Chapter 10 Chemical Bonding II: Molecular Geometry & Hybridization

Chemistry by Chang and Goldsby

Chapter 10: Chemical Bonding II

You will be expected to predict the shapes of molecules for three systems used for modeling atoms using-- VSEPR, atomic orbitals, and hybridization.

10.1 VSEPR Molecular Geometry

You should be able to predict the shape of a molecule using the **V**alence **S**hell **E**lectron **P**air **R**epulsion model.

Steps for applying the VSEPR model:

(1) Draw the Lewis Structure of the molecule. Only the central atom's bonded and unbonded pairs of electrons will be used in determining the shape.

(2) Count the number of sigma bonds and the lone (unbonded) pairs of electrons. These are "electron domains".
Ignore the pi bonds as pi bonds don't alter the shape of the molecule.
The total count of the electron domains is the steric number[1], SN.
The domains arrange in three dimensions as far apart from one another as possible because of the Coulombic repulsion of electrons between the domains.

(3) Use *AP08 C10 Molecular Geometry* table to predict the shape of the molecule.

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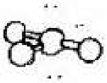
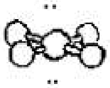
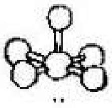
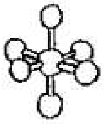
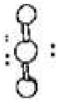
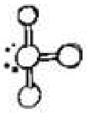
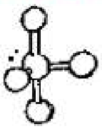
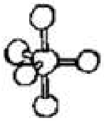
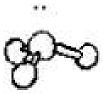
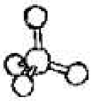
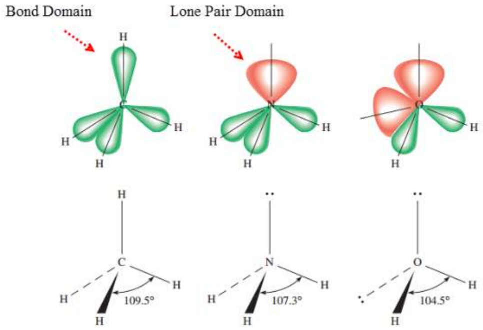
[1] Electron domain and steric number are terms that are not used in most textbooks, but they have been used on AP Chemistry exams.

AP08 C10 Molecular Geometry Table ***Symmetrical Shapes are italicized***

Steric number SN=6 6 Electron Domains[1] 90°					
Bonding Pair	2	3	4	5	6
Lone Pair	4	3	2	1	0
Name	***Linear***	T-shaped	***Square Planar***	Square Pyramidal	***Octahedral***
SN=5 5 Electron Domains 120°& 90°					
Bonding Pair	2	3	4	5	
Lone Pair	3	2	1	0	
Name	***Linear***	T-shaped	Distorted Tetrahedron (Seesaw)	***Trigonal Bipyramidal***	
SN=4 4 Electron Domains 109°				sp^3 **hybrid orbitals**	
Bonding Pair	2	3	4		
Lone Pair	2	1	0		
Name	Nonlinear (Bent)	Trigonal Pyramidal	***Tetrahedral***		
SN=3 3 Electron Domains 120°			sp^2 **hybrid orbitals**		
Bonding Pair	2	3			
Lone Pair	1	0			
Name	Nonlinear (Bent)	***Trigonal Planar***			
SN=2 2 Electron Domains 180°		sp **hybrid orbitals**			
Bonding Pair	2				
Lone Pair	0 ***Linear***				

When predicting bond angles, the lone pair of electrons of a domain are considered to repel more strongly than a bonding pair domain and the bond angles can be distorted[2].

The lone pair domain warps the tetrahedral angle of the H-N-H from the ideal 109° down to a lesser angle such as 104°.



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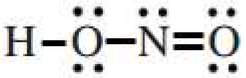
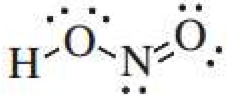
[2] This may not actually true but is the expected explanation in AP Chemistry and most textbooks.

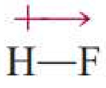
Memorize the shapes, angles, and names on *AP08 C10 Molecular Geometry* table.
Also, you must also know which molecular shapes are symmetrical.

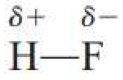
Note: The AP Chem exam will often give the Kekulé structure or diagrams. A Kekulé diagram does not show unpaired electrons and will have misleading angles.

Kekulé structure	Lewis electron dot diagram	Approximate molecular shape
H–O–N–O		
Kekulé diagrams do not include the lone pairs of electrons around atoms. Thus, **Kekulé diagrams do not provide enough information for bond angle predictions.**	Lewis dot diagrams include unpaired electrons and bonds. However, Lewis electron dot diagrams do not show bond angles.	Using the shape table with Lewis electron dot diagrams allows for the determination of the bond angles. In the case of this molecule, the bond angles would be 109° and 120°.

10.2 Dipole Moments

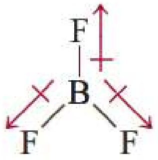
Dipole moments involve polar bonds and unsymmetrical molecular shapes.

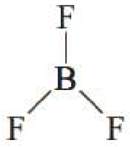




Unsymmetrical molecules will have unequal sharing of electrons causing partial charges. The fluorine atom has a higher electronegativity than hydrogen so the electrons in this molecule will be drawn to fluorine as shown by the vector arrow that shows the direction and magnitude of the separation of charge.

This results in a partial charge negative charge on the fluorine atom and a partial positive charge on the hydrogen atom. The lower case delta, δ, is used to indicate the partial charges. The partial charge is measured in Debyes.





However, if a molecule is symmetrical, it is possible for the polar bonds to cancel because the electronegative atoms electron "pulls" cancel one another. Even though the fluorine atoms have a higher electronegativity than boron trifluoride does not have partial charges.

The illustrations with the vectors (directional pulls) showing the polar bonds can be used to show how the polar bonds interact (cancel or amplify) to form a net dipole or cancel to form a nonpolar (0 Debyes) molecule.

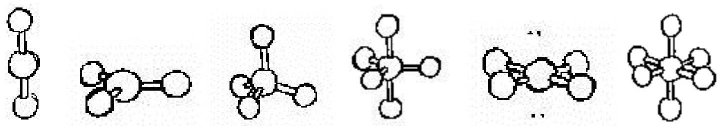
Even though you will not have to calculate the magnitude of the moments, you will be expected to predict if a molecule will be polar (a Debye value of greater than zero) or nonpolar based on the presence of or absence of polar bonds and the shape of the molecule.

General rule: If a molecule has a symmetrical structure both in shape and attached atoms, the polarity of the individual bonds will cancel and the molecule will be nonpolar.

These symmetrical molecules with identical attached atoms will not produce a dipole moment.

Dipole moment, a measure of polarity of a molecule is measured in debyes, D.

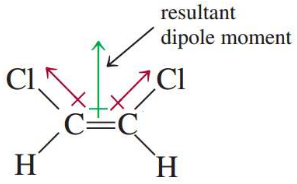
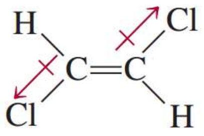
Symmetrical molecules, D = 0 debyes



Symmetrical molecular structure can produce nonpolar molecules despite having polar bonds.

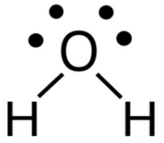
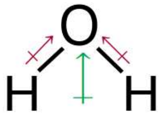
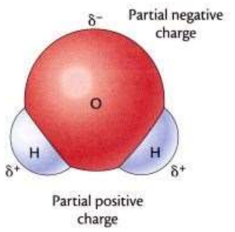
Exception to the Rule: It is possible for an unsymmetrical molecule to be nonpolar.

The dichloroethene molecule has 120° trigonal planar geometry. The H-C bonds are not significantly polar since the electronegativity of H is very close to C. However, chlorine has an electronegativity of 3.0 and carbon has an electronegativity of 2.4, so the C-Cl bond has a significant polarity.

Polar C-Cl bonds in the *cis* position reinforce one another and there is a net dipole moment, μ = 1.7 debyes. The individual polarities (red vectors) combine to make the resultant dipole moment for the molecule.	Polar C-Cl bonds in the *trans* position oppose one another. The individual bond polarities (red vectors) work against one another and cancel. Even though individual bonds may be polar, the molecule itself is nonpolar, μ = 0 debyes.
 *cis*-dichloroethylene	 *trans*-dichloroethylene

The most important example of a polar molecule is the water molecule. The polar O-H bonds and the unsymmetrical shape of the water molecule results in a polar molecule (μ = 1.9 D).

Memorize the unsymmetrical shape and polarity of the water molecule.
Hydrogen atoms of water molecules have a δ+ .
The oxygen atom of water molecules has a δ-.

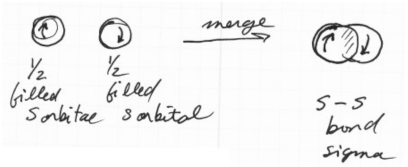
The dipole of the water molecule is used to explain density changes in water, the melting and boiling temperature of water, the solubility of ionic and polar molecular solutes.

10.3 Valence Bond Theory

> "The simpler Lewis theory treats *all* covalent bonds the same way and offers no explanation for the difference among covalent bonds."

The more complex valence bond theory explains why sigma bonds are different from pi bonds and gives a more complete description of bonding.

Sigma bonds (the first bond in all covalent bonds) are made by a simple overlap of half-filled orbitals.

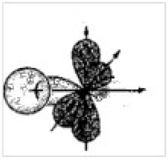
Two half-filled *s* orbitals can overlap.	

For example: in hydrogen atoms becoming H_2, using an *s* orbital–*s* orbital sigma bond.

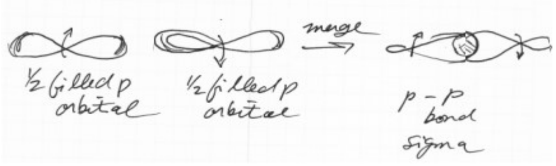
 *s* ↓ Hydrogen	 *s* ↑ Hydrogen	 *s* *s* ↓↑ H-H This is an ***s-s* sigma bond**

A half-filled *s* orbital and a ½ filled *p* orbital can overlap. Note that the unbonded side of the *p* orbital shrinks since the electron spends more time in the bond between the two nuclei.	

For example, a hydrogen atom and fluorine atom overlap half-filled orbitals to make H-F, a *s-p* sigma bond

 *s* ↓ Hydrogen	 p_x p_y p_z ↑ ↑↓ ↑↓ Fluorine The filled *p* orbitals can be ignored.	 s-p_x p_y p_z ↓↑ ↑↓ ↑↓ H-F Hydrogen fluoride This is a ***s-p* sigma bond**

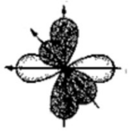
A ½ filled *p* orbital and a ½ filled *p* orbital can sigma overlap.



A fluorine atom and fluorine atom overlap half-filled orbitals to make F-F, a *p-p* sigma bond.

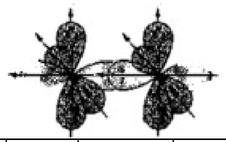
p_z	p_y	P_x
↑↓	↑↓	↑

Fluorine



p_x	p_y	p_z
↑	↑↓	↑↓

Fluorine



p_z	p_y	p_x- p_x	p_y	p_z
↑↓	↑↓	↑↓	↑↓	↑↓

Fluorine-Fluorine

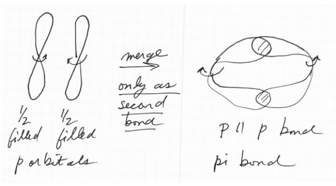
This is a ***p-p*** **sigma bond**

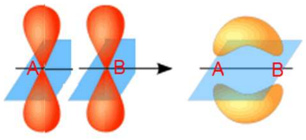
Once a sigma bond is formed, there is no room for more electrons to be shared between the two atoms. For a second or third bond to form, there must be a special way for the bonding electrons to be shared between the two atoms.

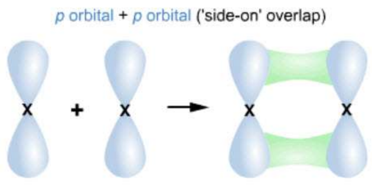
Pi bonds (the second and third bond between two atoms) are made by overlapping half-filled **parallel *p* orbitals.**

A sigma bond first bonds the two atoms together by filling the area directly between the bonded atoms. To form a second bond, the pi, the bond must use another area for bonding. The pi bond forms by using parallel *p* orbitals.

Pi bonds occur with half-filled parallel *p* orbitals merging top and bottom portions of the *p* orbital simultaneously. These three drawings show a single pi bond forming. Examine them carefully understand the pi bond.







Once two molecules create a pi bond, the molecules are locked in position and cannot rotate independently without breaking the pi bond.

By itself, the pi bond has a lower bond energy than a comparable sigma bond. However, since the pi bond only occurs with a sigma bond, **the total bond energy of a double bond (sigma + pi) is greater than a single bond**.

Summarizing **Sigma and Pi bonds**

σ Bonds are the first bond between two atoms

Sigma bonds are simple, direct overlaps of half-filled orbitals.

π Bonds are the second or third bond between two atoms[3]

Pi bonds only form with parallel *p* orbitals.

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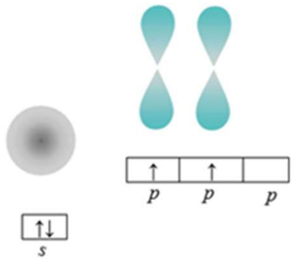
[3] P. Stuart Cohen "As my former student, Tommy DiSantis once said "Why can't we just let pi bonds be pi bonds?" ....I promised Tommy some 40 years ago that every time I told that joke I would mention his name.

10.4 Hybridization of Atomic Orbitals

Hybridization is primarily used with carbon, nitrogen, and oxygen atoms.
You will be responsible for identifying three types of hybrid bonding: sp^3, sp^2, and sp.

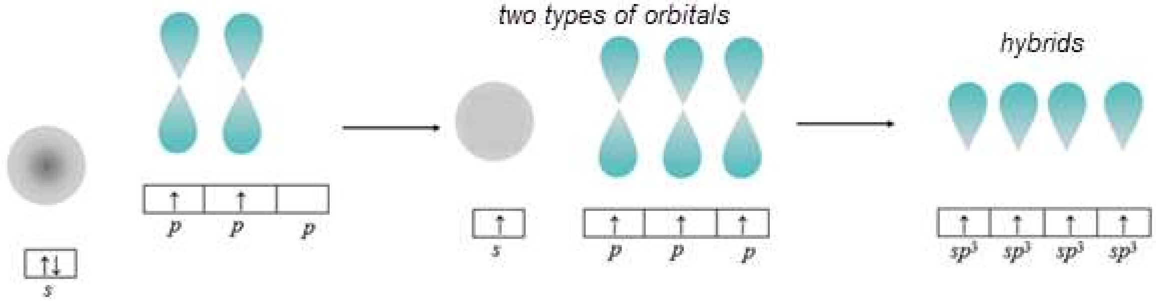
These diagrams explain the formation of hybrids, **but you can skip them and go directly to the Bottom Line on the next page.**

Explanation of hybridization

Based on carbon's electron configuration, carbon would normally have two types of orbitals. Carbon should have one filled *s* orbital, and two half-filled *p* orbitals.	
However, carbon always makes four bonds. So, the orbital structure of carbon must be "hybridized", so it has four half-filled orbitals	

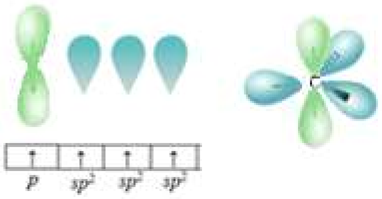
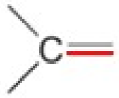
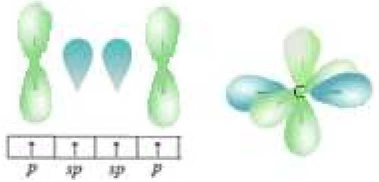
Hybridization provides a model where carbon can form 4 bonds.

The carbon atom starts with $2s^2\ 2p^2$ orbitals and promotes an electron from the s orbital to make $2s^1\ 2p^3$. This provides four half-filled orbitals. Then as a final step, the four orbitals, one *s* and three *p*'s are changed into identical hybrid orbitals each of which is labeled as a sp^3 hybrid orbital.



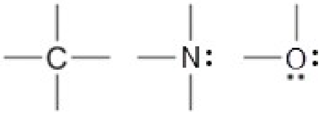
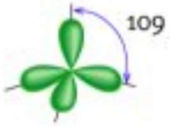
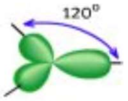
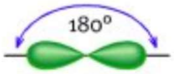
The label ***sp*^{3} indicates the origin of the four hybrid orbitals, *s*^{1}*p*^{3}**.

There are two other types of hybridization used in AP Chemistry. These occur when pi (double) bonds form.

When carbon forms three sigma bonds and one pi bond, a *sp*^{2} hybrid forms since one of the *sp*^{3} hybrids degenerates back into a *p* orbital to make a pi bond. The three remaining hybrid orbitals are *sp*^{2} hybrids.	 1 *p* and 3 *sp*^{2} half-filled orbitals.	 3 *sp*^{2} σ bonds and 1 π bond
When carbon forms two sigma bonds and two pi bonds, two *sp*^{3} hybrids degenerate back into *p* orbitals to make two pi bonds. The two remaining hybrid orbitals are *sp* hybrids.	 2 *p'*s and 2 *sp*^{2} half-filled orbitals.	 2 *sp* σ bonds and 2 π bonds

Bottom line: When asked about hybridization:

1. Draw the Lewis structure of the molecule.
2. Count the sigma bonds and unshared pairs of electrons.
   The number of domains, the steric number, determines hybridization.

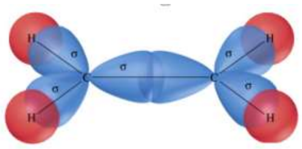
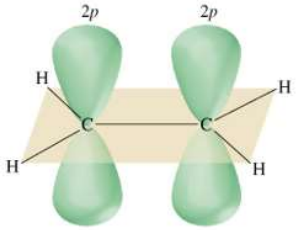
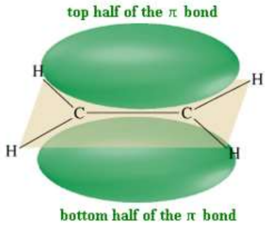
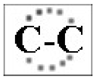
sigma bonds — *and unshared pairs of electrons*: are used in the steric number count	Hybrid designation	Shape and Hybrid Orbitals
pi bonds — are ignored in the steric count		
4 Domains  Each atom has four *sp*^{3} orbitals	***sp*^{3}**	 *sp*^{3}, *sp*^{3}, *sp*^{3}, *sp*^{3} Tetrahedral
3 Domains  Three *sp*^{2} orbitals for sigma bonding one *p* orbital for pi bonding	***sp*^{2}**	 *sp*^{2}, *sp*^{2}, *sp*^{2} Trigonal Planar
2 Domains  Two *sp* orbials for sigma bonding and two *p* orbitals for pi bonding	***sp***	 *sp*, *sp* Linear

Skip the subsection on the hybridization of *d* orbitals. The College Board has decided not to consider *d* orbitals in hybridization. (Most college textbooks still included*d* orbitals in hybrids and so do most college classes.)

10.5 Hybridization in Molecules Containing Double and Triple bonds.

Pi bonding is important in organic chemistry.

This diagram of the molecular structure of $H_2C{=}CH_2$, ethene, shows how double bonds form.

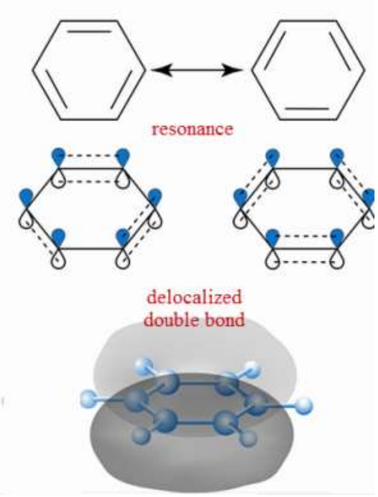
	The carbon atoms are *sp*^{2} hybridized with three *sp*^{2} hybrid orbitals. The three blue *sp*^{2} hybrid orbitals in the drawing form three single, sigma bonds. One sigma bond is C-C (*sp*$^{2-}$*sp*^{2}), and the other two are C-H (*sp*$^{2-}$*s*)
	**To form any pi double bond, you must have two parallel *p* orbitals.** The green parallel *p* orbitals at the left have not bonded. There is a single electron in each of their two-lobed *p* orbitals. Thus, the parallel *p* orbitals are half-filled and ready for bonding.
	The parallel *p* orbitals arch over the top and under the bottom of the carbon atoms to make **one π-bond**. Written as C=C but is more accurately . **This is the method of bond formation for all pi bonds** and explains why there is no independent rotation of each end of the double-bonded carbon compounds.

10.6-10.7 Molecular Orbital Theory.

Skip these two sections with bonding and antibonding diagrams. They are not part of the AP Chemistry curriculum.

10.8 Delocalized Molecular Orbitals-

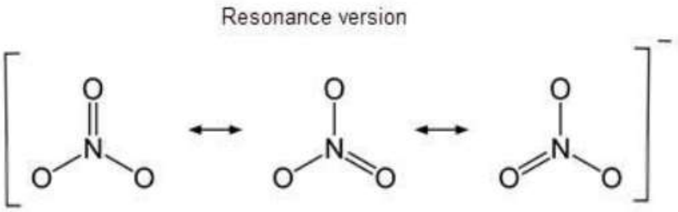
Not on the AP Chemistry exam, but useful in understanding why bonds in resonating structures are of equal length and usually part of college chemistry courses.

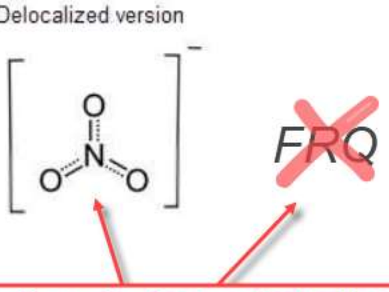


As an alternative to resonance, pi bonds can be thought of as being spread over several atoms.

Instead of having a double bond resonate (two atoms with pi bonds continuously swapping places), the pi bonding is delocalized over the resonating locations.

Often, molecules are drawn with delocalized dotted lines, rather than with alternating resonance diagrams as with this nitrate ion. Do not use the dotted line delocalized drawings on AP FRQ's when questions about resonance are asked.





Makes sense since it shows that all the bond lengths are equal, but not acceptable for diagram FRQ answers on the exam.