

## VALENCE BOND THEORY

VBT was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configuration of elements and the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principle of variation and superposition

Consider two hydrogen atoms A and B approaching each other having nuclei  $N_A$  and  $N_B$  and electrons present in them are represented by  $e_A$  and  $e_B$ . When the two atoms are at large distance from each other, there is no interaction between them.

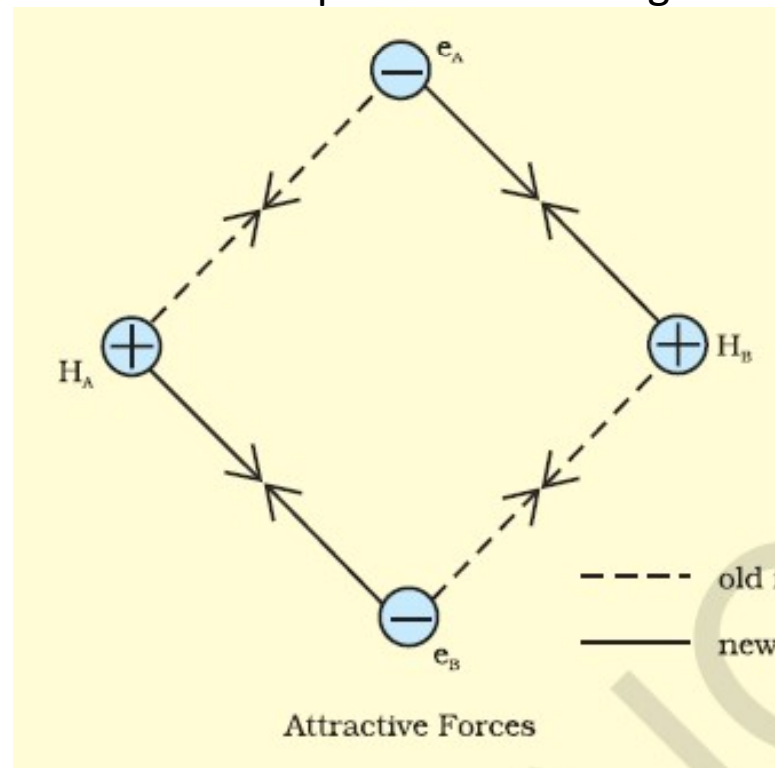
As these two atoms approach each other, new attractive and repulsive forces begin to operate. Attractive forces arise between:

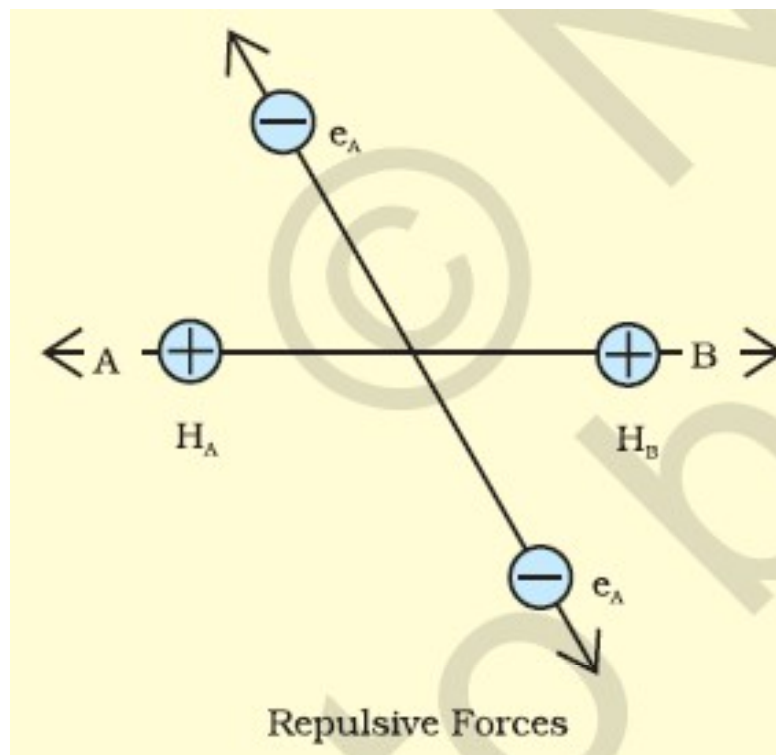
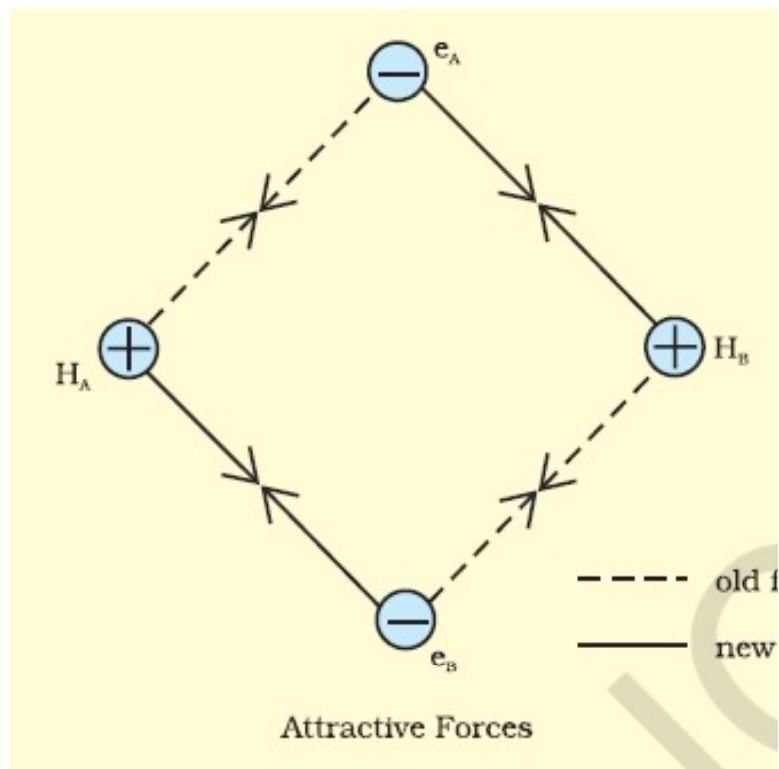
- (i) nucleus of one atom and its own electron that is  $N_A - e_A$  and  $N_B - e_B$ .
- (ii) nucleus of one atom and electron of other atom i.e.,  $N_A - e_B$ ,  $N_B - e_A$ .

Similarly repulsive forces arise between

- (i) electrons of two atoms like  $e_A - e_B$ ,
- (ii) nuclei of two atoms  $N_A - N_{AB}$ .

Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart

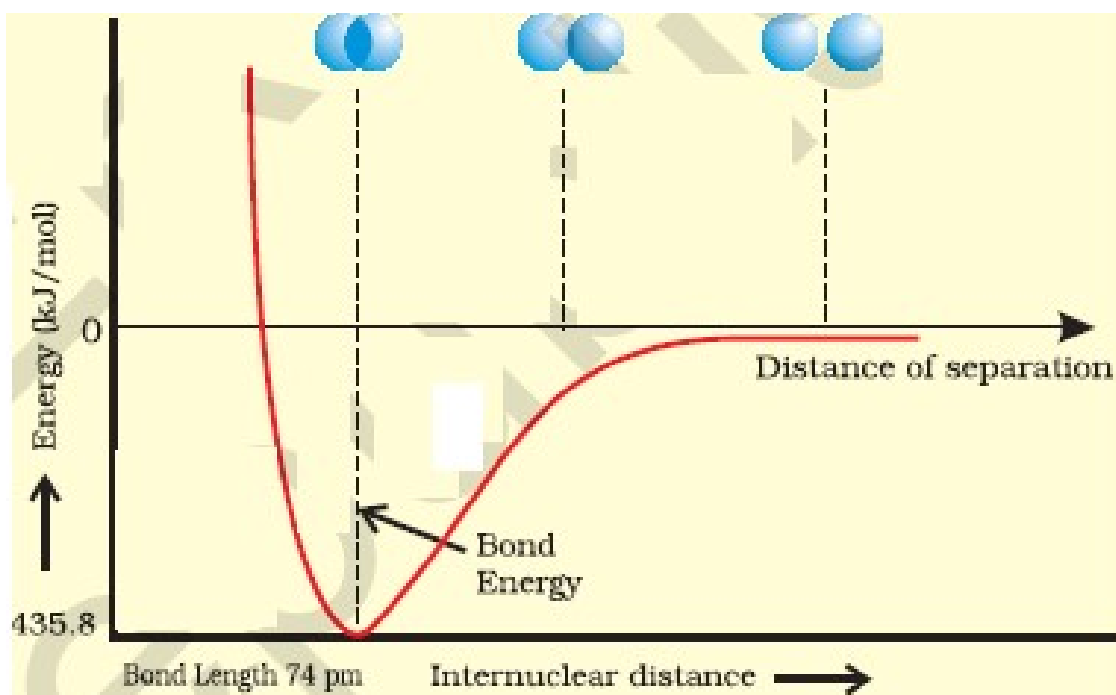




Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potentially energy decreases .

Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded together to form a stable molecule having the bond length of 74 pm.

Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted in Figure. Conversely, 435.8 kJ of energy is required to dissociate one mole of  $\text{H}_2$  molecule.

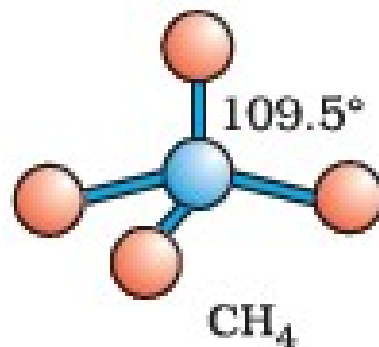


## Orbital overlap concept

In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

### Directional Properties of Bonds

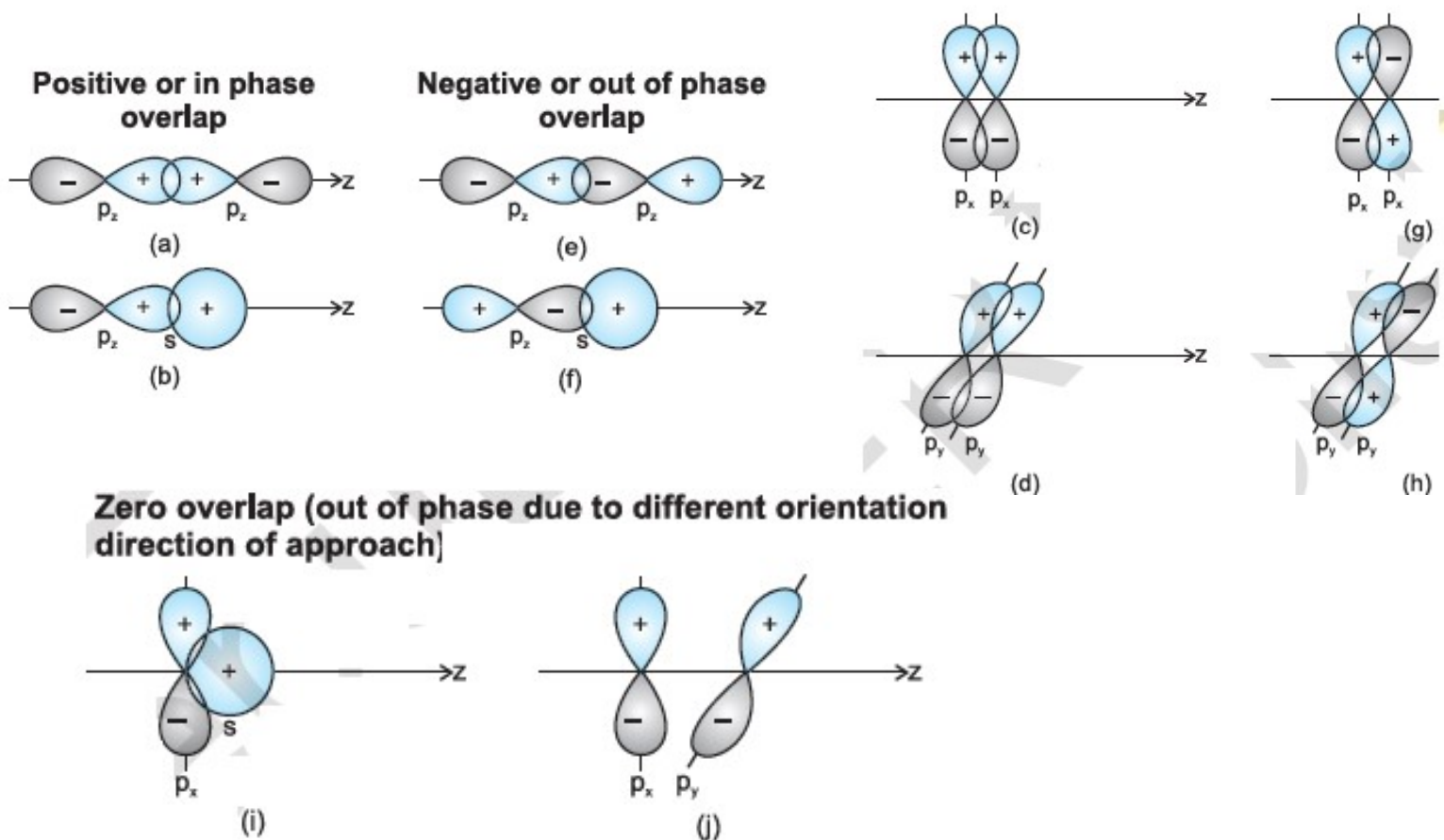
In case of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , the geometry of the molecules is also important in addition to the bond formation. For example why is it so that  $\text{CH}_4$  molecule has tetrahedral shape and HCH bond angles are  $109.5^\circ$ ? Why is the shape of  $\text{NH}_3$  molecule pyramidal?



The valence bond theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , etc. in terms of overlap and hybridisation of atomic orbitals

## Overlapping of Atomic Orbitals

When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space (Figure ). Positive and negative sign on boundary surface diagrams in the Figure show the sign (phase) of orbital wave function and are not related to charge. Orbitals forming bond should have same sign (phase) and orientation in space. This is called positive overlap.



## Discrepancy in the bond angle in methane

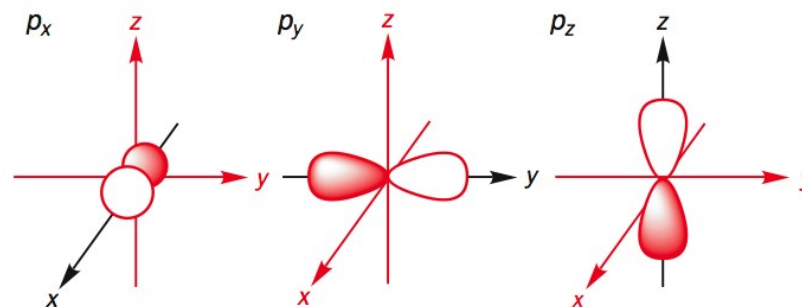
The electronic configuration of carbon in its ground state is  $[\text{He}]2s^2 2p^2$  which in the excited state becomes  $[\text{He}] 2s^1 2p_x^1 2p_y^1 2p_z^1$ .

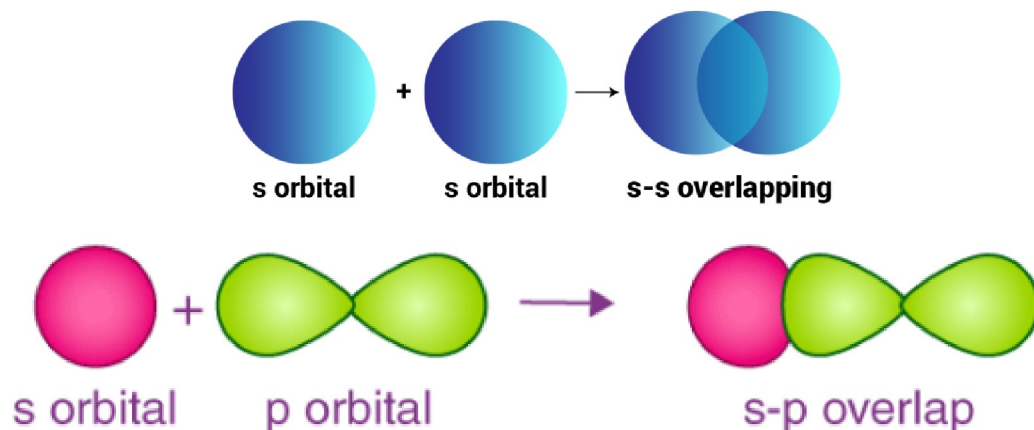
The four atomic orbitals of carbon, each with an unpaired electron can overlap with the *1s orbitals of the four H atoms which* are also singly occupied. This will result in the formation of four C-H bonds.

It will, however, be observed that while the three p orbitals of carbon are at  $90^\circ$  to one another, the HCH angle for these will also be  $90^\circ$ . That is three C-H bonds will be oriented at  $90^\circ$  to one another.

The *2s orbital of carbon and the 1s orbital of H* are spherically symmetrical and they can overlap in any direction. Therefore the direction of the fourth C-H bond cannot be ascertained.

This description does not fit in with the tetrahedral HCH angles of  $109.5^\circ$ .

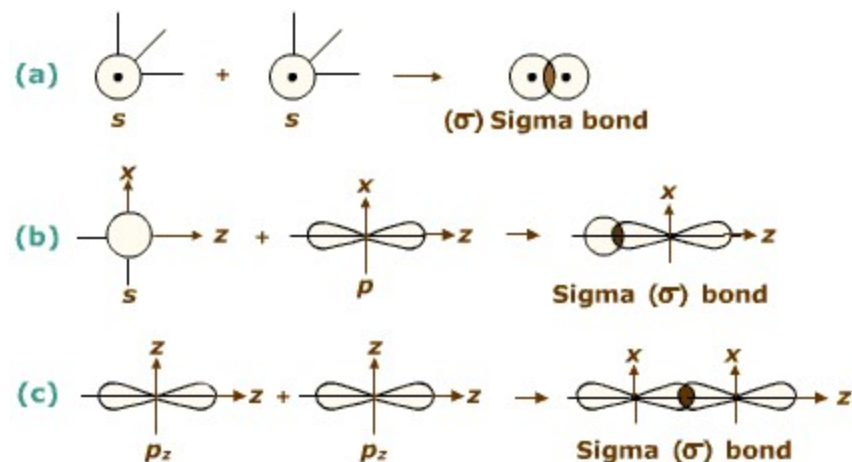




## Types of Overlapping and Nature of Covalent Bonds

(i) Sigma( $\sigma$ ) bond, and (ii) pi( $\pi$ ) bond

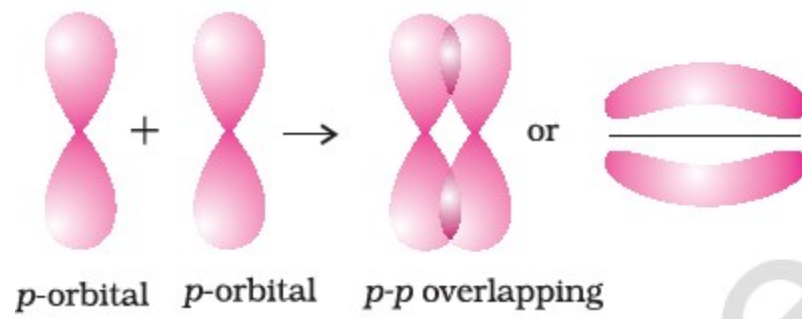
**Sigma( $\sigma$ ) bond** : This type of covalent bond is formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals



Formation of a sigma bond due to (a) The s - s overlap

(b) The s - p overlap (c) The p<sub>z</sub> - p<sub>z</sub> overlap

**$\pi$  Bond:** In the formation of  $\pi$  bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms.



### Strength of Sigma and pi Bonds

Basically the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that in the formation of multiple bonds between two atoms of a molecule, pi bond(s) is formed in addition to a



## 4.6 HYBRIDISATION

In order to explain the characteristic geometrical shapes of polyatomic molecules like  $\text{CH}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  etc., Pauling introduced the concept of hybridisation. According to him the atomic orbitals combine to form new set of equivalent orbitals known as **hybrid orbitals**. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as **hybridisation** which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one  $2s$  and three  $2p$ -orbitals of carbon hybridise, there is the formation of four new  $sp^3$  hybrid orbitals.

***Salient features of hybridisation:***

***The main features of hybridisation are as under :***

1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
2. The hybridised orbitals are always equivalent in energy and shape.

3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.

4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

### **Important conditions for hybridisation**

(i) The orbitals present in the valence shell of the atom are hybridised.

(ii) The orbitals undergoing hybridisation should have almost equal energy.

(iii) Promotion of electron is not essential condition prior to hybridisation.

(iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation

### **Types of Hybridisation**

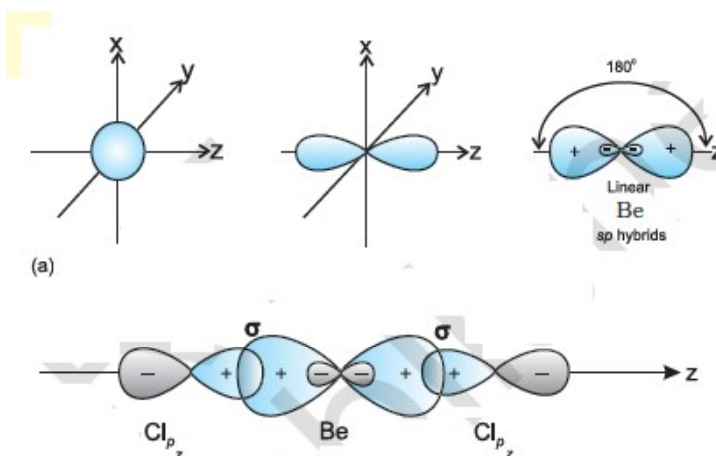
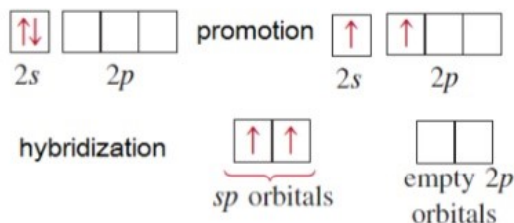
***sp hybridisation:*** This type of hybridisation involves the mixing of one *s* and one *p* orbital resulting in the formation of two equivalent *sp* hybrid orbitals.

## BeCl<sub>2</sub>

The ground state electronic configuration of Be is  $1s^2 2s^2$ . In the excited state one of the  $2s$ -electrons is promoted to vacant  $2p$  orbital to account for its bivalency. One  $2s$  and one  $2p$ -orbital gets hybridised to form two  $sp$  hybridised orbitals. These two  $sp$  hybrid orbitals are oriented in opposite direction forming an angle of  $180^\circ$ . Each of the  $sp$  hybridised orbital overlaps with the  $2p$ -orbital of chlorine axially and form two Be-Cl sigma bonds.

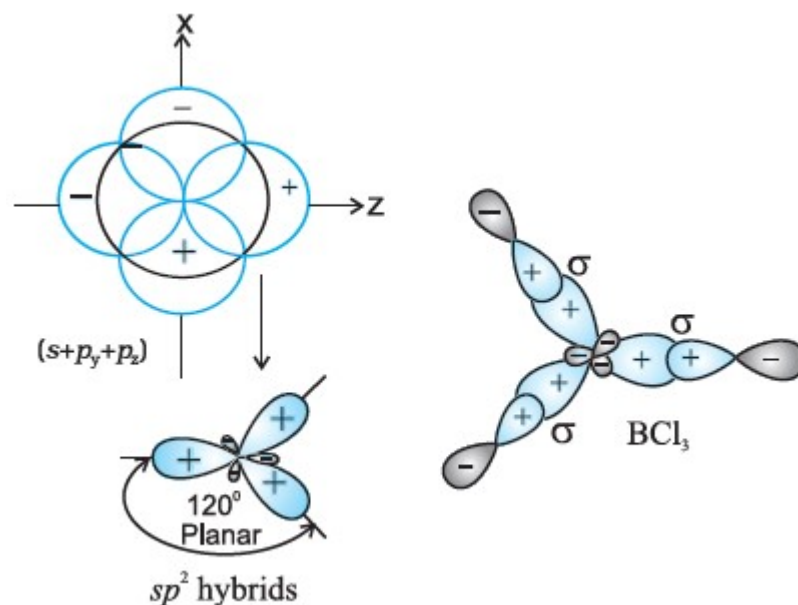
### sp Hybridization

e.g. beryllium chloride (BeCl<sub>2</sub>)



**Sp<sup>2</sup>** In this hybridisation there is involvement of one  $s$  and two  $p$ -orbitals in order to form three equivalent  $sp^2$  hybridised orbitals. For example, in BCl<sub>3</sub> molecule, the ground state electronic configuration of central boron atom is  $1s^2 2s^2 2p^1$ . In the excited state, one of the  $2s$  electrons is promoted to vacant  $2p$  orbital as a result boron has three unpaired electrons.

These three orbitals (one  $2s$  and two  $2p$ ) hybridise to form three  $sp^2$  hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with  $2p$  orbitals of chlorine to form three B-Cl bonds. Therefore, in BCl<sub>3</sub> (Figure) the geometry is trigonal planar with Cl-B-Cl bond angle of  $120^\circ$ .



(III)  $sp^3$  hybridisation: This type of hybridisation can be explained by taking the example of  $CH_4$  molecule in which there is mixing of one  $s$ -orbital and three  $p$ -orbitals of the valence shell to form four  $sp^3$  hybrid orbital of equivalent energies and shape. There is 25%  $s$  character and 75%  $p$ -character in each  $sp^3$  hybrid orbital. The four  $sp^3$  hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between  $sp^3$  hybrid orbital is  $109.5^\circ$  as shown in Figure

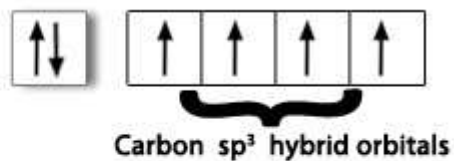
Carbon atom in **ground** state



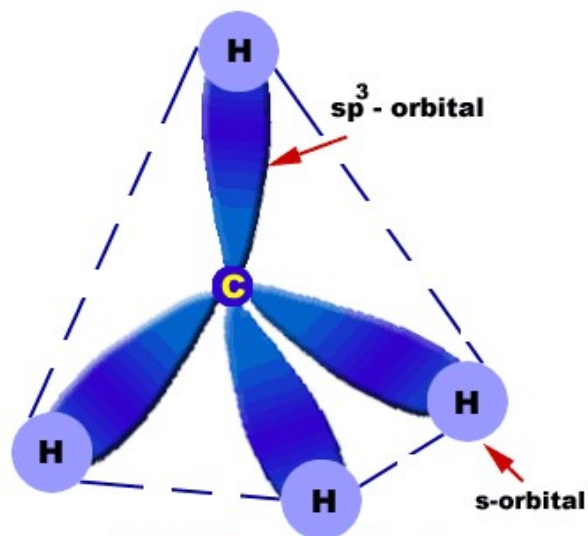
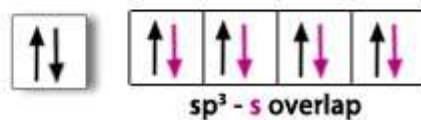
Carbon atom in **excited** state



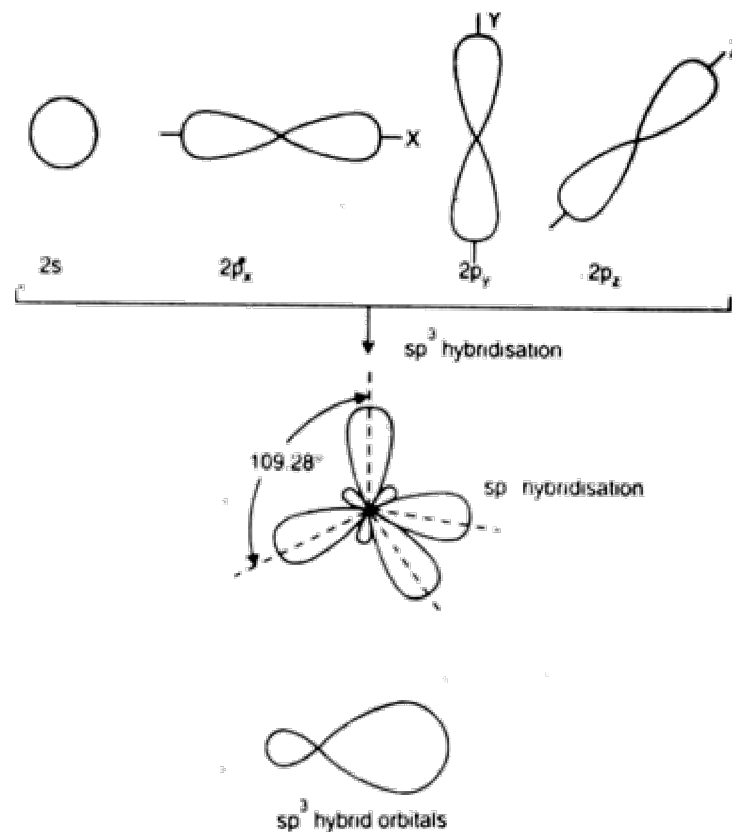
Carbon atom in **hybridized** state

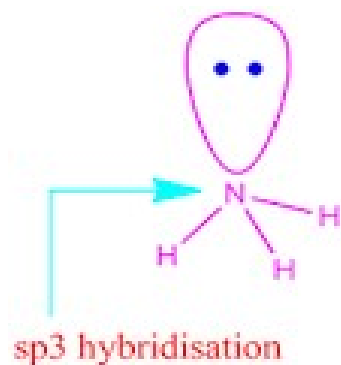


METHANE MOLECULE  
(CH<sub>4</sub>)

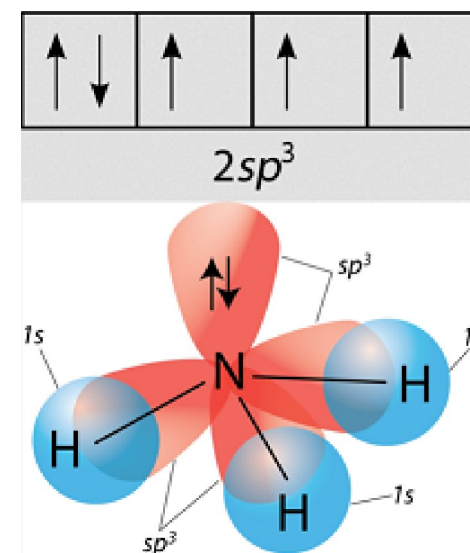
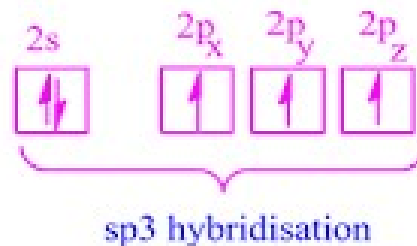


**Orbital structure of methane**

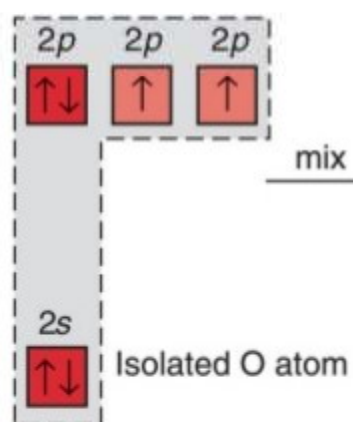




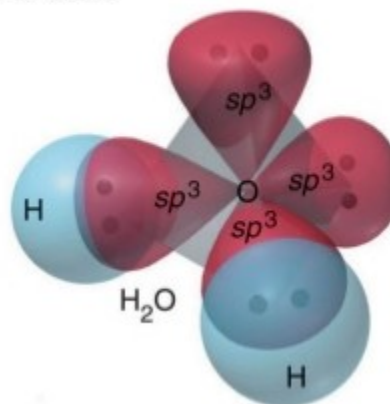
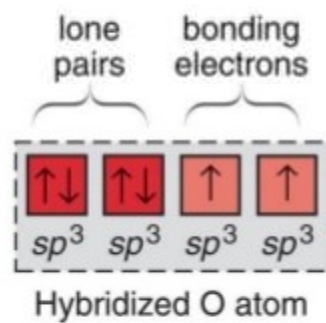
The electronic configuration of N atom 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>3</sup>

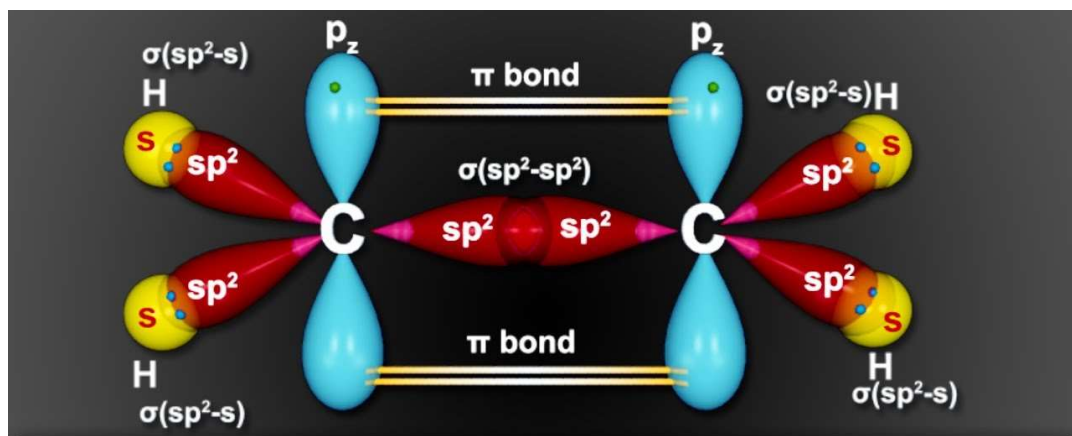


The *sp*<sup>3</sup> hybrid orbitals in H<sub>2</sub>O.



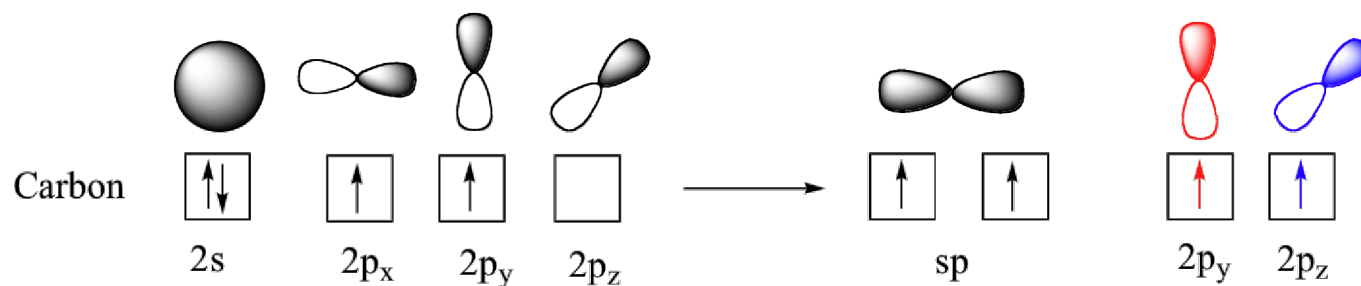
mix



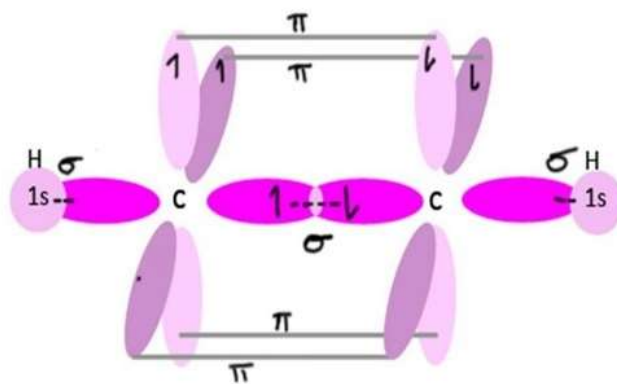


Ethylene

Acetylene



$\text{sp}$  hybridization in Acetylene,  $\text{C}_2\text{H}_2$

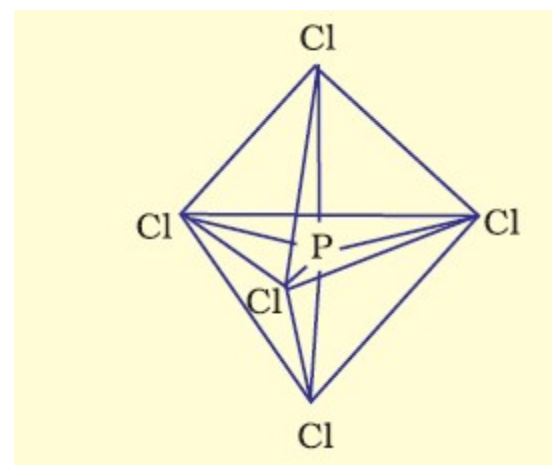
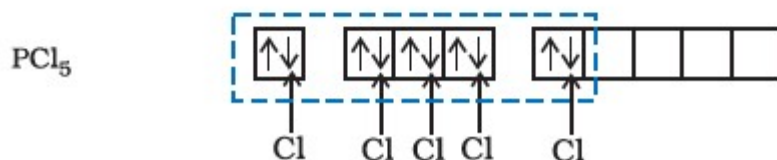
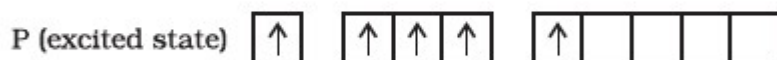
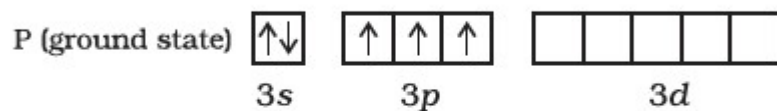




Shape of molecules/ions	Hybridisation type	Atomic orbitals	Examples
Square planar	$dsp^2$	$d+s+p(2)$	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Pt}(\text{Cl})_4]^{2-}$
Trigonal bipyramidal	$sp^3d$	$s+p(3)+d$	$\text{PF}_5$ , $\text{PCl}_5$
Square pyramidal	$sp^3d^2$	$s+p(3)+d(2)$	$\text{BrF}_5$
Octahedral	$sp^3d^2$ $d^2sp^3$	$s+p(3)+d(2)$ $d(2)+s+p(3)$	$\text{SF}_6$ , $[\text{CrF}_6]^{3-}$ $[\text{Co}(\text{NH}_3)_6]^{3+}$

**(i) Formation of  $\text{PCl}_5$  ( $sp^3d$  hybridisation):**

The ground state and the excited state outer electronic configurations of phosphorus ( $Z=15$ ) are represented below.





**(ii) Formation of  $\text{SF}_6$  ( $sp^3d^2$  hybridisation):**

