

Valence bond theory

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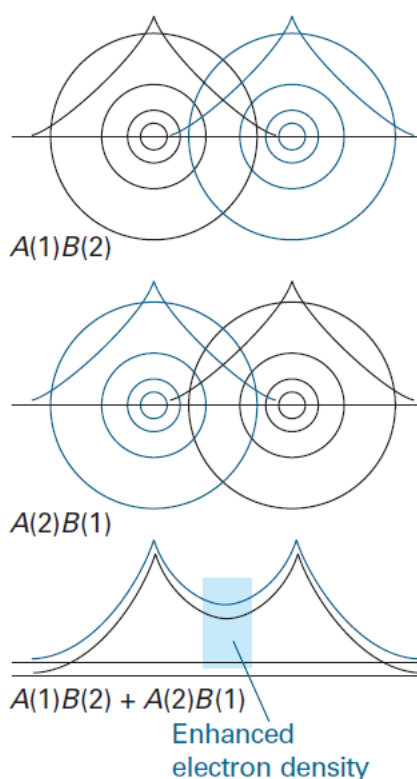
The **valence bond theory** (VBT) of bonding was the first quantum mechanical theory of bonding to be developed. Valence bond theory considers the interaction of atomic orbitals on separate atoms as they are brought together to form a molecule. It was first proposed by W. Hitler and F. London in 1927.

The hydrogen molecule

The two-electron wavefunction for two widely separated H atoms is $\Psi = \Psi_A(1)\Psi_B(2)$, where Ψ_A and Ψ_B are H1s orbitals on atoms A and B. An equally valid description is therefore $\Psi = \Psi_A(2)\Psi_B(1)$, in which electron 2 is on A and electron 1 is on B. When two outcomes are equally probable, quantum mechanics instructs us to describe the true state of the system as a superposition of the wavefunctions for each possibility, so a better description of the molecule than either wavefunction alone is the linear combination of the two possibilities.

$$\Psi = \Psi_A(1)\Psi_B(2) + \Psi_A(2)\Psi_B(1)$$

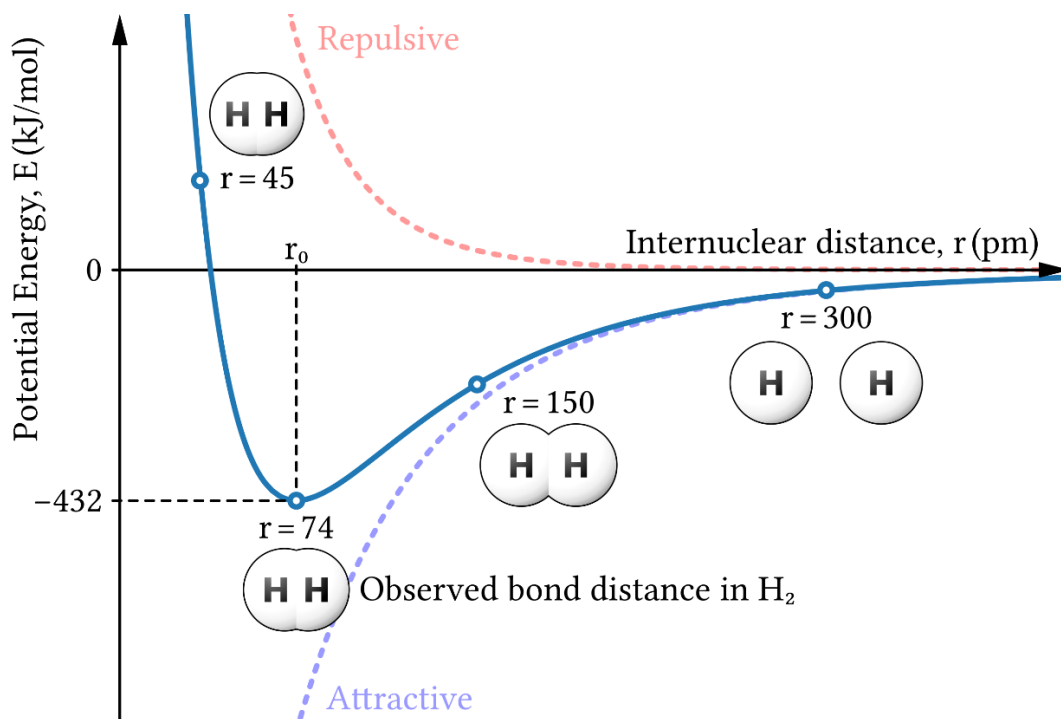
This function is the (unnormalized) VB wavefunction for an H-H bond. The formation of the bond can be pictured as being due to the high probability that the two electrons will be found between the two nuclei and hence will bind them together as shown figure below.



More formally, the wave pattern represented by the term $\Psi_A(1)\Psi_B(2)$ interferes constructively with the wave pattern represented by the contribution $\Psi_A(2)\Psi_B(1)$ and there is an enhancement in the amplitude of the wavefunction in the internuclear region. For technical reasons stemming from the Pauli principle, only electrons with paired spins can be described by a wavefunction of the type written above so only paired electrons can contribute to a bond in VB theory. We say, therefore, that a VB wavefunction is formed by **spin pairing** of the electrons in the two contributing atomic orbitals. The electron distribution described by the wavefunction is called a σ (sigma) **bond**. As shown in above figure, the bond has cylindrical symmetry around the internuclear axis, and the electrons in it have zero orbital angular momentum about that axis.

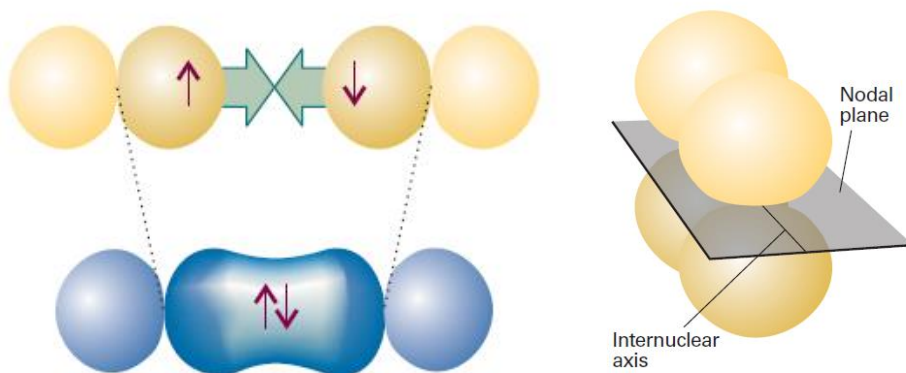
The **molecular potential energy curve** for H_2 molecule, a graph showing the variation of the energy of the molecule with internuclear separation, is calculated by changing the internuclear separation R and evaluating the energy at each selected separation as shown below figure. The energy is found to fall below that of two separated H atoms as the two atoms are brought within bonding distance and each electron becomes free to migrate to the other

atom. However, the resulting lowering of energy is counteracted by an increase in energy from the Coulombic (electrostatic) repulsion between the two positively charged nuclei. This positive contribution to the energy becomes large as R becomes small. Consequently, the total potential energy curve passes through a minimum and then climbs to a strongly positive value at small internuclear separations. The depth of the minimum of the curve is denoted D_e . The deeper the minimum, the more strongly the atoms are bonded together. The steepness of the well shows how rapidly the energy of the molecule rises as the bond is stretched or compressed. The steepness of the curve, an indication of the stiffness of the bond, therefore governs the vibrational frequency of the molecule



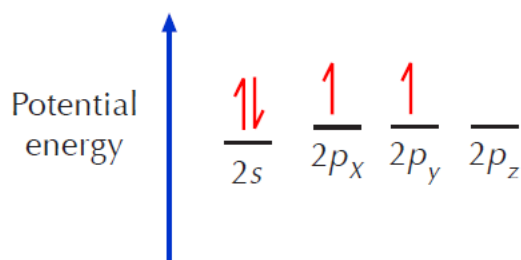
The VB description of H₂ can be applied to other homonuclear diatomic molecules, such as nitrogen, N₂. To construct the valence bond description of N₂, we consider the valence electron configuration of each atom, which is $2s^2 2p_x^1 2p_y^1 2p_z^1$. It is conventional to take the z -axis to be the internuclear axis, so we can imagine each atom as having a $2p_z$ orbital pointing towards a $2p_z$ orbital on the other atom with the $2p_x$ and $2p_y$ orbitals perpendicular to the axis. A σ bond is then formed by spin pairing between the two electrons in the two $2p_z$ orbitals. The remaining $2p$ orbitals cannot merge to give σ bonds as they do not have cylindrical symmetry around the internuclear axis. Instead, they merge to form two π bonds. A π bond arises from the spin pairing of electrons in two p orbitals that approach side-by-side as shown figure below. It is so called because, viewed along the internuclear axis, a π bond resembles a pair of electrons in a p orbital (and π is the Greek equivalent of p).

There are two π bonds in N₂, one formed by spin pairing in two neighbouring $2p_x$ orbitals and the other by spin pairing in two neighbouring $2p_y$ orbitals. The overall bonding pattern in N₂ is therefore a σ bond plus two π bonds which is consistent with the Lewis structure $\text{N} \equiv \text{N}$ for nitrogen.

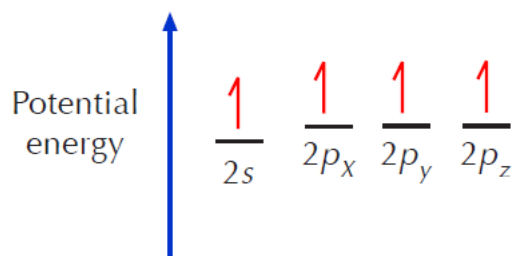


Hybridization Theory

If we look at the valence shell configuration of carbon, we find two paired electrons in the $2s$ orbital, and two unpaired electrons in the $2p_x$ and $2p_y$ orbitals, one in each:



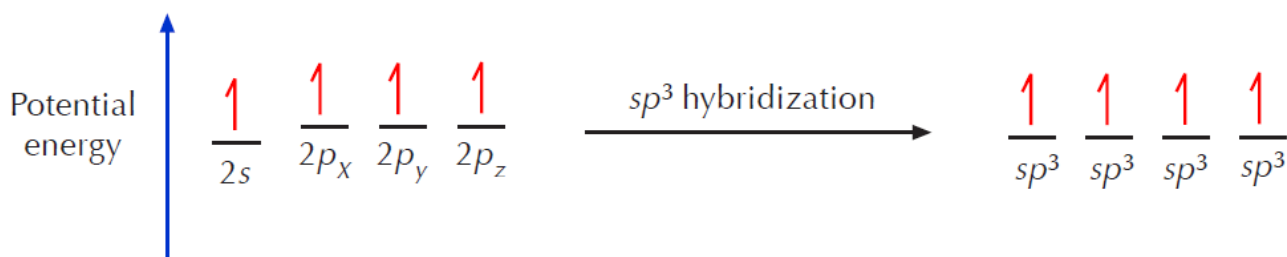
In order to fulfill the octet rule, carbon must use its 4 valence electrons when bonding to other atoms. However, only unpaired electrons can bond. That means that **the two paired electrons occupying the 2s orbital must become unpaired before they can bond**. Since the energy gap between the 2s and 2p orbitals is very small, one of the 2s electrons can be promoted to the empty 2p orbital, leading to the following situation:



Now the four electrons appear to be ready for bonding, but there is a problem. The 2p orbitals are known to be at right angles to each other. If bonding occurs in this state, the 3 equivalent p electrons would form 3 equivalent bonds oriented at 90° to each other, and the s electron would form a bond of a different type and orientation from the other three. No such compound exists. The simplest hydrocarbon –methane (CH₄)– is known to have tetrahedral geometry, where the four C–H bonds are all equivalent and positioned at 109.5° angles to each other. In addition, there are some carbon compounds where the bond angles are 120° or even 180°. **The shapes and relative positions of the valence orbitals in atomic carbon do not explain the shapes and relative positions of the bonds in carbon compounds.**

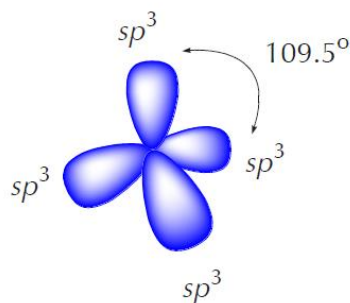
Hybridization Theory Attempts To Explain The Actual Shapes Of Molecules By Invoking The Formation Of Hybrid Orbitals During, Or Prior To, The Bonding Process.

Going back to the carbon model with four unpaired electrons in the valence shell, we can take it as a point of departure for formation of hybrid orbitals. The first step is to take either 2, 3, or all four of those orbitals and equalize their energies. Let's say that we take all four of them and form 4 equivalent new orbitals. These orbitals are now of the same energy, which is intermediate between those of the original 2s and 2p orbitals. At the same time, we cannot name the new orbitals s or p, for they're neither. We have to find a new name that reflects the fact that they were created from **one s orbital and three p orbitals**. We will call them **sp³ orbitals**. The process that leads to their formation is called **sp³ hybridization**.



All four sp³ orbitals that result from this process are **equivalent**. That means that they have **the same size, shape,**

and energy. According to VSEPR (valence shell electron pair repulsion) theory, such orbitals will orient themselves in 3-D space **to be as far apart from each other as possible**. The resulting shape is then a tetrahedron, where the carbon nucleus is at the center and the orbitals point to the corners of the tetrahedron. The ideal angle between orbitals is then 109.5 degrees.



When an sp^3 hybridized carbon bonds to hydrogen, it forms methane, whose geometry is known to be tetrahedral.

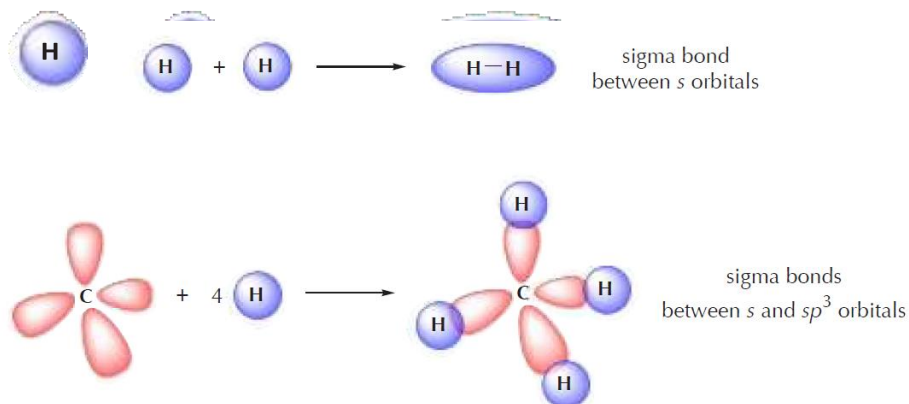
SIGMA BONDING

When atomic orbitals (pure or hybrid) of different atoms overlap to form covalent bonds, they may approach each other in two major ways: **head to head**, or **sideways**. Only head to head overlap is possible with s -orbitals because they are spherical. Hybrid orbitals also undergo mostly head to head overlap when forming covalent bonds. p -orbitals, on the other hand, can approach each other either sideways or head to head.

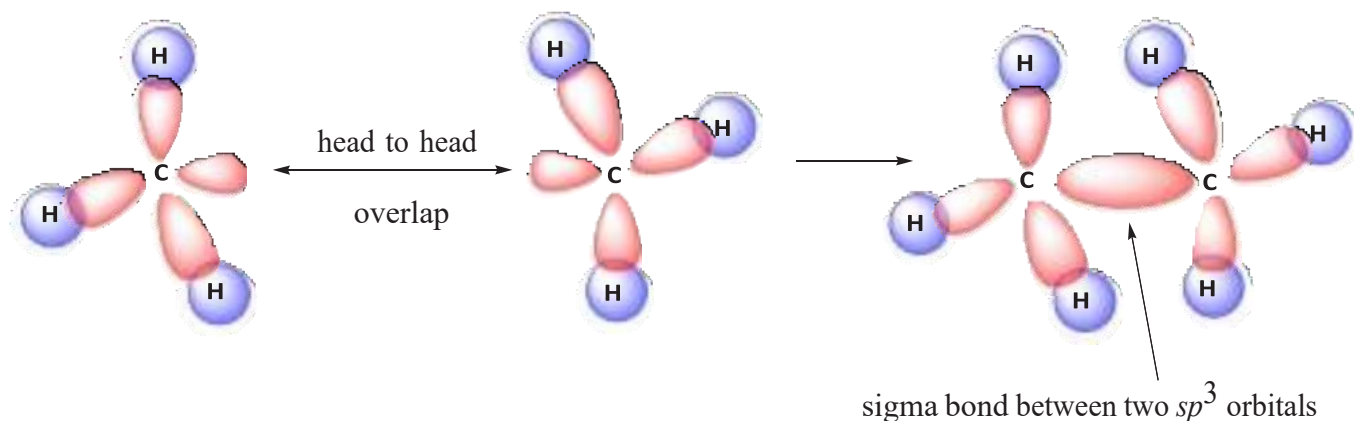
For now, however, we are concerned only with head to head overlap because that's the only type that occurs in alkanes. We'll discuss sideways overlap later in connection with alkenes and alkynes, that is, hydrocarbons that have double and triple bonds respectively.

When orbitals approach each other in a head to head fashion, the resulting covalent bonds are called sigma bonds.

As illustrations, consider the bonds that have already been studied. The bond between two hydrogen atoms is an example of sigma bonding. The bonds between the sp^3 orbitals of hybridized carbon and the s orbitals of hydrogen in methane are also examples of sigma bonds.



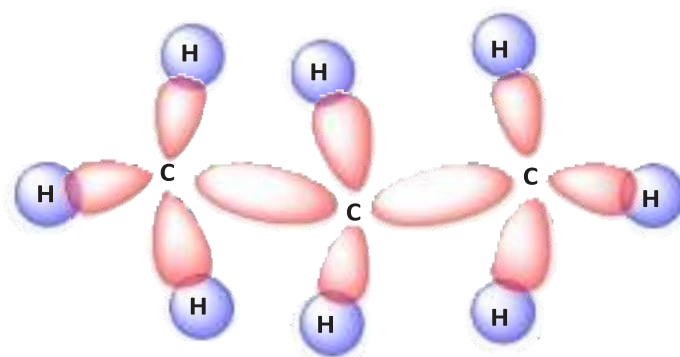
Two sp^3 carbons can also overlap to form a C-C sigma bond where two sp^3 orbitals overlap head to head, such as in the formation of the ethane molecule:



It can be easily seen that **the only type of covalent bonds present in alkanes are sigma bonds**, also loosely known as single bonds.

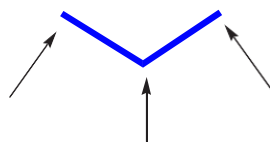
LINE-ANGLE FORMULAS

In alkanes of 3 carbon atoms or more, the main carbon chain acquires a zig-zag structure due to the 109.5° angle between C–C bonds, such as in propane:



Two representations of propane, where the zig-zag structure of the carbon chain becomes apparent

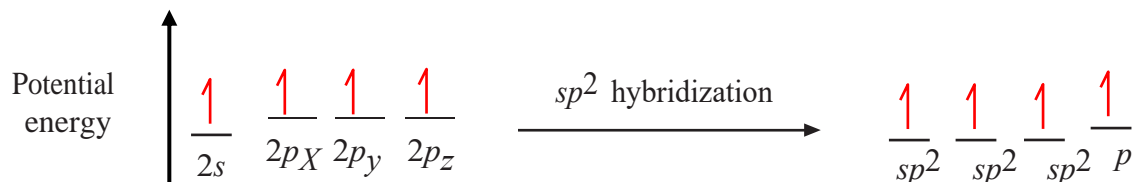
Writing Lewis formulas, or even condensed formulas, for alkanes of many carbon atoms can quickly become cumbersome. A short hand notation that uses zig-zag lines has been developed. The resulting representations are known as **line-angle formulas**. The beginning and the end of the zig-zag line, as well as any breaks in direction represent carbon atoms.



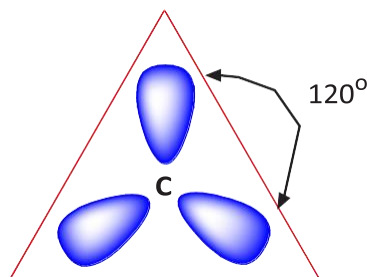
Every carbon atom has to form 4 bonds. **The bonds that are not shown are assumed to be bonds to hydrogen.**
Other examples are:

ALKENES AND sp^2 HYBRIDIZATION OF CARBON

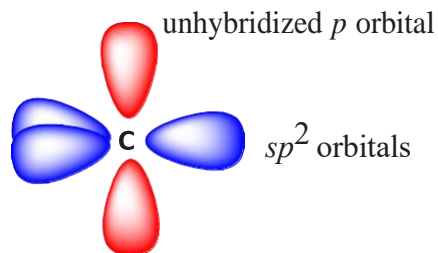
We will now reproduce the sp^3 hybridization process for carbon, but instead of taking one s and three p orbitals to make four equivalent sp^3 orbitals, this time we'll take only **one s and two p orbitals to make three equivalent sp^2 orbitals, leaving one p orbital untouched**. The process is shown below.



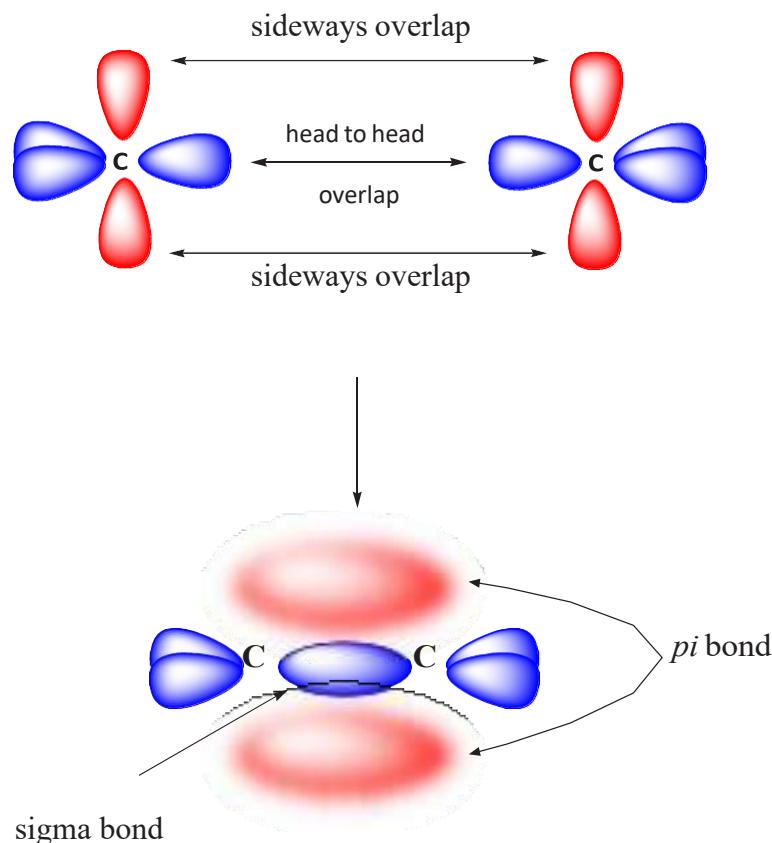
As shown, the three resulting sp^2 orbitals are equivalent in energy, but the remaining p orbital has not been affected. It still retains its original energy and shape. Again, according to VSEPR theory, equivalent orbitals will arrange themselves in 3-D space to be as far apart from each other as possible. Therefore, the three equivalent sp^2 orbitals will arrange themselves in a **trigonal planar** configuration. That is to say, the carbon nucleus will be at the center of an equilateral triangle, and the three sp^2 orbitals will point to the corners of that triangle. **The ideal angle between sp^2 orbitals is therefore 120°** . A **top view** of this arrangement is shown below.



In this top view, the **unhybridized p orbital** cannot be seen because it also arranges itself to be as far apart from the sp^2 orbitals as possible. That is to say, **it is positioned at right angles to those orbitals**, with one lobe coming out of the plane of the page and the other going behind the page. To see this arrangement clearly, we must switch to a **side view** of the orbital system.



When two sp^2 hybridized carbon atoms approach each other to bond, two sp^2 orbitals approach each other head to head, and **two p orbitals approach each other sideways**. The bond formed by the sp^2 orbitals is a sigma bond, and **the bond formed by the p orbitals is called a π bond**. The process is shown below.



The illustration above tries to convey a basic feature of the π bond as compared to the sigma bond. The sigma bond is short and strong. As a rule, **head-to-head overlap is the most efficient way to bond and results in relatively strong and stable bonds**. The π bond, on the other hand, is relatively long and diffuse. **Sideways overlap is less efficient than head to head overlap and results in formation of weaker bonds**.

This has some implications in the properties and chemical reactivity of sigma and π bonds. The electrons in the sigma bond (or sigma electrons) are more tightly bound to the nucleus and don't move too much. In other words, they are more **LOCALIZED**. The electrons in the π bond (or π electrons) are less tightly bound by the nucleus, and therefore **they are relatively mobile**. Under certain conditions, they have the capability to become **DELOCALIZED**, that is to say, they can move in the molecular skeleton from one atom to another, or even become spread over several atoms, according to principles we'll study later.

At the same time, in chemical reactions where electrons are to be traded, **the π electrons are more readily available because they are more exposed and less tightly bound by the nucleus**. It is relatively easy to break a π bond compared to the sigma bond. The principles of all this chemistry will be discussed later in the course.

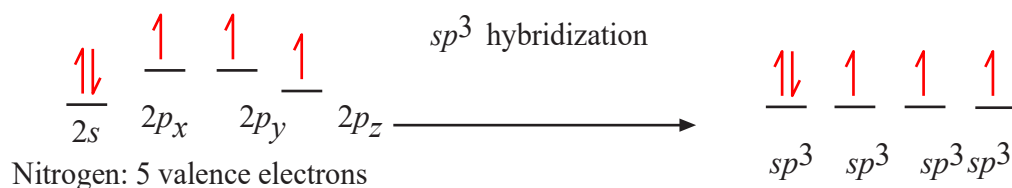
ALKYNES AND sp HYBRIDIZATION OF CARBON

The process for understanding the sp hybridization process for carbon is basically an extension of the other two types (sp^3 and sp^2). You should try to work out this scheme on your own and see if your predictions agree with those presented in the textbook. sp hybridization gives rise to the formation of hydrocarbons known as alkynes. **Alkynes contain at least one triple bond**, and have **linear geometry** around the carbons comprising the triple bond. Therefore, the ideal angle between the sp hybrid orbitals is **180°** . Some examples of alkynes are shown below. For additional information refer to chapter 9 of the Wade textbook.

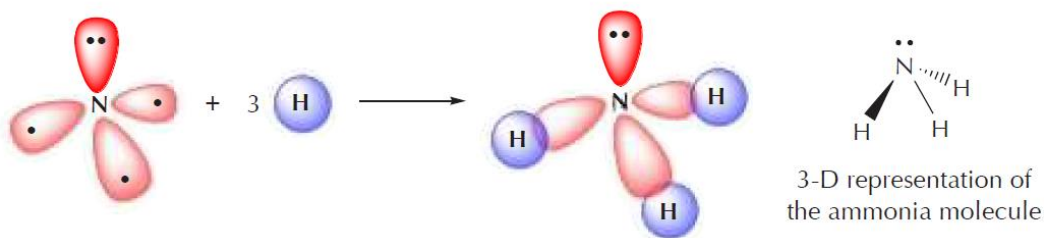
Observe that **the general formula for open chain monoalkynes is C_nH_{2n-2}** where n is the total number of carbon atoms.

ORBITAL HYBRIDIZATION IN NITROGEN AND OXYGEN

The hybridization schemes for nitrogen and oxygen follow the same guidelines as for carbon. For example, sp^3 hybridization for nitrogen results in formation of four equivalent sp^3 orbitals, except that this time only three of them contain unpaired electrons, and one of them contains paired electrons. A similar situation holds true for oxygen, which ends up with two of the sp^3 orbitals occupied with unpaired electrons, and the other two with paired electrons.



The four sp^3 orbitals again orient themselves in 3-D space to be as far apart from each other as possible, but the ideal 109.5° angle becomes distorted because the orbital with two electrons repels the others more strongly than they repel themselves. However the geometry of this arrangement is still fundamentally tetrahedral. When this sp^3 hybridized nitrogen bonds to hydrogen, the three unpaired electrons are used for bonding, and the remaining pair remains as nonbonding electrons.



A similar analysis for oxygen should lead to formation of two sp^3 orbitals with unpaired electrons, and two with paired electrons. Thus, when sp^3 oxygen bonds with hydrogen it forms water, which has a distorted tetrahedral angle, and two pairs of nonbonding electrons in the structure.

