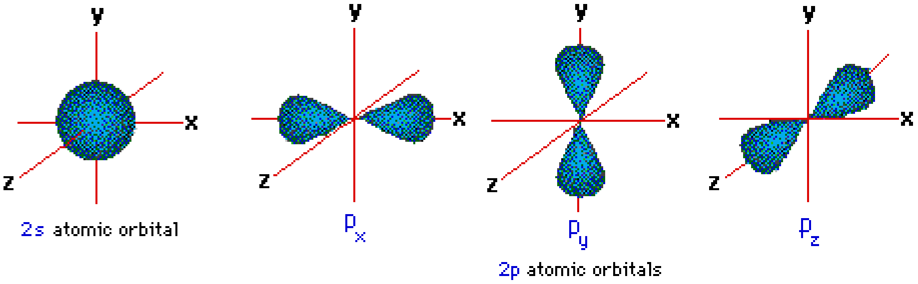
Atomic and Molecular Orbital

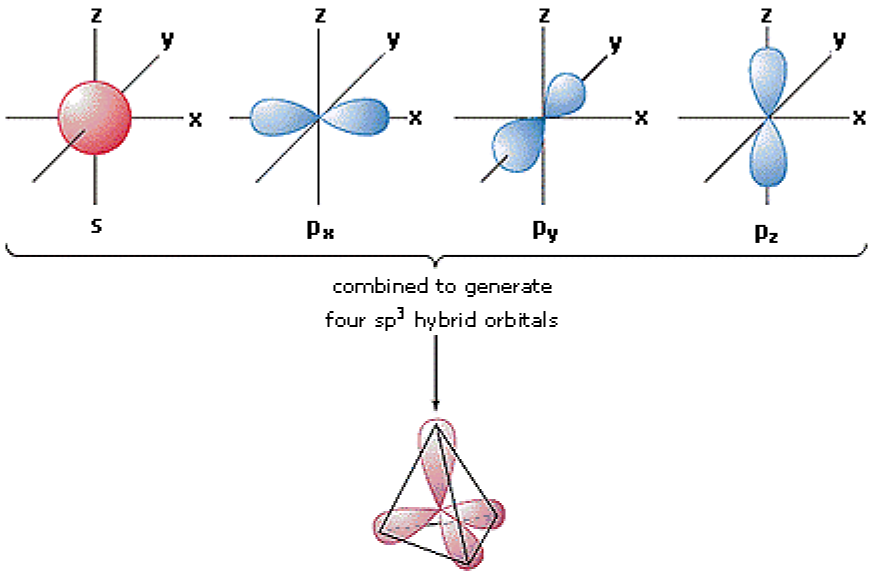
A more detailed model of covalent bonding requires a consideration of valence shell atomic orbitals. For second period elements such as carbon, nitrogen and oxygen, these orbitals have been designated 2_s, $2p_x$, $2p_y$ & $2p_z$. The spatial distribution of electrons occupying each of these orbitals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



The valence shell electron configuration of carbon is 2_s^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. In this case, the valence shell would have six electrons- two shy of an octet. However, the tetrahedral structures of methane and carbon tetrachloride demonstrate that carbon can form four equivalent bonds, leading to the desired octet. In order to explain this covalent bonding, Linus Pauling proposed an orbital hybridization model in which all the valence shell electrons of carbon are reorganized.

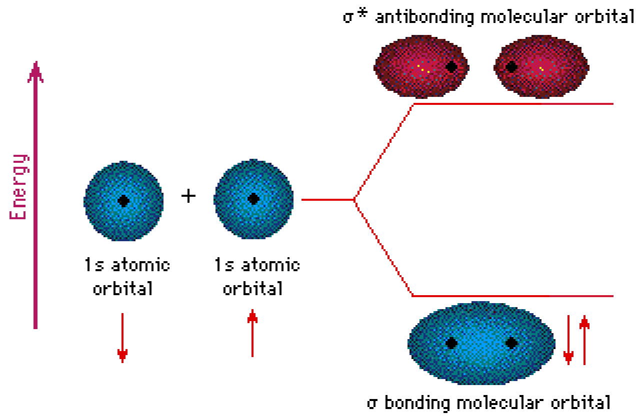
Hybrid Orbitals

In order to explain the structure of methane (CH_4), the 2s and three 2p orbitals are 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. Thus, the four covalent bonds of methane consist of shared electron pairs with four hydrogen atoms in a tetrahedral configuration, as predicted by VSEPR theory.

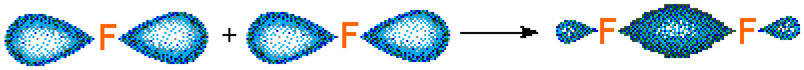


Molecular Orbitals

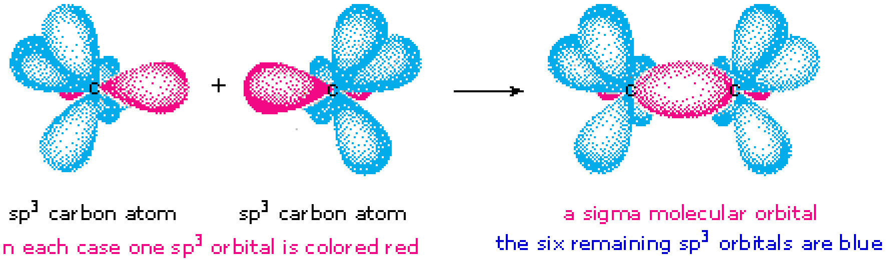
Just as the valence electrons of atoms occupy atomic orbitals (AO), the shared electron pairs of covalently bonded atoms may be thought of as occupying molecular orbitals (MO). It is convenient to approximate molecular orbitals by combining or mixing two or more atomic orbitals. In general, this mixing 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 antibonding 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.



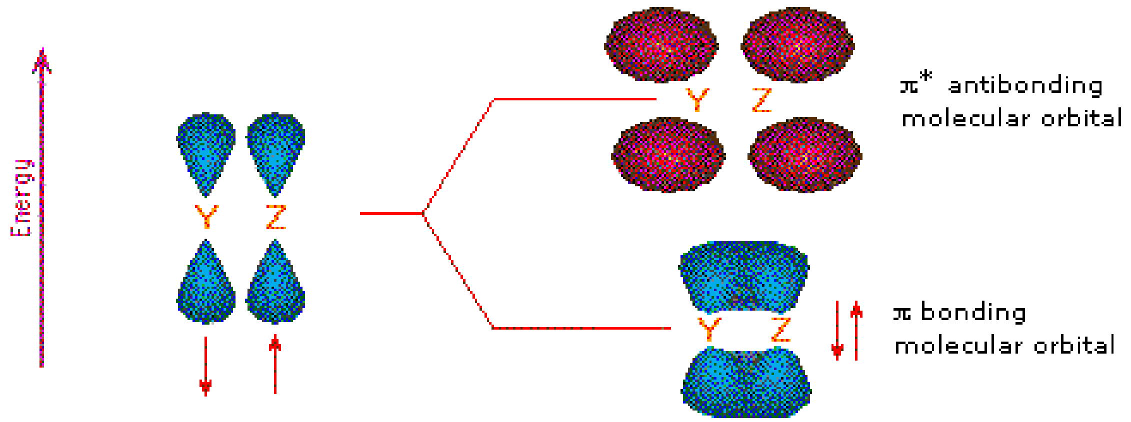
A σ-orbital formation from two p-orbitals



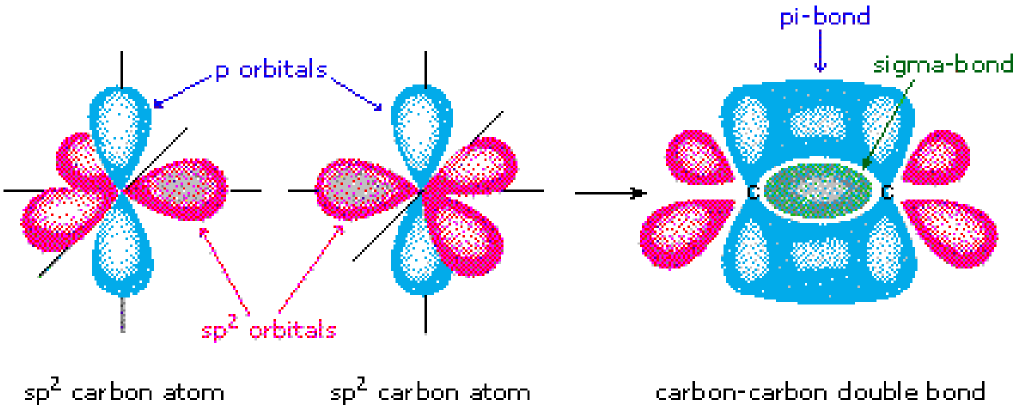
B σ-orbital formation from two sp^3 orbitals

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 actually more complex than the localized examples given above. These are useful models for explaining the structure and reactivity of many organic compounds, but modern molecular orbital theory involves the creation of an orbital **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 antibonding 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 antibonding pair. The overall bonding order depends on the number of antibonding 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.



A π-orbital formation from two p-orbitals

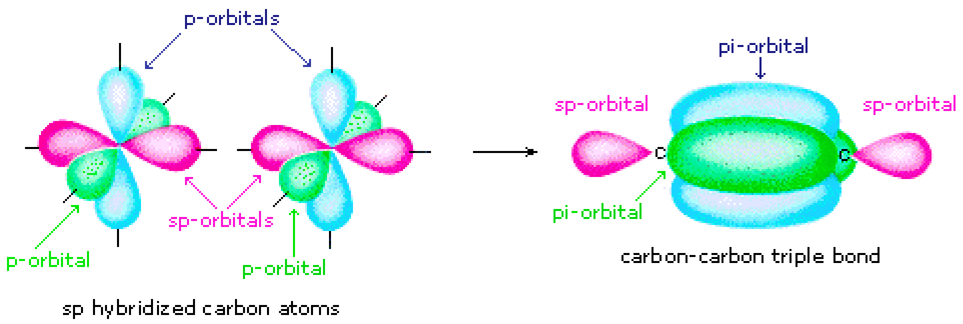


B Formation of σ- and π- molecular orbitals from two sp^2 hybridized carbon atoms

One example of the advantage offered by the molecular orbital approach to bonding is the oxygen molecule. Here, the correlation diagram correctly accounts for the paramagnetic character of this simple diatomic compound. Likewise, the orbital correlation diagram for methane provides another example of the difference in electron density predicted by molecular orbital calculations from that of the localized bond model. Click on the compound names for these displays.

The p-orbitals in these 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 180º 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.



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