

COVALENT BONDS

I. Introduction-

A. Polar Bond: When nonmetals bond covalently with a large difference in electronegativity, a polar bond is formed. A polar bond has a partial separation of charges. Polar bonds are symbolized with an arrow pointing towards the more electronegative element and a crossed tail by the less electronegative element.

ex. NH_3

B. Isomers and Resonance

Isomers are compounds with the same chemical formula but different chemical structure.

Resonance occurs when a double bond can be placed in more than one place in a structure without creating isomers.

C. BONDING Theories:

The **Valence Shell Bonding Theory** assumes that bonds are formed when atomic orbitals overlap. Direct overlap leads to sigma bonds and parallel overlap leads to pi bond.

The **Hybridization Theory** says that the sigma bonds are all identical around an atom, therefore the orbitals forming them must be identical. Therefore, any atomic orbitals involved in sigma bonds hybridize into identical orbitals to bond.

(not covered much on the AP Chem) The **Molecular Orbital Theory** says that rather than overlapping atomic orbitals, or hybridized atomic orbitals, new orbitals are formed in the molecule that are separate. Some of the new orbitals formed pull the two nuclei together and are bonding orbitals. However, some of them pull the two orbitals apart and are anti-bonding orbitals. The bond order is the number of bonding orbital electrons – the number of antibonding orbital electrons divided by 2. The bond order can be used to determine the type of bond (single, double, triple).

II. Electron Sharing

- Most of the substances we encounter are not ionic. Rather than existing as collections of electrically charged particles (ions), they occur as electrically neutral combinations of atoms called molecules. Water, H_2O , consists of molecules, table sugar $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ and gasoline C_8H_{18} are also examples.
- When the IE of all the atoms involved is large, as happens when non-metals combine with other non-metals, nature uses a different way to lower the energy - electron sharing.
- ex. H_2 *What happens when two hydrogen atoms join together to form an H_2 molecule?* As the two atoms approach each other, the electron of each atom begins to feel the attraction of both nuclei. This causes the electron density around each nucleus to shift toward the region between the two atoms. Therefore, as the distance between the nuclei decreases, there is an increase in

the probability of finding either electron near either nucleus. In effect, then, each of the hydrogen atoms in this H₂ molecule now has a share of two electrons. When the electron density shifts to the region between the two hydrogen atoms, it attracts each of the nuclei and pulls them together. Being of the same charge, however, the two nuclei also repel each other, as do the two electrons. In the molecule that forms, therefore, the atoms are held at a distance at which these attractions and repulsions are balanced. Overall, the nuclei are kept from separating, and the net force of attraction produced by the sharing of the pair of electrons is called a covalent bond.

- Every covalent bond is characterized by two quantities, the average distance between the nuclei held together by the bond, and the energy needed to separate the two atoms to produce neutral atoms again. In the hydrogen molecule, the attractive forces pull the nuclei to a distance of 75 pm, and this distance is called the bond length or bond distance. Because a covalent bond holds atoms together, work must be done to separate them. When a bond is formed, an equivalent amount of energy is released. The amount of energy released when the bond is formed is called the bond energy. Formation of a covalent bond releases the bond energy, which means that as the bond forms, the energy of the atom decreases. In the diagram below you can see how the energy changes when two hydrogen atoms form H₂. The minimum energy occurs at a bond distance of 75 pm, and that 1 mol of hydrogen molecules is more stable than 2 mol of hydrogen atoms by 435 kJ. In other words the bond energy of H₂ is 435 kJ/mole.

A. Structural Formulas:

Covalent bonds which are sharing an electron pair bond are indicated with a dash, just like what was used in the organic unit.

H· + ·H ---> H:H which is shown as H-H. (the line indicates a covalent bond pair of electrons)

B. The Octet Rule

The valence shell of the noble gases other than helium all contain eight electrons, and the tendency of many atoms to acquire such an outer shell electron configuration forms the basis of the octet rule.

Octet Rule: *When atoms react, they tend to achieve an outer shell having eight electrons.*

C. Multiple Bonds

The bond produced by the sharing of one pair of electrons between two atoms is called a **single bond**. This first bond is designated a **sigma bond**. There are however many molecules in which more than one pair of electrons are shared between two atoms. For example, we that nitrogen, is diatomic, N₂. Each N atom has the Lewis symbol of

and each nitrogen needs three electrons to complete its octet. When the N₂ molecule is formed, each nitrogen atom shares three electrons with the other. This is a **triple bond**.



In the triple bond above the middle bond is a **sigma type bond and the other two are Pi bonds**. The **pi bonds** are slightly different because they have to be bent out of shape in order to connect properly.

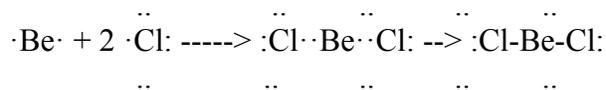
Double bonds are also possible. eg. CO_2

D. When the Octet Rule Fails (exceptions)

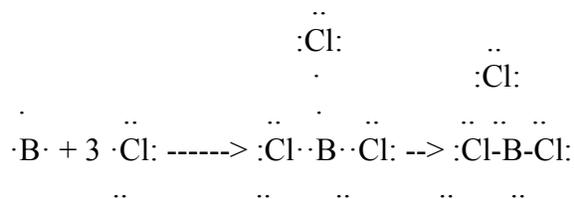
Sometimes it is just impossible to write a Lewis structure in which all of the atoms in a molecule obey the octet rule. This happens most often when an atom forms more than four bonds. Examples are PCl_5 and SF_6 , in which there are five P-Cl bonds and six S-F bonds, respectively. Since each covalent bond requires the sharing of a pair of electrons, P and S must exceed eight electrons in their outer shells. The Lewis formula of these two molecules are shown below.

Elements in period 2 such as carbon or nitrogen, never exceed an octet simply because their valence shell, having $n=2$, can hold a maximum of only 8 electrons. Elements in periods below period 2, however, sometimes do exceed an octet, because their valence shells can hold more than 8 electrons. For example, the valence shell for elements in period 3, for which $n=3$, can hold a maximum of 18 electrons, and the valence shell for period 4 elements can hold as many as 32 electrons.

In some molecules (but not many), an atom has less than an octet. The most common examples are compounds of beryllium and boron.



Note: there is only $4e^-$ around Be



E. How to Write Lewis Structures

Step 1: Decide which atoms are bonded.

Step 2: Count all valence electrons

Step 3: Place two electrons in each bond.

Step 4: Complete the octets of the atoms attached to the central atom by adding e^- 's in pairs.

Step 5: Place any remaining electrons on the central atom in pairs.

Step 6: If the central atom does not have an octet, form double bonds. If necessary form triple bonds.

F. Resonance: When Lewis Structures Fail There are some molecules and ions for which we cannot write Lewis structures that agree with experimental measurements of bond length and bond energy. One example is the formate ion, CHO_2^- , which is produced by neutralizing formic acid, HCHO_2 . The skeletal structure for this ion is:

????O and, following the usual steps, we would write its Lewis structure as This structure suggests that one carbon-oxygen bond should be longer than the other, but experimental evidence shows that they are in fact identical. In fact, the C-O bond lengths are about halfway between that expected for a single bond and that expected for a double bond. The Lewis structure doesn't match the experimental evidence, and there's no way to write one that does unless we use 1.5 electrons per bond. We get around this problem with resonance. The Lewis structure can be shown as two structures The term resonance is often misleading. The word itself suggests that the actual structure flip-flops back and forth between the two structures shown. This is not the case. There is a simple way to determine when resonance should be applied to Lewis structures. **If you find that you must move electrons to create a double bond while following the procedure, the number of resonance structures is equal to the number of equivalent choices for the location of the double bond.** eg 2. An SO_3 molecule showing resonance structures

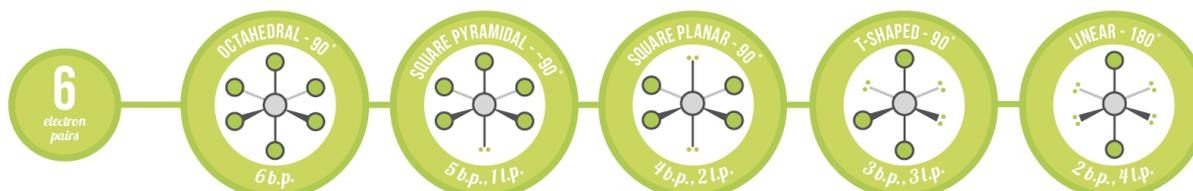
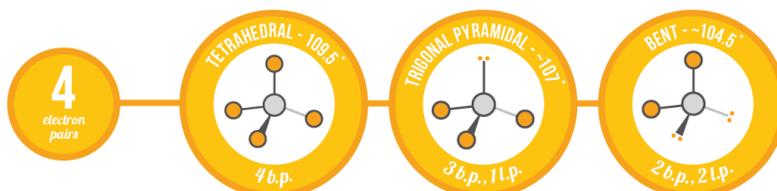
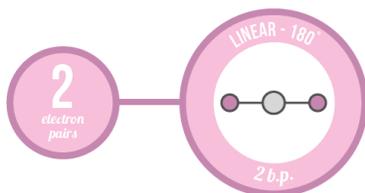
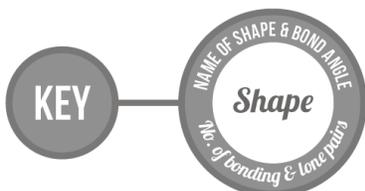
G. Coordinate Covalent Bonding

**Sometimes one atom supplies both of the electrons that are shared in a covalent bond.

When ammonia, NH_3 , is placed in an acidic solution, it picks up a hydrogen ion, H^+ , and becomes NH_4^+ . The H^+ ion has a vacant valence shell that can accommodate two electrons. When the H^+ is bonded to the nitrogen of NH_3 , the nitrogen donates both of the electrons to the bond. This type of bond, in which both electrons of the shared pair come from one of the atoms, is called a *coordinate covalent bond*. Even though we are making a distinction about where the electrons come from, once the NH_4^+ forms all four of the N-H bonds are identical. Another example of a coordinate bond occurs when a molecule having an incomplete valence shell reacts with a molecule having valence shell electrons that aren't being used in bonding.

VSEPR & THE SHAPES OF MOLECULES

A SUMMARY OF THE MOLECULE SHAPES PREDICTED BY VALENCE SHELL ELECTRON PAIR REPULSION THEORY



Using Valence Shell Electron Pair Repulsion Theory

VSEPR is a model used to predict shapes of molecules. Electron pairs repel each other, and adopt an arrangement that minimises repulsion. To find the shape, a Lewis structure can be drawn, or use the following method (assumes single bonds only):

- 1 Find the number of electrons the central atom normally has in its valence shell.
- 2 Add one electron for every atom that the central atom is bonded to.
- 3 Add or subtract electrons to account for charges if the molecule is charged.
- 4 Divide the number arrived at by two to find the number of electron pairs.
- 5 Subtract no. of atoms bonded to the central atom to find no. of lone pairs.
- 6 Arrange electron pairs in the correct shape.

Bonding Pairs & Lone Pairs

Lone pairs lie closer to the central atom, and hence repel more than a bonded pair. The order of strengths of repulsion is:

LONE PAIR/LONE PAIR > BONDED PAIR/LONE PAIR > BONDED PAIR/BONDED PAIR

Lone Pair Repulsion

Each lone pair reduces the bond angle by

APPROXIMATELY 2.5 DEGREES

(if there are 4+ electron pairs arranged around the central atom, ignore repulsions at >90° angles)

FAILS FOR:

Isoelectronic species
Transition metal compounds

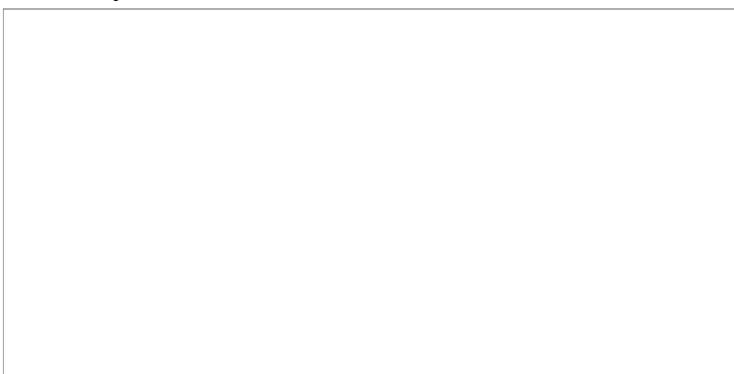


III. Polar Bonds and Electronegativity

When two identical atoms form a covalent bond, as in H_2 or Cl_2 , each has an equal share of the electron pair in the bond. The electron density at both ends of the bond is the same, because the electrons are equally attracted to both nuclei.



When different kinds of atoms combine, as in HCl , the attractions usually are not equal. Generally one of the nuclei attracts the electrons more strongly than the other.



*The effect of unequal attractions for the bonding electrons is an unbalanced distribution of electron density within the bond. It has been found that a chlorine atom attracts the electrons more strongly than does a hydrogen. In the HCl molecule, therefore, the electron cloud is pulled more tightly around the Cl , and that end of the molecule experiences a slight buildup of negative charge. The electron density that shifts toward the chlorine atom is removed from the hydrogen, which causes the hydrogen end to acquire a slight positive charge.

In HCl the electron transfer is incomplete. The electrons are still shared, but unequally. The charges on either end of the molecule are less than full $+1$ and -1 charges; they are partial charges, normally indicated by the lowercase Greek letter delta.

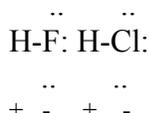
* A bond that carries partial positive and negative charges on opposite ends is called a polar bond, or polar covalent bond. The term *polar* comes from the notion of poles of opposite charge at either end of the bond. Because there are two poles of charge involved, the bond is said to be a dipole.

*The polar bond in HCl causes the molecules as a whole to have opposite charges on either end, so we say that HCl is a polar molecule. The HCl molecule as a whole is also a dipole.

The degree to which a covalent bond is polar depends on the relative abilities of bonded atoms to attract electrons. The term that we use to describe this relative attraction of an atom for the electrons in a bond is called the electronegativity of the atom. In HCl the chlorine is more electronegative than hydrogen. The electron pair of the covalent bond spends more of its time around the more electronegative atom, which is why that end of the bond acquires a

partial negative charge.

*The concept of electronegativity has been put on a quantitative basis - as numerical values have been assigned for each element. Refer to your periodic table for these assigned values. This information is useful because the *difference* in electronegativity values provides an estimate of the degree of polarity of a bond. In addition, the relative magnitudes of the electronegativities indicate which end of the bond carries the negative charge. For instance, fluorine is more electronegative than chlorine. Therefore, we would expect an HF molecule to be more polar than an HCl molecule. In addition, hydrogen is less electronegative than either fluorine or chlorine, so in both of these molecules the hydrogen bears the positive charge.



The concept of electronegativity shows that there is no sharp dividing line between ionic and covalent bonding.

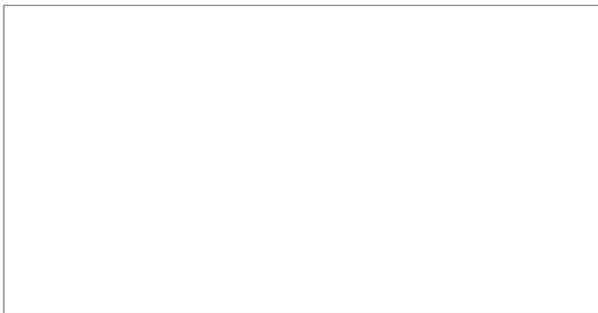
Ionic bonding and nonpolar covalent bonding simply represent the two extremes. Ionic bonding occurs when the difference in electronegativity between two atoms is very large; the more electronegative atom acquires essentially complete control of the bonding electrons. In a nonpolar covalent bond, there is no difference in electronegativity, so the pair of bonding electrons is shared equally.

The degree of polarity, which is the amount of ionic character of the bond varies in a continuous way with changes in the electronegativity difference. The bond becomes more than 50% ionic when the electro-negativity difference exceeds 1.7

Within the periodic table, electronegativity varies in a more or less systematic way, and the trends follow those for the ionization energy (IE). Atoms with large ionization energies also have large electronegativities. An atom that has a small IE will give away an electron more easily than an atom with a large IE, just as an atom with a small electronegativity will lose its share of an electron pair more readily than an atom with a large electronegativity.

A Molecular Shapes and the Polarity of Molecules

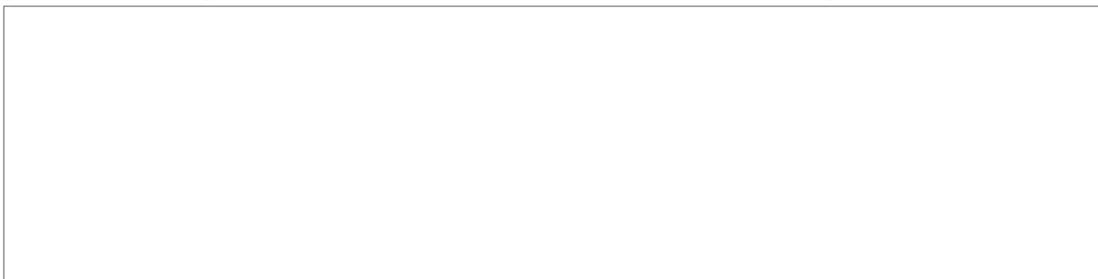
One of the main reasons you should be concerned about the polarity of molecules is because many physical properties, such as melting point and boiling point, are affected by it. This is because polar molecules attract each other - the positive end of one polar molecule attracts the negative end of another.



The strength of the attraction depends both on the amount of charge on either end of the molecule and on the distance between the charges. There are many molecules that are not dipoles even though they contain bonds that are polar. The reason for this is that can be seen if you look at the key role that molecular structure plays in determining molecular polarity.

H-Cl molecule, which has only two atoms and therefore only one bond. This bond is polar, and opposite ends of the bond carry partial charges of opposite sign. Because there are only two atoms in this molecule, which are located at the ends of the bond, the molecule as a whole has ends with equal but opposite charges. A molecule with equal but opposite charges on opposite poles is polar, so HCl is a polar molecule. In fact, any molecule composed of just two atoms that differ in electronegativity must be polar.

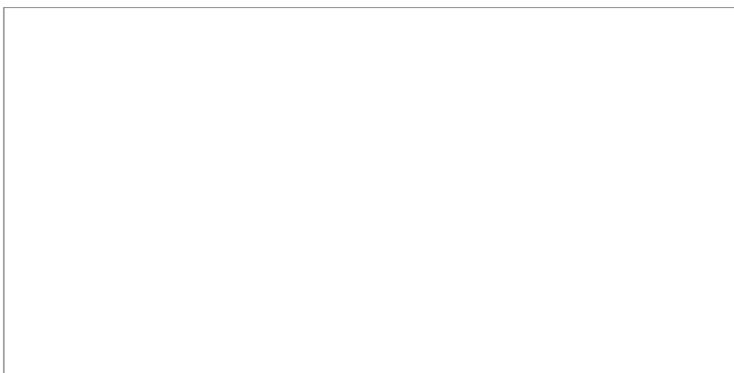
For molecules that contain more than two atoms, consider the combined effects of all the polar bonds. Sometimes, when all the atoms attached to the central atom are the same, the effects of the individual polar bonds cancel and the molecule as a whole is non-polar. In the diagram below the $+ \dashrightarrow$ sign is used to show the direction of the dipole. The arrow head points to the negative end of the bond and the crossed end is the positive end.



In CO_2 both bonds are identical, so each bond dipole is of the same magnitude. Because CO_2 is a linear molecule, these bond dipoles point in opposite directions and work against each other. The net result is that their effects cancel, and CO_2 is a non-polar molecule.

Although it is not as easy to visualize, the same thing also happens in BCl_3 and CCl_4 . In each of these molecules the effects of one of the bond dipoles is cancelled by the effects of the others.

If all the atoms attached to the central atom are not the same, or if there are lone pairs in the valence shell of the central atom, the molecule will usually be polar.



Not every structure that contains lone pairs on the central atom produces polar molecules. The following are two exceptions.

IV. Hybrid Orbitals

The mixing of orbitals of different energy levels gives rise to new orbital types of intermediate energy that are able to form stronger bonds.

The approach that we have taken so far has worked well with some simple molecules. their shapes are explained very nicely by the overlap of simple atomic orbitals. It does not take long to find molecules with shapes and bond angles that fail to fit the model that has been developed. For example, CH_4 , has a shape that the VSEPR theory predicts to be tetrahedral.

The H-C-H bond angles in this molecule are 109.5° . No simple atomic orbitals are oriented at this bond angle. So what kinds of orbitals are CH_4 molecules using?

When some atoms form bonds, their simple s, p, and d orbitals often *mix* to form new atomic orbitals, called *hybrid atomic orbitals*. These new orbitals have new shapes and new directional properties. The reason for this mixing can be seen if we look at their shapes.

One kind of hybrid atomic orbital is formed by mixing a s orbital with a p orbital. This creates *two* new orbitals called *sp hybrid orbitals* (the *sp* is used to designate the kinds of orbitals from which the hybrid was formed).

Notice that each of the hybrid orbitals has the same shape - each has one large lobe and another much smaller lobe. The large lobe extends further from the nucleus than either the s or p orbital from which the hybrid orbital was formed. This allows the hybrid orbital to overlap more effectively with an orbital on another atom when a bond is formed. In general, the greater the overlap of two orbitals, the stronger the bond.

Another point to notice is that the large lobes of the two *sp* hybrid orbitals point in opposite directions - that is, they are 180° apart.

Let's look at a specific example, the linear beryllium hydride molecule, BeH_2 , as it would be formed in the gas phase.

****Note: 2s orbital is filled and the three 2p orbitals are empty. For bonds to form at a 180° angle between beryllium and the two hydrogen atoms, two conditions must be met: (1) the two orbitals that beryllium uses to form the Be-H bonds must be aligned oppositely at 180° , and (2) each of the beryllium orbitals must contain only one electron. The reason for the first requirement is obvious. The reason for the second is that each bond must contain two electrons, one from the beryllium and one from the hydrogen. The net effect of all this is that when the Be-H bonds form, the electrons from the beryllium unpaired, and the resulting half-filled s and p atomic orbitals become hybridized.

Other Hybrid Orbitals

Hybrid orbitals can be formed by mixing more than just two simple atomic orbitals. If an s and two p orbitals combine, *three* hybrid orbitals, each similar in shape to the sp hybrids, are formed. They are called *sp² hybrid orbitals*, the superscript 2 specifying the *number* of p orbitals taking part in the formation of the hybrids. Also, notice that the number of hybrids in the set is equal to the number of simple atomic orbitals from which the hybrids are formed.

BCl_3 is a molecule in which the central boron atom uses sp^2 hybrids for bonding. A boron atom has the valence shell configuration

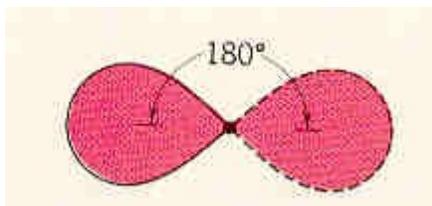
To form three bonds, boron must have three half-filled orbitals, so its 2s electrons must become unpaired. The resulting half-filled s and p orbitals then become hybridized.

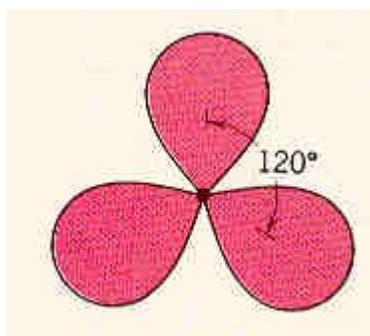
A chlorine atom has the valence shell configuration $1s^2 2s^2 2p^5$, the half-filled 3p_z orbital of each chlorine overlaps with one of the sp^2 hybrids of boron to give the molecule.

These bonds are illustrated below. The geometry of the BCl_3 molecule is planar triangular because all three hybrid orbitals fit nicely into the plane of the equator, 120° apart.

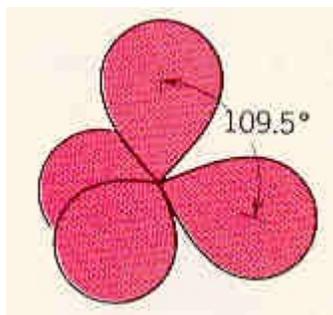
The list below shows important types of hybrid orbitals. The directional properties of the various hybrids are also shown.

sp hybrids

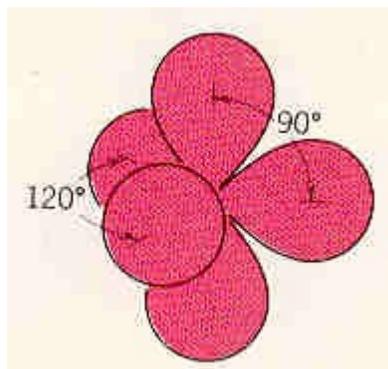




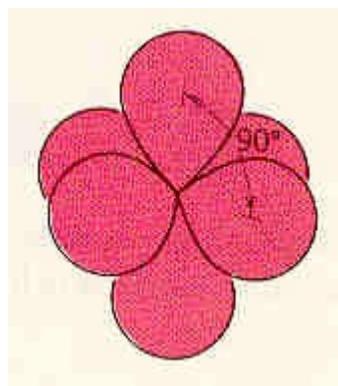
sp^2 hybrids



sp^3 hybrids

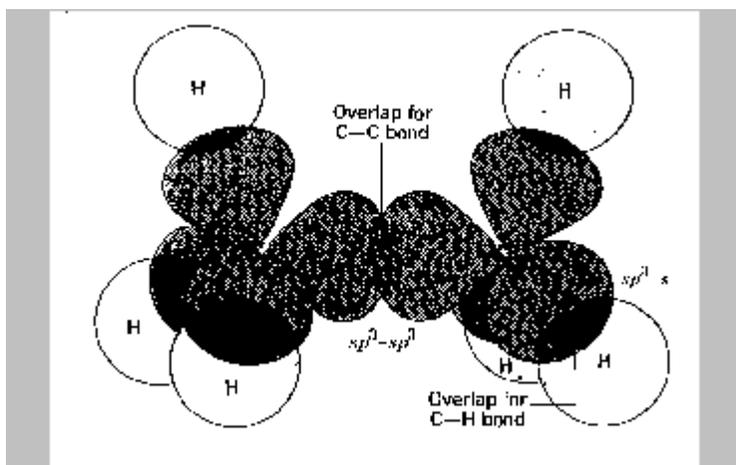


sp^3d hybrids



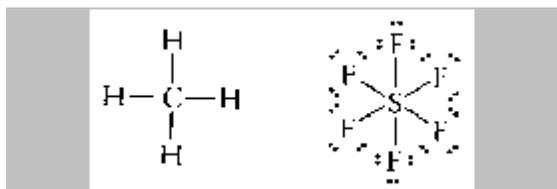
sp^3d^2 hybrids

The bonds in the ethane molecule. Notice the overlap in the orbitals. The degree of overlap of the sp^3 orbitals in the carbon-carbon bond does not appreciably affect the rotation of the two CH_3 - groups.



Using VSEPR Theory to Predict Hybridization

If we know the geometry of a molecule, we can predict the kind of hybrid orbitals that are used. Since VSEPR works so well in predicting geometry, we can use it to help us obtain information on the hybrid orbitals. For example, the Lewis structures of CH_4 and SF_6 are



In CH_4 , there are four electron pairs around carbon. The VSEPR model tells us that they should be arranged tetrahedrally. The only hybrid orbitals that are tetrahedral are sp^3 hybrids, and we have seen that they explain the structure of this molecule well. Similarly, the VSEPR theory tells us that the six electron pairs around sulphur should be arranged octahedrally. The only octahedrally orientated hybrids are sp^3d^2 - the sulphur in the SF_6 molecules must have these hybrids.