

These Notes are to SUPPLEMENT the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test! The author is not responsible for typos in these notes.

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.

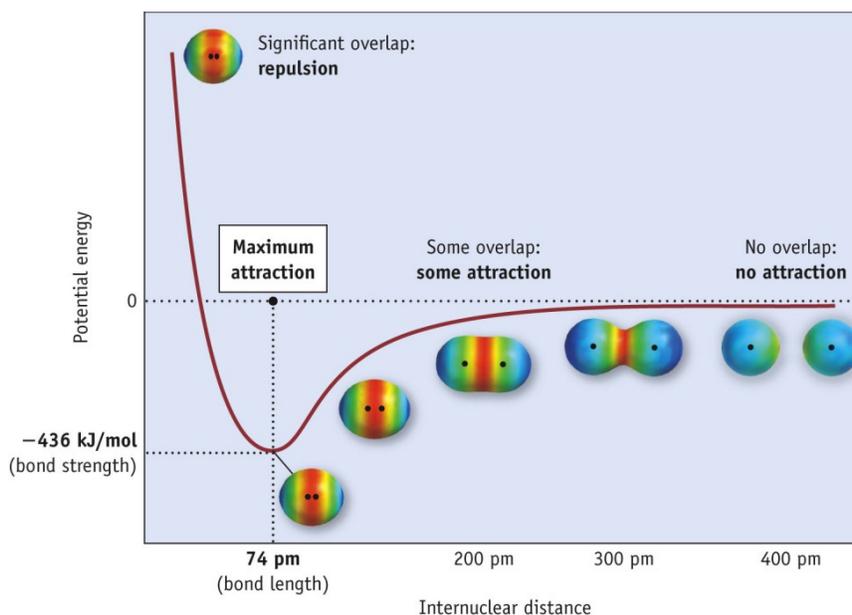
VB approach provides:

- 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 O₂.

VB approach bringing together two Hydrogen to form H₂.



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 H₂.

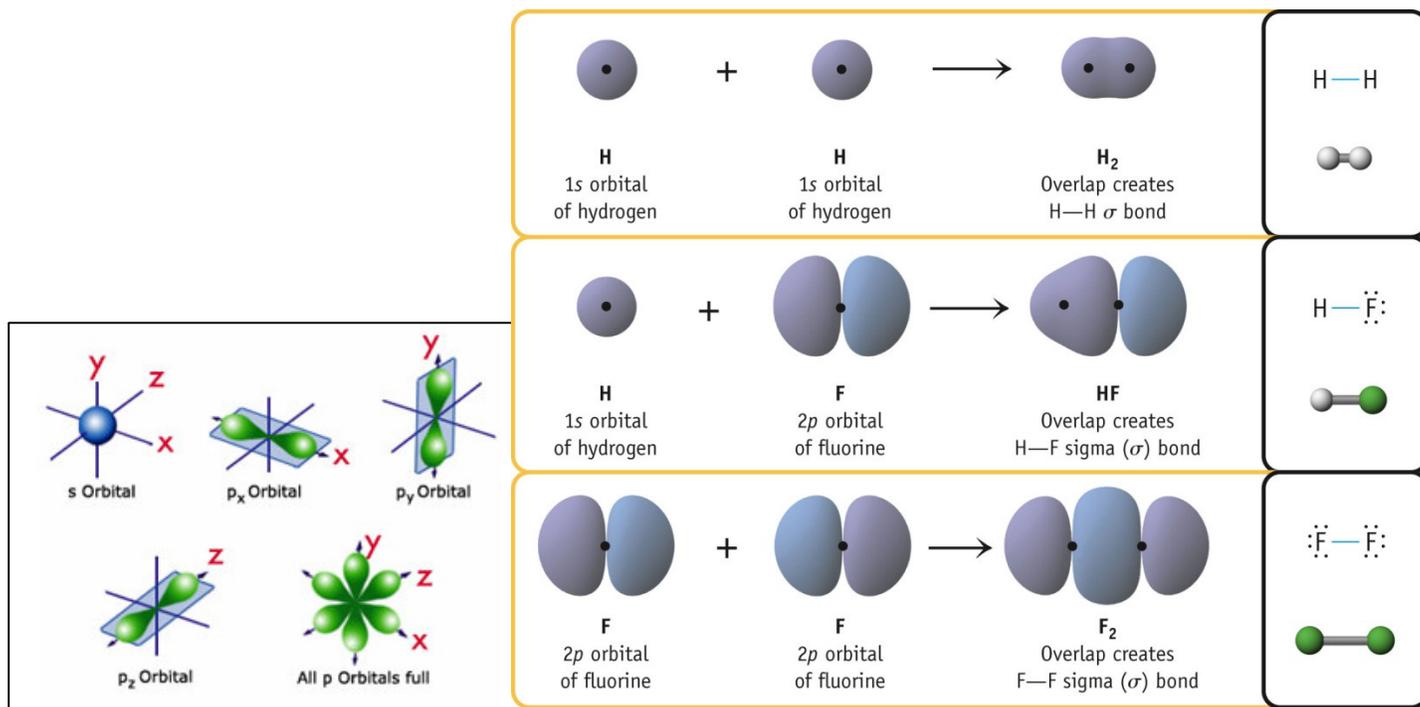
Per the graph below, the bonding electrons spend most of their time between the two hydrogen nuclei in a bonding function. This **Orbital Overlap** comes from the bonds formed by overlap of the atomic orbitals based on the VB theory. The bond is called a sigma (σ) bond. A σ bond has the electron density 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 σ 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° 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 ⁻	180°	Linear
sp ²	s^1 and p^2	3 e ⁻	120°	Trigonal Planer
sp³	s¹ and p³	4 e⁻	109.5°	Tetrahedral (Carbon)
sp ³ d	s^1 and p^3 and d^1	5 e ⁻	120° and 90°	Trigonal Bipyramidal
sp ³ d ²	s^1 and p^3 and d^2	6 e ⁻	90°	Octahedral

Hybrid Orbitals	Arrangement of Hybrid Orbitals	Geometry	Example
Two electron pairs <i>sp</i>			Linear BeCl ₂
Three electron pairs <i>sp²</i>			Trigonal-planar BF ₃
Four electron pairs <i>sp³</i>			Tetrahedral CH ₄
Five electron pairs <i>sp³d</i>			Trigonal-bipyramidal PF ₅
Six electron pairs <i>sp³d²</i>			Octahedral SF ₆

VB Theory for Methane, CH₄

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.

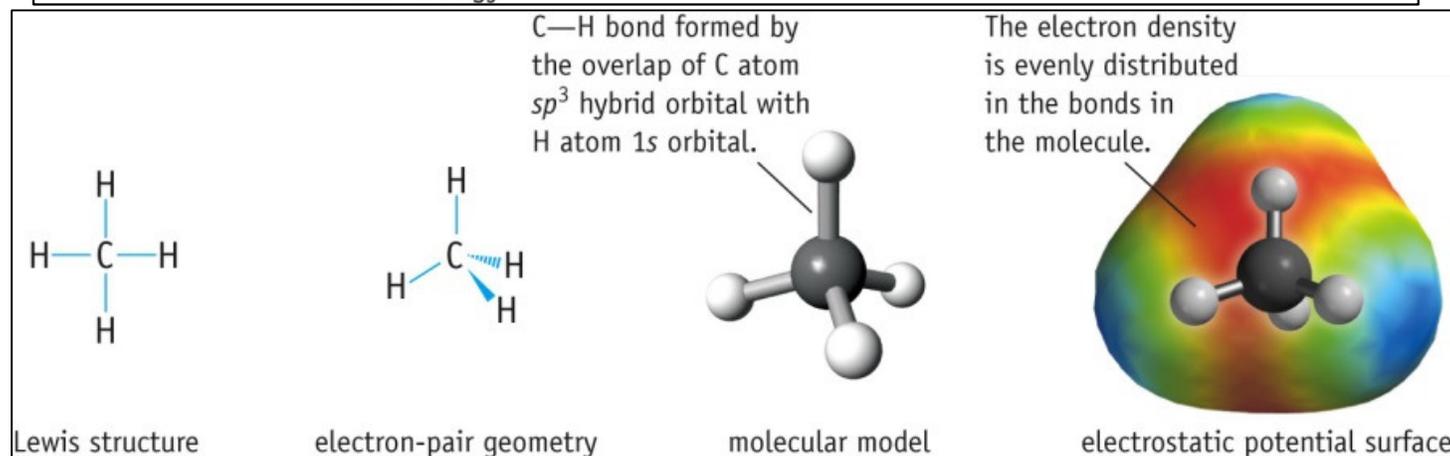
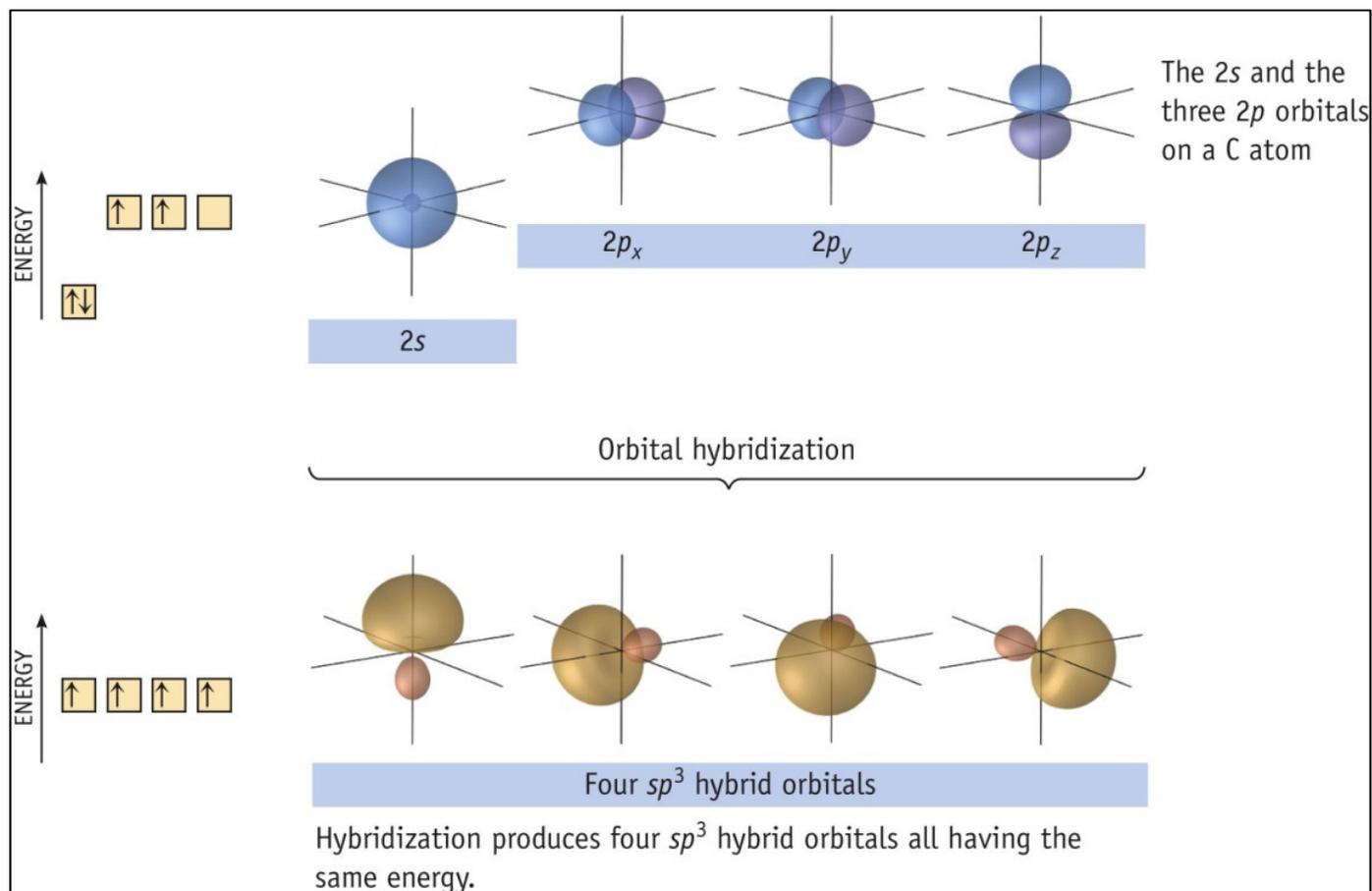
From:



To:



Carbon sp^3 hybrid model



VB Theory for Ammonia, NH₃

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

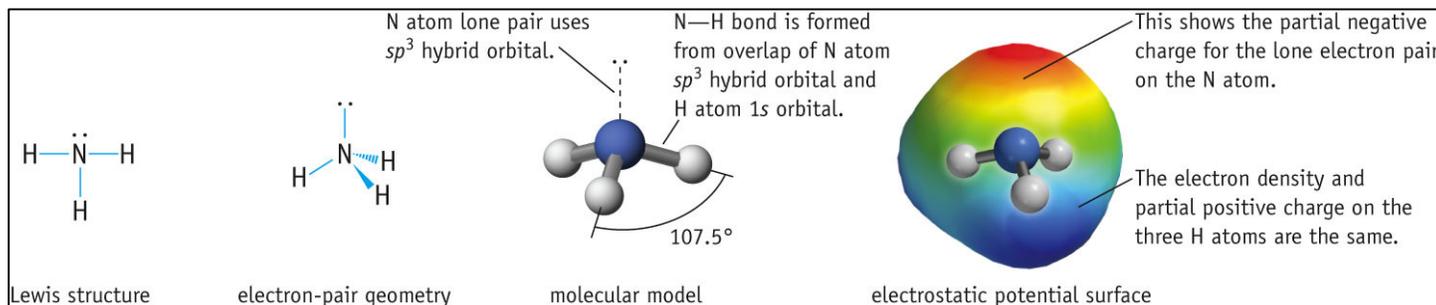
From: 2s² is a sphere (see carbon above) and 2p³ which are 3 dumbbell lobes in the p_x, p_y, p_z

To: sp³ hybrid where all bonds are equivalent (see Carbon sp³ hybrid model above)

From N 1s² 2s² 2p³ $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow \uparrow \uparrow [He] 2s² 2p³

To: N 1s² sp³ $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow \uparrow \uparrow sp³ 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 sp³.

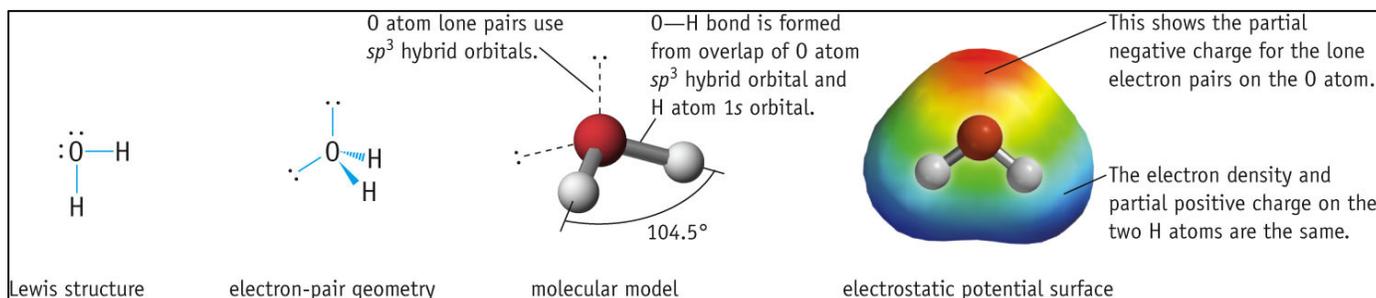


VB Theory for Water, Hydrogen Hydroxide H-OH, DiHydrogen Oxide H₂O

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 sp³ hybrid 3D structure with the lone electron pairs pushing the hydrogen's away forming an **H-O-H angle of 104.5°**.

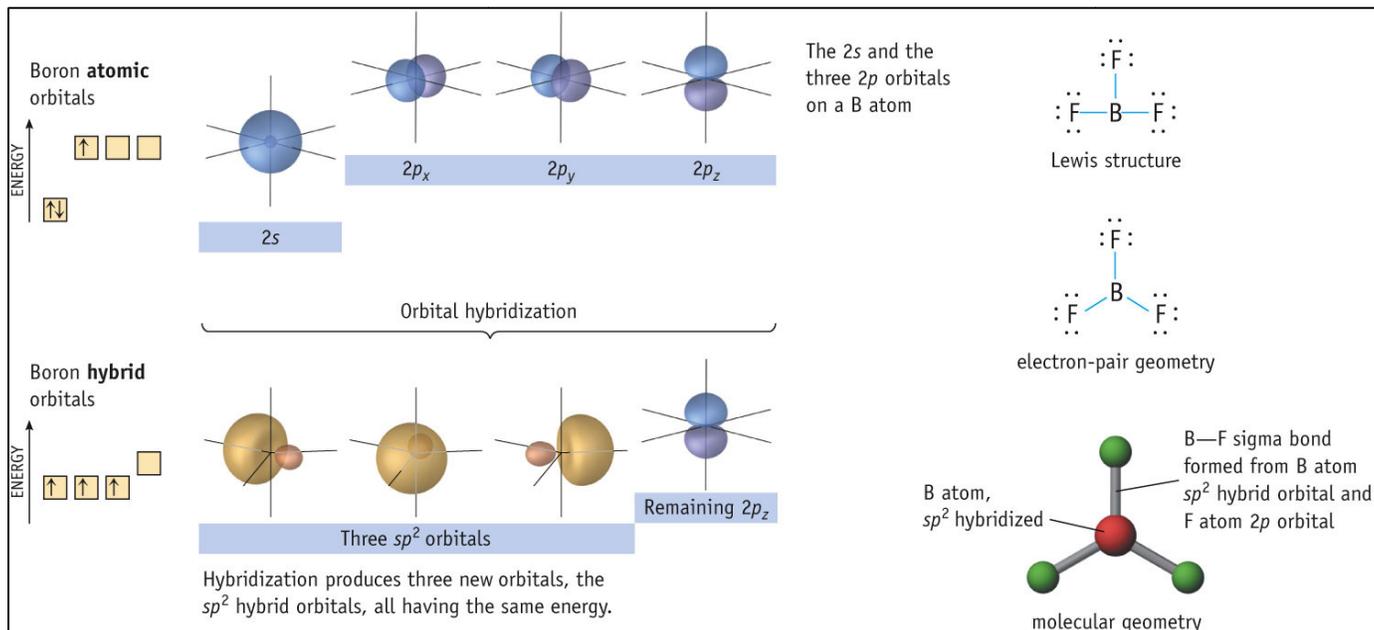
From: O 1s² 2s² 2p³ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow \uparrow 2s² 2p⁴

To: O 1s² 2s² 2p⁴ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow \uparrow sp³ 3D Hybrid

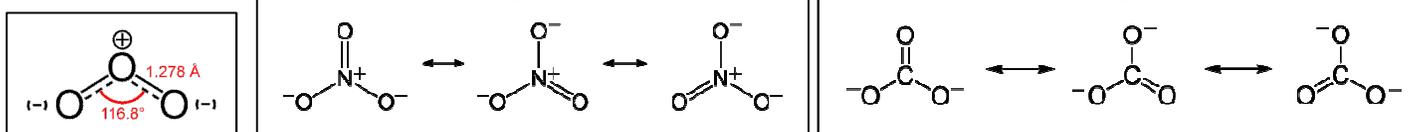


Trigonal-Planar or sp^2 hybrid = 3 electron pair = flat with 3 bonds

Trigonal-Planer geometry is a central atom with 3 hybrid orbitals 120° apart.

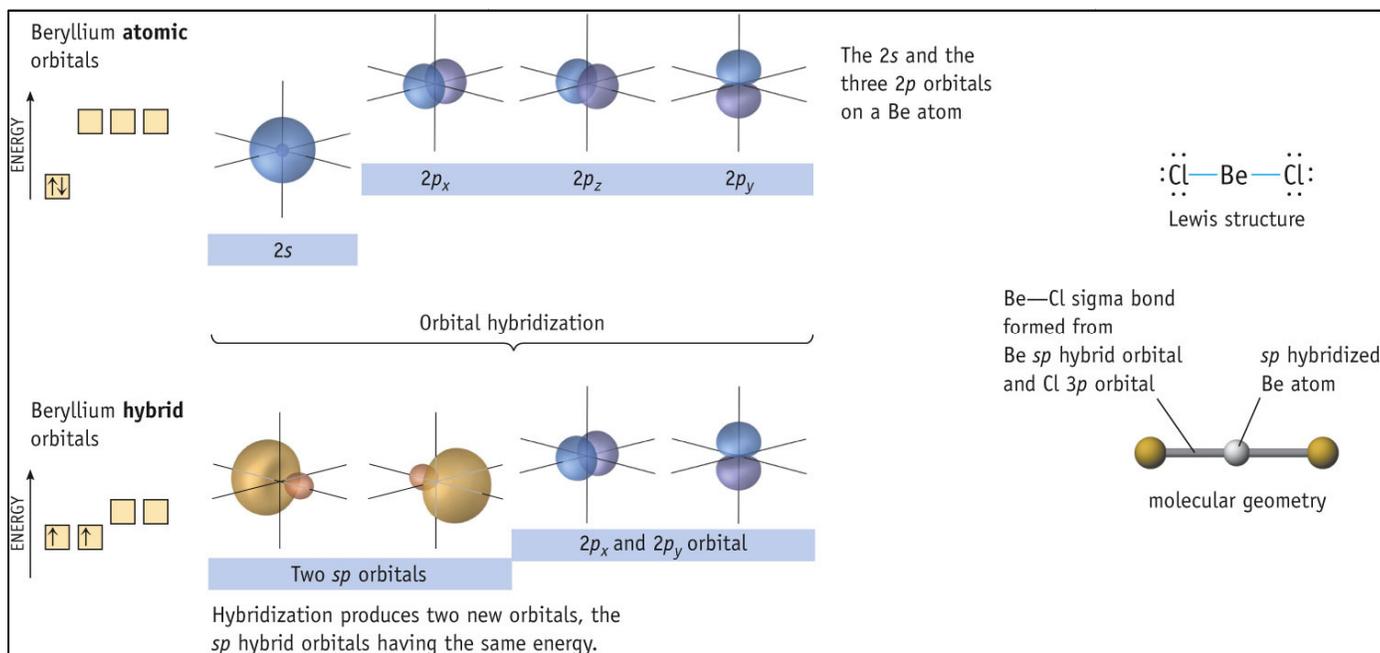


BF_3 , O_3 , NO_3^- and CO_3^{2-} are Trigonal planar. There is an unfilled $2p_z$ orbital – see picture above.



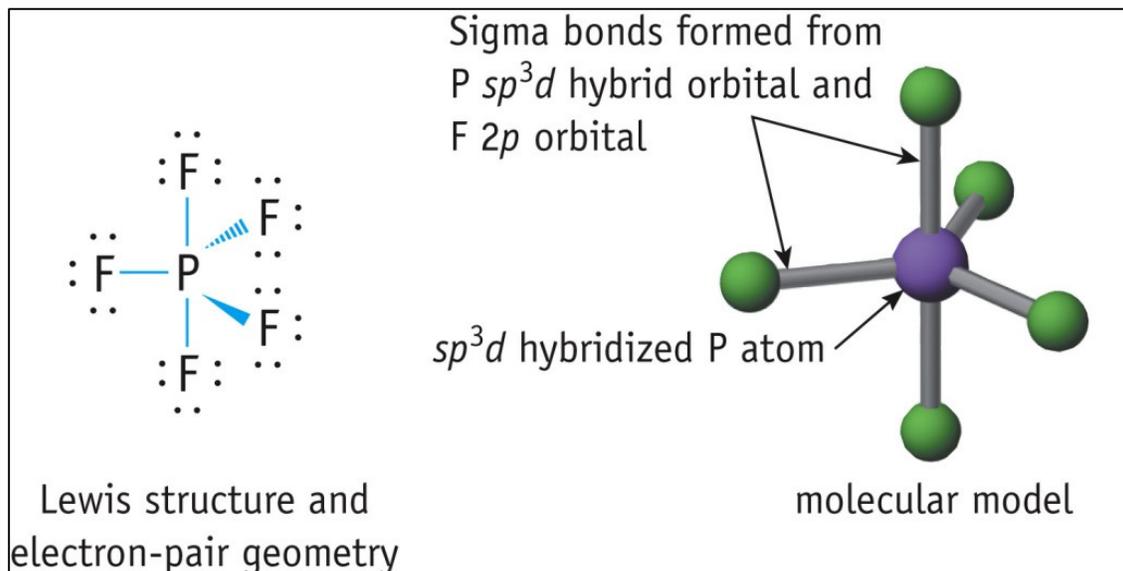
Linear or sp hybrid = 2 electron pair = flat with 2 bonds

sp hybrid molecules have two bonds that are 180° apart.

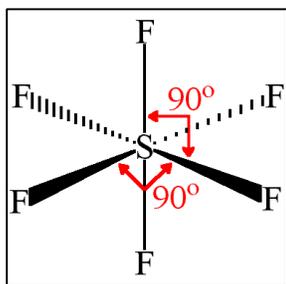


BeCl₂ is an example. Note there are 2 sp bonding orbital's (see brown orbital's above) and 2 unfilled p orbital's (see blue 2px and 2py orbital's in picture above). Note in the picture above that Be has 2 2s electrons. As such it cannot form a bond. The fact that Be forms BeCl₂, shows that one of the 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 electron pairs such as PF₅ are Trigonal-Bipyramidal. Five electron pairs: One s, three p and one d orbital combine to form the **sp³d hybrid** as shown below.



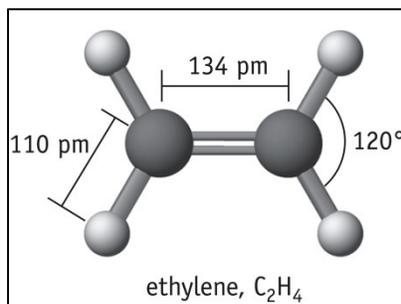
Six electron pairs: One s, three p and two d orbitals combine to form the Octahedral **sp³d² hybrid** as shown below.



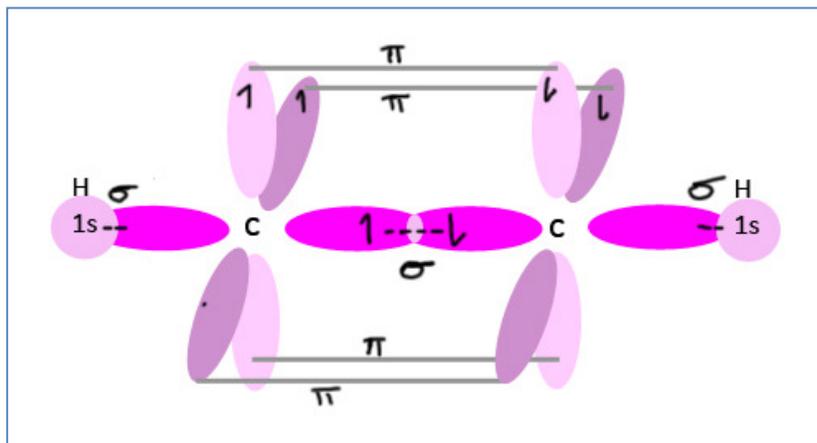
SF₆ is Octahedral

Multiple Bonds: Double Bonds

Two orbitals on adjacent atoms overlap. Ethylene is H₂C=CH₂ and has bond angles of 120°.

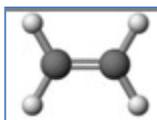


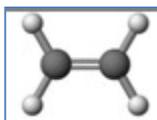
Again, we have a good picture of Acetylene below. The dark pink are the sp hybridized bonds that join the H-C, the center bond in the C \equiv C, and the C-H. The two lighter orbits are the normal 2p_y and 2p_z unhybridized orbits. As expected, they are 90° to each other. These two unhybridized orbits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

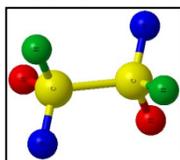


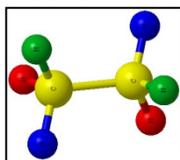
A Double bond will always consist of a sigma, σ , or normal bond; and a Pi Π bond. A triple bond will always consist of a sigma, σ , or normal bond; and two Pi Π bonds.

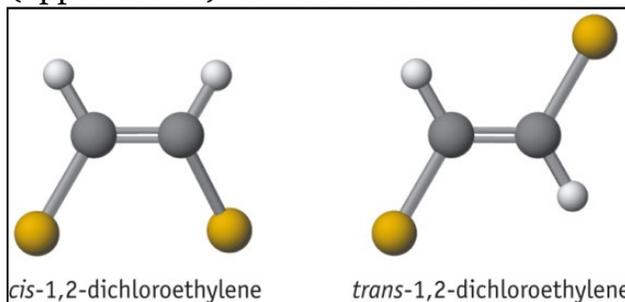
Cis-Trans Isomers



Ethylene, H₂C=CH₂ or  with the Pi bond has restricted rotation about the Carbon-Carbon bond. Ethane, H₃C-CH₃ on the other hand with just a sigma bond holding the C-C together has free

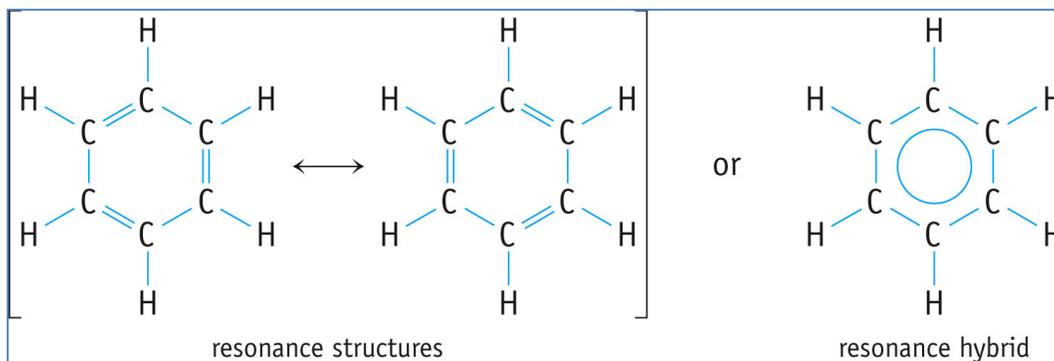


rotation about this C-C bond. . With no rotation about the C=C bond in ethylene, there are cis (same side) and trans (opposite side) isomers that can be formed:

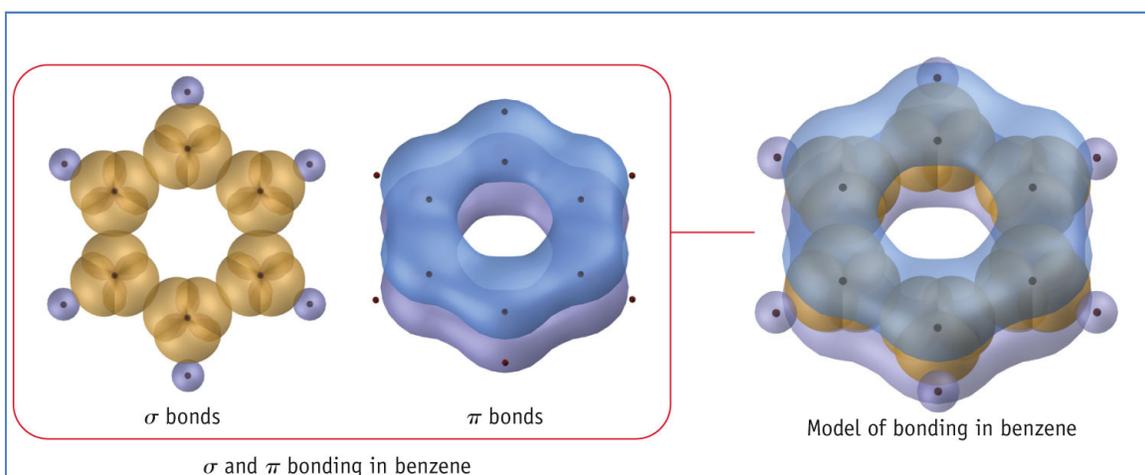


Benzene: pi bonding

Benzene is C₆H₆ 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.

1st 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.

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

3rd 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)