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## Chapter 9 Bonding and Molecular Structure

There are two common approaches to chemical bonding: The **Valence Bond (VB)** theory and the **Molecular Orbital (MO)** theory.

The **VB approach**, by Linus Pauling, says there are bonding electron pairs between atoms and lone pairs of electrons on a particular atom.

The **MO approach**, by Robert Mulliken, holds the molecular orbitals are delocalized over the molecule, so a set of separate atomic orbitals form a set of orbitals that are “the property of the molecule” and distributes the electrons within the orbitals of the molecule.

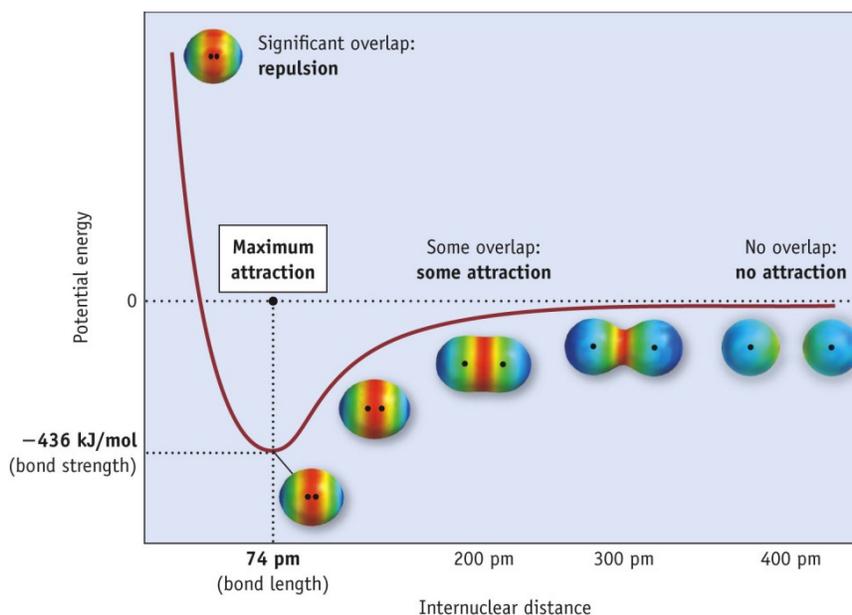
**VB approach** provides:

- A qualitative visual picture of the molecular structure and bonding
- A good description of bonding in in the ground state

**MO theory** provides:

- A quantitative picture of bonding
- A good description of bonding in higher energy or excited states
- The only theory to explain molecules such as NO and O<sub>2</sub>.

VB approach bringing together two Hydrogen to form H<sub>2</sub>.



Using the VB approach and the graph above, as two separate hydrogen atoms approach each other, the electron clouds touch. As the atoms get closer the electron cloud of one atom is attracted by the nucleus, one proton, of the other hydrogen atom. At 74 pm, the molecule is most stable. Closer, the nucleus start to repel each other. At 74 pm bond length distance, we have a very happy molecule of H<sub>2</sub>.

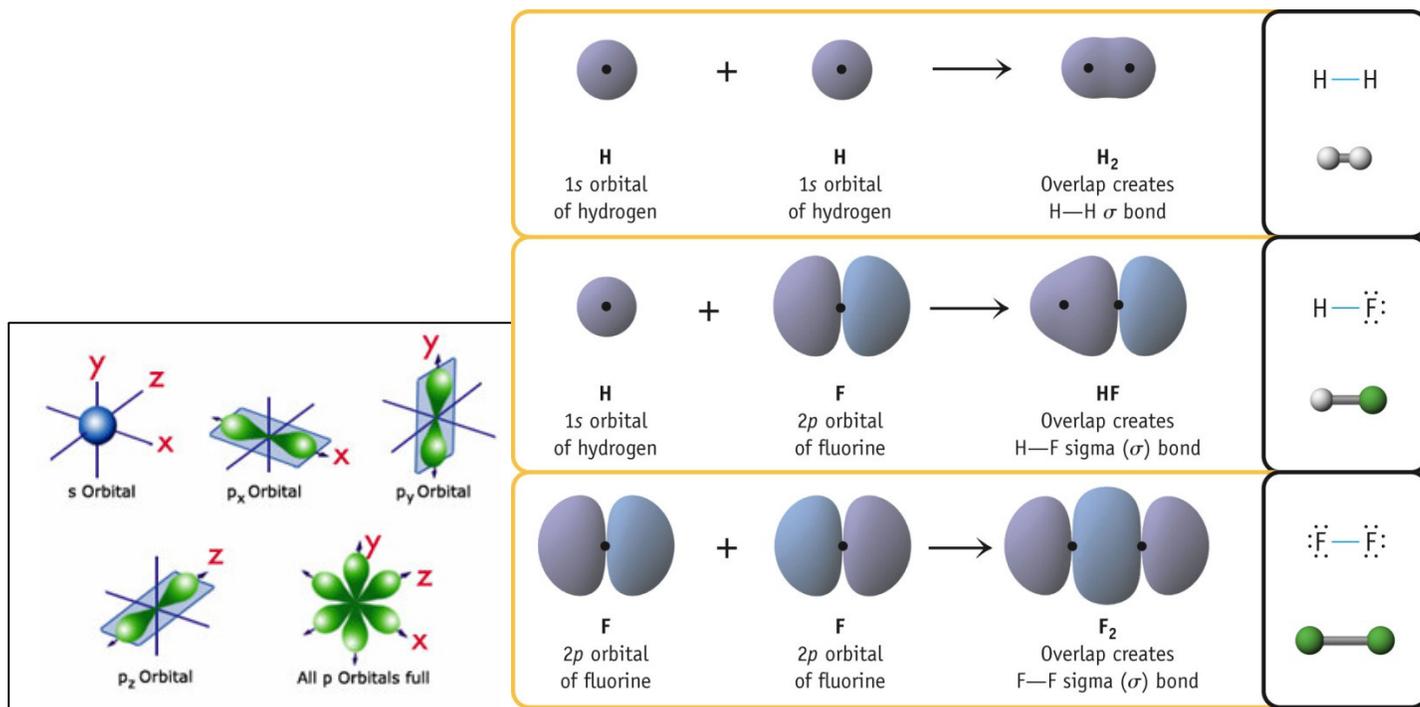
Per the graph below, the bonding electrons spend most of their time between the two hydrogen nuclei in a bonding function. This **Orbital Overlap** comes from the bonds formed by overlap of the atomic orbitals based on the VB theory. The bond is called a sigma ( $\sigma$ ) bond. A  $\sigma$  bond has the electron density greatest along the axis of the bond.

The **VB** approach:

- Orbitals overlap to form a bond between the atoms
- Two electrons, of opposite spin, are in the overlapping orbital.
- Due to orbital overlap, the bonding electrons have a higher probability of being found in the region of space between the two nuclei.

For HF, Hydrogen is  $1s^1$  and F is  $1s^2 2s^2 2p^5$ . The electron from the Hydrogen bonds to the Fluorine in its  $2p^5$  orbital to form a  $2p^6$  orbital. This also forms a sigma bond, but the Fluorine will still have 3 lone pair of **non-bonding** electrons.

Picture on left shows the 3D electron orbits for the  $P_x$ ,  $P_y$ , and  $P_z$ . One of the p orbitals, the  $P_x$  will bond with the Hydrogen in the HF molecule, the other two ( $P_y$  and  $P_z$ ) do not bond and are called nonbonding electrons. With  $F_2$ , the  $P_x$  from each Fluorine will bind to form a  $\sigma$  bond. The  $P_y$  and  $P_z$  do are nonbonding electrons.



## Hybridization of Atomic Orbitals

Carbon's electron configurations is:  $1s^2 2s^2 2p^2$  -or-  $\uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \underline{\quad}$ .

We would expect carbon to form  $CH_2$ , but it doesn't. Carbon forms  $CH_4$  and all bond angles are  $109.5^\circ$  and all 4 Hydrogen are equal. So you can't have one Hydrogen bonded to the Carbon via a 2s orbital and three by a 2p orbital – the Hydrogen's would be different, and they are not.

**Orbital Hybridization** involves the creation of a new set of orbitals from the old ones. These

**Hybrid Orbital's**, are created from the mixing of the original s and p orbits.

- The number of hybrid orbits is always equal to the number of atomic orbitals that are mixed to form the hybrid orbit set
- Hybrid Orbital's sets are combined s and as many p orbital's (sometimes d), to have enough hybrid orbital's to accommodate the bond and lone pairs on the central atom.
- The Hybrid Orbital's are directed towards the terminal atoms. This leads to a better orbit overlap and stronger bond.

The hybrid orbital's required by a molecule are chosen to match the electron-pair geometry of the atom – how many and what kind of things is it joined to?

sp	The s orbital & p orbital ( $s^1$ & $p^1$ )	2 e <sup>-</sup>	180°	Linear
sp <sup>2</sup>	$s^1$ and $p^2$	3 e <sup>-</sup>	120°	Trigonal Planer
<b>sp<sup>3</sup></b>	<b>s<sup>1</sup> and p<sup>3</sup></b>	<b>4 e<sup>-</sup></b>	<b>109.5°</b>	<b>Tetrahedral (Carbon)</b>
sp <sup>3</sup> d	$s^1$ and $p^3$ and $d^1$	5 e <sup>-</sup>	120° and 90°	Trigonal Bipyramidal
sp <sup>3</sup> d <sup>2</sup>	$s^1$ and $p^3$ and $d^2$	6 e <sup>-</sup>	90°	Octahedral

Hybrid Orbitals	Arrangement of Hybrid Orbitals	Geometry	Example
Two electron pairs <i>sp</i>			
Three electron pairs <i>sp<sup>2</sup></i>			
Four electron pairs <i>sp<sup>3</sup></i>			
Five electron pairs <i>sp<sup>3</sup>d</i>			
Six electron pairs <i>sp<sup>3</sup>d<sup>2</sup></i>			

## VB Theory for Methane, CH<sub>4</sub>

Methane has 4 orbitals (forms 4 bonds); the Carbon is hybridized from  $s^2p^2$  to  $s^1p^3$  ( $sp^3$ ) and is tetrahedral with **bond angles of 109.5°**. It is a very symmetric molecule.

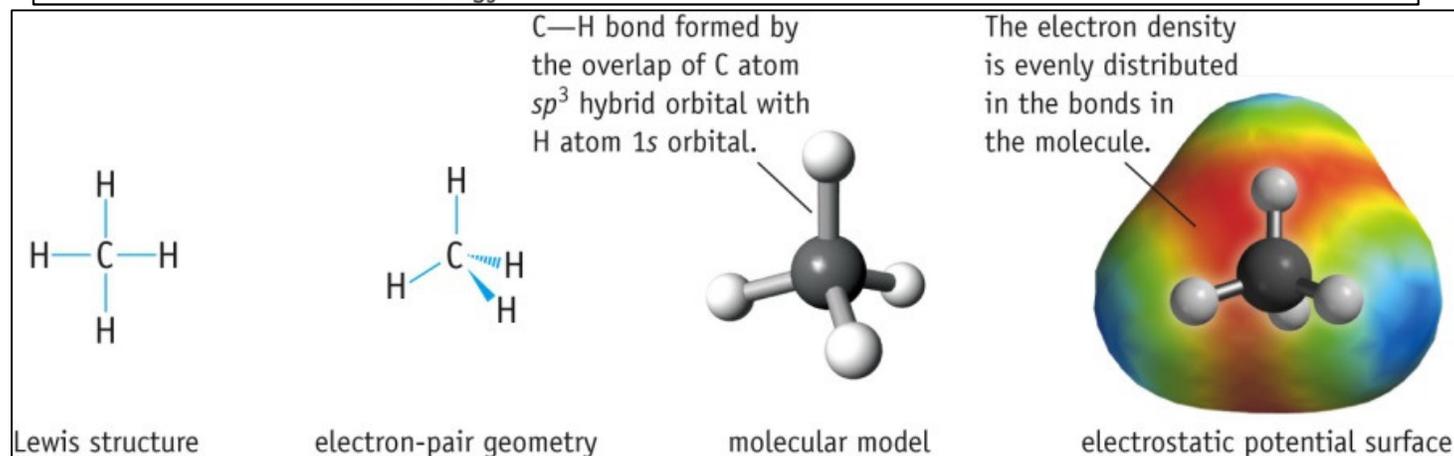
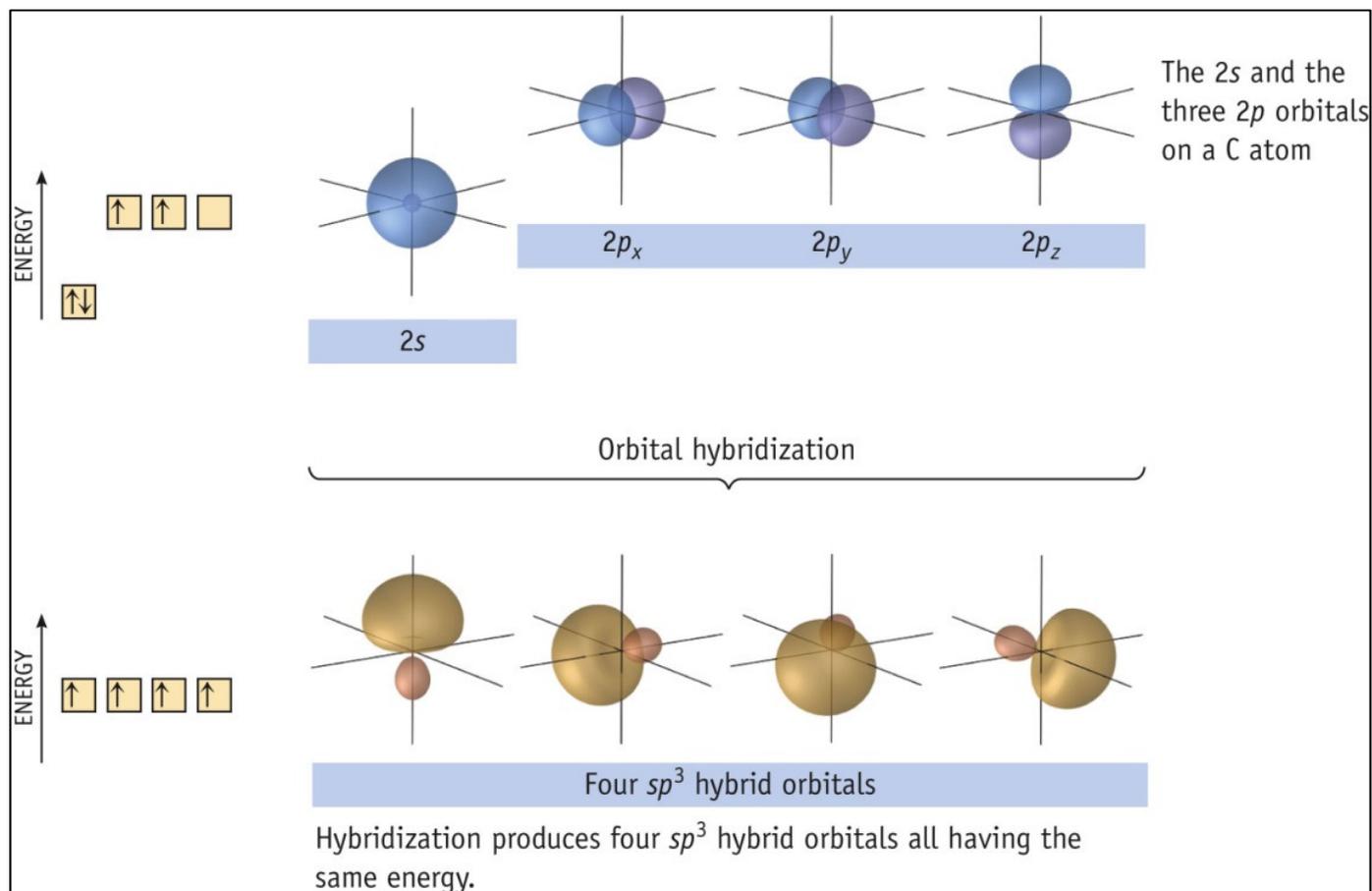
**From:**



**To:**



Carbon  $sp^3$  hybrid model



## VB Theory for Ammonia, NH<sub>3</sub>

Ammonia also has 4 bonds, but one holds a lone pair of electrons. It also hybridizes or changes shape:

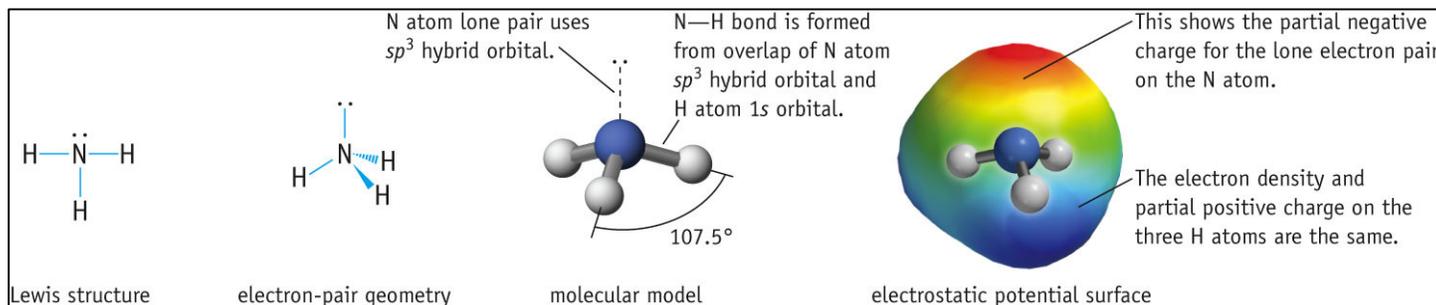
**From:** 2s<sup>2</sup> is a sphere (see carbon above) and 2p<sup>3</sup> which are 3 dumbbell lobes in the p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub>

**To:** sp<sup>3</sup> hybrid where all bonds are equivalent (see Carbon sp<sup>3</sup> hybrid model above)

**From N** 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>3</sup>  $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow$   $\uparrow$   $\uparrow$  [He] 2s<sup>2</sup> 2p<sup>3</sup>

**To:** N 1s<sup>2</sup> sp<sup>3</sup>  $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow$   $\uparrow$   $\uparrow$  sp<sup>3</sup> 3D Hybrid

The 3D structure is almost tetrahedral as is Methane, but the lone pair of electrons pushes the Hydrogen's away, making the **H-N-H bond angle 107.5°**. Ammonia also is hybridized to sp<sup>3</sup>.

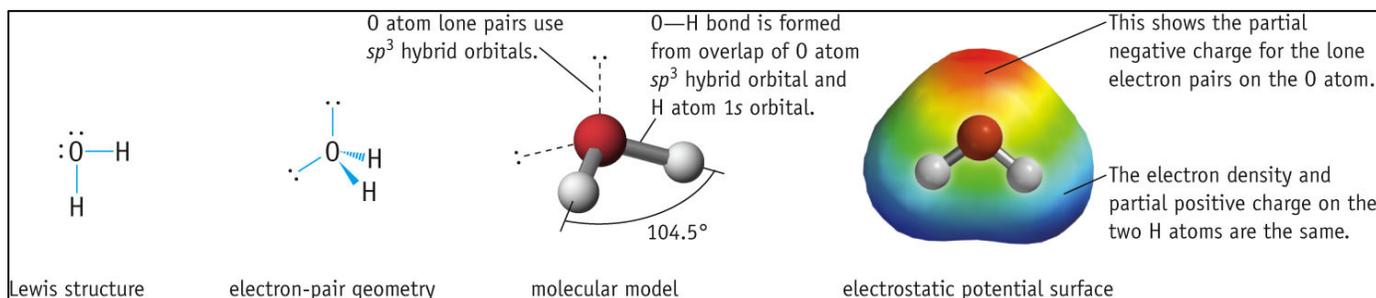


## VB Theory for Water, Hydrogen Hydroxide H-OH, DiHydrogen Oxide H<sub>2</sub>O

Water Oxygen has 2 bonding pair and 2 electron lone pair. Nitrogen above has 2 bonding pair and 1 electron lone pair. Water also assumes a sp<sup>3</sup> hybrid 3D structure with the lone electron pairs pushing the hydrogen's away forming an **H-O-H angle of 104.5°**.

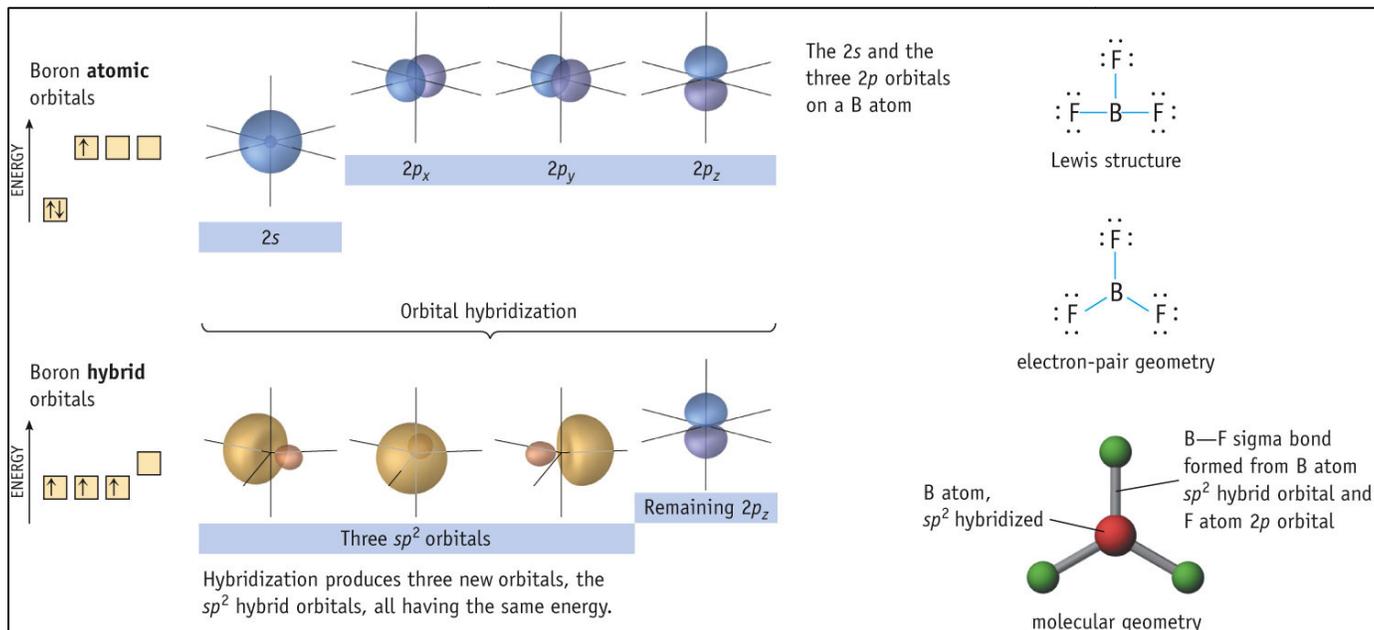
**From:** O 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>3</sup>  $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow$   $\uparrow$  2s<sup>2</sup> 2p<sup>4</sup>

**To:** O 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>  $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow\downarrow$   $\uparrow$   $\uparrow$  sp<sup>3</sup> 3D Hybrid

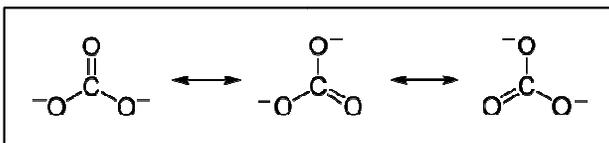
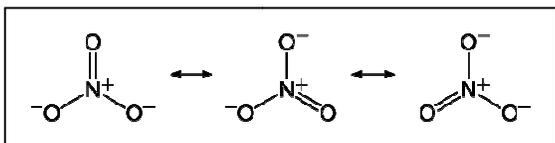
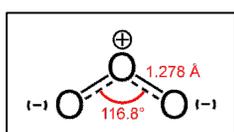


**Trigonal-Planar or  $sp^2$  hybrid = 3 electron pair = flat with 3 bonds**

Trigonal-Planer geometry is a central atom with 3 hybrid orbitals  $120^\circ$  apart.

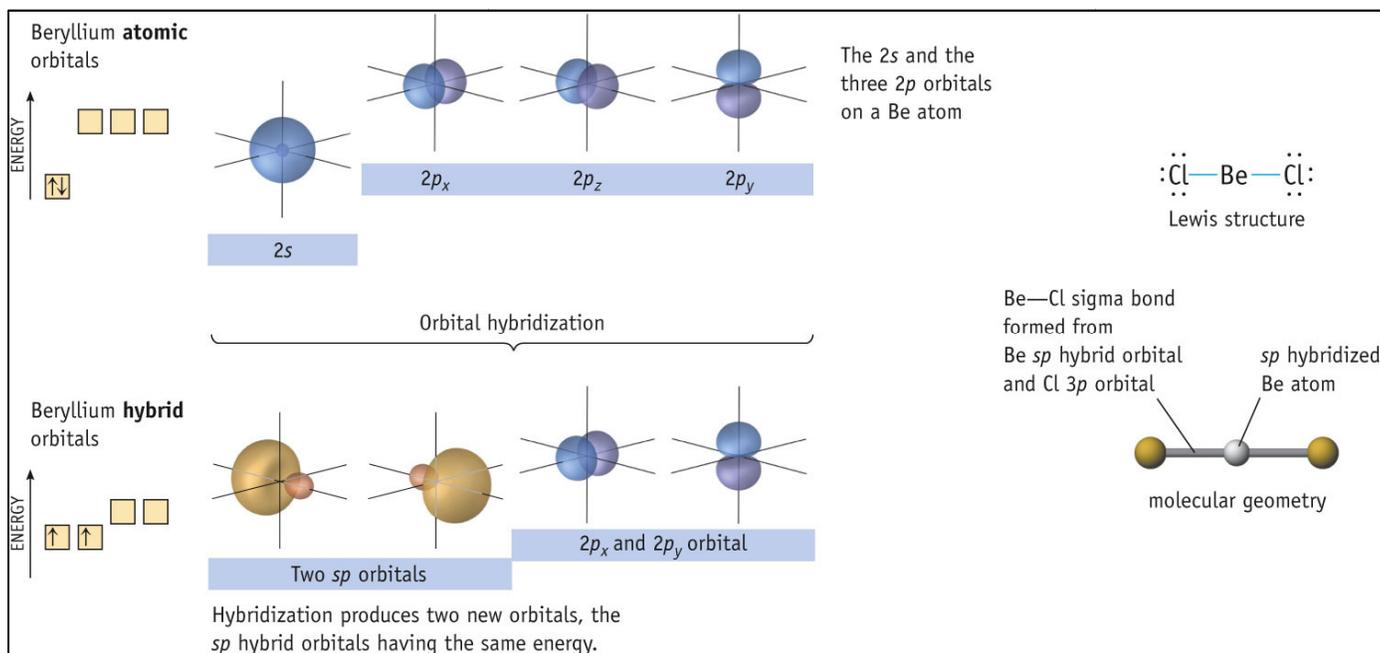


$BF_3$ ,  $O_3$ ,  $NO_3^-$  and  $CO_3^{2-}$  are Trigonal planar. There is an unfilled  $2p_z$  orbital – see picture above.



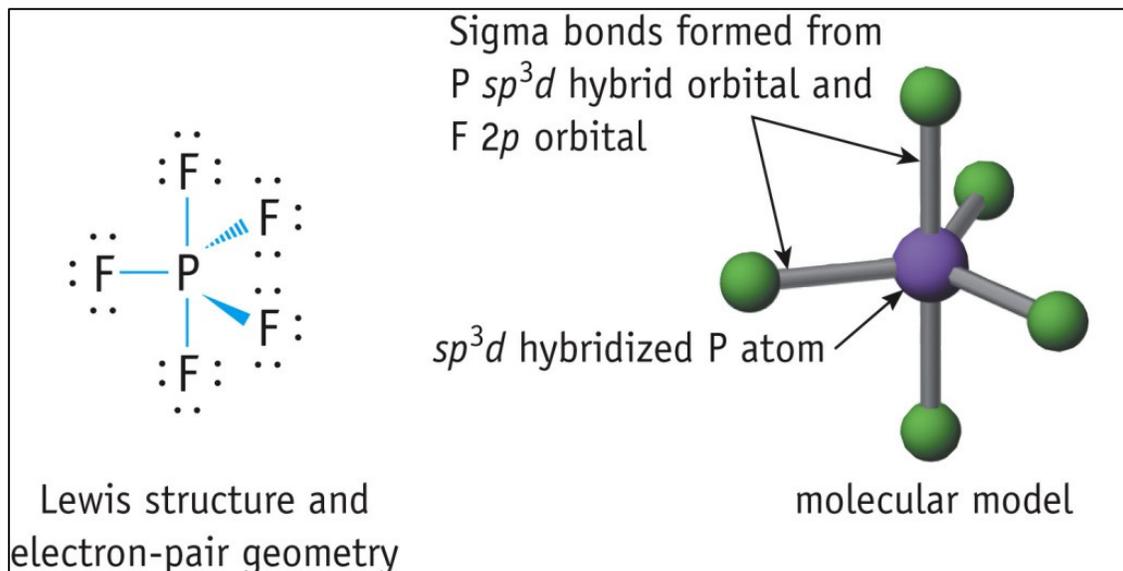
**Linear or  $sp$  hybrid = 2 electron pair = flat with 2 bonds**

$sp$  hybrid molecules have two bonds that are  $180^\circ$  apart.

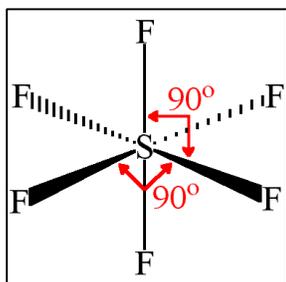


BeCl<sub>2</sub> is an example. Note there are 2 sp bonding orbital's (see brown orbital's above) and 2 unfilled p orbital's (see blue 2px and 2py orbital's in picture above). Note in the picture above that Be has 2 2s electrons. As such it cannot form a bond. The fact that Be forms BeCl<sub>2</sub>, shows that one of the 2s electrons is promoted to the 2p level.

**Trigonal-Bipyramidal or 5 electron pair or Octahedral electron pair or added d orbital participation.** Molecules with 5 electrons such as PF<sub>5</sub> are Trigonal-Bipyramidal. Five electrons: One s, three p and one d orbital combine to form the **sp<sup>3</sup>d hybrid** as shown below.



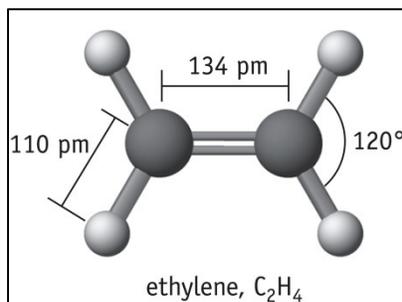
Six electrons: One s, three p and two d orbital combine to form the Octahedral **sp<sup>3</sup>d<sup>2</sup> hybrid** as shown below.



SF<sub>6</sub> is Octahedral

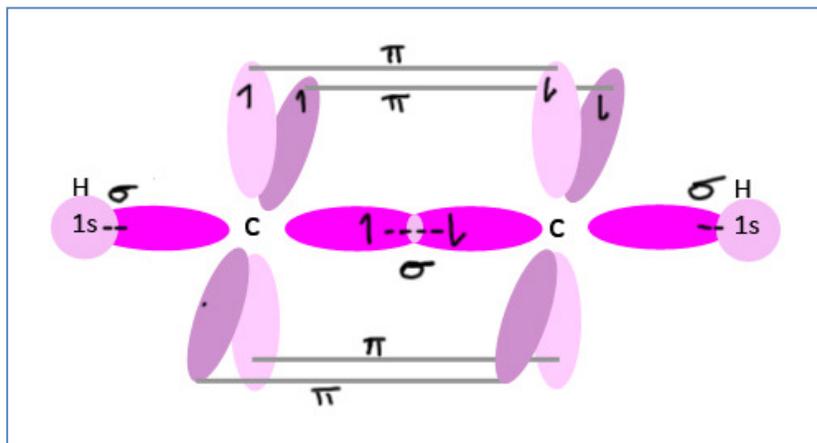
**Multiple Bonds:** Double Bonds

Two orbital's on adjacent atoms overlap. Ethylene is H<sub>2</sub>C=CH<sub>2</sub> and has bond angles of 120°.



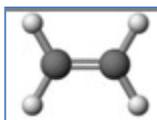


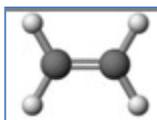
Again, we have a good picture of Acetylene below. The dark pink are the sp hybridized bonds that join the H-C, the center bond in the C≡C, and the C-H. The two lighter orbits are the normal 2py and 2pz unhybridized orbits. As expected, they are 90° to each other. These two unhybridized orbits form two π (Pi) bonds. The py and pz bonds on each of the two Carbons will bond to form these Pi bonds.

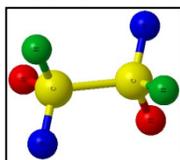


A Double bond will always consist of a sigma,  $\sigma$ , or normal bond; and a Pi  $\pi$  bond. A triple bond will always consist of a sigma,  $\sigma$ , or normal bond; and two Pi  $\pi$  bonds.

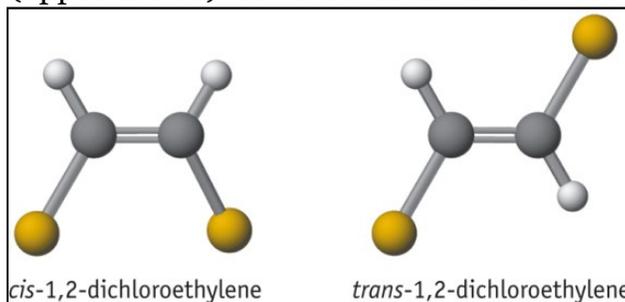
### Cis-Trans Isomers



Ethylene,  $\text{H}_2\text{C}=\text{CH}_2$  or  with the Pi bond has restricted rotation about the Carbon-Carbon bond. Ethane,  $\text{H}_3\text{C}-\text{CH}_3$  on the other hand with just a sigma bond holding the C-C together has free

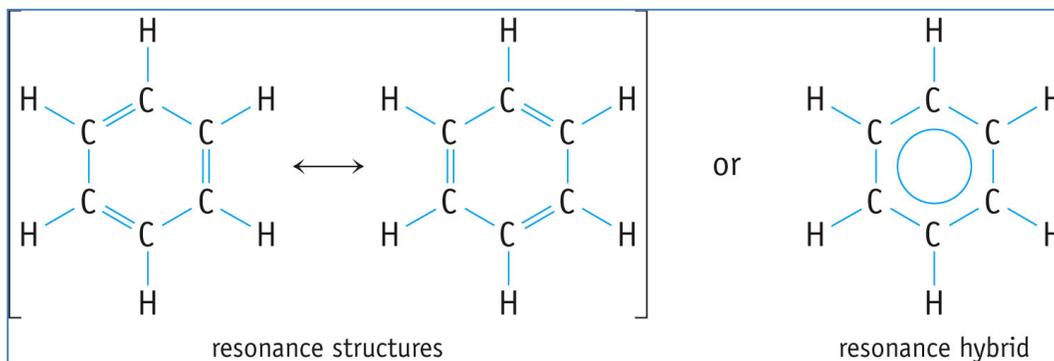


rotation about this C-C bond. With no rotation about the C=C bond in ethylene, there are cis (same side) and trans (opposite side) isomers that can be formed:

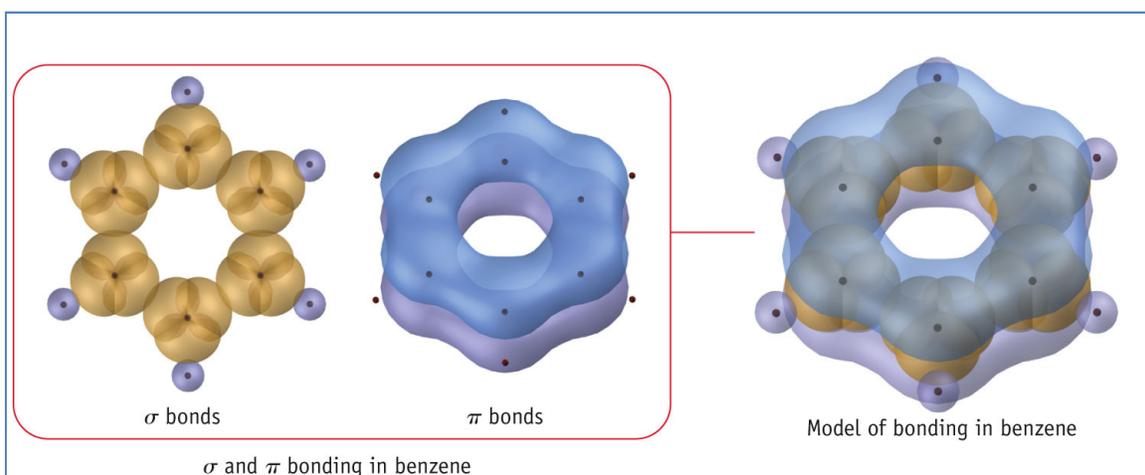


## Benzene: pi bonding

Benzene is C<sub>6</sub>H<sub>6</sub> and is a 6 membered cyclic ring with alternating single and double bonds.



Studies show all of the C-C bond lengths are the same, there is no C-C and C=C. Therefore the resonance hybrid structure is assumed. The bond lengths are 139 pm which is between the 154 pm single bond length and the 134 pm double bond length. The sigma bonds join all of the carbons together and the pi bonds form a donut cloud above and below the ring:



**Molecular Orbital Theory** or MO theory is the alternative way to show electron orbits. The Valence Bond Theory assumes electrons around the central atoms for bonding. The MO Theory says the atomic orbitals in the molecule combine and spread out over the entire molecule to form Molecular Orbitals.

**1<sup>st</sup> Principal** of MO Theory: the total number of molecular orbitals is always equal to the number of atomic orbitals contributed by the atoms that have combined.

This leads to bonding and antibonding molecular orbitals.

**2<sup>nd</sup> Principal** states that the bonding molecular orbital is lower in energy than the parent orbitals, and the antibonding orbital is higher in energy.

**3<sup>rd</sup> Principal** is the electrons of the molecule are assigned to orbitals of successively higher energy according to the Pauli Exclusion Principal and Hund's Rule.

## Bond Order

Bond Order =  $\frac{1}{2}$  (Number of electrons in bonding MO's) – number of electrons in antibonding MO's)