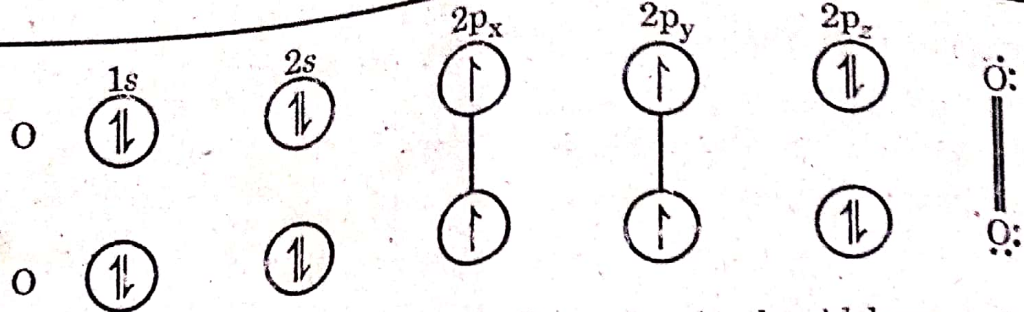


According to valence bond theory, O_2 molecule should have a double bond with no unpaired electrons. But the paramagnetic nature and magnetic moment value of O_2 indicates the presence of two unpaired electrons. This is an example of the failure of the VB theory in predicting the electronic structure.

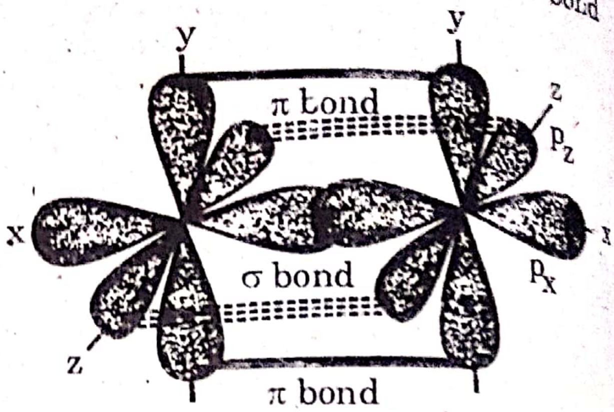


Fig. 2.25 Formation of one σ bond and two π bonds in N_2 molecule.

As already pointed out, the π MO formed here is a pair of 'sausage-like' regions lying parallel to the σ bond. The π bond is analogous to the classical **double bond** of organic chemistry. The formation of N_2 molecule is shown in Fig. 2.25.

We conclude that every simple double bond consists of a sigma (σ) and a pi (π) bond and every triple bond contains one σ-bond and two π-bonds.

2.14 Hybridization of Orbitals

Many elements, such as Be, B and C, form compounds whose formation cannot be explained on the basis of ground-state electronic configuration. Beryllium whose electronic configuration is $1s^2 2s^2$ would be inert and forms no bond at all. In fact, Be is not an inert element as it reacts with other elements to form compounds showing its bivalency e.g. BeH_2, $BeCl_2$. Boron which has the electronic configuration $1s^2 2s^2 2p_x^1$, should behave as a monovalent element, but actually B forms trivalent compounds such as BF_3, BCl_3. Carbon with electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1$ has two unpaired electrons and it should be divalent, but it is found to be tetravalent in its compounds such as CH_4, CCl_4.

Pauling and slater resolved this discrepancy by introducing the concept of **orbital hybridization** which involves mixing of different orbitals (say *s* and *p*) of an atom to form new **hybrid orbitals,** before overlapping and bond formation. These hybrid orbitals are identical in directional character and have the same shape and energy. *The total number of hybrid orbitals formed after mixing, is always equal the number of atomic orbitals mixed.* The hybrid orbitals are just atomic orbitals, although they arise only during the process of bonding and do not exist in the free atom. A bonding process can then be considered as a process of overlapping the hybrid orbitals of one atom with a pure or hybrid atomic orbital of another.

"The process of mixing of orbitals of an atom of nearly equal energy giving rise to entirely new orbitals equal to the number of mixing orbitals and having identical shape and same energy content is called **hybridization".**

The hybrid orbitals are named by indicating the *number* and *kind* of atomic orbitals hybridized. For example, hybridization of *one 2s* orbital and *one 2p* orbital gives two *sp hybrid orbitals.*

Types of the hybridization are:

(i) sp (ii) sp^2 (iii) sp^3 (iv) dsp^2 (v) dsp^3 (vi) sp^3d^2 or d^2sp^3 (vii) sp^3d^3

(i) *sp* hybridization (the formation of $BeCl_2$)

The divalency of Be can be explained by assuming that one of the 2*s* electrons is promoted to a vacant 2*p* orbital to give the configuration $1s^2\,2s^1\,2p_x^1$. The Be atom now has two half-filled orbitals which can form two covalent bonds by overlapping with the half-filled $3p_x$ orbitals of two chlorine atoms. The two Be-Cl bonds thus formed would be *nonequivalent,* because the Be 2s and 2*p* orbitals are not expected to overlap Cl $3p_x$ orbital with equal effectiveness. This is contrary to the fact that both Be-Cl bonds are equivalent in bond length and bond strength. Thus Be atom does not use simple 2*s* and 2*p* orbitals individually, but 2s and 2p orbitals are mixed to form two new equivalent orbitals called **sp hybrid orbitals.** These sp orbitals are oriented at an angle of 180°. The sp hybrid orbital has two lobes, one with greater extension in space than the other.

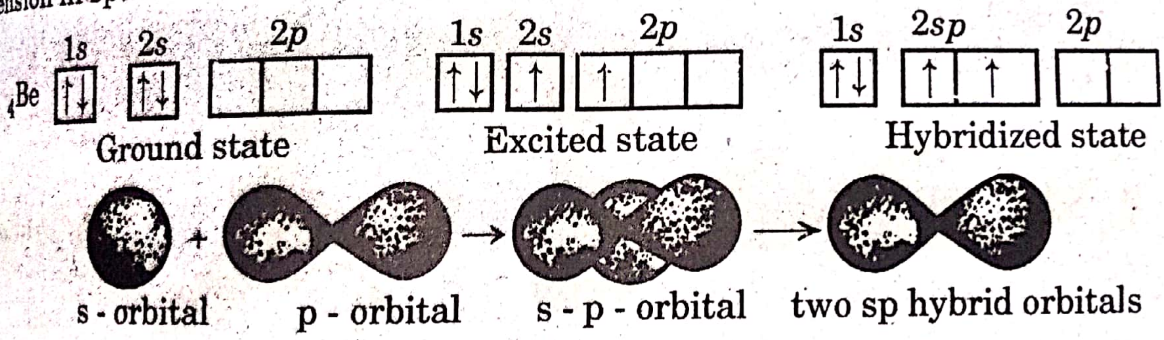


Fig. 2.26. Formation of *sp* hybrid orbitals

The formation of $BeCl_2$ can be visualized as the overlap of the $2p_x$ orbitals of chlorine atoms with the two equivalent collinear sp hybrid orbitals of Be atom. The two Cl – Be – Cl bonds must be equivalent and collinear.

Cl – Be – Cl

Fig. 2.27. Bond formation in $BeCl_2$ using *sp* hybrid orbitals

In general, *sp* hybridization occurs at the central atom of a molecule or a polyatomic ion, whenever there are two regions of high electron density around the central atom. This kind of hybridization is called **digonal hybridization.** The structures of BeF_2, $BeBr_2$ and BeI_2 are similar to that of $BeCl_2$. The chlorides, bromides and iodides of Cd and Hg are also linear covalent molecules.

(ii) sp^2 Hybridization (BF_3 molecule)

The mixing of one s orbital and two p orbitals on the same atom to form three new equivalent hybrid orbitals is called sp^2 **hybridization.** These three sp^2 hybrid orbitals lie in the same plane and are directed towards the three corners of an equilateral triangle forming a mutual angle of 120°. It is for this reason that sp^2 orbitals are also called **trigonal hybrid,** the process being referred to as **trigonal hybridization.**

The electronic configuration of boron is $1s^2, 2s^2\, 2p_x^1$. It has only one unpaired electron, which demands the formation of only one covalent bond. Trivalency of boron can be explained on the basis of sp^2 hybridization. Boron must, therefore, exist in the excited state when one s electron is promoted to p orbital to give the configuration $1s^2, 2s^1, 2p_x^1\, 2p_y^1$. Now in the excited boron, we have three unpaired orbitals, so it can form three covalent bonds. However, not only would we predict that two of the bonds would be different from the third (because two 2p orbitals on B and one 2s orbital on B would be involved), but also we could not account for the observed 120° bond angles. So the evidence in favour of hybridization is very strong. Therefore, boron utilizes its 2s, $2p_x$ and $2p_y$ orbitals for the formation of $3sp^2$ hybrid orbitals. These three hybrid orbitals overlap with three p orbitals from three different F atoms to form three B-F bonds at an angle of 120° with each other.

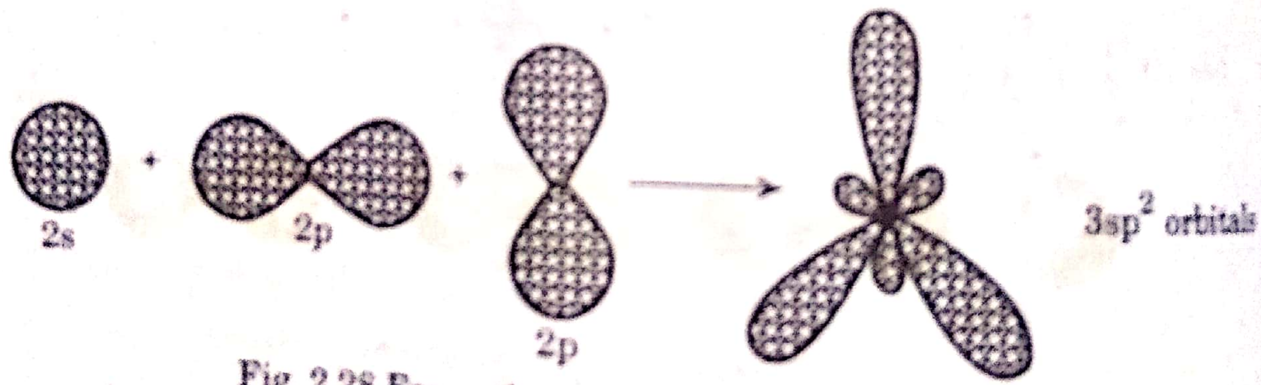


Fig. 2.28 Formation of three sp^2 hybrid orbitals

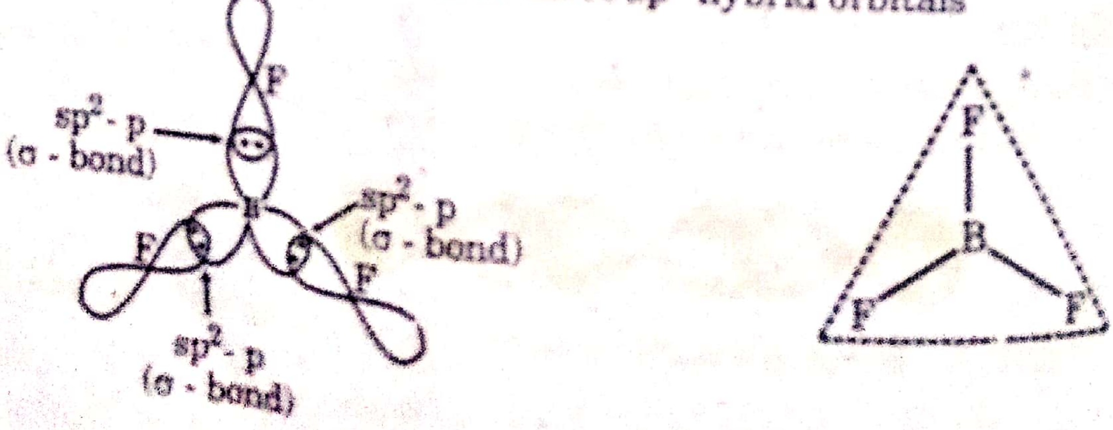


Fig. 2.29. Form...

In general, sp^2 hybridization occurs at the central atom whenever there are three regions of high electron density around the central atom.

(iii) sp^3 Hybridization (methane, CH_4)

The mixing of one s and three p orbitals on a single atom to form four equivalent sp^3 hybrid orbitals is called sp^3 **hybridization.** The tetravalency of carbon can be explained on the basis of sp^3 hybridization.

Carbon with an electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1$ has two unpaired electrons and would form two covalent bonds, but forms four bonds in most of its compounds. This has been explained that one of the two *s* electrons is promoted to an empty $2p$ orbital giving the excited state a configuration of carbon $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$. In the excited state carbon can form four bonds but these would not be equivalent. In actual practice all the four C–H bonds in CH_4 are equivalent with a bond angle of 109.5°. This has been explained by the process of hybridization in which $2s$ and three $2p$ orbitals combine to form four equivalent sp^3 hybrid orbitals. Each sp^3 orbital is composed of *s* and *p* orbitals in the ratio of 1:3 and is directed toward the corners of a regular tetrahedron, forming an angle of 109.5° to each other. This type of hybridization is called **tetrahedral hybridization.**

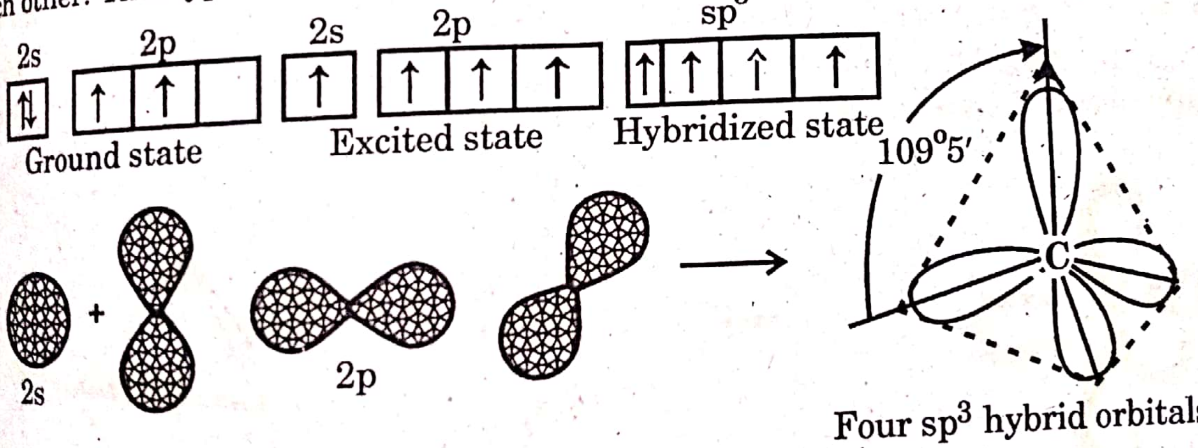


Fig. 2.30. Formation of $4sp^3$ hybrid orbitals.

The methane molecule is formed by the overlap of four carbon sp^3 orbitals with $1s$ orbitals of four hydrogen atoms. The structure of CH_4 is considered tetrahedral.

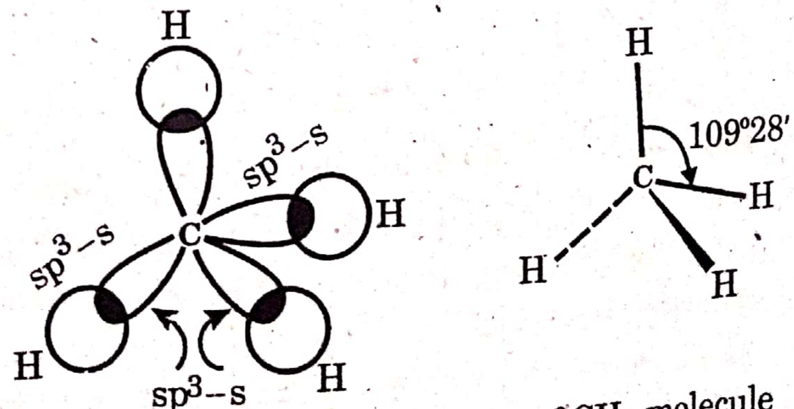


Fig. 2.31 Tetrahedral shape of CH_4 molecule

Hybridization involving *d* orbitals

There are several types of hybridization involving d orbitals. Since the *d* orbitals have a relatively complex shape, we will consider here only some of the common types. The most important of these are *dsp*^{2} hybridization, *dsp*^{3} hybridization and *d*^{2}*sp*^{3} hybridization.

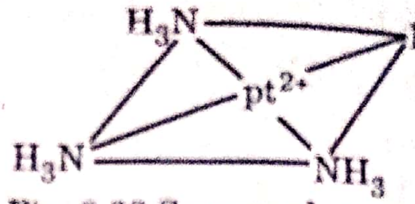
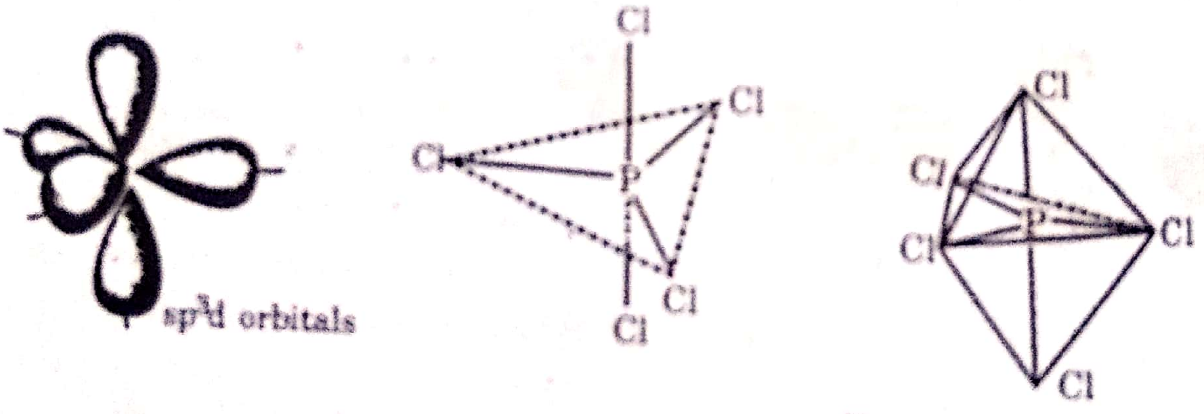


Fig. 2.32 Square planar strcutre of $[Pt(NH_3)_4]^{2+}$

(iv) *dsp*^{2} hybridization. would occur when one *s* orbital, two *p* orbitals (p_x, p_y) and one *d* orbital (from the next to outermost shell, $d_{x^2-y^2}$) mix together to give four equivalent hybrid orbitals. These four hybrid orbitals are directed to the corners of a square in the *xy* plane. This gives a square planar arrangement between them and the hybridization is, therefore, called *square planar hybridization*. Many compounds of nickel and platinum possess this square planar shape e.g., $[Pt(NH_3)_4]^{2+}$, $Ni(CN)_4^{2-}$.

***(v) dsp*^{3} hybridization** would occur when one *s* orbital, 3*p* orbitals and one d(d_{z^2}) of the outermost electronic shell, mix together to give five hybrid orbitals. These hybrid orbitals so formed are not equivalent and consist of one group of two equivalent oppositely directed orbitals and a second group of three equivalent orbitals. The five *sp*^{3}*d* or *dsp*^{3} hybrid orbitals are directed toward the corners of a trigonal bipyramid and this type of hybridization is, therefore, called **trigonal bipyramidal hybridization.** An example is PCl_5 molecule.



Trigonal bipyramidal structure

Fig. 2.33. *dsp*^{3} bonding configuration

***d*^{2}*sp*^{3} or *sp*^{3}*d*^{2} hybridization** occurs when one *s*, three *p* and two *d* orbitals (d_{z^2} and $d_{x^2-y^2}$) mix together to form six equivalent hybrid orbitals. The six *sp*^{3}*d*^{2} hybird orbitals are directed toward the corners of a regular octahedron. Four out of six hybrid orbitals are lying in one plane and are inclined to one another at 90° while the remaining two are directed above and below the plane containing the four hybrid orbitals perpendicularly. The formation of SF_6 molecule is an example of

sp^3d^2 hybridization. Each sp^3d^2 hybrid orbital is overlapped by a half-filled p orbtial from six fluorine atoms to form a total of six covalent bonds.

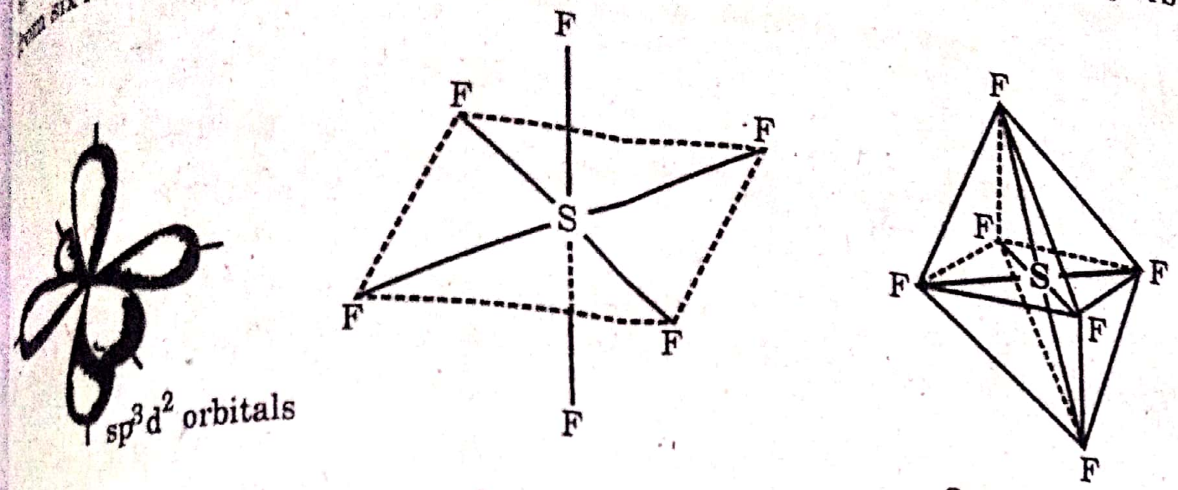


Fig. 2.34 d^2sp^3 bonding configuration

(vii) sp^3d^3 **Hybridization** ($s + p_x + p_y + p_z + d_{xy} + d_{yz} + d_{xz}$ AO's). Mixing of one s, three p and three d atomic orbitals gives seven sp^3d^3 hybrid orbitals which are directed towards the corners of a pentagonal-bipyramid. These are not equivalent hybrid orbitals. Five of them point towards the vertices of a regular pentagon while the other two are oriented perpendicular (90°) to the plane containing the first set of five hybrids. Examples are IF_7 molecule and XeF_6 molecule.

IF_7 molecule. The valence electronic configuration of iodine atom (central atom) in the ground state is $5s^2, 5p_x^2, 5p_y^2, 5p_z^1$. In order to make available seven singly-occupied orbitals for sp^3d^3 hybridization one 5s and two 5p electrons are promotated to the vacant high energy $5d_{xy}$, $5d_{yz}$ and $5d_{xz}$ orbitals. These seven atomic orbitals then hybridize to form seven sp^3d^3 hybrid orbitals all of which are singly-filled and, therefore overlap with seven singly-occupied $2p_z$ atomic orbitals of seven fluorine atoms to form seven I–F σ bonds. All these are $sp^3d^3 - p_z$ σ bonds and the molecule is pentagonal bipyramidal in shape (see Fig).

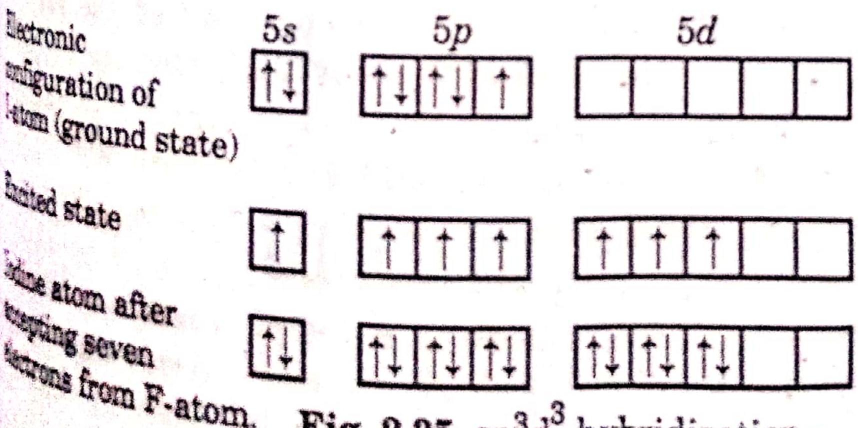


Fig. 2.35 sp^3d^3 hybridization

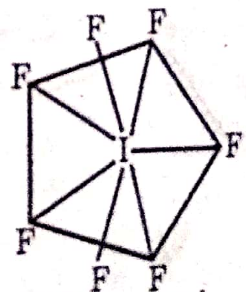


Fig. 2.36 Pentagonal bipyramidal IF_7 molecule.

Axial I-F distances are not the same as equatorial I-F distances. This confirms the nonequivalent nature of sp^3d^3 hybrid orbitals.

Table 2.3. Hybrid orbitals and their geometrical orientation

No. of electron pairs in outer shell	Hybrid orbitals	Orientation	Bond Angle	Examples
2	sp	Linear	180°	$BeCl_2$, C_2H_2
3	sp^2	Trigonal	120°	BF_3, GaI_3
4	sp^3	Tetrahedral	109.5°	CH_4, CCl_4, SiF_4
4	dsp^2	Square planar	90°	$Pt(NH_3)_4^{2+}$, $Ni(CN)_4^{2-}$
5	dsp^3	Trigonal planar	120° & 90°	PCl_5
6	d^2sp^3	Octahedral	90°	SF_6, $[Co(NH_3)_6]^{2+}$
7.	sp^3d^3	Pentagonal bipyramidal		IF_7, XeF_6

Summary of bridization

The important steps in hybridization are summarized as follows:

1. The formation of an excited state which involves unpairing of electrons followed by promotion of electrons to orbitals of higher energy. The promotion of electrons may take place between orbitals with the same principal quantum number *n* or between orbitals with different n values.
2. The pure atomic orbitals in the excited state are mixed or hybridized to form equivalent hybrid orbitals.
3. These hybrid orbitals have a definite orientations in space.

2.15 Molecular Orbital Theory (MOT)

The valence bond theory is based upon the assumption that the formation of a molecule involves an interaction between the electron waves of only the atomic orbitals of participating atoms which are half-filled. These bonding orbitals (half-filled) merge into one another to give a new orbital of a bigger size which is responsible for the stability of the system. All other orbitals on the atoms remain undisturbed.

According to the molecular orbital theory (developed by Hund, Mulliken and Huckel), all the valence electrons in molecule are associated with all the nuclei concerned. In other words, all the valence electrons have an influence on the stability of the molecule. (Inner-shell electrons may also make a contribution to the bonding but for many simple molecules the effect is small). Further more, MO theory considers that valence-shell atomic orbital cease to exist when a molecule is formed. They are replaced by a new set of energy levels with corresponding new charge-cloud distributions. These new energy levels are a property of the molecules as a whole, and are called, consequently, *molecular orbitals*. "*An electronic energy level in a molecule and the corresponding charge-cloud distribution in space is called*

...ular orbital". Molecular orbitals may be obtained by the linear combination of atomic orbitals (LC AO method) belonging to each atom in the molecule. The wave functions of the atomic orbitals are combined mathematically to produce wave functions for the resulting molecular orbitals. The molecular orbitals are polycentric and not monocentric as in the case of an atom. The number of molecular orbitals produced is equal to the number of original atomic orbitals combined. The rules for filling the electrons in these molecular orbitals are the same as for filling the atomic orbitals.

Let us consider the formation of a simple homonuclear diatomic molecule such as hydrogen molecule in which two identical atoms are linked by an electron pair. Although the atoms are identical but it will be convenient to distinguish the two atoms by writing, H_A and H_B. Each hydrogen atoms has a single electron in 1 s orbital. Let the wave functions for describing the two 1s atomic orbitals be Ψ_A and Ψ_B for hydrogen atoms H_A and H_B. The effective overlap of the wave functions Ψ_A and Ψ_B will take place only if (i) the orbitals have similar energy state (ii) the orbitals overlap to a considerable extent, and (iii) orbitals have the same symmetry. If these conditions are fulfilled by atomic orbitals of both the hydrogen atoms. The molecular orbital wave function ψ will be obtained by the linear combination of the atomic orbital wave function Ψ_A and Ψ_B.

$$\psi = C_A \Psi_A \ (1s) \pm C_B \Psi_B \ (1s) \tag{6}$$

where C_A end C_B are mixing coefficients which may be replaced by single coefficient, λ. Thus

$$\psi = \Psi_A \ (1s) \pm \lambda \ \Psi_B \ (1s) \tag{7}$$

λ gives the relative proportions of $\Psi_A(1s)$ and $\Psi_B(1s)$ in the molecular orbital in the ratio of $1^2 : \lambda^2$. Since both H_A and H_B are identical, thus atomic orbitals must make equal contributions to the molecular orbitals so that $\lambda^2 = 1$ or $\lambda = \pm 1$. Thus by substituting the values of λ in equation (7), two possible molecular orbitals wave functions are obtained, one from the addition and other from the subtraction i.e.,

$$\psi_{bonding} = \Psi_A \ (1s) + \psi_B \ (1s) \tag{8}$$

$$\psi_{antibonding} = \Psi_A \ (1s) - \psi_B \ (1s) \tag{9}$$

Since the probability of finding an electron in a particular space is expressed by ψ^2, squaring of equations (8) and (9) will give the expression for the probability of finding an electron at any point within the molecular orbitals and from this expression the corresponding boundary surfaces and also energy levels can be found.

$$\psi_b^2 = \psi_A^2 \ (1s)^2 + \psi_B^2 \ (1s)^2 + 2\psi_A \ (1s) \ \psi_B \ (1s) \tag{10}$$

$$\psi_a^2 = \psi_A^2 \ (1s)^2 + \psi_B^2 \ (1s)^2 - 2\psi_A \ (1s) \ \psi_B \ (1s) \tag{11}$$

The boundary surfaces and the relative energies of two MOs which are formed by combining two 1s AOs are shown in Fig. 2.37.