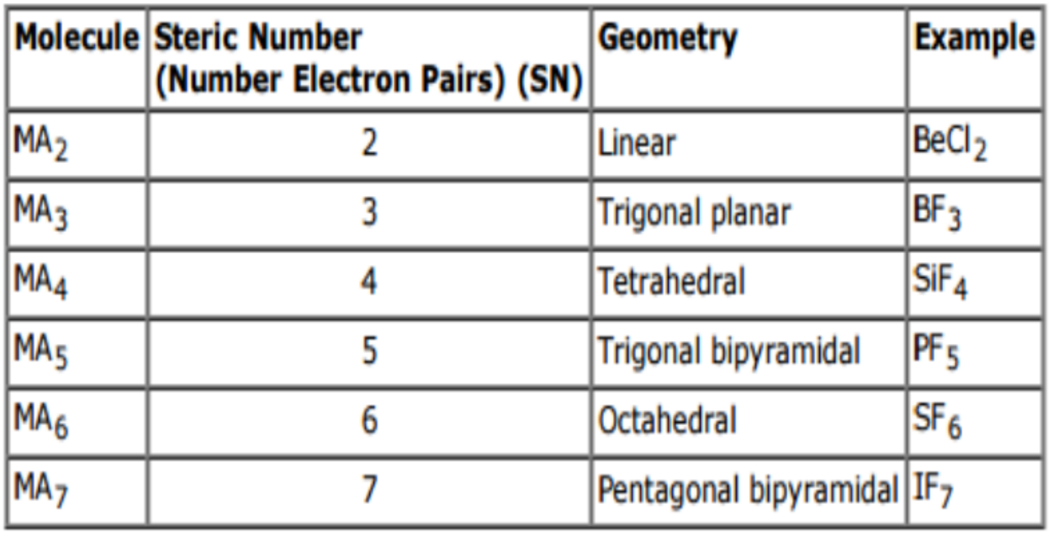
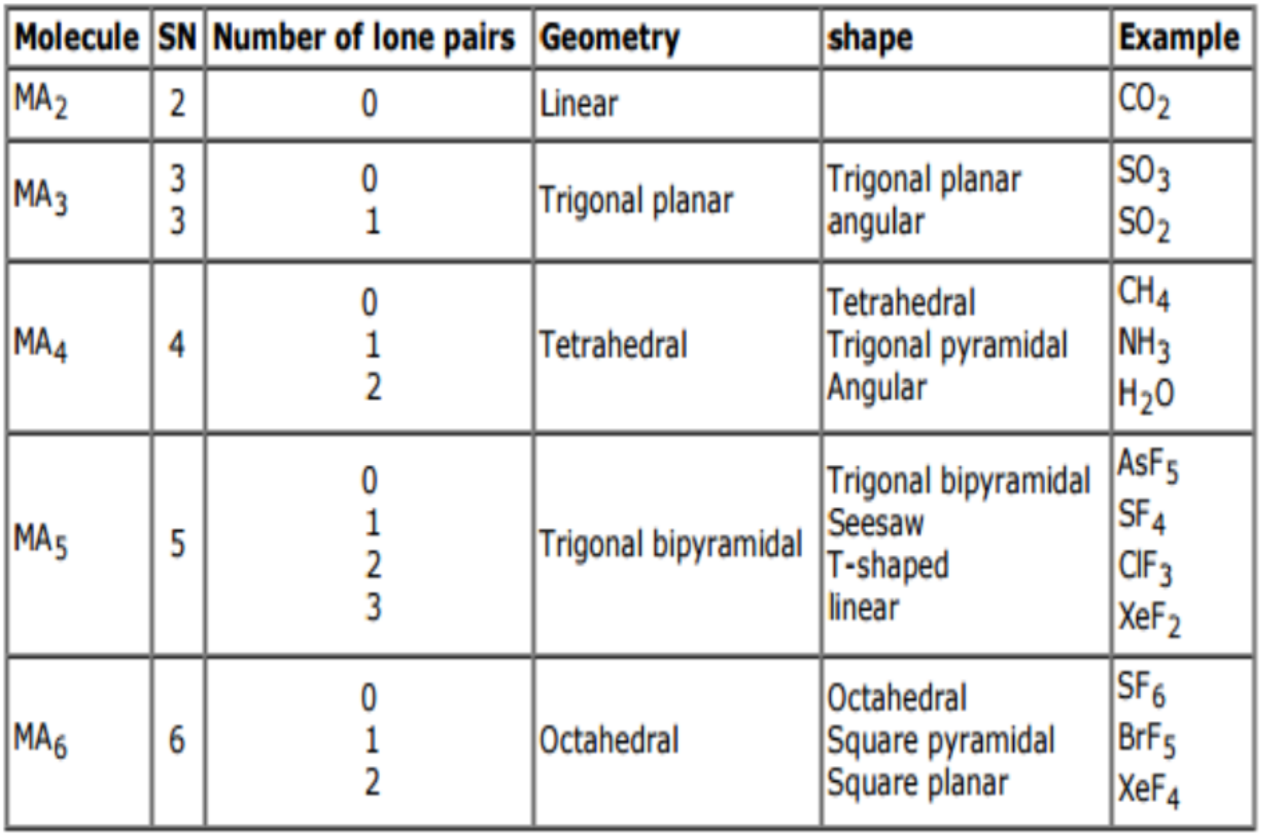
Molecular shapes determined by VSEPR theory



Molecule	Steric Number (Number Electron Pairs) (SN)	Geometry	Example
MA_2	2	Linear	$BeCl_2$
MA_3	3	Trigonal planar	BF_3
MA_4	4	Tetrahedral	SiF_4
MA_5	5	Trigonal bipyramidal	PF_5
MA_6	6	Octahedral	SF_6
MA_7	7	Pentagonal bipyramidal	IF_7

Molecular shapes determined by VSEPR theory (contd..)

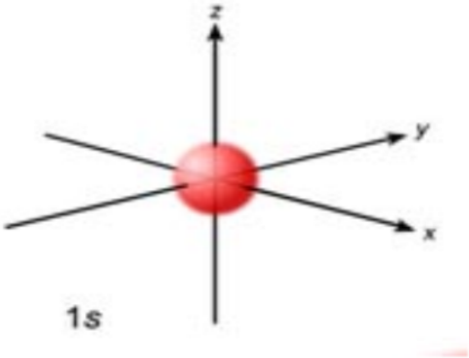


Molecule	SN	Number of lone pairs	Geometry	shape	Example
MA_2	2	0	Linear		CO_2
MA_3	3 3	0 1	Trigonal planar	Trigonal planar angular	SO_3 SO_2
MA_4	4	0 1 2	Tetrahedral	Tetrahedral Trigonal pyramidal Angular	CH_4 NH_3 H_2O
MA_5	5	0 1 2 3	Trigonal bipyramidal	Trigonal bipyramidal Seesaw T-shaped linear	AsF_5 SF_4 ClF_3 XeF_2
MA_6	6	0 1 2	Octahedral	Octahedral Square pyramidal Square planar	SF_6 BrF_5 XeF_4

Valence bond theory describes a chemical bond as the overlap of atomic orbitals. In the case of the hydrogen molecule, the 1s orbital of one hydrogen atom overlaps with the 1s orbital of the second hydrogen atom to form a molecular orbital called a sigma bond. Attraction increases as the distance between the atoms gets closer but nuclear-nuclear repulsion becomes important if the atoms approach too close.

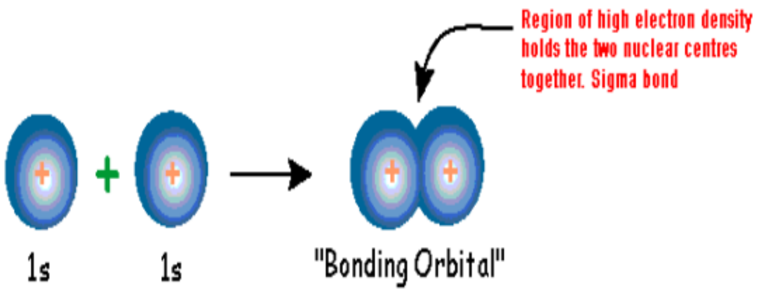
An orbital is a region of space in which there is a 99% probability of finding an electron with a specific quantity of energy. The shape plotted out by this probability is accepted to be the region of space where the electron is, as this makes discussions of electrons and their movements much easier to understand.

For example electrons with the lowest energy are 99% likely to be within a region of spherical shape around the nucleus of an atom. It is convenient for us to describe this region of space as the orbital in which a maximum of two electrons may be housed. We call it an 's' orbital. If it is the lowest energy level, then it is designated 1s.



When two s orbitals overlap, the electrostatic forces of attraction for the nucleus of one atom will attract the electrons of the other atom and vice versa. This produces an overall force that holds the two nuclei together. We call this a chemical bond.

If two s orbitals directly overlap then the bond formed is linear between the two nuclear centres and is called a sigma bond.



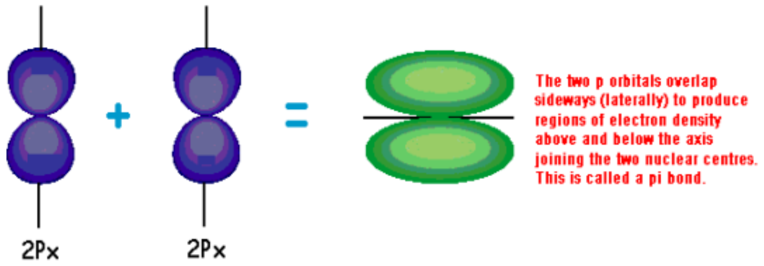
Region of high electron density holds the two nuclear centres together. Sigma bond

Sigma bonds are produced by any direct orbital overlap along the axis joining the two nuclear centres together.

Although it is convenient to show this overlap using two 1s orbitals, in fact this is the exception rather than the rule. Direct orbital overlap usually happens by overlap of a hybridised orbital with a 1s orbital (in hydrogen) or between two hybridised orbitals.

Pi bonds:

When a sigma bond is formed by direct orbital overlap and this brings two parallel 'p' orbitals into close proximity then these can overlap sideways (laterally) to form a region of electron density that is not directly between the two nuclear centres but which nevertheless contributes to bonding. This is called a pi bond.

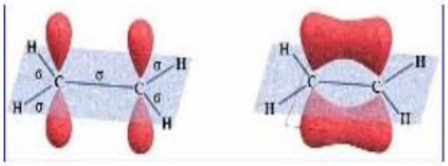


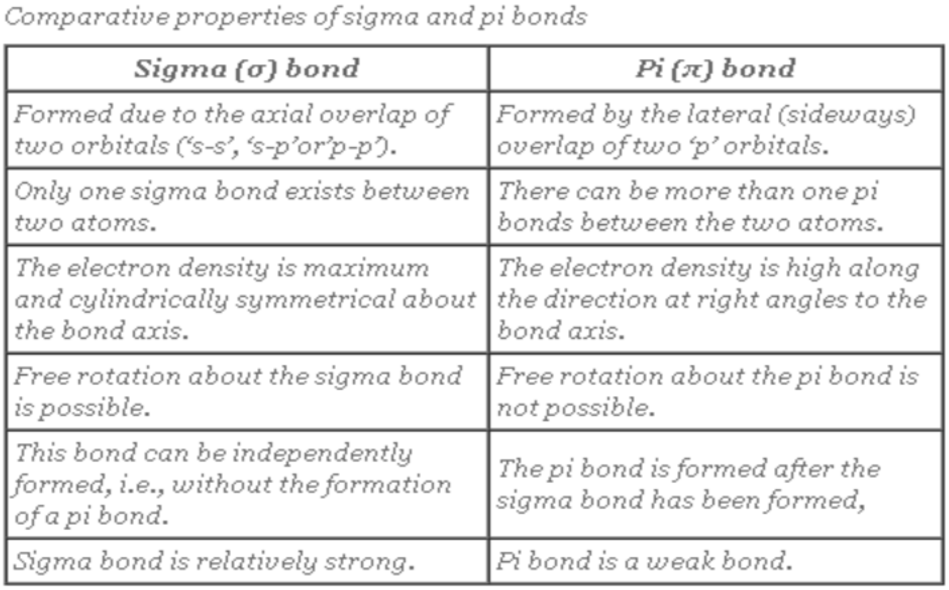
The two p orbitals overlap sideways (laterally) to produce regions of electron density above and below the axis joining the two nuclear centres. This is called a pi bond.

It should be emphasised that a pi bond can only form after a sigma bond has already formed. It is always part of a double or triple bond.

Double and Triple Bonds:

As stated above a pi bond can only form after a sigma bond. Consequently the pi bond must be part of a double (or triple) bond system. Whenever there is a double bond it is made up of one sigma (direct orbital overlap) bond and one pi (lateral orbital overlap) bond.





Comparative properties of sigma and pi bonds

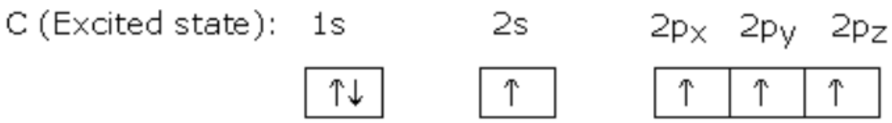
Sigma (σ) bond	***Pi (π) bond***
Formed due to the axial overlap of two orbitals ('s-s', 's-p'or'p-p').	*Formed by the lateral (sideways) overlap of two 'p' orbitals.*
Only one sigma bond exists between two atoms.	*There can be more than one pi bonds between the two atoms.*
The electron density is maximum and cylindrically symmetrical about the bond axis.	*The electron density is high along the direction at right angles to the bond axis.*
Free rotation about the sigma bond is possible.	*Free rotation about the pi bond is not possible.*
This bond can be independently formed, i.e., without the formation of a pi bond.	*The pi bond is formed after the sigma bond has been formed,*
Sigma bond is relatively strong.	*Pi bond is a weak bond.*

Hybridization

The structures of different molecules can be explained on the basis of hybridization. For e.g., in case of carbon, the ground state electronic

configuration is $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$.

To explain the tetravalency of carbon, it was proposed that one of the electrons from 2s filled orbital is promoted to the 2p empty orbital ($2p_z$), which is in a higher energy state. Thus, four half-filled orbitals form in the valence shell this accounts for the bonding capacity of four carbon atoms. This state is known as excited state and the configuration of carbon in the excited state is:



The above configuration reveals that all the four bonds formed by carbon will not be identical. For e.g., in the formation of CH_4 molecule, one C-H bond will be formed by the overlapping of 2s-orbital of C and 1s-orbital of H whereas the other three C-H bonds will be formed by the overlapping of 2p-orbitals of C and 1s-orbital of H. Therefore, all the bonds will not be equivalent.

But actually, in most of the carbon compounds, such as methane (CH_4), carbon tetrachloride (CCl_4) etc., all the four bonds of carbon atom are equivalent. The equivalent character of the bonds can be explained with the help of hybridisation.

Hybridisation may be defined as the phenomenon of intermixing of the orbitals of slightly different energies so as to redistribute their energies and to give new set of orbitals of equivalent energy and shape. The new orbitals formed as a result of hybridization are called hybrid or hybridized orbitals. Thus, to form four equivalent bonds, one 2s and three 2p-orbitals of carbon hybridize and form four new orbitals.such orbitals are called **sp^3 hybrid orbitals**.

The important characteristics of hybridisation are listed below:

(i) The number of hybridized orbitals formed is equal to the number of orbitals that get hybridized.

(ii) The hybridized orbitals are always equivalent in energy and shape.

(iii) The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.

(iv) The hybrid orbitals are directed in space in some preferred directions to have stable arrangements.

Therefore, the type of hybridization gives the geometry of the molecule. Depending upon the different combinations of s- and three p-orbitals, three types of hybridizations are known.

sp hybridization

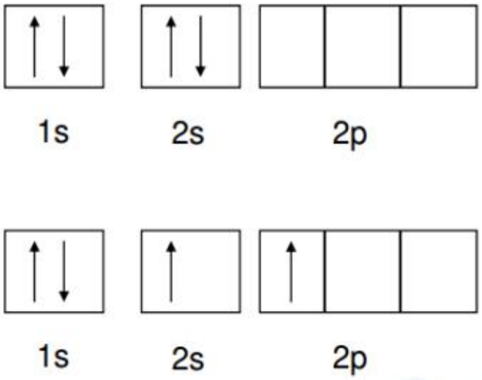
This involves the mixing of one s- and one p-orbital forming two sp-hybrid orbitals. The two sp-hybrid orbitals are oriented in a linear arrangement and bond angle is 180°. For e.g., BeF_2 involves sp-hybridization and is, therefore, linear.2-hybridization">

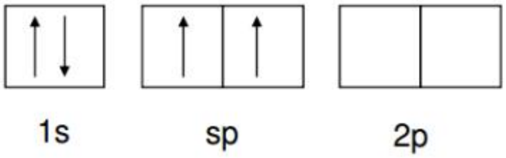
For polyatomic atoms we need to explain bonds *and* geometry

We can assume that atomic orbitals mix to form new orbitals called HYBRID orbitals. The total number of atomic orbitals always equals the total number of hybrid orbitals

BeF_2: F has one unpaired electron, Be doesn't

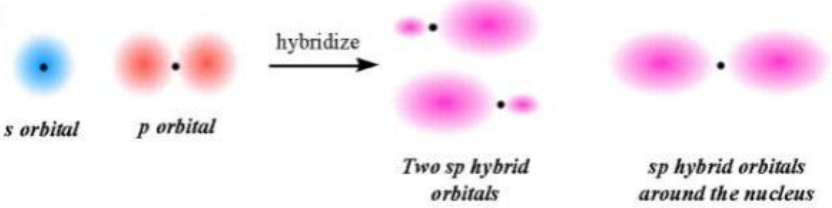
Ground state Be

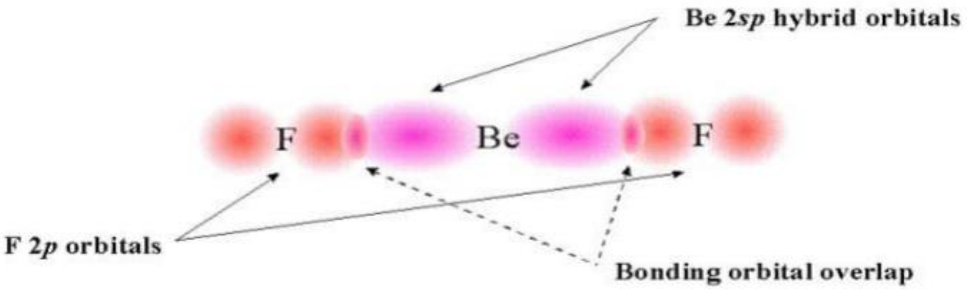




sp hybridisation

Promote one 2s electron



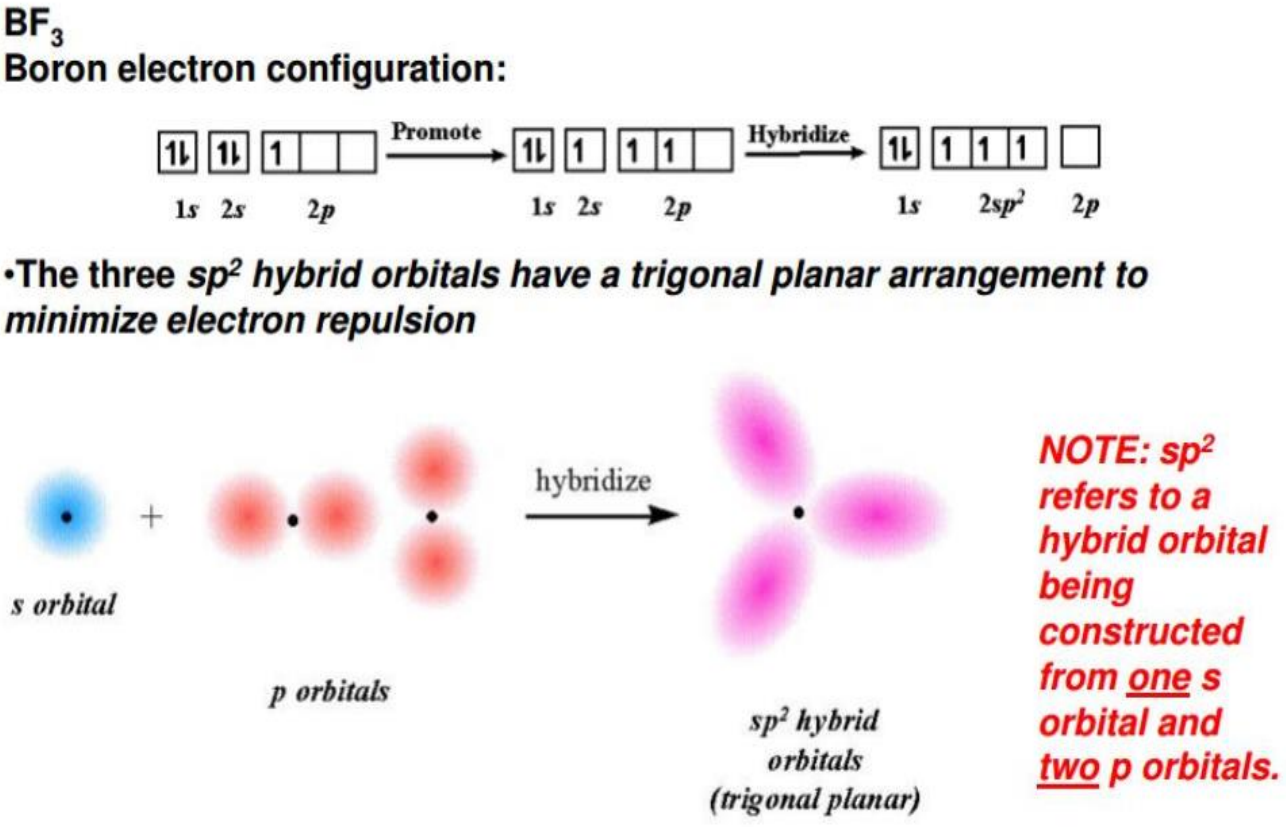


By combining an s and a p orbital the hybrid must be linear therefore the molecular geometry in BeF_2 must linear

the two steps often observed when constructing hybrid orbitals is to 1) promote a valence electron from the ground state configuration to a higher energy orbital, and then 2) hybridize the appropriate valence electron orbitals to achieve the desired valence electron geometry (i.e. the correct number of hybrid orbitals for the appropriate valence electron geometry)

sp^2 hybridization

In this case, one s- and two p-orbitals hybridize to form three sp^2 hybrid orbitals. These three sp^2 hybrid orbitals are oriented in a trigonal planar arrangement. For e.g., in BF_3 boron atom undergoes sp^2hybridization and therefore, BF_3 has trigonal planar geometry and HBH bond angle is 120°.3-hybridization">



BF_3
Boron electron configuration:

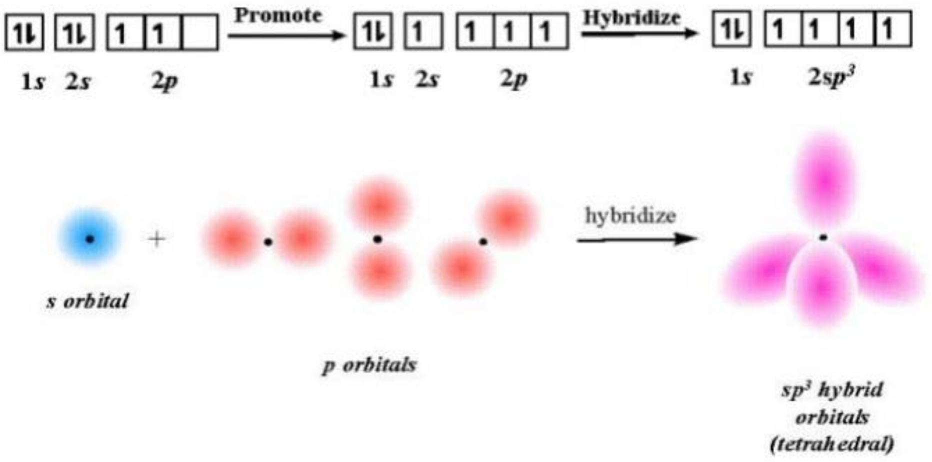
•The three *sp^2 hybrid orbitals have a trigonal planar arrangement to minimize electron repulsion*

NOTE: sp^2 refers to a hybrid orbital being constructed from one s orbital and two p orbitals.

sp^3 hybridization

In this case, one s- and three p-orbitals hybridize to form four sp^3 hybrid orbitals. These four sp^3-hybrid orbitals are oriented in a tetrahedral arrangement. The common example of molecule involving sp^3-hybridisation is methane (CH_4). Therefore, CH_4 has tetrahedral geometry and HCH bond angle is 109.5°.

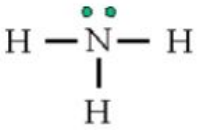
CH$_4$



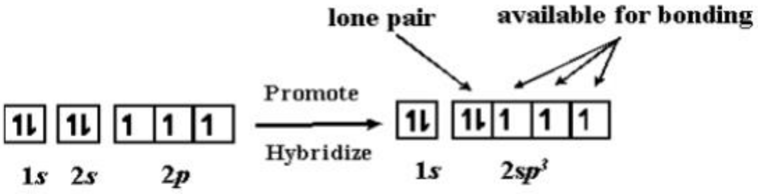
- Using **valence bond theory**, we would describe the bonds in methane as follows: each of the carbon *sp*^{3} hybrid orbitals can overlap with the 1s orbitals of a hydrogen atom to form a bonding pair of electrons

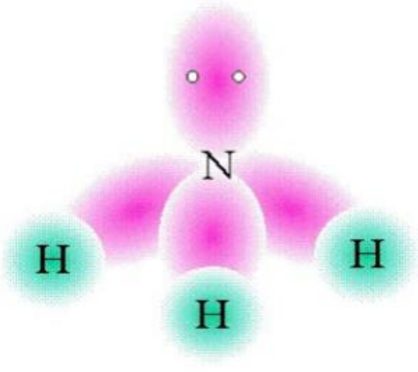
Hybrid Orbitals – sp^3

Ammonia?



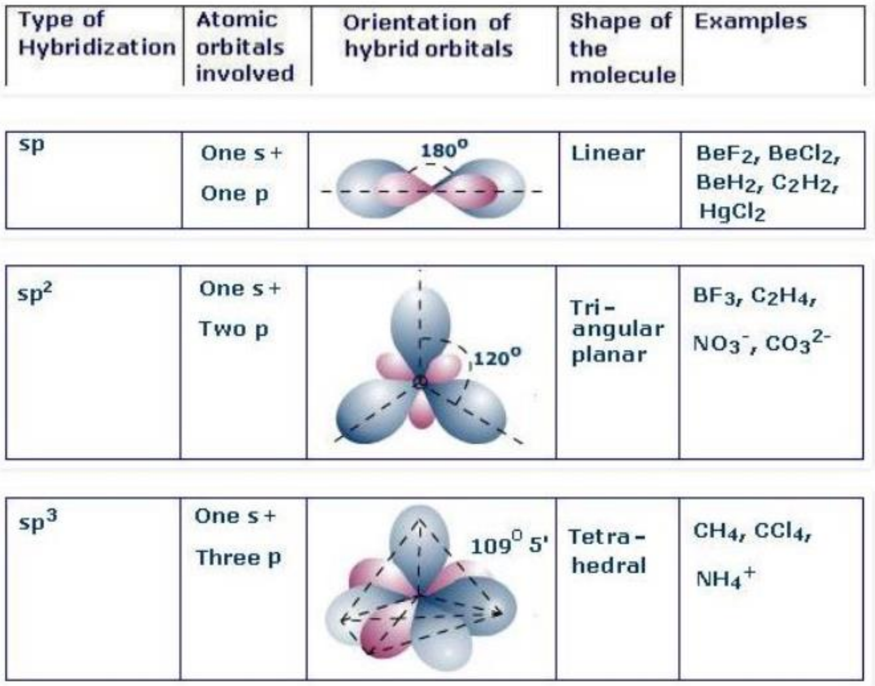
VSEPR indicates *tetrahedral geometry* with one non-bonding pair of electrons (structure itself will be *trigonal pyramidal*)





sp^3 *hybrid orbitals (tetrahedral)*

Hybrid orbitals and molecular shapes involving s and p-orbitals

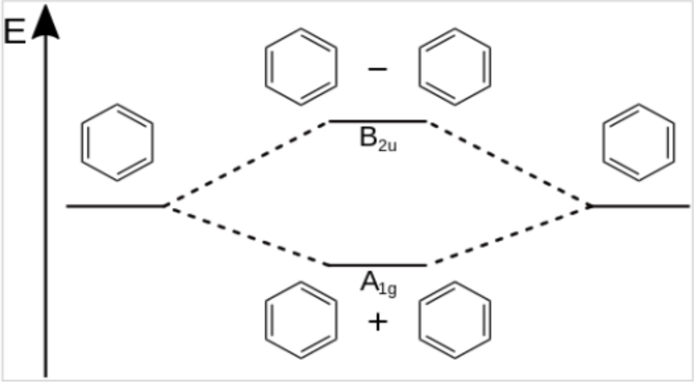


Type of Hybridization	Atomic orbitals involved	Orientation of hybrid orbitals	Shape of the molecule	Examples
sp	One s + One p	180°	Linear	BeF_2, $BeCl_2$, BeH_2, C_2H_2, $HgCl_2$
sp^2	One s + Two p	120°	Tri-angular planar	BF_3, C_2H_4, NO_3^-, CO_3^{2-}
sp^3	One s + Three p	109° 5'	Tetra-hedral	CH_4, CCl_4, NH_4^+

RESONANCE

Resonance theory is one of the most important theories that helps explain many interesting aspects of chemistry ranging from differences in reactivity of related compounds to physical properties such a the absorption of light by molecules.

Resonance structures are two forms of a molecule where the **chemical**connectivity is the same but the electrons are distributed differently around the structure.**Resonance** occurs when electrons can flow through neighboring pi systems. Each contributing structure can be represented by a Lewis structure, with only an integer number of covalent bonds between each pair of atoms within the structure.[3] Several Lewis structures are used collectively to describe the actual molecular structure, which is an approximate intermediate between the canonical forms called a **resonance hybrid**. Contributing structures differ only in the position of electrons, not in the position of nuclei. Electron delocalization lowers the potential energy of the substance and thus makes it more stable than any of the contributing structures. The difference between the potential energy of the actual structure and that of the contributing structure with the lowest potential energy is called the **resonance energy** or delocalization energy.



VB mixing diagram of benzene.[20] The A_{1g} and B_{2u} labels define the symmetries of the two states, as defined by the character table for the D_{6h} symmetry group.

Resonance has a deeper significance in the mathematical formalism of valence bond theory (VB). Quantum mechanics requires that the wavefunction of a molecule obeys its observed symmetry. If a single contributing structure does not achieve this, resonance is invoked.

For example, in benzene, valence bond theory begins with the two Kekulé structures and constructs the actual wave function of the molecule as a linear superposition of the wave functions representing the two structures. As both Kekulé structures have equal energy, they are equal contributors to the overall structure – the superposition is an equally weighted average, or a 1:1 linear combination of the two – but this need not be the case. The symmetric combination gives the ground state while the antisymmetric combination gives the first excited state as shown.

In general, the superposition is written with undetermined coefficients, which are then variationally optimized to find the lowest possible energy for the given set of basis wave functions. When more contributing structures are included, the molecular wave function becomes more accurate and more excited states can be derived from different combinations of the contributing structures.