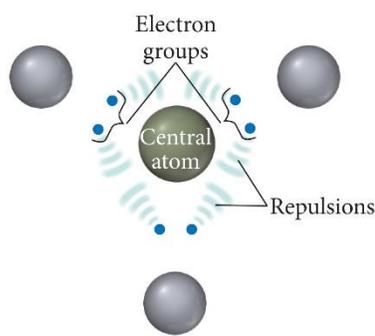


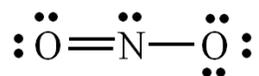
MOLECULAR SHAPES

- Properties of molecular substances depend on the structure of the molecule. The structure includes many factors:
 - The skeletal arrangement of the atoms
 - The kind of bonding between the atoms (ionic, polar covalent, or nonpolar covalent)
 - The shape of the molecule
- Bonding theory allows us to predict the shapes of molecules. Molecules are three-dimensional objects. We often describe the shape of a molecule with terms that relate to geometric figures.
- These geometric figures have characteristic “corners” that indicate the positions of the surrounding atoms around a central atom in the center of the geometric figure. The geometric figures also have characteristic angles that we call **bond angles**.
- Lewis theory predicts regions of electrons in an atom. Some regions result from placing shared pairs of valence electrons between bonding nuclei. Other regions result from placing unshared valence electrons on a single nuclei.
- Lewis theory states that these regions of electron groups should repel each other, because they are regions of negative charge. This idea can then be extended to predict the shapes of the molecules.
- The position of atoms surrounding a central atom will be determined by where the bonding electron groups are. The positions of the electron groups will be determined by trying to minimize repulsions between them.

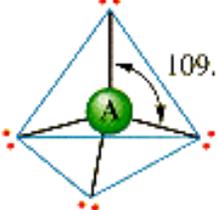


VSEPR THEORY

- Electron groups around the central atom will be most stable when they are as far apart as possible. We call this **valence shell electron pair repulsion (VSEPR)** theory.
- Because electrons are negatively charged, they should be most stable when they are separated as much as possible. The resulting geometric arrangement will allow us to predict the shapes and bond angles in the molecule.
- The Lewis structure predicts the number of valence electron pairs around the central atom(s). Each lone pair of electrons constitutes one electron group on a central atom. Each bond constitutes one electron group on a central atom, regardless of whether it is single, double, or triple.



- Based on VSEPR, there are five basic electron-pair geometries. The actual geometry of the molecule might be different from these if one or more of the electron pairs are lone pairs. The 3 electron-pair geometries discussed earlier are listed below.

Number of electron-pairs on central atom	Arrangement of electron-pairs	Electron-pair Geometry
2		Linear
3		Trigonal Planar
4		Tetrahedral

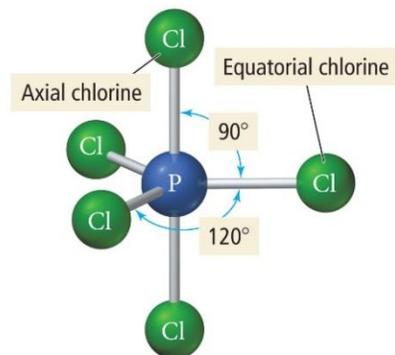
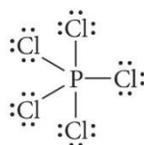
- Note that the bond angles listed above are idealized bond angles—where all electron pair groups are the same. The actual bond angles differ slightly from these when the electron-pair groups are not the same.

GEOMETRIES WITH FIVE & SIX ELECTRON-PAIR GROUPS

- When there are five electron groups around the central atom, they will occupy positions in the shape of two tetrahedra that are base to base with the central atom in the center of the shared bases. This results in the electron groups taking a **trigonal bipyramidal geometry**.



Trigonal bipyramid

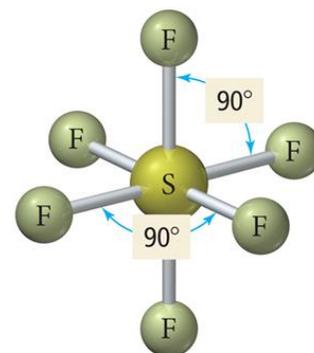
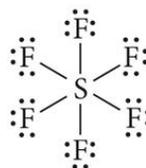


Trigonal bipyramidal geometry

- The positions above and below the central atom are called the **axial** positions. The positions in the same base plane as the central atom are called the **equatorial** positions. The bond angle between equatorial positions is 120° . The bond angle between axial and equatorial positions is 90° .
- When there are six electron groups around the central atom, they will occupy positions in the shape of two square-base pyramids that are base-to-base with the central atom in the center of the shared bases. This results in the electron groups taking an **octahedral geometry**. This shape is called octahedral because the geometric figure has eight sides.



Octahedron

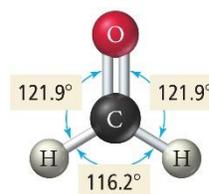
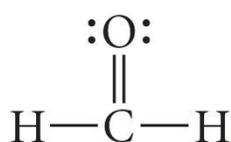


Octahedral geometry

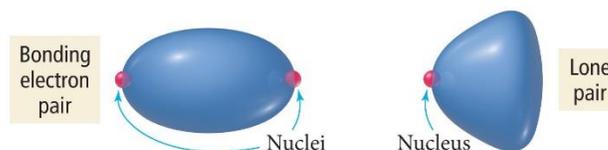
- All positions are equivalent with bond angle of 90° .

MOLECULAR GEOMETRY

- The actual geometry of the molecule may be different from the electron geometry. When the electron groups are attached to atoms of different size, or when the bonding to one atom is different than the bonding to another, this will affect the molecular geometry around the central atom.
- For example, consider the formaldehyde molecule (H_2CO), shown below. Because the bonds and atom sizes are not identical in formaldehyde, the observed angles are slightly different from ideal angle (120°) for trigonal planar shape.

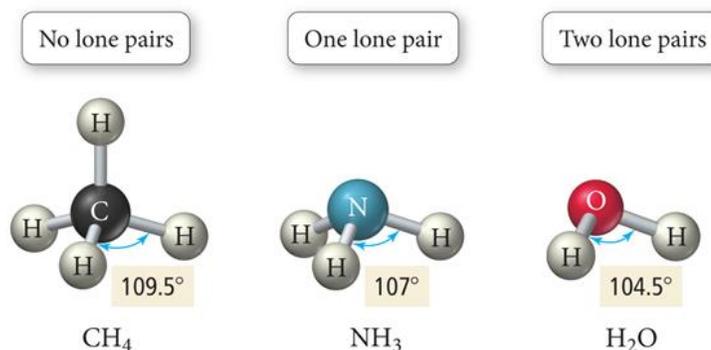


- Lone pairs also affect the molecular geometry. They occupy space on the central atom, but are not “seen” as points on the molecular geometry.
- Lone pair groups “occupy more space” on the central atom because their electron density is exclusively on the central atom, rather than shared, like bonding electron groups. The bonding electrons are shared by two atoms, so some of the negative charge is removed from the central atom.
- Relative sizes of repulsive force interactions is as follows:



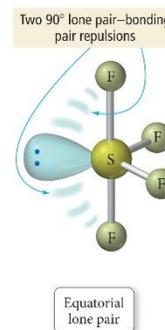
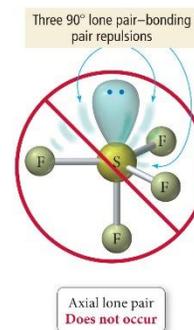
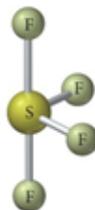
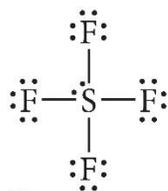
Lone Pair – Lone Pair > Lone Pair – Bonding Pair > Bonding Pair – Bonding Pair

- This affects the bond angles, making the bonding pair angles smaller than expected.

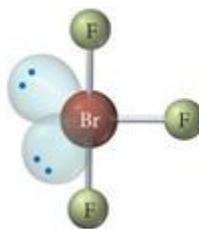
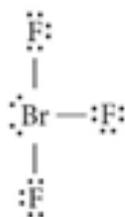


DERIVATIVES OF TRIGONAL BIPYRAMIDAL ELECTRON-PAIR GEOMETRY

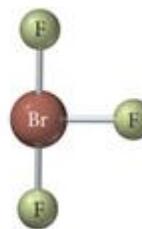
- When there are five electron groups around the central atom, and some are lone pairs, they will occupy the equatorial positions because there is more room.
- When there are five electron groups around the central atom, and one is a lone pair, the result is called the **seesaw** shape.



- When there are five electron groups around the central atom, and two are lone pairs, the result is **T-shaped**.

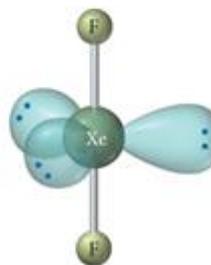


Electron geometry:
trigonal bipyramidal



Molecular geometry:
T-shaped

- For both see-saw and T-shaped, the bond angles between equatorial positions are less than 120° and the bond angles between axial and equatorial positions are less than 90°.
- When there are five electron groups around the central atom, and three are lone pairs, the result is a **linear shape**.



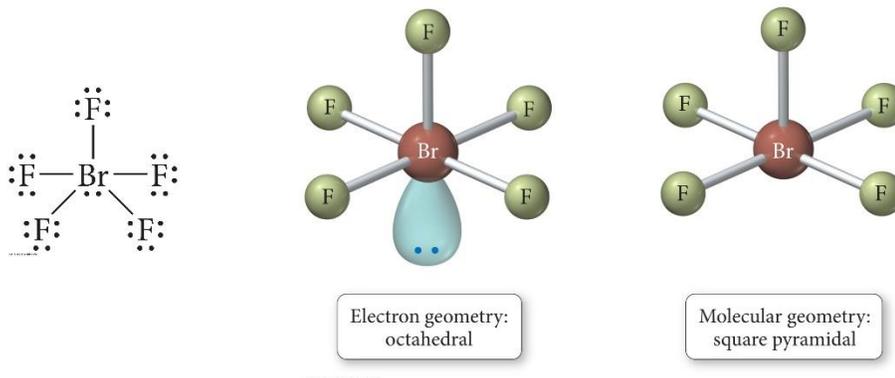
Electron geometry:
trigonal bipyramidal



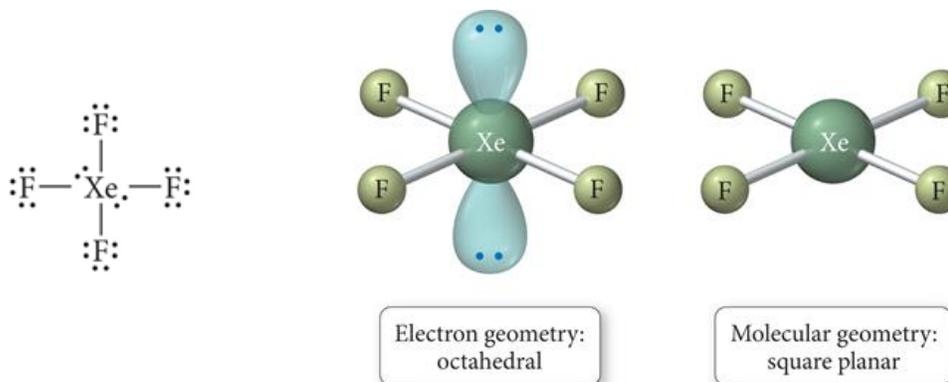
Molecular geometry:
linear

DERIVATIVES OF OCTAHEDRAL ELECTRON-PAIR GEOMETRY

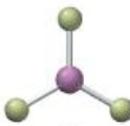
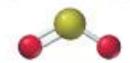
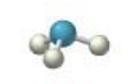
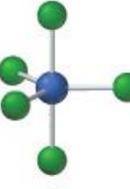
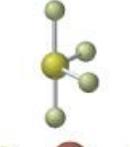
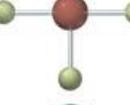
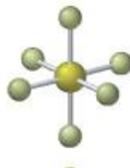
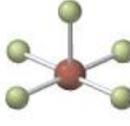
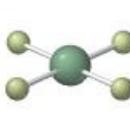
- All six positions in the octahedral geometry are equivalent. Therefore, when one of the six electron-pairs around the central atom is a lone pair (as in BrF_5 molecule), it can be situated in any one of these positions. The resulting molecular geometry is *square pyramidal*.



- When two of the six electron-pair groups around the central atom are lone pairs (as in XeF_4), the lone pairs occupy positions across from each other (to minimize repulsions). The resulting molecular geometry is *square planar*.



- The table on the next page summarizes all the possible electron-pair and molecular geometries predicted by VSEPR theory.

TABLE 10.1 Electron and Molecular Geometries						
Electron Groups*	Bonding Groups	Lone Pairs	Electron Geometry	Molecular Geometry	Approximate Bond Angles	Example
2	2	0	Linear	Linear	180°	$\text{:}\ddot{\text{O}}=\text{C}=\ddot{\text{O}}\text{:}$ 
3	3	0	Trigonal planar	Trigonal planar	120°	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{---B---}\ddot{\text{F}}\text{:} \end{array}$ 
3	2	1	Trigonal planar	Bent	<120°	$\text{:}\ddot{\text{O}}=\text{S}\text{---}\ddot{\text{O}}\text{:}$ 
4	4	0	Tetrahedral	Tetrahedral	109.5°	$\begin{array}{c} \text{H} \\ \\ \text{H---C---H} \\ \\ \text{H} \end{array}$ 
4	3	1	Tetrahedral	Trigonal pyramidal	<109.5°	$\begin{array}{c} \text{H} \\ \\ \text{H---N---H} \\ \\ \text{H} \end{array}$ 
4	2	2	Tetrahedral	Bent	<109.5°	$\text{H---}\ddot{\text{O}}\text{---H}$ 
5	5	0	Trigonal bipyramidal	Trigonal bipyramidal	120° (equatorial) 90° (axial)	$\begin{array}{c} \text{:}\ddot{\text{Cl}}\text{:} \\ \text{:}\ddot{\text{Cl}}\text{---P---}\ddot{\text{Cl}}\text{:} \\ \text{:}\ddot{\text{Cl}}\text{:} \end{array}$ 
5	4	1	Trigonal bipyramidal	Seesaw	<120° (equatorial) <90° (axial)	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{---S---}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$ 
5	3	2	Trigonal bipyramidal	T-shaped	<90°	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{---Br---}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$ 
5	2	3	Trigonal bipyramidal	Linear	180°	$\text{:}\ddot{\text{F}}\text{---Xe---}\ddot{\text{F}}\text{:}$ 
6	6	0	Octahedral	Octahedral	90°	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{---S---}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$ 
6	5	1	Octahedral	Square pyramidal	<90°	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{---Br---}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$ 
6	4	2	Octahedral	Square planar	90°	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{---Xe---}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$ 

*Count only electron groups around the central atom. Each of the following is considered one electron group: a lone pair, a single bond, a double bond, a triple bond, or a single electron.

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SUMMARIZING VSEPR THEORY

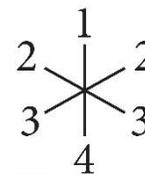
- The geometry of a molecule is determined by the number of electron-pair groups on the central atom (or the interior atoms, if there is more than one central atom).
- The number of electron-pair groups is determined from the Lewis structure of the molecule. If the Lewis structure contains resonance structures, use any of the resonance structures to determine the number of electron-pair groups.
- Each of the following count as one electron-pair group: lone pair, a single bond, a double bond, a triple bond, or a single electron (as in a free radical).
- The geometry of the electron-pair groups is determined by their repulsions as summarized in Table 10.1. In general, electron-pair groups repulsions vary as follows:

Lone pair–lone pair > lone pair–bonding pair > bonding pair–bonding pair

- Bond angles can vary from the idealized angles because double and triple bonds occupy more space than single bonds (they are bulkier even though they are shorter), and lone pair occupy more space than bonding pairs. The presence of lone pairs usually makes bond angles smaller than the ideal angle for the particular geometry.

Examples:

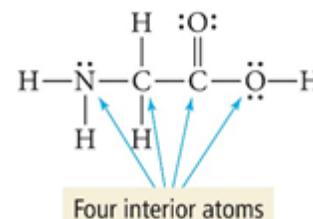
1. Suppose that a molecule with six electron-pair groups were confined to two dimensions and therefore had a hexagonal planar electron-pair geometry (shown on the right). If two of the six groups were lone pairs, where would they be located? Why?



2. Predict the molecular geometry and bond angle of ICl_4^- .

PREDICTING SHAPE OF LARGER MOLECULES

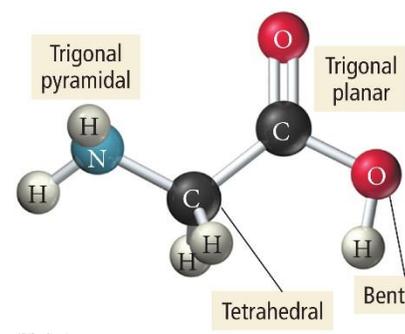
- Larger molecules may have two or more interior atoms. When predicting the shape of these molecules, apply the principles discussed to each interior atom.
- For example, glycine, an amino acid found in many proteins, contains four interior atoms: one N, two C's, and an O atom. To determine the shape of glycine, the shape about each interior atom is determined as follows:



Atom	Number of Electron Groups	Number of Lone Pairs	Molecular Geometry
Nitrogen	4	1	Trigonal pyramidal
Leftmost carbon	4	0	Tetrahedral
Rightmost carbon	3	0	Trigonal planar
Oxygen	4	2	Bent

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- Using the geometries of each of the interior atoms, the entire 3-dimensional shape of the molecule is determined.

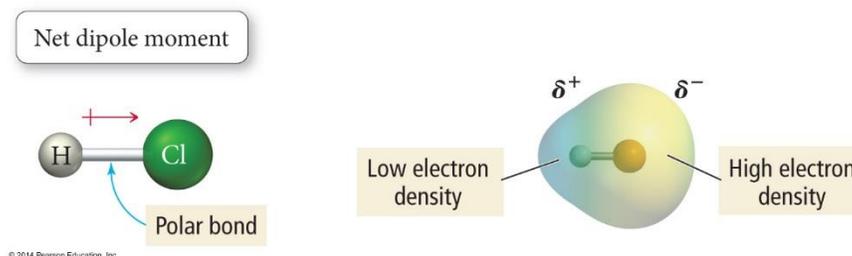


Examples:

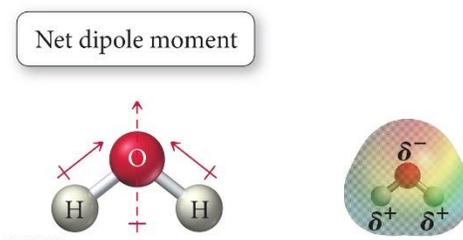
- Predict the geometry about each interior atom in methanol (CH_3OH) and make a sketch of the molecule.

MOLECULAR SHAPE AND POLARITY

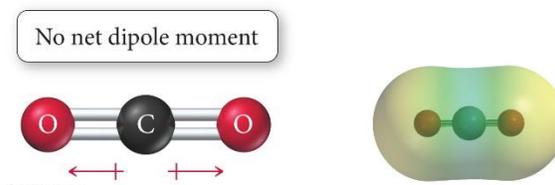
- Earlier we discussed polar bond. Entire molecules can also be polar, depending on their shape and the nature of their bonds. For example, if a diatomic molecule has a polar bond, the molecule as a whole would be polar.



- In polyatomic molecules, presence of polar bonds may or may not result in a polar molecule, depending on the molecular geometry. If the molecular geometry is such that the dipole moments of individual polar bonds sum together to a net dipole moment, then the molecule will be polar. But if the molecular geometry is such that the dipole moments of the individual polar bonds cancel each other and sum to zero, then the molecule will be nonpolar.
- For example, the polar O–H bonds of water do not cancel one another due to its bent shape and lead to a net dipole moment, making water a polar molecule.

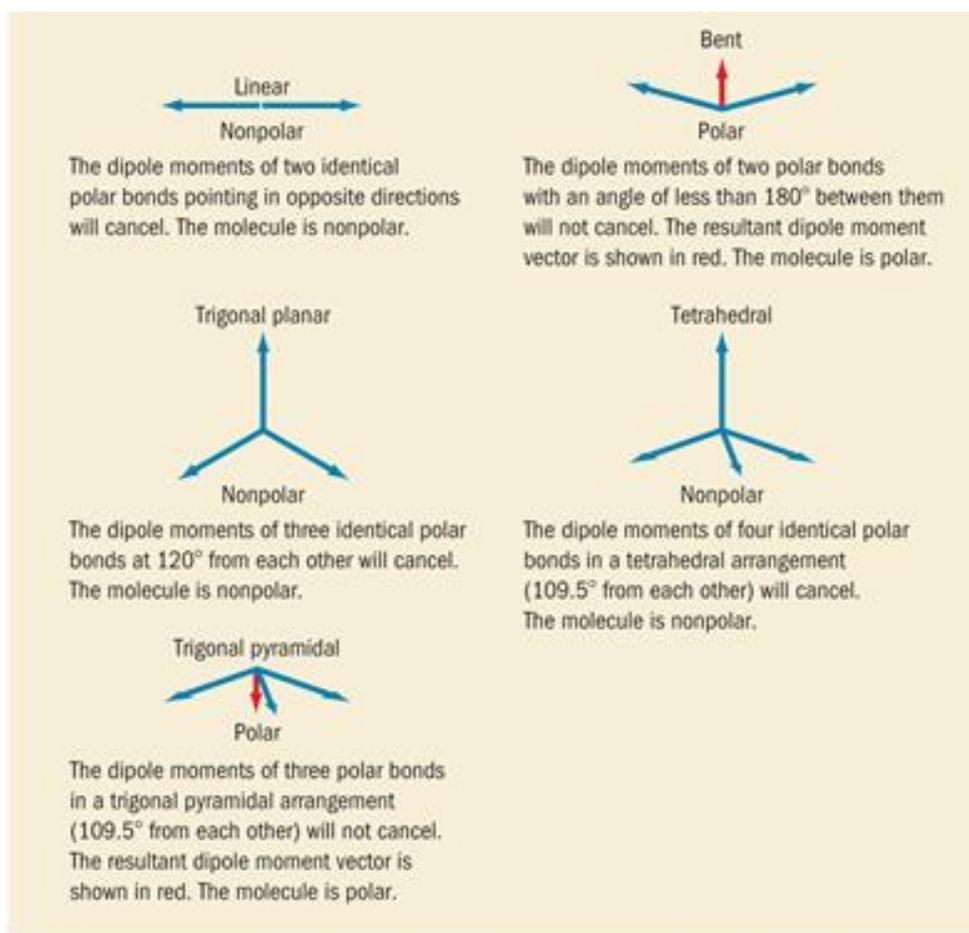


- On the other hand, the polar C=O bonds in CO₂ cancel one another due to its linear shape and lead to no net dipole moment, making CO₂ a nonpolar molecule.



MOLECULAR SHAPE AND POLARITY

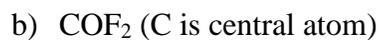
- To determine the polarity of a molecule,
 - Draw the Lewis structure for the molecule and determine its molecular geometry.
 - Determine if the molecule contains polar bonds. The bond is polar if the two bonding atoms have sufficiently different electronegativities. The dipole moment for each bond can be represented as a vector with its length proportional to the magnitude of the ΔEN .
 - Determine if the polar bonds add together to form a net dipole moment. Sum the dipole moment vectors together. If the vectors sum to zero, the molecule is non-polar. If the vectors sum to a net vector, the molecule is polar.
- Some common molecular geometries and polarities are shown below. Note that in all cases which dipoles of two or more bonds cancel, the bonds are assumed to be identical. If one or more of the bonds are different from the other(s), the dipoles will not cancel and the molecule will be polar.



MOLECULAR SHAPE AND POLARITY

Examples:

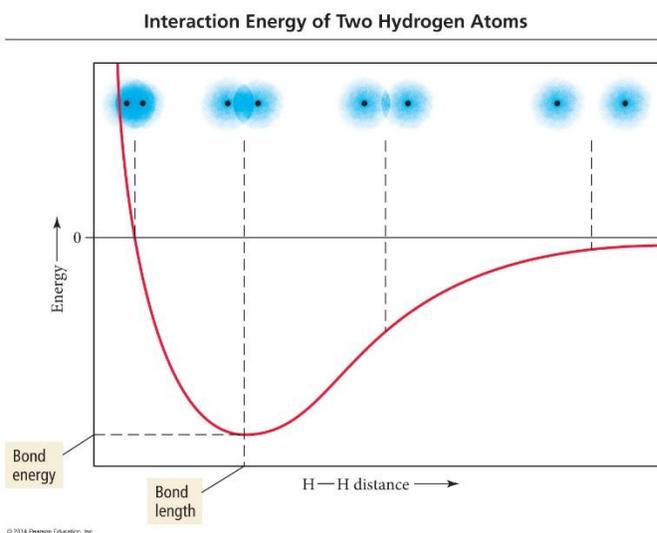
1. Determine whether each molecule shown below is polar or nonpolar:



2. The PF_3 molecule has a dipole moment of 1.3 D, but BF_3 has a dipole moment of zero. How can this difference be explained?

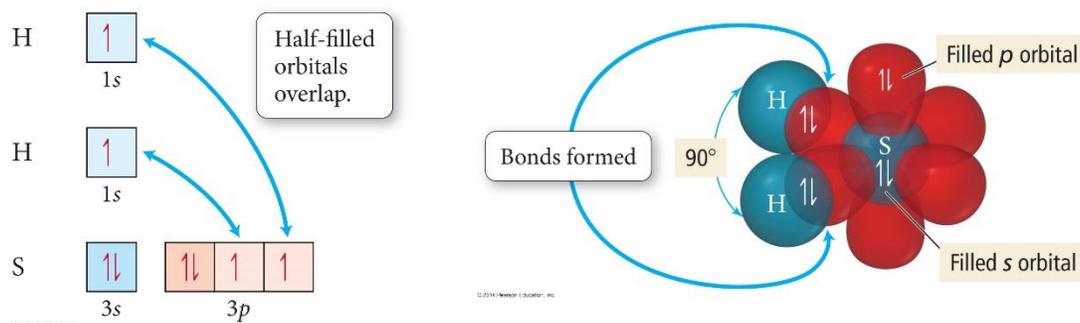
VALENCE BOND THEORY

- In the Lewis model, “dots” are used to represent electrons as they are transferred or shared between bonding atoms. Based on quantum mechanical theory, however, such a treatment is oversimplification.
- More advance bonding theories treat electrons in a quantum mechanical manner, and are actually extensions of quantum mechanics, applied to molecules. One such theory is the **valence bond (VB) theory**. A quantitative treatment of this theory is not the scope of this course. However, a qualitative description of the theory is discussed in this section.
- According to valence bond theory, electrons reside in quantum mechanical orbitals localized on individual atoms. In many cases, these orbitals are the standard s, p, d, and f orbitals we discussed earlier in Chapter 7. In other cases, these orbitals are **hybridized atomic orbitals**, a kind of blend or combination of two or more standard orbitals.
- When two atoms approach each other, the electrons and nucleus of one atom interact with the electrons and nucleus of the other atom. In VB theory, the effect of these interactions on the energies of the electrons are calculated. If the energy of the system is lowered because of the interactions, then the chemical bond is formed. If the energy of the system is raised by the interactions, then the chemical bond does not form.
- For example, as the diagram below shows, the potential energy of two hydrogen atoms is lowest when they are separated by a distance that allows their 1s orbitals substantial overlap without too much repulsion between their nuclei. This distance, at which the system is most stable, is the bond length of the H₂ molecule.

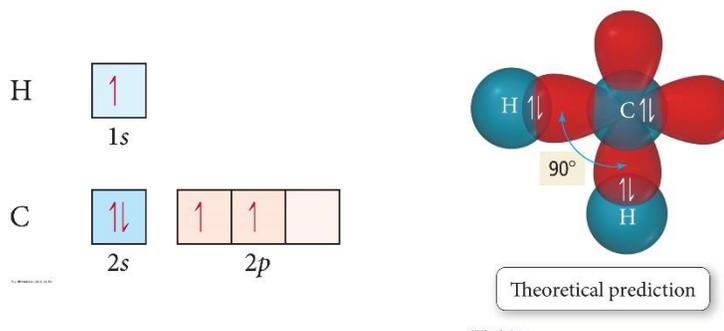


VALENCE BOND THEORY

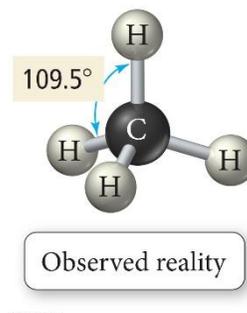
- When the concepts of VB theory are applied to a number of atoms and their corresponding molecules, the following general observation is found:
 - The interaction energy is usually negative (or stabilizing) when the interacting atomic orbitals contain a total of two electrons (oriented with opposing spins).
 - Most commonly, the two electrons come from two half-filled orbitals, but in some cases, the two electrons come from one filled orbital overlapping with a completely empty orbital (called *coordinate covalent* bond).
- Applying the principles above to explain the bonding in H_2S molecule shows how the half-filled $1s$ orbitals of the two H atoms overlap with the two half-filled $3p$ orbitals of to form the two bonds.



- If the same principles above are applied to explain the bonding between C and H, one would predict that the half-filled $1s$ orbital from 2 H atoms overlap with the two half-filled $2p$ orbitals of C, forming two bonds between C and H.

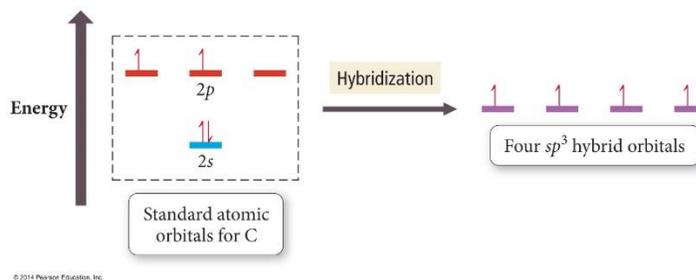


- However, experimental results show that the stable compound formed between C and H is CH_4 with bond angles of 109.5° . These observations deviate from the prediction in two ways: 1) Carbon forms 4 bonds with hydrogen, not two; 2) bond angles between atoms is larger than the one predicted between two p orbitals (90°).



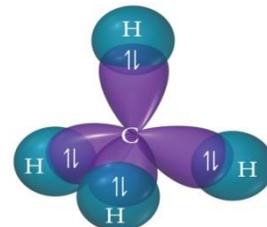
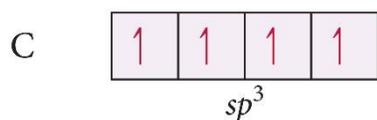
HYBRIDIZATION OF ATOMIC ORBITALS

- VB theory accounts for the bonding in CH₄ and many other polyatomic molecules by incorporating an additional concept called *orbital hybridization*.
- Hybridization is a mathematical procedure in which the standard atomic orbitals are combined to form new atomic orbitals, called *hybrid orbitals*, that correspond more closely to the actual distribution of electrons in chemically bonded atoms.
- Hybrid orbitals are still localized on individual atoms, but they have different shapes and energies from those of standard atomic orbitals. In hybrid orbitals, the electron probability density is more concentrated in a single directional lobe, allowing greater overlap with the orbitals of other atoms.
- In VB theory, the chemical bond is the overlap of two orbitals that together contain two electrons. The greater the overlap, the stronger the bond and the lower the energy.
- The mathematical procedure for obtaining hybrid orbitals is beyond the scope of this course. However, the following general statements can be made regarding hybridization:
 - The number of atomic orbitals added together always equals the number of hybrid orbitals formed. The total number of orbitals is conserved.
 - The particular combination of standard atomic orbitals added together determines the shapes and energies of the hybrid orbitals.
 - The particular type of hybridization that occurs is the one that yields the lowest overall energy for the molecule. To simplify this process, the electron geometries determined by VSEPR theory are used to predict the type of hybridization.
- Using the general concepts above, we can now account for the tetrahedral geometry of CH₄ by hybridization of one 2s orbital and three 2p orbitals of the carbon atom.
- The four new hybrid orbitals that result are called sp³. This hybridization process is shown in the energy diagram to the right.
- Carbon's four valence electrons occupy the four hybrid sp³ orbitals singly with parallel spins (as dictated by Hund's rule).

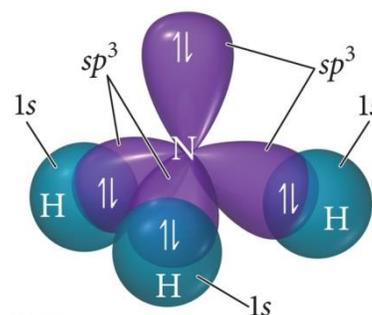


HYBRIDIZATION OF ATOMIC ORBITALS

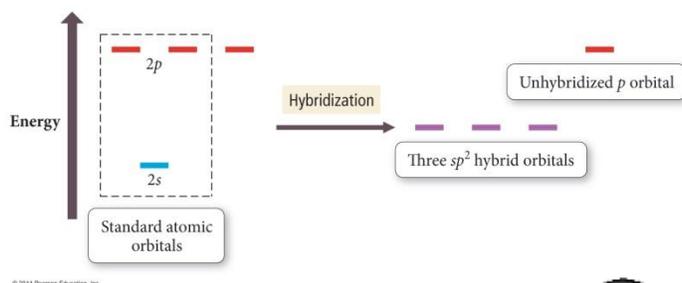
- With this electron configuration, carbon has four half-filled orbitals and can form four bonds with four hydrogen atoms. The resulting geometry of the overlapping orbitals is tetrahedral with angles of 109.5° between the orbitals.



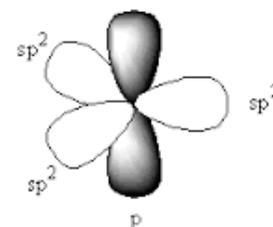
- Hybridized orbitals can readily form chemical bonds because they tend to maximize overlap with other orbitals. However, if the central atom of a molecule contains lone pairs, hybrid orbitals can also accommodate them. For example, nitrogen orbitals in NH_3 are sp^3 hybrids.



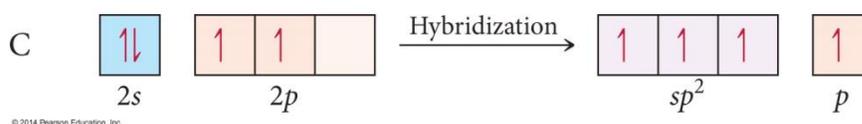
- Similarly, when one s and two p orbitals combine, they form three sp^2 hybridized orbitals and one leftover unhybridized orbital.



- When an s and two p orbitals are mixed to form a set of sp^2 orbitals, one p orbital remains unchanged and is perpendicular to the plane of the hybrid orbitals.

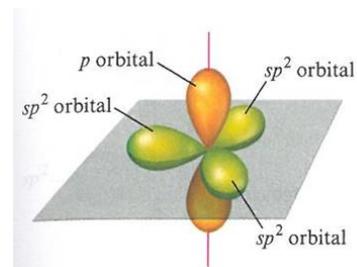
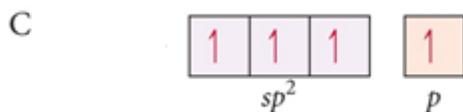


- For example, in formaldehyde molecule, (H_2CO), the hybridization of the central atom (C) is shown below:

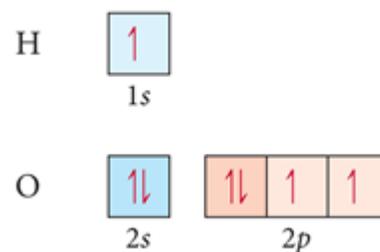


HYBRIDIZATION OF ATOMIC ORBITALS

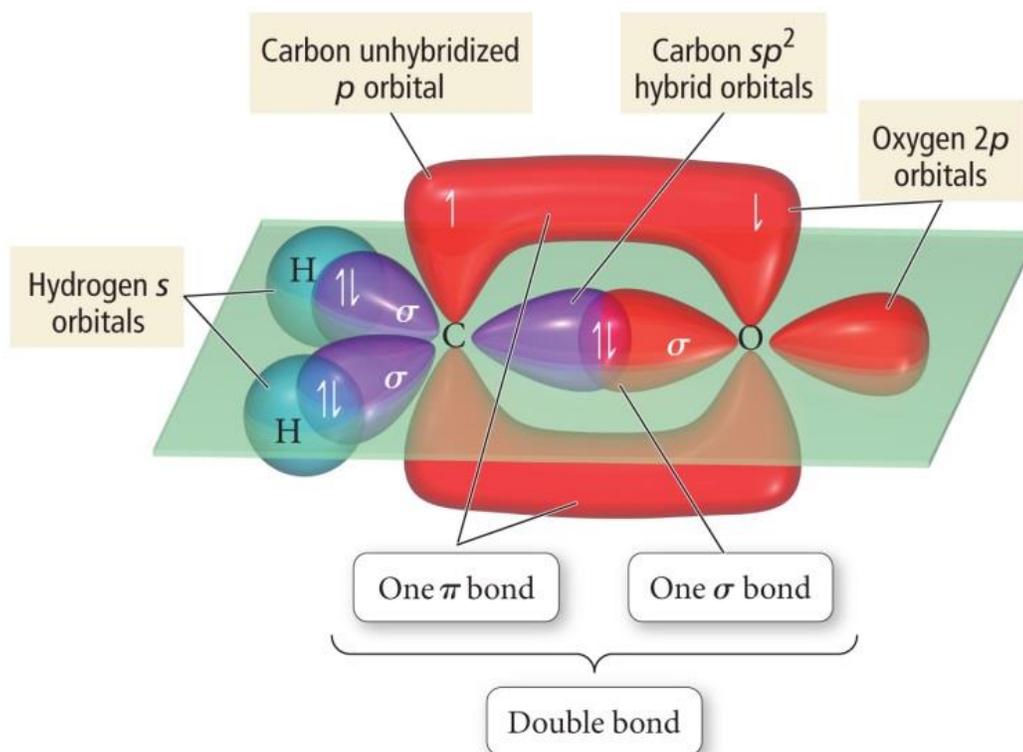
- After hybridization, carbon has four unpaired electrons (three occupying hybrid sp^2 orbitals and one occupying a standard p orbital).



- Carbon can then form four bonds, two with hydrogen and two with oxygen.

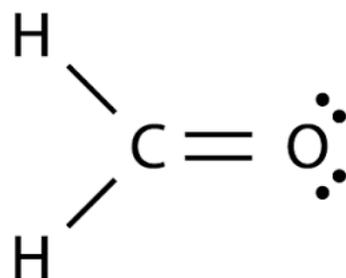


- The overlap of the two unhybridized orbitals between C and O (double bond) is called a π (**pi**) **bond**, while the overlap of the hybridized orbitals with s and p orbitals are called σ (**sigma**) **bonds**.



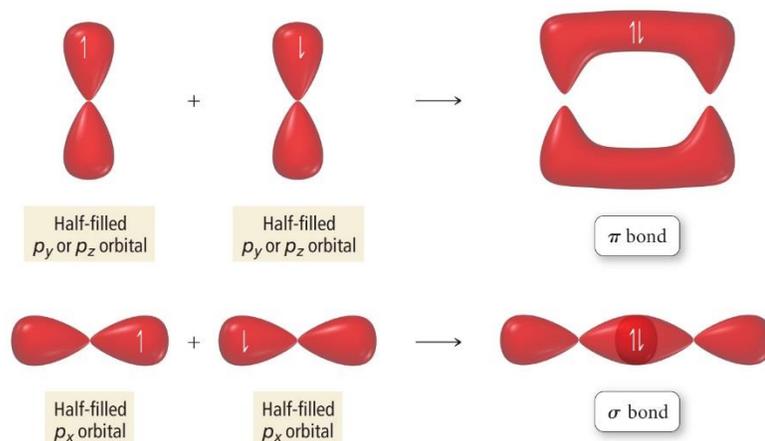
BONDING SCHEMES

- When writing bonding schemes for molecules, identify the bond type (σ or π) and label each atom and orbital used by that atom to form the bond.
- For example formaldehyde shown below, has the following bonding scheme.



SIGMA (σ) AND PI (π) BONDS

- Overlap of orbitals end-to-end results in formation of a *sigma* (σ) bond, while overlap of orbitals side-by-side results in formation of *pi* (π) bonds.

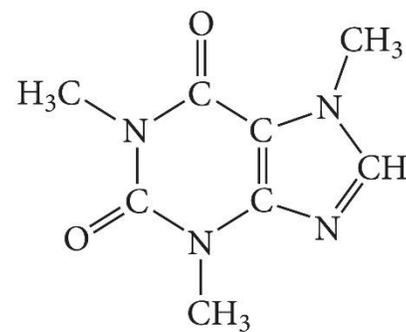


- The interaction between parallel orbitals is not as strong as between orbitals that point at each other; therefore, **σ bonds are stronger than π bonds**.
- Single bonds are composed of one σ bond, while multiple bonds (double or triple) consist of one σ bond and 1 or 2 π bonds, respectively. For example, the bonding for HCN molecule is shown on the right.



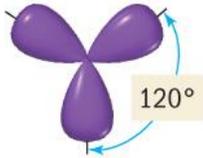
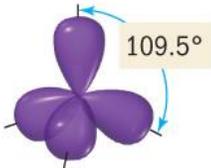
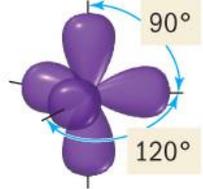
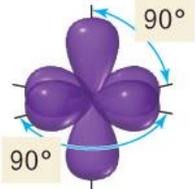
Examples:

- Earlier we learned that while double bonds are stronger than single bonds, their bond energy is not twice that of single bonds. Use VB theory to explain this fact.
- The structure of caffeine, present in coffee and many soft drinks, is shown on the right. How many sigma and pi bonds are present in a molecule of caffeine?



HYBRIDIZATION OF ATOMIC ORBITALS

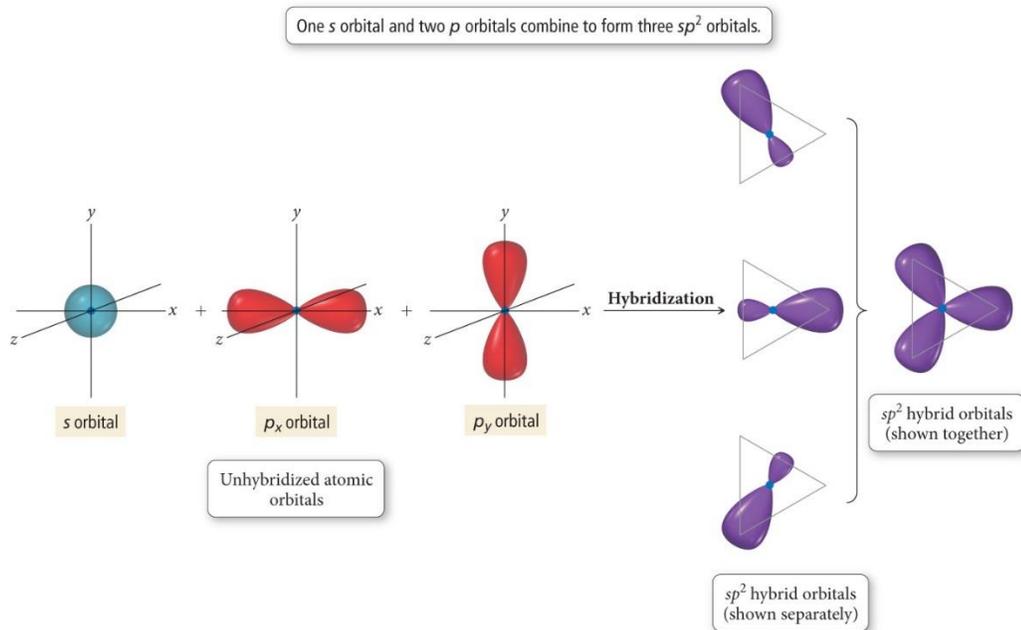
- The table below lists the five VSEPR geometries and the corresponding hybridization schemes.

TABLE 10.3 Hybridization Scheme from Electron Geometry		
Number of Electron Groups	Electron Geometry (from VSEPR Theory)	Hybridization Scheme
2	Linear	sp 
3	Trigonal planar	sp^2 
4	Tetrahedral	sp^3 
5	Trigonal bipyramidal	sp^3d 
6	Octahedral	sp^3d^2 

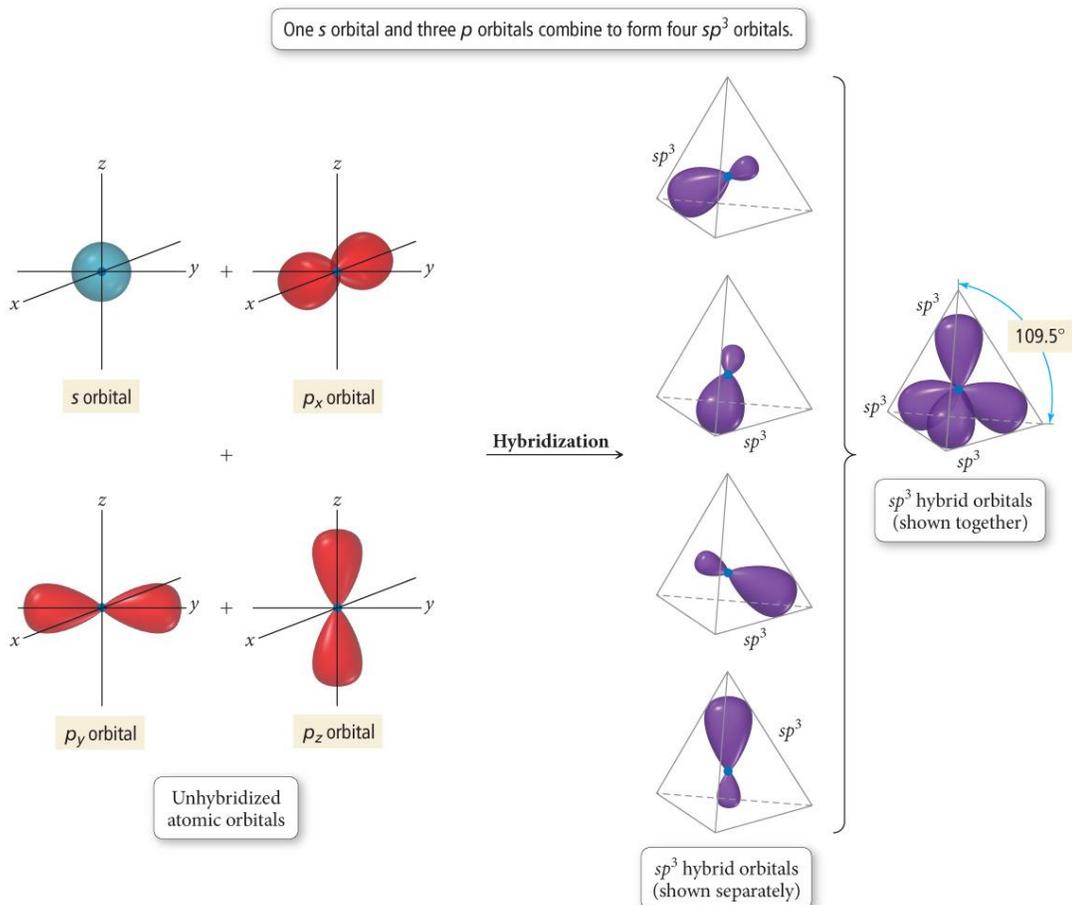
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HYBRIDIZATION OF ATOMIC ORBITALS

Formation of sp^2 Hybrid Orbitals



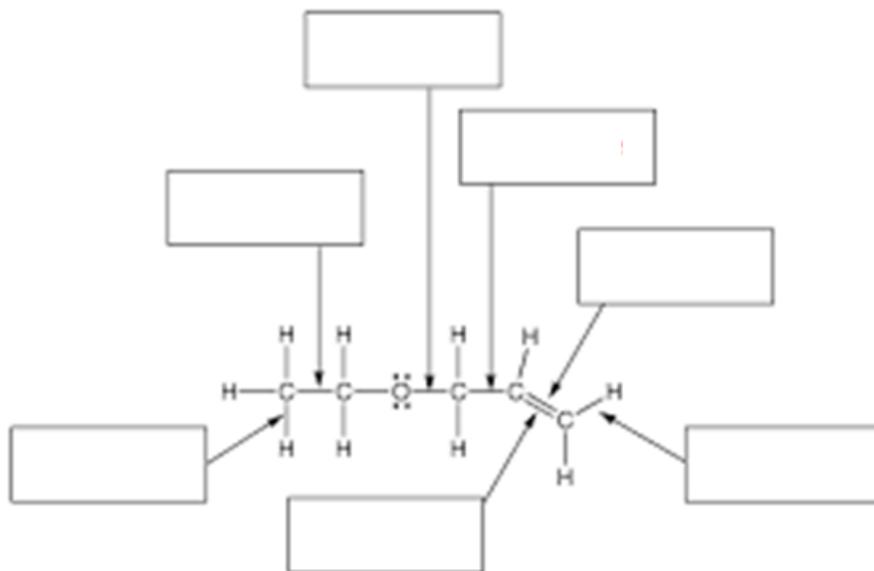
Formation of sp^3 Hybrid Orbitals



Examples:

1. Consider the three molecules C_2H_6 , C_2H_4 and C_2H_2 . How many sigma and pi bonds does each molecule contain?

2. Identify the hybridization of each interior atom and write bonding scheme for all bonds indicated by arrows:



3. Shown below is the structural formula for the amino acid aspartic acid. Indicate the hybridization about each interior atom.

