formaldehyde has the Lewis structure



Describe how the bonds in formaldehyde are formed in terms of overlaps of appropriate hybridized and unhybridized orbitals.

Practice Exercise

- Consider the acetonitrile molecule:



$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-C\equiv N:}$$

a. Predict the bond angles around each carbon atom.

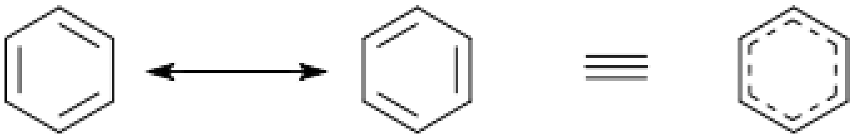
Practice Exercise Con’t

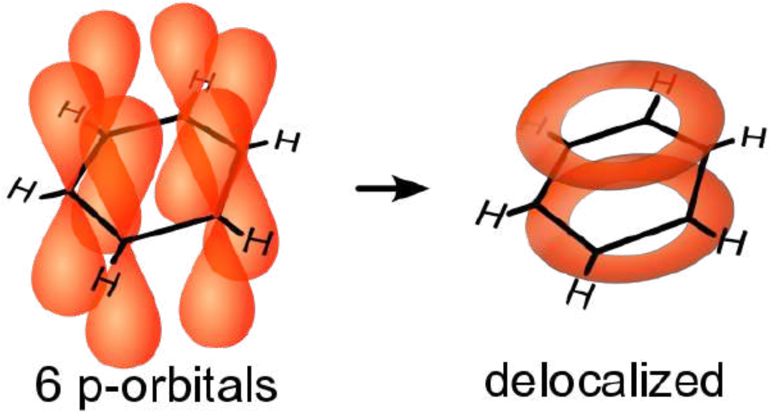
b. Describe the hybridization at each carbon atom.

c. Determine the total number of σ and π bonds in the molecule.

Localized and Delocalized Electrons

- Localized electrons belong to the two atoms that form the bond.
- When resonance structures exist for a molecule, the electrons move around and are called delocalized.





Sample Exercise 9.7

- Describe the bonding in the nitrate ion, NO_3^-. Does this ion have delocalized π bonds?

Practice Exercise

- Which of the following molecules or ions will exhibit delocalized bonding: SO_3, SO_3^{2-}, H_2CO, O_3, NH_4^+?

Sample Integrative Exercise

- Elemental sulfur is a yellow solid that consists of S_8 molecules. The structure of the S_8 molecule is an eight-membered ring. Heating elemental sulfur to high temperatures produces gaseous S_2 molecules:

$$S_{8(s)} \rightarrow 4S_{2(g)}$$

a. With respect to electronic structure, which element in the second row of the periodic table is most similar to sulfur?

Sample Integrative Exercise

b. Use the VSEPR model to predict the S – S – S bond angles in S_8, and the hybridization at S in S_8.

Sample Integrative Exercise

d. Use average bond enthalpies (Table 8.4) to estimate the enthalpy change for the reaction just described. Is the reaction exothermic or endothermic?