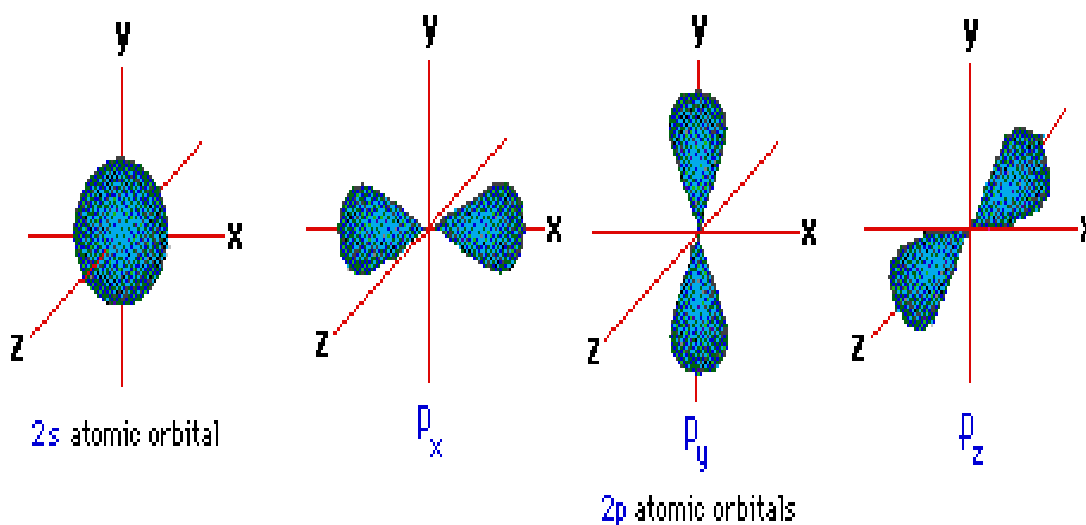


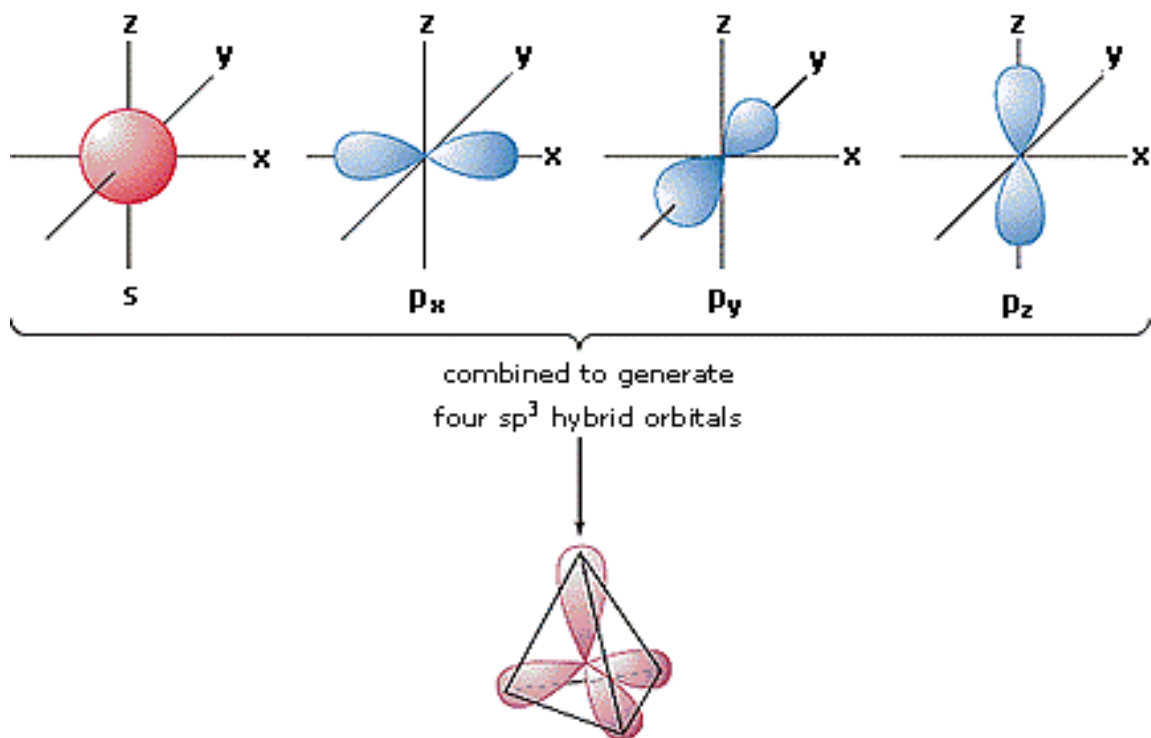
Orbital

Atomic and Molecular Orbitals

- A more detailed model of covalent bonding requires a consideration of valence shell atomic orbitals. For second period elements such as carbon, nitrogen and oxygen, these orbitals have been designated $2s$, $2p_x$, $2p_y$ & $2p_z$. The spatial distribution of electrons occupying each of these orbitals is shown in the diagram below.

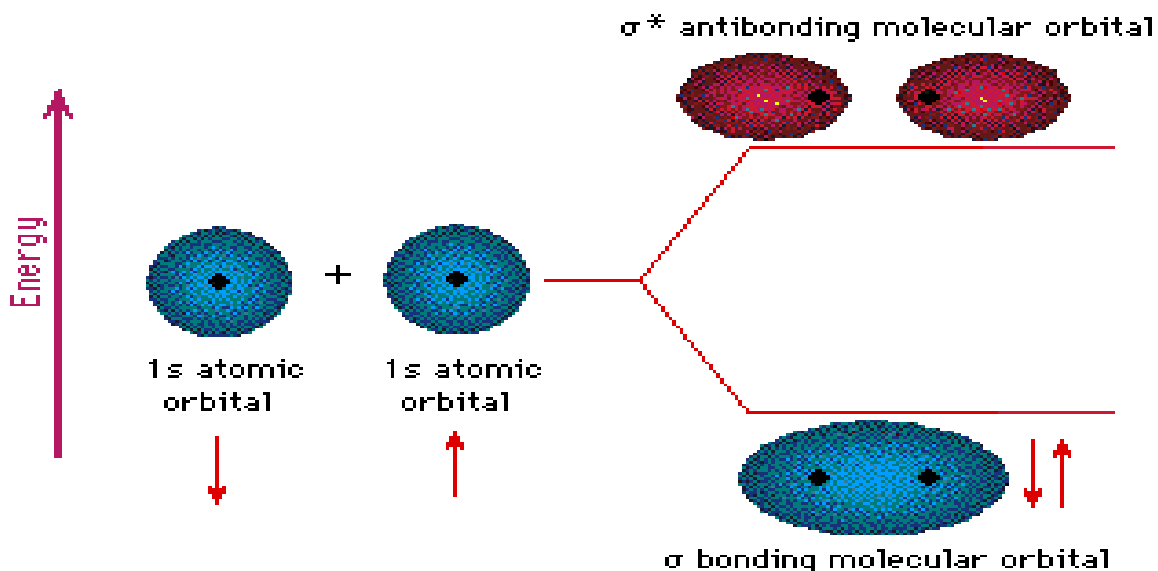


- The valence shell electron configuration of carbon is $2s^2$, $2p_x^1$, $2p_y^1$ & $2p_z^0$. If this were the configuration used in covalent bonding, carbon would only be able to form two bonds.
- **Hybrid Orbitals**
In order to explain the structure of methane (CH_4), the 2s and three 2p orbitals must be converted to four equivalent **hybrid atomic orbitals**, each having 25% s and 75% p character, and designated sp^3 . These hybrid orbitals have a specific orientation, and the four are naturally oriented in a tetrahedral fashion.

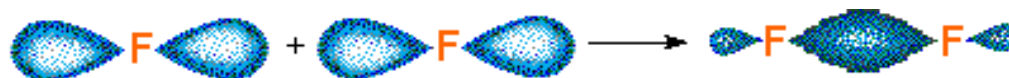


- **Molecular Orbitals:**

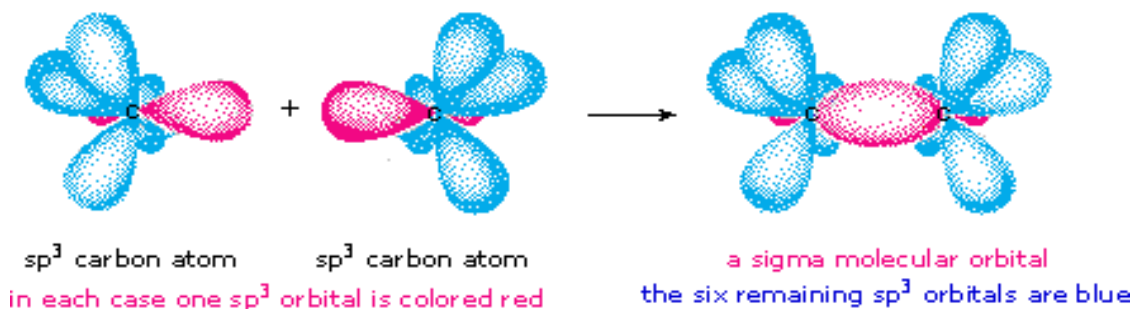
Just as the valence electrons of atoms occupy atomic orbitals (AO), the shared electron pairs of covalently bonded atoms may be thought of as occupying molecular orbitals (MO). It is convenient to approximate molecular orbitals by combining or mixing two or more atomic orbitals. In general, this mixing of n atomic orbitals always generates n molecular orbitals. The hydrogen molecule provides a simple example of MO formation. In the following diagram, two $1s$ atomic orbitals combine to give a sigma (σ) bonding (low energy) molecular orbital and a second higher energy MO referred to as an anti-bonding orbital. The bonding MO is occupied by two electrons of opposite spin, the result being a covalent bond.



- The notation used for molecular orbitals parallels that used for atomic orbitals. Thus, s-orbitals have a spherical symmetry surrounding a single nucleus, whereas σ -orbitals have a cylindrical symmetry and encompass two (or more) nuclei. In the case of bonds between second period elements, p-orbitals or hybrid atomic orbitals having p-orbital character are used to form molecular orbitals. For example, the sigma molecular orbital that serves to bond two fluorine atoms together is generated by the overlap of p-orbitals (part A below), and two sp^3 hybrid orbitals of carbon may combine to give a similar sigma orbital. When these bonding orbitals are occupied by a pair of electrons, a covalent bond, **the sigma bond** results. Although we have ignored the remaining p-orbitals, their inclusion in a molecular orbital treatment does not lead to any additional bonding, as may be shown by activating the fluorine correlation diagram below.

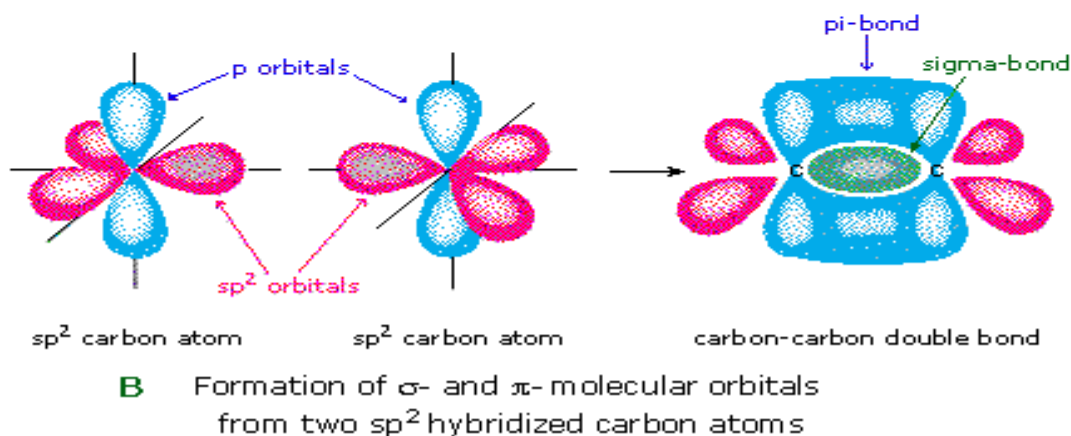
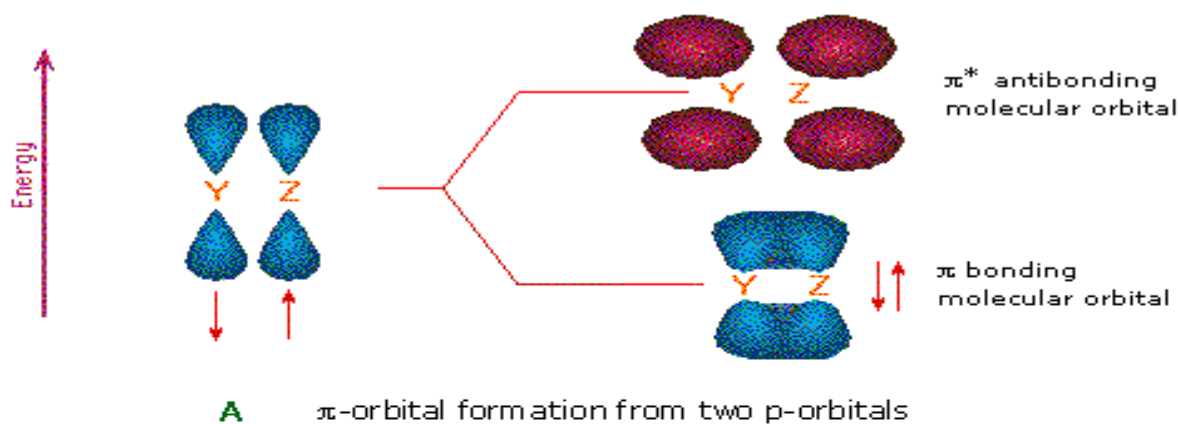


A σ -orbital formation from two p-orbitals



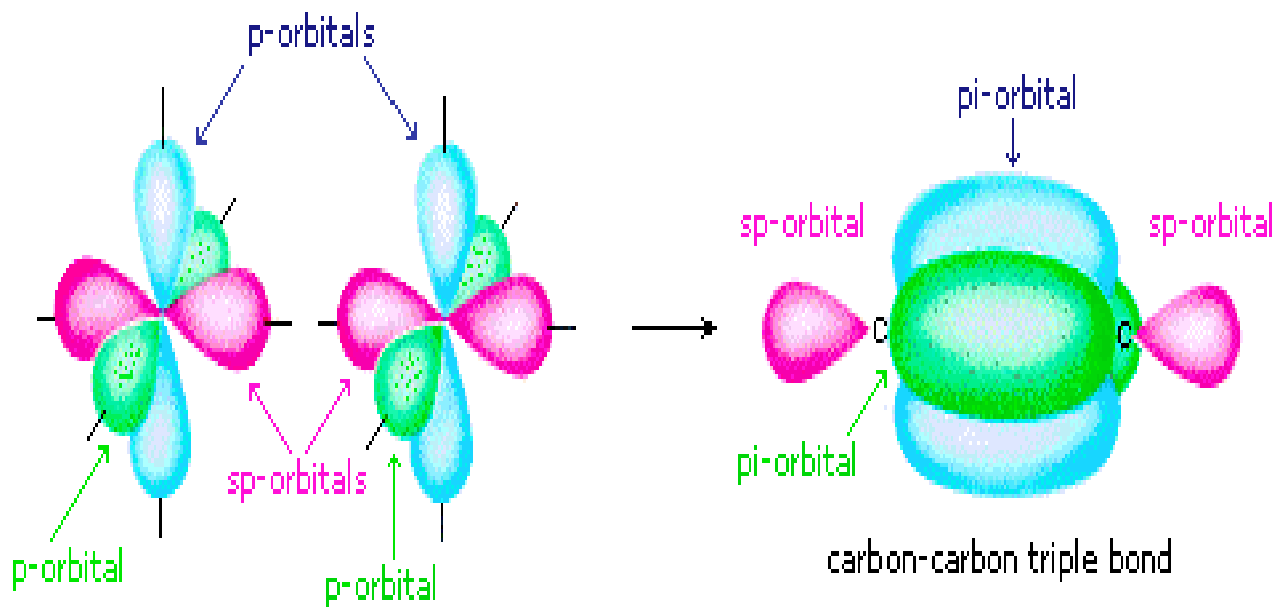
• B σ -orbital formation from two sp^3 orbitals

- Another type of MO (the π orbital) may be formed from two p-orbitals by a lateral overlap, as shown in part A of the following diagram. Since bonds consisting of occupied π -orbitals (**pi-bonds**) are weaker than sigma bonds, pi-bonding between two atoms occurs only when a sigma bond has already been established. **Thus, pi-bonding is generally found only as a component of double and triple covalent bonds.** Since carbon atoms involved in double bonds have only three bonding partners, they require only three hybrid orbitals to contribute to three sigma bonds. A mixing of the 2s-orbital with two of the 2p orbitals gives three sp^2 hybrid orbitals, leaving one of the p-orbitals unused. Two sp^2 hybridized carbon atoms are then joined together by sigma and pi-bonds (a **double bond**), as shown in part B.

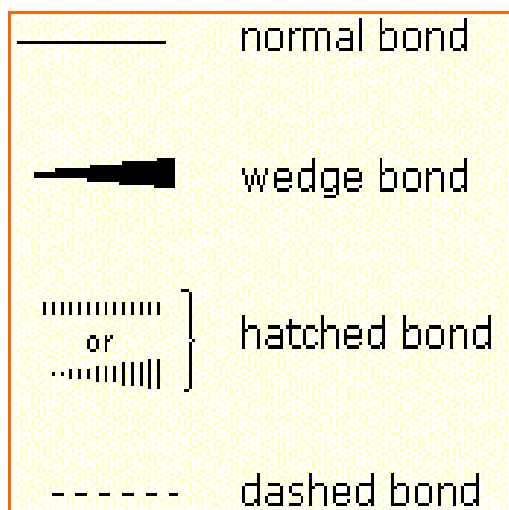


- The manner in which atomic orbitals overlap to form molecular orbitals is commonly illustrated by a **correlation diagram**. Two examples of such diagrams for the simple diatomic elements F_2 and N_2 will be drawn above when the appropriate button is clicked. The 1s and 2s atomic orbitals do not provide any overall bonding, since orbital overlap is minimal, and the resulting sigma bonding and anti-bonding components would cancel. In both these cases three 2p atomic orbitals combine to form a sigma and two pi-molecular orbitals, each as a bonding and anti-bonding pair. The overall bonding order depends on the number of anti-bonding orbitals that are occupied.

- The subtle change in the energy of the σ_{2p} bonding orbital, relative to the two degenerate π -bonding orbitals, is due to s-p hybridization that is unimportant to the present discussion. An impressive example of the advantages offered by the molecular orbital approach to bonding is found in the oxygen molecule.
- **A model of the π orbitals of ethene .**
- The p-orbitals in this model are represented by red and blue colored spheres or ellipses, which represent different phases, defined by the mathematical wave equations for such orbitals.
- Finally, in the case of carbon atoms with only two bonding partners only two hybrid orbitals are needed for the sigma bonds, and these sp hybrid orbitals are directed 180° from each other. Two p-orbitals remain unused on each sp hybridized atom, and these overlap to give two pi-bonds following the formation of a sigma bond (a triple bond), as shown below.

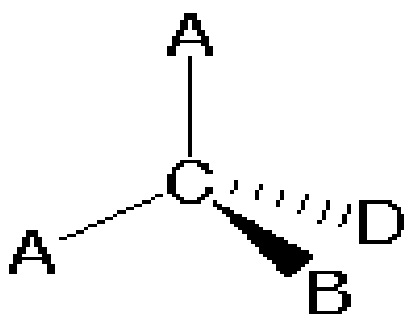


- sp hybridized carbon atoms



The Shape of Molecules

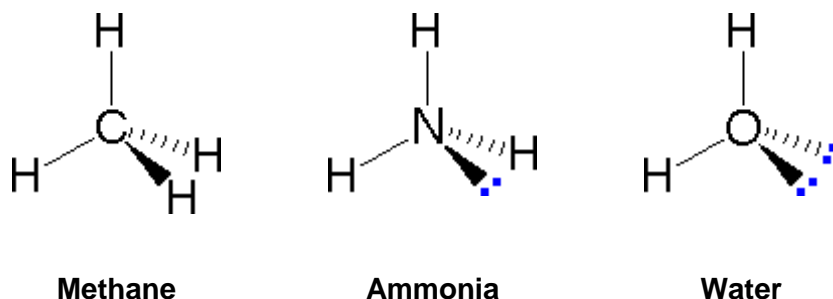
The three dimensional shape or **configuration** of a molecule is an important characteristic. This shape is dependent on the preferred spatial orientation of covalent bonds to atoms having two or more bonding partners. Three dimensional configurations are best viewed with the aid of models. In order to represent such configurations on a two-dimensional surface (**paper, blackboard or screen**), we often use **perspective drawings**



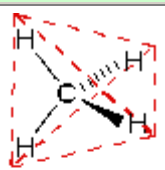
in which the direction of a bond is specified by the line connecting the bonded atoms. In most cases the focus of configuration is a carbon atom so the lines specifying bond directions will originate there. As defined in the diagram on the right, a simple straight line represents a bond lying approximately in the surface plane. The two bonds to substituent A in the structure on the left are of this kind. A wedge shaped bond is directed

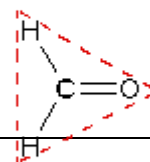
in front of this plane (**thick end toward the viewer**), as shown by the bond to substituent **B**; and a hatched bond is directed in back of the plane (**away from the viewer**), as shown by the bond to substituent **D**. Some texts and

other sources may use a dashed bond in the same manner as we have defined the hatched bond, but this can be confusing because the dashed bond is often used to represent a partial bond (i.e. a covalent bond that is partially formed or partially broken). The following examples make use of this notation, and also illustrate the importance of including non-bonding valence shell electron pairs (colored blue) when viewing such configurations



Bonding configurations are readily predicted by valence-shell electron-pair repulsion theory, commonly referred to as **VSEPR** in most introductory chemistry texts. This simple model is based on the fact that electrons repel each other, and that it is reasonable to expect that the bonds and non-bonding valence electron pairs associated with a given atom will prefer to be as far apart as possible. The bonding configurations of carbon are easy to remember, since there are only three categories.

Configuration	Bonding Partners	Bond Angles	Example
Tetrahedral	4	109.5°	



[Orbitals & Hybridization (Concept / structure)]

Trigonal	3	120°	
Linear	2	180°	

In the three examples shown above, the central atom (**carbon**) does not have any non-bonding valence electrons; consequently the configuration may be estimated from the number of bonding partners alone. For molecules of water and ammonia, however, the non-bonding electrons must be included in the calculation. In each case there are four regions of electron density associated with the valence shell so that a tetrahedral bond angle is expected. The measured bond angles of these compounds (**H₂O 104.5° & NH₃ 107.3°**) show that they are closer to being tetrahedral than tri-gonal or linear. Of course, it is the configuration of atoms (**not electrons**) that defines the shape of a molecule, and in this sense ammonia is said to be pyramidal (**not tetrahedral**). The compound boron tri-fluoride, BF₃, does not have non-bonding valence electrons and the configuration of its atoms is tri-gonal.