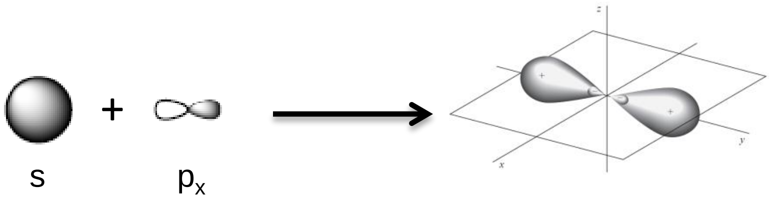
Notes on
Hybridization- Shapes of organic molecules

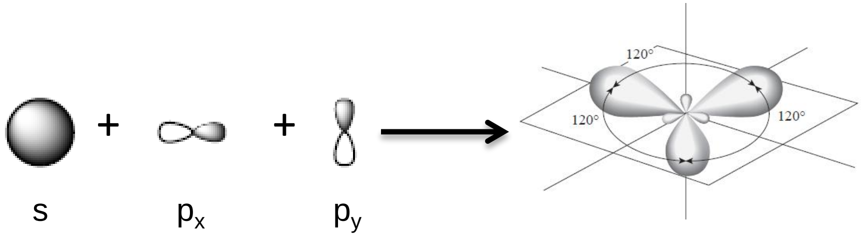
Hybridization is the concept of mixing atomic orbitals that are close in energy to form same number of new hybrid orbitals with equal energy and definite geometry. These newly formed orbitals are called hybrid orbitals.

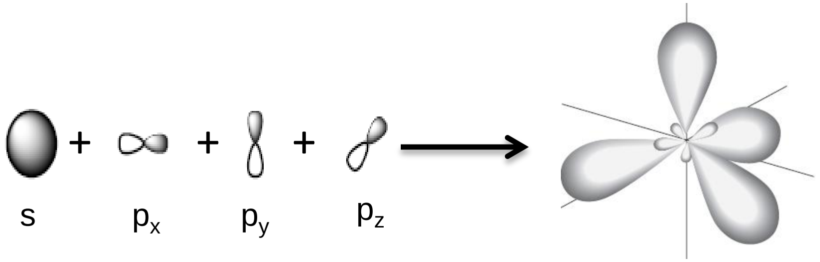
The concept of hybridization was first proposed by Linus Pauling in 1931.

Important points of hybridization-

- The hybridization of atomic orbitals takes place either by reshuffling of all or some of the orbitals in the excited state.
- The hybrid orbitals have same shape, size and energy i.e. they are equivalent to each other.
- The number of hybrid orbitals is equal to the number of reshuffled pure atomic orbitals.
- The shape, size, orientation and energy content of the hybrid orbitals are different from the pure atomic orbitals.
- The labels given to hybrid orbitals reflect the contributing atomic orbitals. For example- an sp hybrid orbital possess equal amounts of s and p orbital character.

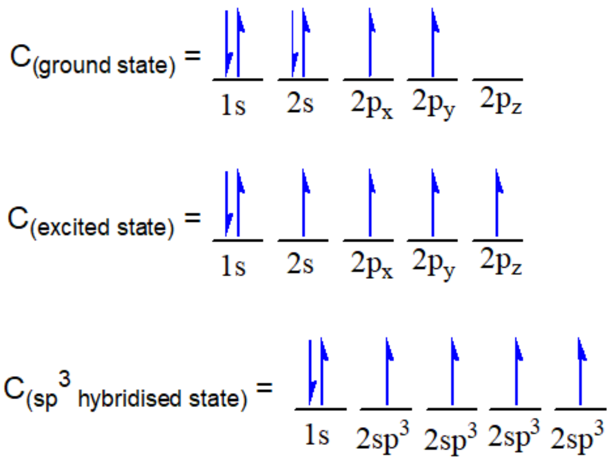




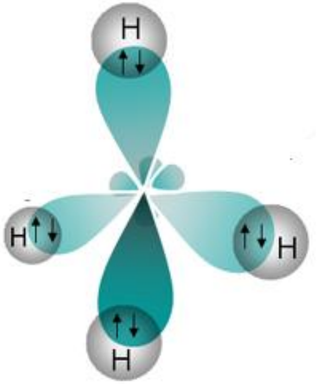


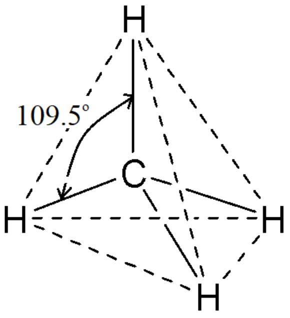
Bonding in methane

In methane, carbon is in sp^3 hybridised state where it has four sp^3 hybridised orbitals



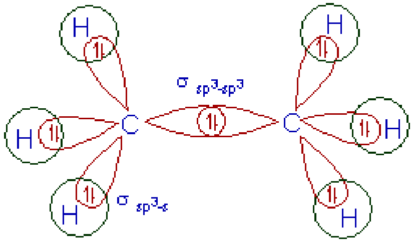
Each four sp^3 hybrid orbitals of carbon overlap with half-filled 1s orbitals of four H atoms to form four C-H bonds. All the four C-H bonds in methane are equivalent with 1.10 Å. All of the H-C-H bond angles are 109.5º

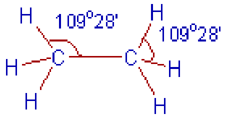




Bonding in ethane

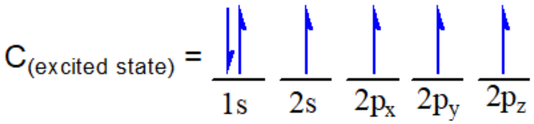
In ethane, both the carbon atoms are sp^3 hybridised. In its structure, three of the sp^3 hybrid orbitals of each carbon atom overlap with the 1s orbitals of H to form a total of six C-H bonds, while the remaining sp^3 hybrid orbital of carbon overlap with the sp^3 hybrid orbital of adjacent carbon to form C-C sigma bond.

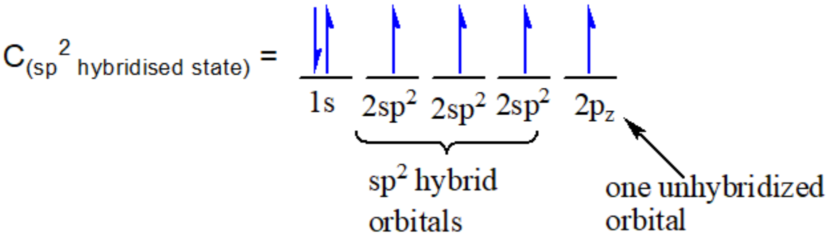




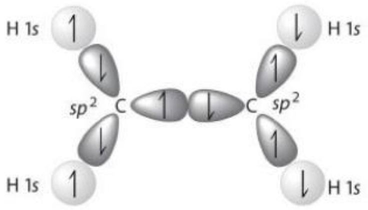
Bonding in ethylene

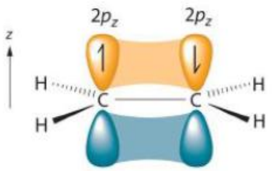
In ethylene, each carbon atom is in sp^2 hybridised state.





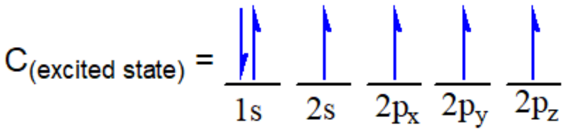
In its structure, each carbon atom utilized two of its three sp^2 hybrid orbitals to form two C-H bonds by overlaping with the 1s orbitals of H. The remaining sp^2 hybrid orbitals of each carbon overlap with each other along the axis to form C-C sigma bond. The unhybridised $2p_z$ orbital, perpendicular to the plane of sp^2 hybrid orbitals overlap sidewise with the other $2p_z$ orbital on the adjacent carbon.

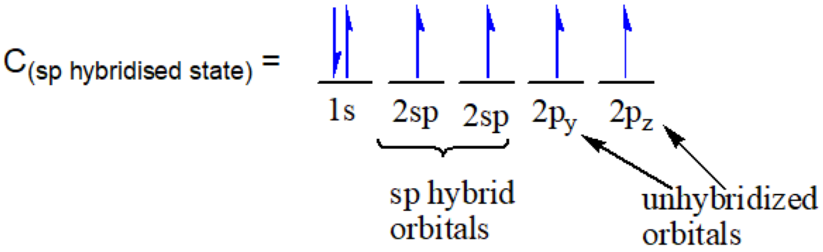




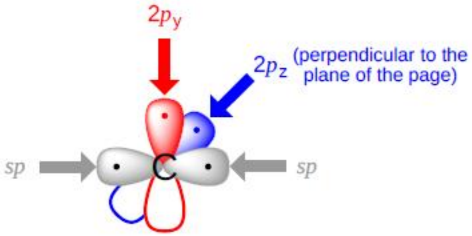
Bonding in acetylene

In acetylene, carbon atoms are sp hybridised.





In the formation of acetylene, one sp hybrid orbital on each carbon overlaps with 1s orbital of hydrogen to form C-H sigma bond, while the other sp hybrid orbital of carbon atom overlaps with the sp hybrid orbital of adjacent carbon atom along the axis to form C-C sigma bond. The remaining two unhybridised 2p orbitals ($2p_y$ and $2p_z$) of each carbon overlap with each other side wise to form two pi bonds.



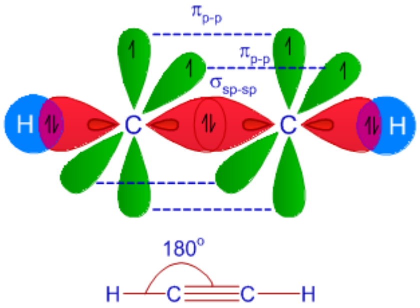


Table 1: Shape of the molecules depending on hybridisation

Hybridisation	Molecular geometry	Example
sp^3	Tetrahedral	CH_4
sp^2	Planar trigonal	C_2H_4, BCl_3
sp	Linear	C_2H_2, BeH_2

Influence of hybridization on bond properties

Table 2: Comparison of bond angles, bond length and bond strengths of C-C and C-H bonds in ethane, ethene and ethyne

Molecule	Hybridisation of carbon	Bond angles	C-C bond length (Å)	Strength of C-C bond (Kcalmol^{-1})	C-H bond length (Å)	Strength of C-H bond (Kcalmol^{-1})
Ethane	sp^3	109.5°	1.54	88	1.10	101
Ethene	sp^2	120°	1.33	152	1.08	107
Ethyne	sp	180°	1.20	200	1.06	131

- When comparing lengths and strengths of C-C single, double and triple bonds, the more bonds holding two carbon atoms together, the shorter and stronger the C-C bond.

- ***The more s character in hybridisation, the shorter and stronger the bond, because an s orbital is closer to the nucleus than a p orbital.***

- C-H bond is shorter and stronger than C-C sigma bond. The s orbital of H is closer to the nucleus than is the sp^3 orbital of carbon, so the carbon and H nuclei are closer together in sp^3-s overlap than are the carbon nuclei in sp^3-sp^3 overlap, causing C-H bond to be shorter than a C-C bond.

- **Bond angle** in a molecule depends primarily on the shape of the molecule. The more s character in an orbital used by carbon or any atom to form the bond has, the larger the bond angle of the molecule.

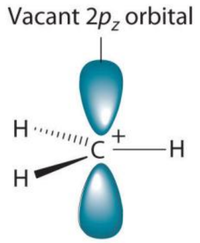
Important points of hybridization-

- **The hybridization of C, O or N atom can be determined by the number of pi bonds it forms. If it forms no pi bonds, it is sp^3 hybridised; if it forms one pi bond, it is sp^2 hybridised and; if it forms two pi bonds, it is sp hybridised.**

- ***The hybridisation of C, O or N is $sp^{(3\text{-number of pi bonds})}$.***

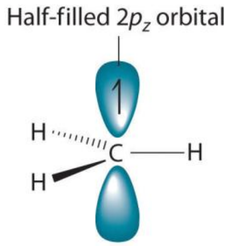
Bonding in methyl cation (CH_3^+)

A positively charged carbon forms three covalent bonds, so it hybridizes three orbitals- one s and two p orbitals. Therefore, it forms three covalent bonds by using the three sp^2 orbitals. The unhybridized p orbital remains empty. So, the structure of carbocation is trigonal planar. The p orbital stands perpendicular to the plane.



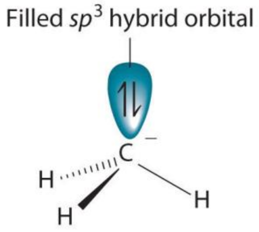
Bonding in methyl radical ($CH_3^\cdot$)

The carbon atom in methyl radical is also sp^2 hybridised. The unpaired electron is in the p orbital.



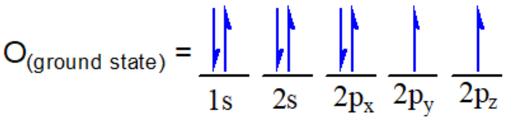
Bonding in methyl anion (CH_3^-)

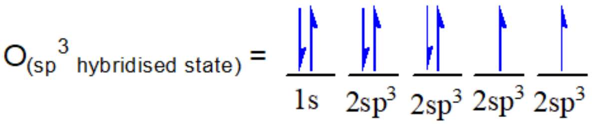
The negatively charged carbon has three bonding and one nonbonding electron pairs. Since, pairs of electrons should be placed as far apart from each other as possible, the four orbitals containing the electron pairs point towards the corners of a tetrahedron. In other words, the negatively charged is sp^3 hybridised. Three of the sp^3 hybrid orbitals overlap with the s orbital of H and the fouth sp^3 orbital holds the non-bonding electron pair.



Bonding in water (H_2O)

In water, oxygen atom is sp^3 hybridised. Each of the two O-H bonds is formed by the overlap of an sp^3 orbital of oxygen with 1s orbital of hydrogen. The remaining two sp^3 hybridised orbitals are occupied by the two nonbonding pair of electrons.





The bond angle in water is a little smaller (104.5º) than the tetrahedral angle, because of the lone pair-bond pair and lone pair-lone pair repulsion which reduces the bond angle.