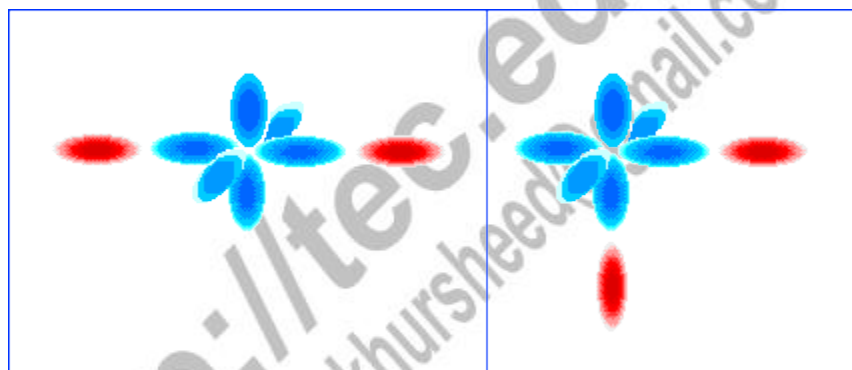


Hybridization Theory

VSEPR theory adequately describes all of the situations we will encounter in this course. Unfortunately, organic chemists still use the language of an older theory, hybridization theory, in the literature and in textbooks. We will take a pragmatic approach to hybridization theory:

If there are two regions of electron density around a central atom, that atom is said to be sp hybridized; if there are three regions of electron density around a central atom, that atom is said to be sp^2 hybridized; if there are four regions of electron density around a central atom, that atom is said to be sp^3 hybridized.

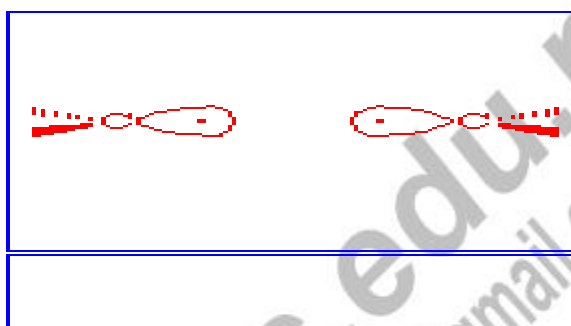
Alternative Atomic Orbital Overlap



According to hybridization theory, there are two types of bonds, sigma (σ) and pi (π). Sigma bonds are single bonds. They are formed by the **head-to-head overlap** of hybridized orbitals. Multiple bonds are combinations of one sigma bond and one or two pi bonds. **The pi bonds** are formed by the **side-to-side overlap** of un-hybridized p orbitals. **Thus a double bond is considered to be a combination of one sigma bond and one pi bond, while a triple bond is formed from one sigma bond and two pi bonds.**

Figure 3 animates the way organic chemists envision the formation of a double bond between two sp^2 hybridized carbon atoms. Only the sp^2 orbitals that are involved in the formation of the **C-C sigma bond** are shown explicitly.

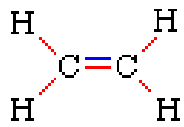
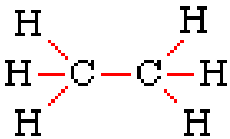
Imagining the Formation of a Double Bond



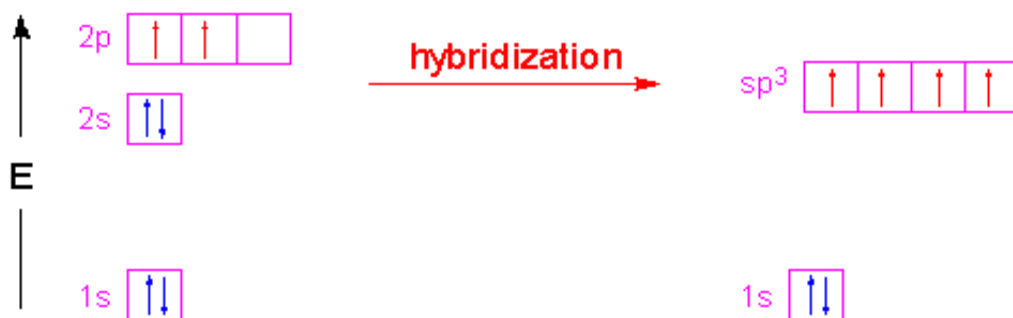
Since **head-to-head overlap localizes the electron pair** in the inter-nuclear region more than **side-to-side overlap does**, the electrons in a sigma bond experience greater nuclear attraction than the electrons in a pi bond. Hence, electrons in sigma bonds have lower energy than electrons in pi bonds. Both sigma-bonded electrons and pi-bonded electrons are lower in energy than non-bonded electrons because non-bonded electrons are localized on a single atom and therefore experience the nuclear attraction of only that atom.

Table 1 summarizes the bonding arrangements that are possible for the three most common hybridizations. Each entry in columns 1-5 of the table refers to a single carbon atom. You should be certain you understand the relationships between the information in these two tables.

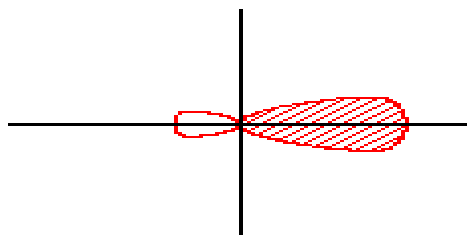
A Summary of Hybridization and Bonding

Hybridization	Hybridizing Orbitals	Un-hybridized Orbitals	σ Bonds	π Bonds	Example
sp	s + p = 2 sp	2 p	2	2	H-C \equiv C-H
sp ²	s + 2p = 3 sp ²	1 p	3	1	
sp ³	s + 3p = 4 sp ³	none	4	none	

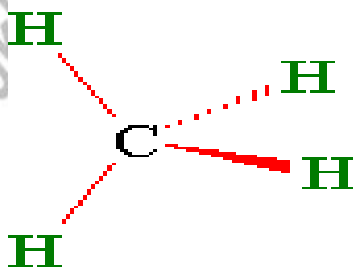
In the case of methane CH₄, the three 2p orbitals of the carbon atom are combined with its 2s orbital to form four new orbitals called "**sp³**" hybrid orbitals. The name is simply a tally of all the orbitals that were blended together to form these new hybrid orbitals. Four hybrid orbitals were required since there are four atoms attached to the central carbon atom. These new orbitals will have energy slightly above the 2s orbital and below the 2p orbitals as shown in the following illustration. Notice that no change occurred with the 1s orbital.



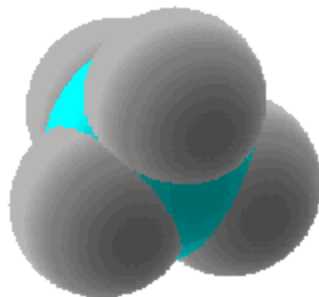
These hybrid orbitals have 75% p-character and 25% s-character which gives them a shape that is shorter and fatter than a p-orbital. The new shape looks a little like...



A stick and wedge drawing of methane shows the tetrahedral angles...(The wedge is coming out of the paper and the dashed line is going behind the paper. The solid lines are in the plane of the paper.)



A space-filling model of methane would look like...

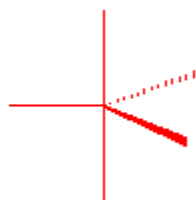


A stick and wedge drawing of ammonia showing the non-bonding electrons in a probability area for the hybrid orbital...

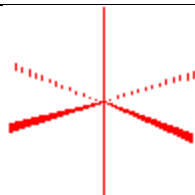
Hybridization Involving d-Orbitals

As we discussed earlier, some 3rd row and larger elements can accommodate more than eight electrons around the central atom. These atoms will also be hybridized and have very specific arrangements of the attached groups in space. The two types of hybridization involved with d orbitals are sp^3d and sp^3d^2 .

The groups will be arranged in a trigonal bi-pyramidal arrangement with sp^3d hybridization...bond angles will be 120° in the plane with two groups arranged vertically above and below this plane.



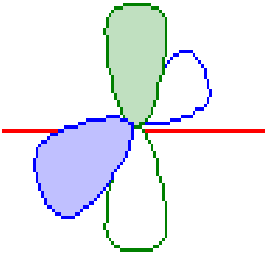
There will be an octahedral arrangement with sp^3d^2 hybridization...all bond angles are at 90° .

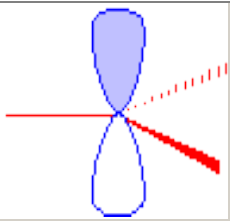
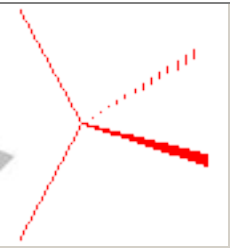
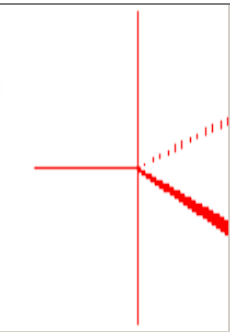
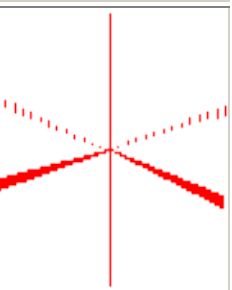


Non-bonded electron pairs are always placed where they will have the most space...in the trigonal plane for sp^3d hybridization.

Try drawing the 3-dimensional electron-dot picture for each of the following molecules...First draw an electron-dot formula. Remember to put all the extra electrons on the central atom as pairs when drawing this initial electron-dot formula. Now count the groups around the central atom. If there are six groups (Remember to count non-bonding electron pairs as groups.) it will have sp^3d^2 hybridization. If it has five groups it will have sp^3d hybridization.

Summary of Hybridization...In the following summary, groups are considered to be atoms and/or pairs of electrons and hybrid orbitals are the red lines and wedges. When the octet of an element is exceeded, then hybridization will involve d-orbitals. Unhybridized p-orbitals are shown as probability areas in blue and green for sp hybridization and blue for sp^2 hybridization. A single electron as found in a radical would occupy an unhybridized p-orbital.

Number of Groups Attached to a Central Atom	Description and 3-Dimensional Shape
Two Groups... sp	<p>2 groups = sp hybridization 180 degree bond angle linear electron-pair geometry</p> 

<p>Three Groups...sp^2</p>	<p>3 groups = sp^2 hybridization 120 degree bond angles trigonal planar electron-pair geometry</p>	
<p>Four Groups...sp^3</p>	<p>4 groups = sp^3 hybridization 109.5 degree bond angles tetrahedral electron-pair geometry</p>	
<p>Five Groups...sp^3d</p>	<p>5 groups = sp^3d hybridization 120 and 90 degree bond angles trigonal bipyramidal electron-pair geometry</p>	
<p>Six Groups...sp^3d_2</p>	<p>6 groups = sp^3d_2 hybridization 90 degree bond angles octahedral electron-pair geometry</p>	

Hybridization Involving Multiple Bonds

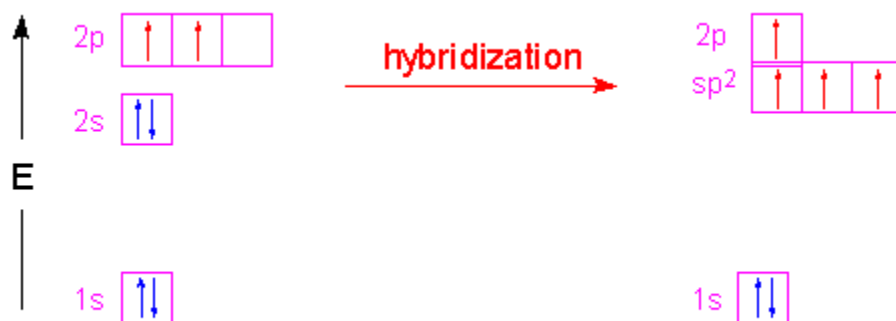
Only a maximum of two electrons can occupy any orbital whether it is an atomic orbital or a molecular orbital due to electron-electron repulsion. When we draw a double or a triple-bond between two atoms, we imply that either four or six electrons are directly between these two atoms. Since this is impossible, we must have these

extra electrons off to the side in what we refer to as pi bonds. Therefore, all multiple bonds are composed of two different kinds of molecular bonds called pi-bonds and sigma-bonds.

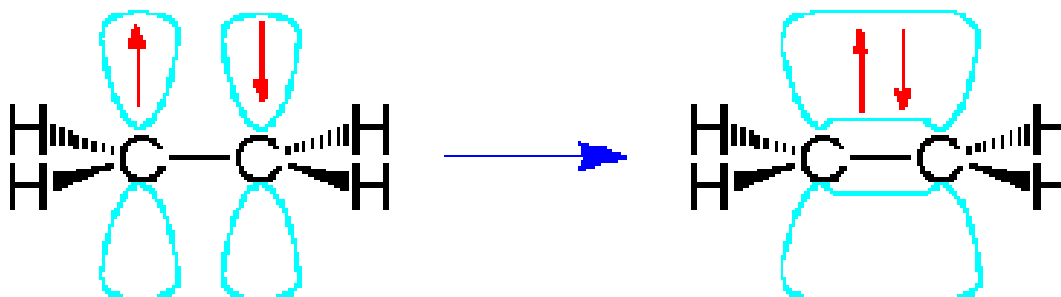
The sigma-bond is defined as the linear overlap of atomic orbitals (hybrids except for hydrogen) in which two electrons are directly between the two bonded nuclei.

Pi-bonds are defined as the parallel overlap of p-orbitals. A double bond has one sigma-bond and one pi-bond. A triple bond thus consists of a sigma-bond and two pi-bonds with the pi-bonds in different planes.

In the molecule C₂H₄, Ethene both carbon atoms will be sp² hybridized and has one unpaired electron in a non-hybridized p orbital.

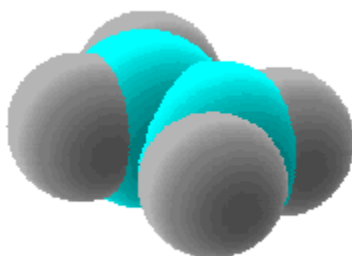


These p-orbitals will undergo parallel overlap and form one pi bond with bean-shaped probability areas above and below the plane of the six atoms. **This pair of bean-shaped probability areas constitutes one pi-bond and the pair of electrons in this bond can be found in either bean-shaped area.**

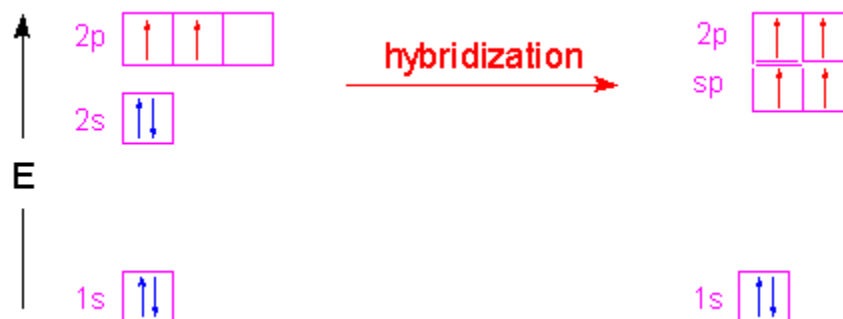


The 3-dimensional model of ethene is therefore planar with H-C-H and H-C-C bond angles of 120° ...

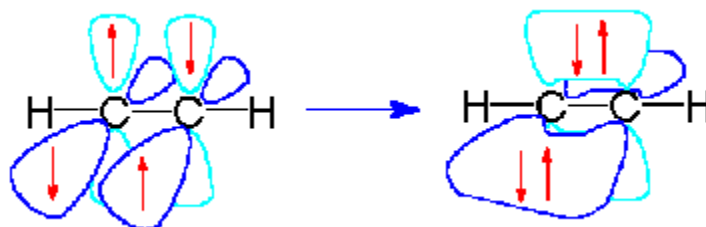
(The pi-bond is not shown in this picture)



Now let's look at H_2C_2 (acetylene). Both carbon atoms will be sp hybridized and have one electron in each of two un-hybridized p orbitals.



These p orbitals will undergo parallel overlap to form two pi-bonds at right angles to each other.



The 3-dimensional model of acetylene is therefore linear...the pi-bonds are not shown in this picture.

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