2.7 VSEPR and Bond Hybridization

Essential knowledge statements from the AP Chemistry CED:

- VSEPR theory uses the Coulombic repulsion between electrons as a basis for predicting the arrangement of electron pairs around a central atom.
- Both Lewis diagrams and VSEPR theory must be used for predicting electronic and structural properties of many covalently bonded molecules and polyatomic ions, including the following:
  - Molecular geometry
  - Bond angles
  - Relative bond energies based on bond order
  - Relative bond lengths (multiple bonds, effects of atomic radius)
  - Presence of a dipole moment
  - Hybridization of valence orbitals of the molecule
- The terms "hybridization" and "hybrid atomic orbital" are used to describe the arrangement of electrons around a central atom. When the central atom is sp hybridized, its ideal bond angles are 180^o; for sp^2 hybridized atoms the bond angles are 120^o; and for sp^3 hybridized atoms the bond angles are 109.5^o.
- Bond formation is associated with overlap between atomic orbitals. In multiple bonds, such overlap leads to the formation of both sigma and pi bonds. The overlap is stronger in sigma than pi bonds, which is reflected in sigma bonds having greater bond energy than pi bonds. The presence of a pi bond also prevents the rotation of the bond and leads to structural isomers.

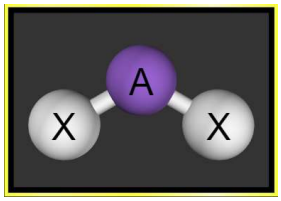
Visit the following website: bit.ly/PhET_shapes

Or you can search online for "PhET shapes"

Once the website loads, you should have the following options.

"Model" "Real Molecules"

Choose the "Model" icon located on the left.



On the bottom side of the screen, select the box for "Molecule Geometry."

On the right side of the screen, select the boxes for "Show Lone Pairs" and "Show Bond Angles."

1. (a) Use a separate sheet of paper to draw the correct Lewis electron dot structures for each of the following: CO_2 NO_2^+ HCN

   (b) Now use the PhET simulation to build each molecule/ion. Fill in the information below.

   Geometry (or Shape) = _____ and bond angle = _____

2. (a) Use a separate sheet of paper to draw the correct Lewis electron dot structures for each of the following: BF_3 SO_3 NO_3^-

   (b) Now use the PhET simulation to build each molecule/ion. Fill in the information below.

   Geometry (or Shape) = _____ and bond angle = _____

3. (a) Use a separate sheet of paper to draw the correct Lewis electron dot structures for each of the following: CF_4 NH_4^+ SO_4^{2-}

   (b) Now use the PhET simulation to build each molecule/ion. Fill in the information below.

   Geometry (or Shape) = _____ and bond angle = _____

4. (a) Use a separate sheet of paper to draw the correct Lewis electron dot structure for PF_5.

   (b) Now use the PhET simulation to build that molecule. Fill in the information below.

   Geometry (or Shape) = _____ and bond angle = 90° and 120°

5. (a) Use a separate sheet of paper to draw the correct Lewis electron dot structure for SF_6.

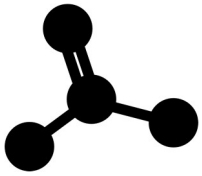
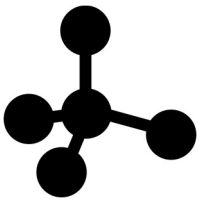
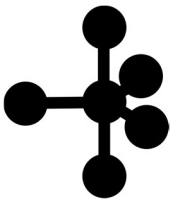
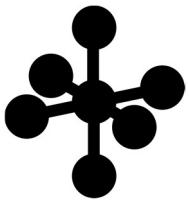
   (b) Now use the PhET simulation to build that molecule. Fill in the information below.

   Geometry (or Shape) = _____ and bond angle = _____

An **electron domain** refers to a bond (single, double, or triple) or a lone pair of electrons.

- A single bond (or a multiple bond) counts as one electron domain.
- A lone pair (nonbonding pair) of electrons counts as one electron domain.

VSEPR stands for Valence Shell Electron Pair Repulsion. The electron domains that are connected to the central atom are arranged in three-dimensional space in such a way that they are located as far apart from each other as possible, in order to minimize the repulsions between them.

2 electron domains	3 electron domains	4 electron domains	5 electron domains	6 electron domains
				
linear	trigonal planar	tetrahedral	trigonal bipyramidal	octahedral
180°	120°	109.5°	90° and 120°	90°

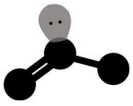
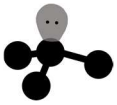
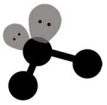
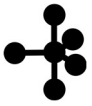
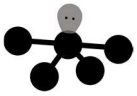
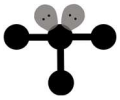
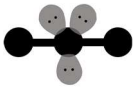
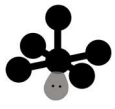
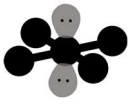
Up until this point in the packet, each substance that has been used as an example has had a central atom with no lone pairs of electrons on it. In other words, all of the electron domains connected to the central atom have been bonding domains only. Now we will consider how the shape of a molecule is affected by the presence of nonbonding electron domains on the central atom.

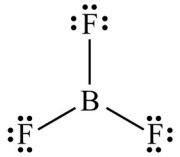
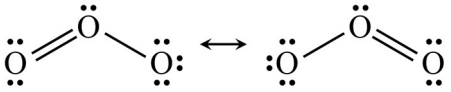
6. Each example in the table below represents a molecule with at least one lone pair of electrons on the central atom. Use the PhET simulation to build each molecule according the information in the table. Fill in the information for molecular geometry in the table below.

Bonding Domains (single bonds) connected to the central atom	Nonbonding Domains (lone pairs) connected to the central atom	Molecular Geometry
2	1	
3	1	
2	2	
4	1	
3	2	
2	3	
5	1	
4	2	

7. Fill in the table below with one of the following example molecules.

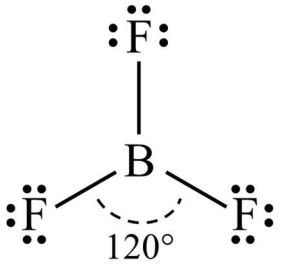
CO_2 SO_2 SF_2 XeF_2 SO_3 PF_3 ClF_3 CF_4 SF_4 XeF_4 PF_5 BrF_5 SF_6

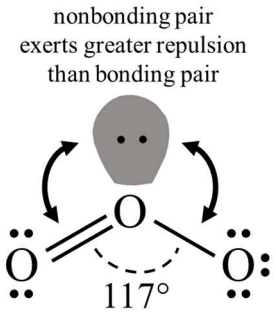
Total Electron Domains	Bonding Domains	Nonbonding Domains	Molecular Geometry	Picture	Example Molecule
2	2	0	linear		
3	3	0	trigonal planar		
3	2	1	bent		
4	4	0	tetrahedral		
4	3	1	trigonal pyramidal		
4	2	2	bent		
5	5	0	trigonal bipyramidal		
5	4	1	seesaw		
5	3	2	T-shaped		
5	2	3	linear		
6	6	0	octahedral		
6	5	1	square pyramidal		
6	4	2	square planar		

	
F–B–F bond angle = 120°	O–O–O bond angle = 117°

As shown in the table above, the bond angle in the O_3 molecule is slightly less than the bond angle in the BF_3 molecule. This difference in bond angle can be explained as follows.

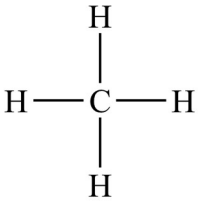
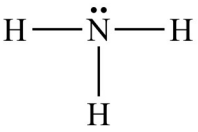
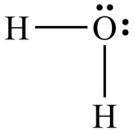
Let's compare the amount of space occupied by a bonding pair of electrons with the amount of space occupied by a nonbonding pair (lone pair) of electrons.





A bonding pair of electrons is attracted by the nuclei of two atoms. Therefore the bonding electrons are likely to be located in the space between the two atoms that share them.

A nonbonding pair (lone pair) of electrons can spread out more, occupying more space than a bonding pair. As a result, it tends to exert greater repulsive forces on the nearby bonding pairs, reducing the bond angle slightly.

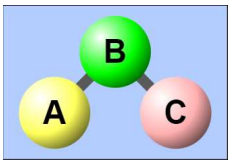
		

8. The Lewis structures for CH_4, NH_3, and H_2O are shown above. Arrange these three molecules in order from the smallest bond angle to largest bond angle.

Visit the following website: bit.ly/PhET_polarity

Or you can search online for “PhET polarity”

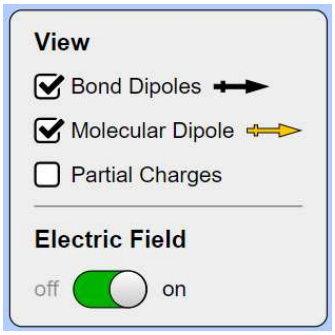
Once the website loads, you should have the following three options.



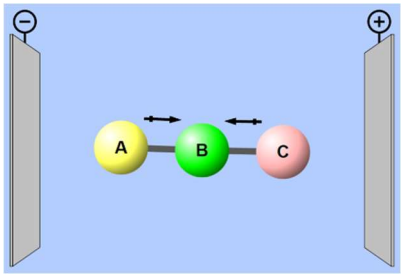
“Two Atoms” “Three Atoms” “Real Molecules”

Choose the “Three Atoms” icon located in the middle of the screen.

On the right side of the screen, select the following settings.

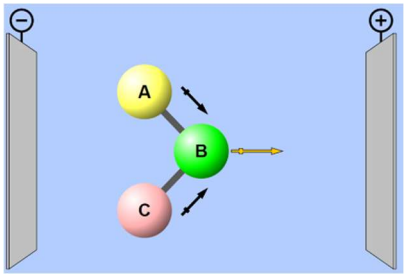


Arrange the atoms A, B, and C so that a linear molecule is formed. The two black arrows represent the dipoles for each polar bond. These two arrows are equal in magnitude, but they point in opposite directions. These two dipoles cancel each other out. The yellow arrow representing the molecular dipole has disappeared. The molecule rotates randomly within the electric field, because it is not attracted to either the positive plate or the negative plate.



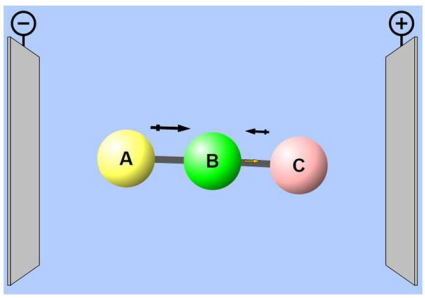
The molecule is nonpolar. Its dipole moment is equal to zero.

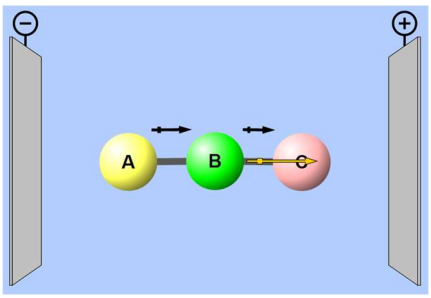
Now arrange the atoms A, B, and C so that a bent molecule is formed. The two black arrows represent the dipoles for each polar bond. These two arrows are equal in magnitude, but now they do not point in opposite directions. The two dipoles do not cancel each other out. The yellow arrow representing the molecular dipole is visible. The molecule does not rotate around randomly within the electric field. It is locked in place, because the negative end of the molecular dipole points toward the positive plate.



This molecule is polar, and has a nonzero value for its dipole moment.

It is possible to create a linear molecule that is polar. Use the sliders to adjust the electronegativity of the atoms. If the two bond dipoles (represented by black arrows) do not cancel each other out, then the molecule is classified as polar. If the yellow arrow (molecular dipole) is visible, the molecule is polar.



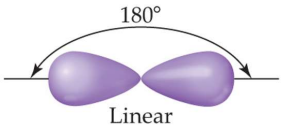
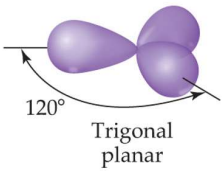
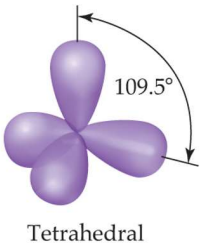


9. Use a separate sheet of paper to draw the correct Lewis electron dot structures for each of the following molecules in the table below. Identify the molecular shape and classify each molecule as polar or nonpolar.

- If all of the bond dipoles cancel each other out, the molecule is classified as nonpolar.
- If the bond dipoles do not cancel each other out, the molecule is classified as polar.

Substance	Molecular Shape	Polar or Nonpolar?
CO_2		
HCN		
BF_3		
CCl_2O		
SO_2		
CF_4		
CH_2F_2		
NH_3		
H_2O		
PF_5		
PF_4Cl		
SF_4		
ClF_3		
XeF_2		
SF_6		
BrF_5		
XeF_4		

In order to explain how the atomic orbital for an atom forms chemical bonds to create molecules with certain molecular shapes, we assume that the atomic orbitals on an atom undergo a "mixing" process that is known as **hybridization**. The three types of hybrid orbitals are summarized in the table below.

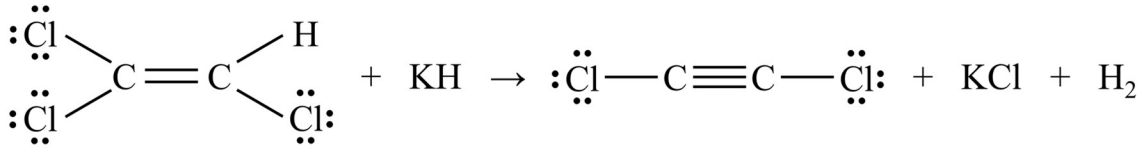
Hybridization	Origin of the Term	Total Number of Electron Domains Around the Central Atom	What it looks like
sp	one s orbital and one p orbital are mixed together	2	
sp^2	one s orbital and two p orbitals are mixed together	3	
sp^3	one s orbital and three p orbitals are mixed together	4	

10. Identify the hybridization of the valence orbitals (*sp*, sp^2, or sp^3) around the central atom in each of the following substances. Draw the Lewis diagram in order to determine the total number of electron domains around the central atom.

BeF_2 _____ CO_2 _____ NH_3 _____ NO_2^+ _____

BF_3 _____ SO_2 _____ NH_4^+ _____ NO_2^- _____

CF_4 _____ SF_2 _____ H_2O _____ NO_3^- _____



11. In the reaction shown above, how does the hybridization of the carbon atoms change?

(A) It changes from sp^3 to sp^2.

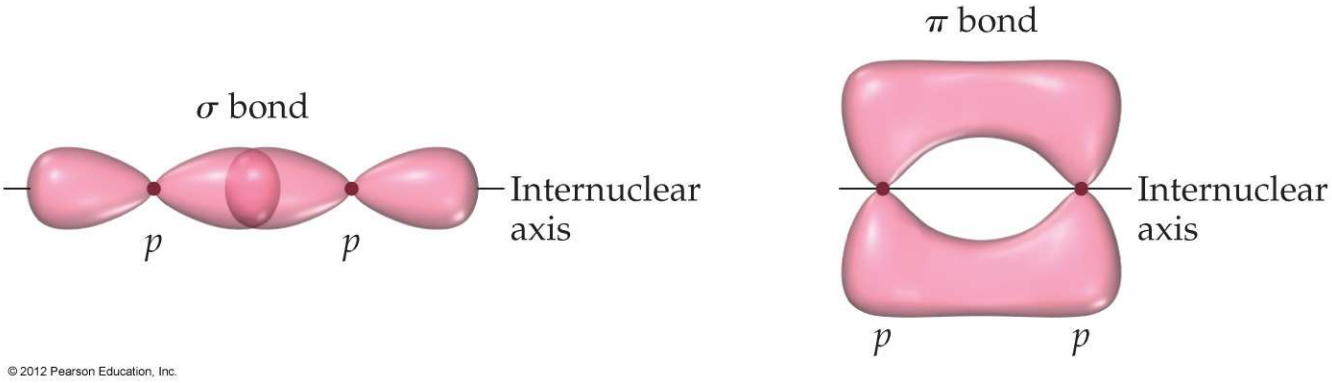
(B) It changes from sp^3 to *sp*.

(C) It changes from sp^2 to sp^3.

(D) It changes from sp^2 to *sp*.

A **sigma (σ) bond** is a bond formed by the overlap of orbitals in an end-to-end fashion, with the electron density concentrated between the nuclei of the bonding atoms.

A **pi (π) bond** is a bond formed by the overlap of orbitals in a side-by-side fashion, with the electron density concentrated above and below the plane of the nuclei of the bonding atoms.



- A single bond represents one sigma (σ) bond.
- A double bond represents one sigma (σ) bond and one pi (π) bond.
- A triple bond represents one sigma (σ) bond and two pi (π) bonds.

12. Fill in the missing information in the following table.

Molecule	Total Number of Sigma (σ) Bonds	Total Number of Pi (π) Bonds