The basic ideas can be summarized as follows :

Valence shell pairs of electrons are arranged about the central atoms so that repulsion among them is minimised, or so that there is maximum separation among the regions of high electron density (bond pairs) about the atom. For instance, two regions of high electron density would be most stable on opposite side of the central atom (*Linear arrangement*), while three regions would be most stable when they are arranged at the corners of an equilateral triangle *Trigonal planar arrangement)*. The resulting arrangement of these regions is referred to as the electronic geometry of the central atom.

Number of Bond Pairs	Electronic Geometry	Bond Angles
2	Linear	180°
3	Trigonal planar	120°
4	Tetrahedral	109° 28′
5	Trigonal Bi-pyramidal	90°, 120°, 180°
6	Octahedral	90°, 180°

As mentioned earlier, there are two distinct types of electron pairs around the central atom : Bonding electron pairs (bp) and Nonbonding electron pairs or lone pairs (–*l*p). The strength of repulsion between the electron pairs varies as :

–*l*p-–*l*p > –*l*p-bp > bp-bp

This is very significant while deciding the final geometry of a molecule. We will divide our study of shapes in two categories :

- *The molecules containing only bond–pairs of electrons and*
- *The molecules containing both bond–pairs and lone (non-bonding) pairs.*

Note : Before we go into the details of shapes, first let us discuss the *Theory of Covalent Bonding*.

THEORIES OF COVALENT BONDING — Section - 6

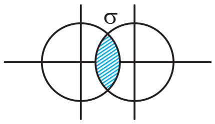
Orbital theory of Covalent Bonding :

As discussed earlier that covalent bonding is the result of sharing of electrons between atoms. The main requirement for sharing of electrons is: *only a single electron must be present in an orbital of the outer shell.* Such an orbital (i.e. containing an odd electron) will combine with another orbital (containing an odd electron *but of opposite spin*) of same kind or of another kind of atom to form covalent bond. This combination of orbitals is known as *overlapping of orbitals.* So according to atomic orbital theory, *the covalent bond is formed by the overlapping of atomic orbitals having electrons with opposite spins, belonging to the external shells of two atoms of same or of different kinds*. After overlapping the electron–pair now belongs to both the orbitals of two atoms.

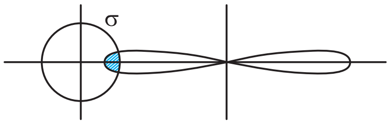
Depending upon the types of orbitals which take part in overlapping, we can classify overlapping as follows:

(a) s–s overlapping **(b)** s–p overlapping **(c)** p–p overlapping

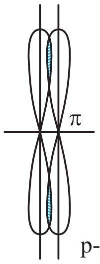
From above, we observe that overlapping can further be analysed as lateral and end to end. s–s, s–p and one of p–p type overlapping is of end-to-end type and one of the p–p overlapping is of lateral type.



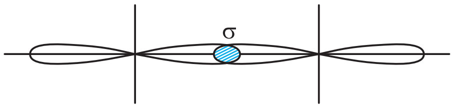
s-s overlap (end to end)



s-p overlap (end to end)



p-p overlap (lateral)



p-p overlap (end to end)

Sigma (σ) bond : The bond formed as a result of end to end type of overlapping is called as σ bond**.** Here overlapping of orbitals takes place along the same axis. The bond formed by this type of overlapping is very strong as the extent of overlapping is sufficiently high. *The extent of overlapping determines the strength of covalent bond.* In sigma bond, the electron density accumulates between the centres of the atoms being bonded and lies on the imaginary line joining the nuclei of bonded atoms.

Pi (π) bond : The bond formed between two atoms by the sideways overlapping (also called lateral overlapping) of the two half–filled orbitals is called a pi (π) bond. The extent of overlapping in case of a pi bond is much less than in sigma bond, so strength of pi bond is low. In this bond, the electron density lies above and below the imaginary line joining the centres of nuclei of bonded atoms. Whenever there is multiple bonding, i.e., double and triple bonds, pi bond is formed.

Hybridisation and Hybrid Orbital :

The electronic configuration of carbon (C), $1s^2\ 2s^2 2p^2$, is rather misleading if we talk about the tetravalency of carbon (which is its most common valency in its compounds). Its configuration predicts the carbon to divalent due to two unpaired p electrons. This is actually not the case. In bond formation, the atomic orbitals of carbon atom are mixed in such a manner as to produce *four equivalent orbitals*, which are confined to the corners of a regular tetrahedron, in order to maximise the separation among them (VSEPR theory). The mixing of atomic orbitals in order to produce new orbitals is called as Hybridisation. This concept was given by Linus Pauling in 1937. This concept not only predicts the correct shapes but also explains the actual microscopic observations of the geometry of molecules. The different cases of hybridisation arise by mixing of s, p and d orbitals are discussed below.

sp^3 Hybridisation :

This type of hybridisation results from mixing of one *s*, three *p* orbitals of outer (valence) shell of an atom. To understand the concept clearly, let us consider the formation of CH_4 molecule. The outer-shell configuration of C atom in ground state is $2s^2 2p_x^1 2p_y^1$. Note that $2p_z$ orbital is empty. One of the electrons in the $2s^2$ orbital is excited (or promoted) to this vacant $2p_z$ orbital. This results in the following picture.

Ground state **Excited state**

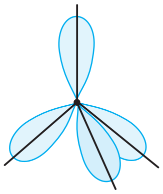
$2s^2\,2p_x^{\;1}\,2p_y^{\;1} \longrightarrow$ *one electron excited to a* $2p_z$ *orbital* $\longrightarrow 2s^1\,2p_x^{\;1}\,2p_y^{\;1}\,2p_z^{\;1}$

(This step requires energy)

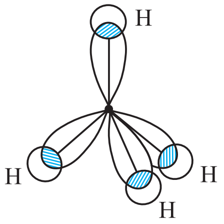
After the electron is promoted, all the four orbitals are mixed to give four equivalent hybrid orbitals (in sense that all of them are of equal energy) called as sp^3 hybrid orbitals.

$2s^1\,2p_x^{\;1}\,2p_y^{\;1}\,2p_z^{\;1} \longrightarrow$ *mixed or hybridised* $\longrightarrow$ four sp^3 hybrid orbitals

These four hybrid orbitals are of same energy and equivalent in every other way. They are directed at the corners of a regular tetrahedron. This is best geometry for four bonded pairs to be at the maximum distance apart and thus minimise the repulsion and hence the energy of the system is minimised. Each of four sp^3 orbitals in carbon can now combine with a 1*s* orbital of a hydrogen atom, forming four equivalent CH bonds involving sp^3–s overlapping and forming four sigma bonds. The extent of overlapping by hybrid orbitals is very high due to their strong orientation in space or one can now imagine a bond formed by hybrid orbital to be highly stable. This additional stability accounts for the energy required in the promotion step before mixing.



4 sp^3 hybrid orbitals



CH_4 (Methane) molecule

sp^3 –s overlapping
tetrahedral shape
Bond angle 109.5°

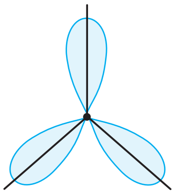
sp^2 hybridisation :

To account for the shapes of molecules like BF_3, BCl_3 etc., let us consider the valence-shell configuration of Boron: $2s^2\,2p_x^{\;1}$. Note that p_y and p_z orbitals are vacant, so promotion of one 2s electron takes place to $2p_y$ orbital to account for three B-F bonds in BF_3.

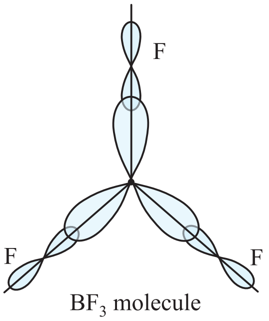
Ground state **Excited state**

$2s^2\,2p_x^{\;1} \longrightarrow$ *one electron excited to a* $2p_y^{\;1}$ *orbital from a* 2*s orbital* $\longrightarrow 2s^1\,2p_x^{\;1}\,2p_y^{\;1}$

The three orbitals in excited state are mixed to give three sp^2 hybrid orbitals of equivalent energy. These are all in a same plane with central atom (Boron) at the centre of an equilateral triangle with three sp^2 orbitals at its corners. This is the best possible geometry for three bond–pairs to be at maximum distance (VSEPR theory). Each of these orbitals now form three sigma bonds with three 2*p* orbitals of F atoms to form B–F bonds and hence forms a BF_3 molecule.



sp^2 hybrid orbitals



BF_3 molecule

sp^2 –p overlapping
trigonal planar shape
Bond angle 120°

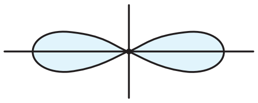
sp hybridization :

A sp hybrid orbital is formed when in an atom *one s* and *one p* orbital mix with each other to form two equivalent orbitals. Two such orbitals, i.e., sp hybrid orbitals are most stable when they adopt an angle of 180° between them so that they are at the maximum distance apart. It means that the molecule involving sp hybrid orbitals will be *linear in shape*. The geometry of BeF_2 is linear and is explained by sp hybridisation of Be atom. The valence shell configuration of Be is $2s^2$ which means one electron from 2*s* orbital can be promoted to vacant 2p orbital and form the excited state.

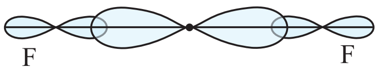
Ground state **Excited state**

$2s^2 \longrightarrow$ *promotion of one s electron* $\longrightarrow 2s^1\,2p_x^{\ 1}$
to a p_x orbital

The $2s^1$ and $2p_x^{\ 1}$ electron can now mix or hybridised to give two sp hybrid orbitals, which form two sigma bonds with F atoms (as in BF_3) to form BeF_2 molecule.



2 *sp* hybrid orbitals



BeF_2 molecule sp-p
overlapping linear shape
Bond angle 180°

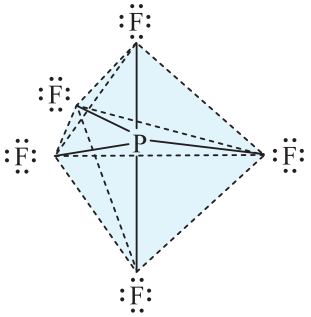
*sp*³*d* hybridisation (PF_5 molecule) :

Since phosphorus is the central element in PF_5 molecules, it must have five half–filled orbitals to form bonds with five Fluorine atoms. Hybridisation is again the answer. This time using one d orbital from the vacant set of 3d orbitals in addition ot the 3s and 3p orbitals of the phosphorus atom.

Ground state **Excited state**

$3s^2\,3p^3\,3d^0 \longrightarrow$ *promotion of one s electron* $\longrightarrow 3s^1 3p_x^{\ 1}\,3p_y^{\ 1} 3p_z^{\ 1}\,3d^1$
to a vacant d orbital

The five sp^3d hybrid orbitals are directed toward the corners of a trigonal bipyramid. Each is overlapped by the (only) 2p orbital of a Fluorine atom that contains a single electron. The resulting pairing of P and F electrons forms a total of five covalent bonds.



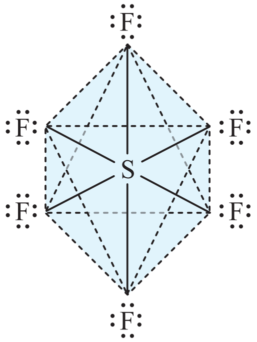
*sp*³*d*² hybridisation (SF_6) :

The sulphur atoms can form six hybrid orbitals to accommodate six electron pairs, and in Valence Bond theory terminology, we have :

Ground state **Excited state**

$3s^2\,3p^4\,3d^0 \longrightarrow$ *promotion of one s electron* $\longrightarrow 3s^1 3p_x^{\ 1}\,3p_y^{\ 1} 3p_z^{\ 1}\,3d^1 3d^1$
and p electron to a vacant d orbitals

The six sp^3d^2 hybrid orbitals are directed toward the corners of a regular octahedron. Each sp^3d^2 hybrid orbital is overlapped by a half–filled 2p orbital from Fluorine to form a total of six covalent bonds.



We should note the sp^3d hybridisation involves utilisation of an available d orbital in the outermost shell of the central atom, P. The heavier Group 15 elements P, As, and Sb, can form five co–ordinate compounds utilising this hybridisation. But it is not possible for Nitrogen (also in Group 15) to form such five–coordinate compounds. Why ?

(i) Nitrogen is too small to accommodate five (even very small) substituents without excessive crowding which causes instability.

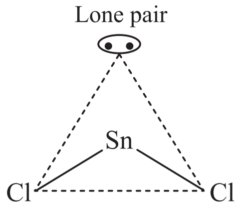
(ii) It has no low-energy *d* orbitals.

In fact, we can generalise; no elements of the second period can be central element in five–coordinate molecules (or higher–coordinate ones) because they have no low energy d orbitals available for hybridisation, and because they are too small.

It is important to realise that the set of s and p orbitals in a given energy level, and therefore any set of hybrids composed only of them, can accommodate a maximum of eight electrons and participate in a maximum of four covalent bonds.

In the following section, we will discuss the hybridisation of molecules in which the central atom has lone pair(s). The actual geometry of the molecule containing one or more lone pairs of electrons is different from the geometry (distorted Geometry) which is expected from the type of hybridisation involved in the molecule.

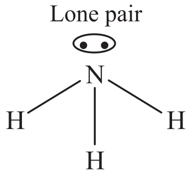
sp^2 hybridisation in $SnCl_2$:



The outer electronic configuration of Sn is $5s^2\ 5p_x^1\ 5p_y^1$. To explain the shape of $SnCl_2$, the concept of hybridisation is applied. Here one 5*s*, two 5*p* orbitals hybridise to give three sp^2 hybridised orbitals of equivalent energy.

In this case one of the hybrid orbitals contains a lone pair, whereas other two contain an electron each. These two orbitals containing one electron overlap with two 3p orbitals of two chlorine atoms to form two Sn–Cl bonds. The geometry of $SnCl_2$ molecule should have been Trigonal planer, but due to presence of lone pair over the central atom (Sn), there is some distortion in the shape of the molecule. The bond angle is slightly less than 120° and the molecule is *bent or V–shaped*. The reason is the *greater repulsion between a bp and a –!p* than normal bp–bp repulsion.

sp^3 hybridisation in NH_3 and H_2O molecule :

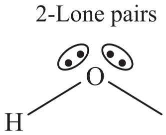


Ammonia
(Pyramidal)

In Ammonia, NH_3 : N is the central atom and its outer–shell configuration is $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$. One s orbital (containing a lone pair) hybridises with three p orbitals (containing one electron each) to give four sp^3 hybrid orbitals. Of these four hybrid orbitals, the three orbitals containing one electron each overlap with three 1s orbitals of three H–atoms to form N–H bonds.

Due to lone pair over N, the geometry of the molecule gets distorted from regular tetrahedron (which is the exact geometry for sp^3 hybrid orbitals) and the bond angle changes from 109.5° to 107° The final shape is *pyramidal* where N is at the centre with three H–atoms forming the base and the lone pair forming the apex of the pyramid.

In Water, H_2O : O is the central atom with $2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ as its outer–shell configuration. Here, one s orbital (containing a ℓp), one *p* orbital (containing a ℓp) and two *p* orbitals (containing one electron each) hybridises to give four sp^3 hybrid orbitals of equivalent energy. Of these two orbitals (containing one electron each) overlap with two 1*s* orbitals of H atoms to form two O–H bonds.



Water
(V-shaped)

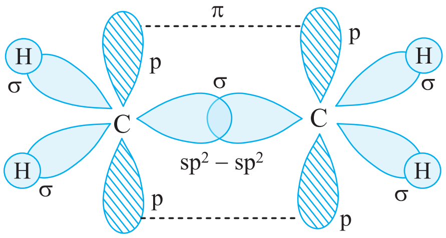
Due to two ℓps over O atom, the actual geometry of molecule is distorted. Apart from ℓp–bp repulsion, ℓp–ℓp repulsion also exists in this molecule, so the distortion is much greater than the ammonia molecule. The bond angle changes form 109.5° to 104.5° in water and the final is *bent or V–shaped.*

Note : The actual geometry of the molecule containing one or more ℓp of electrons is different form the geometry which is expected from the type of hybridisation involved in the molecule.

Hybridisation and Multiple Bonding : (Shapes of C_2H_4 and C_2H_2)

Geometry of C_2H_4 molecule :

In ethylene (C_2H_4), two carbon atoms in the excited state undergo hybridisation in a different manner than the carbon atom in C_2H_4 molecule. After the promotion of one 2*s* electron to the vacant 2*p* orbital, one *s* orbital and two *p* orbitals of two carbon atoms hybridises to form three sp^2 hybrid orbitals (leaving one *p* orbital in unhybridised state).

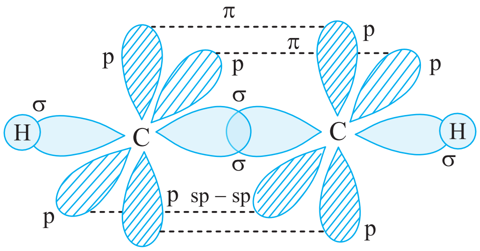


Now one of the sp^2 hybrid orbitals of each carbon atom overlaps with each other to form one C–C bond (sigma bond) and other two hybrid orbital of two carbons overlaps with 1*s* orbitals of H atoms to form *four* C–H bond (sigma bonds) in total. It is important to note that two unhybridised *p* orbitals are perpendicular to the plane of three sp^2 orbitals. These two *p* orbitals form a *pi* (π) bond with each other (Recall the formation of pi bond).

We, now observe that two covalent bonds that make up the double bond between the carbon atoms are not equivalent, they are different. One of them is a sigma (σ) bond and other is the pi (π) bond.

Geometry of C_2H_2 molecule :

In acetylene (C_2H_2), after achieving the excited states, both the carbon atoms undergo sp hybridisation. One *s* orbital and one *p* orbital hybridise to form two *sp* hybrid orbitals (leaving two *p* orbitals in unhybridised state perpendicular to the plane of *sp* hybrid orbitals). Now one sp hybrid orbital belonging to each carbon atom form a C–H sigma bond and other *sp* hybrid orbital form sigma bond with 1*s* orbital of H atom (in all two C–H bonds).



Two unhybridised *p* orbitals of each carbon atom form two *pi* bonds with each other. This means that a carbon-carbon triple bond comprises of one sigma bond and two *pi* bonds.

METHOD TO DETERMINE TYPE OF HYBRIDISATION :

Hybridization never takes place in isolated atoms but takes place only at the time of bond formation.

Hybrid orbitals form stronger bonds than pure atomic orbitals.

Type of hybridization of central atom of a simple molecule or ion can be determined with the help of the value of 'H' which is equal to:

$$H = \frac{1}{2}\left[\begin{matrix}\text{number of valence electrons} \\ \text{of central atom}\end{matrix} + \begin{matrix}\text{number of monovalent atom} \\ \text{attached to central atom}\end{matrix} + \begin{matrix}\text{Charge on} \\ \text{anion}\end{matrix} - \begin{matrix}\text{Charge on} \\ \text{cation}\end{matrix}\right]$$

Value of H	2	3	4	5	6	7
Hybridization	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

Find the hybridization of the central atom in the molecules given below:

(i) $BeF_2 : H = \frac{1}{2}[2+2] = 2 \Rightarrow sp$

(ii) $BCl_3 : H = \frac{1}{2}[3+3] = 3 \Rightarrow sp^2$

(iii) $CH_4 : H = \frac{1}{2}[4+4] = 4 \Rightarrow sp^3$

(iv) $H_2O : H = \frac{1}{2}[6+2] = 4 \Rightarrow sp^3$

(v) $NH_4^+ : H = \frac{1}{2}[5+4-1] = 4 \Rightarrow sp^3$

(vi) $NH_3 : H = \frac{1}{2}[5+3] = 4 \Rightarrow sp^3$

(vii) $CO_3^{2-} : H = \frac{1}{2}[4+2] = 3 \Rightarrow sp^2$

(viii) $NO_3^- : H = \frac{1}{2}[5+1] = 3 \Rightarrow sp^2$

(ix) $H_2SO_4 : H = \frac{1}{2}[6+2] = 4 \Rightarrow sp^3$

(x) $PCl_5 : H = \frac{1}{2}[5+5] = 5 \Rightarrow sp^3d$

(xi) $ClO_3^- : H = \frac{1}{2}[7+1] = 4 \Rightarrow sp^3$

(xii) $ClO_4^- : H = \frac{1}{2}[7+1] = 4 \Rightarrow sp^3$

(xiii) $CO_2 : H = \frac{1}{2}[4] = 2 \Rightarrow sp$

(xiv) $SF_6 : H = \frac{1}{2}[6+6] = 6 \Rightarrow sp^3d^2$

(xv) $XeOF_2 : H = \frac{1}{2}[8+2] = 5 \Rightarrow sp^3d$