HYBRIDIZATION

A linear ombination of the orbitals of same atom is called "hybridization". The combination of n-atomic orbitals of an atom generates 'n' hybrid orbitals.

The hybrid orbitals have better directional properties and can form stronger bonds.

The important consideration is that.

I. The hybrid orbitals must be equivalent, which means that a symmetry operation of the molecule can transform one hybrid orbital into another
II. It must be normalized
III. It must be orthogonal

s-p hybridization

the combination of **one** 2s and **one** 2p orbital, giving two hybrid orbitals Ψ_1 and Ψ_2 may be expressed as.

$$\Psi_1 = a_1\Psi_{2s} + b_1\Psi_{2p} \qquad (1)$$

$$\Psi_2 = a_2\Psi_{2s} + b_2\Psi_{2p} \qquad (2)$$

The values of the linear combination coefficient a_1, b_1, a_2, b_2 may be determined by the following considerations.

I. Ψ_1 & Ψ_2 are normalized
II. Ψ_1 & Ψ_2 are orthogonal, and
III. Ψ_1 & Ψ_2 are equivalent

From Ist condition (normalization)

$$\int \Psi_1{}^2\, d\tau = a_1{}^2 \int \Psi_{2s}{}^2\, d\tau + b_1{}^2 \int \Psi_{2p}{}^2\, d\tau + 2a_1b_1 \int \Psi_{2s}\Psi_{2p}\, d\tau = 1$$

$$\Rightarrow\ a_1{}^2 + b_1{}^2 = 1 \qquad (3)$$

$$\int \Psi_2{}^2\, d\tau = a_2{}^2 \int \Psi_{2s}{}^2\, d\tau + b_2{}^2 \int \Psi_{2p}{}^2\, d\tau + 2a_2b_2 \int \Psi_{2s}\Psi_{2p}\, d\tau = 1$$

$$\Rightarrow\ a_2{}^2 + b_2{}^2 = 1 \qquad (4)$$

From (ii) condition (orthogonality)

$$\int \Psi_1\Psi_2\, d\tau = \int (a_1\Psi_{2s} + b_1\Psi_{2p})\,(a_2\Psi_{2s} + b_2\Psi_{2p})d\tau = 0$$

$$\Longrightarrow a_1a_2 \int \Psi_{2s}{}^2\, d\tau + a_1b_2 \int \Psi_{2s}\Psi_{2p}\, d\tau + b_1a_2 \int \Psi_{2p}\Psi_{2s}\, d\tau + +b_1b_2 \int \Psi_{2p}{}^2\, d\tau = 0$$

$$\Rightarrow\ a_1a_2 + b_1b_2 = 0 \qquad (5)$$

Sine the s-orbital is sperically symmetrical and the two hybrid orbitals $\Psi_1 \& \Psi_2$ are equivalent, the share of 's' function is equal in both $\Psi_1 \& \Psi_2$ i.e.

$$a_1{}^2 = a_2{}^2 = \frac{1}{2} \text{ or } a_1 = a_2 = \frac{1}{\sqrt{2}} \qquad (6)$$

Then from equation (3) we have

$$a_1{}^2 + b_1{}^2 = 1$$

We have

$$\frac{1}{2} + {b_1}^2 = 1$$

Or

$$b_1 = \frac{1}{\sqrt{2}} \qquad (7)$$

So that,

$$\Psi_1 = \frac{1}{\sqrt{2}}\left(\Psi_{2s} + \Psi_{2p}\right) \qquad (8)$$

Further from equation (5)

$$a_1 a_2 + b_1 b_2 = 0$$

we have

$$\frac{1}{\sqrt{2}} \times \frac{1}{\sqrt{2}} + \frac{1}{\sqrt{2}}\ b_2 = \frac{1}{\sqrt{2}}$$

$$\Rightarrow\ b_2 = -\frac{1}{\sqrt{2}} \qquad (9)$$

Therefore

$$\Psi_2 = \frac{1}{\sqrt{2}}\left(\Psi_{2s} - \Psi_{2p}\right) \qquad (10)$$

Where $\Psi_2 \& \Psi_2$ are given by equations (8) and (10) represent two sp-hybrid orbitals.

Directional characteristics of s-p hybrid orbitals can be determined as follows.

Using the normalized $f_2(\theta) \times f_3(\phi)$ *i.e* $Y(\theta, \phi)$ for 2s and 2p- orbitals and choosing $2p_z$, for example , as 2p orbital, we get the two sp-hybrid orbitals as:

$$\Psi_1 = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{4\pi}} + \sqrt{\frac{3}{4\pi}}\cos\theta\right]$$

and

$$\Psi_2 = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{4\pi}} - \sqrt{\frac{3}{4\pi}}\cos\theta\right] \qquad (11)$$

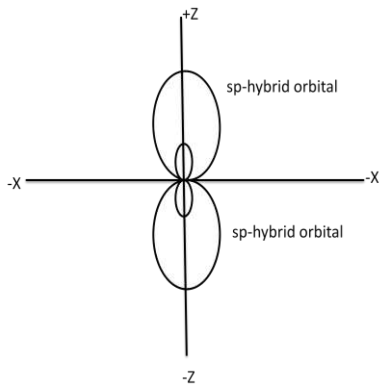
Taking out the factor $\frac{1}{\sqrt{4\pi}}$, we get the functions which determine the directions of the two hybrid orbitals

$$f_1 = \frac{1}{\sqrt{2}}\left[1 + \sqrt{3}\cos\theta\right]$$

and

$$f_2 = \frac{1}{\sqrt{2}}\left[1 - \sqrt{3}\cos\theta\right] \qquad (12)$$

The function f_1& f_2 are maximum for $\theta = 0$ (i.e in the +z direction) and $\theta = \pi$ (i.e in the -z direction) respectively. The value of maximum in either case is $\frac{1+\sqrt{3}}{\sqrt{2}} = 1.932$, which is greater than that for the pure 2s orbital ($f = 1$) or a 2p orbital ($f = \sqrt{3} = 1.732$. While the simple p_z – orbital is directed along both +z and -z directions, an sp-hybrid orbital is directed towards only either +z or -z and the angle between the two being 180^o. The polar plots of f_1 and f_2 for various values of θ are shown below.



Polar plots of sp-hybrid orbitals

The angle between two hybrid orbital is calculated using the relation.

$$\cos\theta = -\frac{s\ character\ of\ hybrid\ orbital}{1 - s\ character\ of\ hybrid\ orbital}$$

sp-hybridization is responsible for linear structure of acetylene

$sp^2 - HYBRIDIZATION$

Wave function of sp² hybrid orbitals

For the three hybrid orbitals, we may write

$$\Psi_1 = a_1\Psi_S + b_1\Psi_{p_x} + c_1\Psi_{p_y}$$

$$\Psi_2 = a_2\Psi_S + b_2\Psi_{p_x} + c_2\Psi_{p_y}$$

$$\Psi_3 = a_3\Psi_S + b_3\Psi_{p_x} + c_3\Psi_{p_y}$$

i. Since the charge density of s orbital is equally divded among the three hybrid orbitals, we get

$$a_1{}^2 = a_2{}^2 = a_3{}^2 = \tfrac{1}{3} \text{ i.e } a_1 = a_2 = a_3 = \tfrac{1}{\sqrt{3}}$$

ii. If we assume Ψ_1 to point towards x-axis, then the contribution of p_y orbital in this will be zero, i.e

$$c_1 = 0$$

iii. Normalization condition of Ψ_1 gives

$$a_1{}^2 = b_1{}^2 = 1$$

Since $a_1 = \frac{1}{\sqrt{3}}$ we get

$$b_1 = \sqrt{\frac{2}{3}}$$

iv. Orthogonal conditions of Ψ_1 & Ψ_2 and Ψ_1 & Ψ_3 gives

$$a_1a_2 + b_1b_2 = 0$$
$$a_1a_3 + b_1b_3 = 0$$

Hence

$$b_2 = -\frac{a_1a_2}{b_1} = -\frac{{}^1\!/_3}{\sqrt{{}^2\!/_3}} = -\frac{1}{\sqrt{6}}$$

$$b_3 = -\frac{a_1a_3}{b_1} = -\frac{{}^1\!/_3}{\sqrt{{}^2\!/_3}} = -\frac{1}{\sqrt{6}}$$

v. Normalization condition of Ψ_2 gives $a_2{}^2 + b_2{}^2 + c_2{}^2 = 1$
Hence

$$c_2{}^2 = 1 - \left(a_2{}^2 + b_2{}^2\right) = 1 - \left(\frac{1}{3} + \frac{1}{6}\right) = \frac{1}{2} \; or \; c_2 = \frac{1}{\sqrt{2}}$$

vi. Normalization condition of Ψ_3 gives

$$a_3{}^2 + b_3{}^2 + c_3{}^2 = 1$$

$$c_3{}^2 = 1 - \left(a_3{}^2 + b_3{}^2\right) = 1 - \left(\frac{1}{3} + \frac{1}{6}\right) = \frac{1}{2} \; or \; c_3 = -\frac{1}{\sqrt{2}}$$

(For Ψ_2 and Ψ_3 to be different, we take the mius root of c_3)

Hence three functions are

$$\Psi_1 = \tfrac{1}{\sqrt{3}}\Psi_s + \sqrt{2/3}\,\Psi_{p_x} \qquad (1)$$

$$\Psi_2 = \tfrac{1}{\sqrt{3}}\Psi_s - \tfrac{1}{\sqrt{6}}\Psi_{p_x} + \tfrac{1}{\sqrt{2}}\Psi_{p_y} \qquad (2)$$

$$\Psi_3 = \tfrac{1}{\sqrt{3}}\Psi_s - \tfrac{1}{\sqrt{6}}\Psi_{p_x} + \tfrac{1}{\sqrt{2}}\Psi_{p_y} \qquad (3)$$

Angle between the hybrid orbitals

Utilizing the expressions

$$p_z = \sqrt{3}\cos\theta$$

$$p_x = \sqrt{3}\sin\theta\cos\Psi$$

$$p_y = \sqrt{3}\sin\theta\sin\Psi$$

(Where θ is tha angle which radius vector makes with z-axis and Ψ is tha angle which the projection of radius vector in xy plane makes with x-axis)

we get,

$$\Psi_1 = \frac{1}{\sqrt{3}} + \frac{2}{\sqrt{3}}\sqrt{3}\sin\theta\cos\Psi$$

$$\Psi_2 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}}\sqrt{3}\sin\theta\cos\Psi + \frac{1}{\sqrt{2}}\sqrt{3}\sin\theta\sin\Psi$$

$$\Psi_3 = \frac{1}{\sqrt{3}} - \frac{1}{\sqrt{6}}\sqrt{3}\sin\theta\cos\Psi - \frac{1}{\sqrt{2}}\sqrt{3}\sin\theta\sin\Psi$$

Since the p_z orbital does not appear in the equation (1)-(3), we may conclude that all three orbitals lie in the xy-plane for which angle θ is equal to 90°. thus, the above relation become

$$\Psi_1 = \tfrac{1}{\sqrt{3}} + 2\cos\Psi \qquad (4)$$

$$\Psi_2 = \tfrac{1}{\sqrt{3}} - \tfrac{1}{\sqrt{2}}\cos\Psi + \sqrt{3/2}\,\sin\Psi \qquad (5)$$

$$\Psi_3 = \tfrac{1}{\sqrt{3}} - \tfrac{1}{\sqrt{2}}\cos\Psi - \sqrt{3/2}\,\sin\Psi \qquad (6)$$

Let Ψ_1 have its maximum on x-axis. In order to find the direction of maximum of Ψ_2, we equate $\frac{d\Psi_2}{d\Psi} = 0$. Thus, we have

$$\frac{d\Psi_2}{d\Psi} = \frac{1}{\sqrt{2}}\sin\Psi + \sqrt{3/2}\,\cos\Psi = 0$$

Or

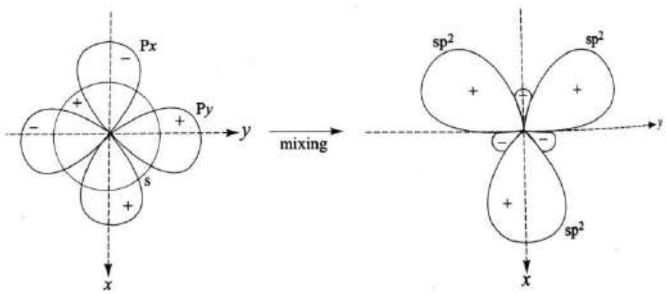
$$\tan\Psi = -\sqrt{3/2}\,.\sqrt{2} = -\sqrt{3} = -1.7322$$

Hence $\Psi = 120°$

Thus the three hybrid orbitals are inclined at an angle of $120°$ with each other.

Shape of the hybrid orbitals

The function Ψ_1 will have its maximum, say on x-axis, for which $\Psi = 0$. This maximum relative to s-orbital has a value of $1 + \sqrt{2} = 2.414$. In comparison to p_x orbital ($\theta = 90°, \Psi = 0$, maximum = 1.732), the sp^2 orbital is better in overlapping with the orbital of another atom. The function $\Psi_1, \Psi_2 \& \Psi_3$ when plotted against different values of Ψ give the orbitals as shown in the following figure.



sp^3 – HYBRIDIZATION

Wave function of sp^3 hybrid orbitals

For the four hybrid orbitals, we may write

$$\Psi_1 = a_1\Psi_S + b_1\Psi_{p_x} + c_1\Psi_{p_y} + d_1\Psi_{p_z}$$

$$\Psi_2 = a_2\Psi_S + b_2\Psi_{p_x} + c_2\Psi_{p_y} + d_2\Psi_{p_z}$$

$$\Psi_3 = a_3\Psi_S + b_3\Psi_{p_x} + c_3\Psi_{p_y} + d_3\Psi_{p_z}$$

$$\Psi_4 = a_4\Psi_S + b_4\Psi_{p_x} + c_4\Psi_{p_y} + d_4\Psi_{p_z}$$

i. Since the charge density of s orbital is to be distributed equally over all the four orbitals, we get

$$a_1{}^2 = a_2{}^2 = a_3{}^2 = a_4{}^2 = \frac{1}{4} \text{ i.e } a_1 = a_2 = a_3 = a_4 = \frac{1}{2}$$

ii. Let us develop Ψ_1 on the x-axis. It is obvious that the combination of Ψ_{p_x}&Ψ_{p_z} in the function Ψ_1 will be zero and hence we may write

$$c_1 = 0 \text{ and } d_1 = 0$$

iii. Normalization condition of Ψ_1 gives

$$a_1{}^2 = b_1{}^2 = 1 \text{ or } b_1{}^2 = 1 - a_1{}^2 = 1 - \frac{1}{4} = \frac{3}{4}$$

Hence

$$b_1 = \frac{\sqrt{3}}{2}$$

iv. Orthogonal conditions of Ψ_1 and Ψ_2, Ψ_1 and Ψ_3, and Ψ_1 & Ψ_4 gives

$$a_1a_2 + b_1b_2 = 0$$
$$a_1a_3 + b_1b_3 = 0$$
$$a_1a_4 + b_1b_4 = 0$$

Hence

$$b_2 = b_3 = b_4 = -\frac{a_1 a_2}{b_1} = -\frac{1/4}{\sqrt{3}/2} = -\frac{1}{2\sqrt{3}}$$

v. We assume that Ψ_2 lies on xz-plane. Hence the contribution of p_y in Ψ will be zero i.e

$$c_2 = 0$$

vi. Normalization condition of Ψ_2 gives ${a_2}^2 + {b_2}^2 + {d_2}^2 = 1$

Hence

$$ {d_2}^2 = 1 - \left({a_2}^2 + {b_2}^2\right) = 1 - \left(\frac{1}{4} + \frac{1}{12}\right) = 1 - \frac{1}{3} \; or \; {d_2}^2 = \sqrt{\frac{2}{3}}$$

vii. Orthogonal conditions of Ψ_2 and Ψ_3 ,and Ψ_2 & Ψ_4 gives

$$a_2 a_3 + b_2 b_3 + d_2 d_3 = 0$$
$$a_2 a_4 + b_2 b_4 + d_2 d_4 = 0$$

Hence

$$d_3 = d_4 = -\frac{a_2 a_3 + b_2 b_3}{d_2} = -\frac{1/4 + 1/12}{\sqrt{\frac{2}{3}}} = -\frac{1}{\sqrt{6}}$$

viii. Normalization condition of Ψ_3 gives

$${a_3}^2 + {b_3}^2 + {c_3}^2 + {d_3}^2 = 1$$

i.e

$$\frac{1}{4} + \frac{1}{12} + {c_3}^2 + \frac{1}{6} = 1$$
$${c_3}^2 = \frac{1}{2} \; or \; c_3 = +\frac{1}{\sqrt{2}}$$

ix. For the normalization condition of Ψ_4, we take

$$c_4 = -\frac{1}{\sqrt{2}}$$

Hence the four functions are

$$\Psi_1 = \tfrac{1}{2}\Psi_s + \tfrac{\sqrt{3}}{2}\Psi_{p_x}$$
$$\Psi_2 = \tfrac{1}{2}\Psi_s - \tfrac{1}{2\sqrt{3}}\Psi_{p_x} + \sqrt{\tfrac{2}{3}}\Psi_{p_z}$$
$$\Psi_3 = \tfrac{1}{2}\Psi_s - \tfrac{1}{2\sqrt{3}}\Psi_{p_x} + \tfrac{1}{\sqrt{2}}\Psi_{p_y} - \tfrac{1}{\sqrt{6}}\Psi_{p_z}$$
$$\Psi_4 = \tfrac{1}{2}\Psi_s - \tfrac{1}{2\sqrt{3}}\Psi_{p_x} - \tfrac{1}{\sqrt{2}}\Psi_{p_y} - \tfrac{1}{\sqrt{6}}\Psi_{p_z}$$

Angle between the hybrid orbitals

Utilizing the expression

$$p_z = \sqrt{3}\cos\theta$$

$$p_x = \sqrt{3}\sin\theta\cos\Psi$$

$$p_y = \sqrt{3}\sin\theta\sin\Psi$$

we get,

$$\Psi_1 = \frac{1}{2} + \frac{\sqrt{3}}{2}\ (\sqrt{3}\sin\theta\cos\Psi)$$

$$\Psi_2 = \frac{1}{2} - \frac{1}{2\sqrt{3}}\ (\sqrt{3}\sin\theta\cos\Psi) + \sqrt{\frac{2}{3}}(\sqrt{3}\cos\theta)$$

$$\Psi_3 = \frac{1}{2} - \frac{1}{2\sqrt{3}}\left(\sqrt{3}\sin\theta\cos\Psi\right) + \frac{1}{\sqrt{2}}\left(\sqrt{3}\sin\theta\sin\Psi\right) - \frac{1}{\sqrt{6}}(\sqrt{3}\cos\theta)$$

$$\Psi_4 = \frac{1}{2} - \frac{1}{2\sqrt{3}}\left(\sqrt{3}\sin\theta\cos\Psi\right) - \frac{1}{2}\left(\sqrt{3}\sin\theta\sin\Psi\right) - \frac{1}{\sqrt{6}}(\sqrt{3}\cos\theta)$$

Let Ψ_1 have its maximum on x-axis, for θ=90° & Ψ=0°. Thus, the relative magnitude of Ψ_1 on x-axis

$$\frac{1}{2} + \frac{3}{2} = 2$$

This may be compared with the value of 1.732 of the p_z orbital.

We have assumed the function Ψ_2 to lie on the xz-plane. We take Ψ=180° for this plane. Substituting this value of Ψ in Ψ_2, we get

$$\Psi_2 = \frac{1}{2} + \frac{1}{2}\ \sin\theta + \sqrt{2}\cos\theta$$

Setting $\frac{d\Psi_2}{d\theta} = 0$, we get

$$\frac{1}{2}\ \cos\theta - \sqrt{2}\sin\theta = 0$$

Or

$$\tan\theta = \frac{1}{2\sqrt{2}} = \frac{1}{2.828} = 0.354$$

Hence $\theta = 19°28'$

Since θ is the angle between the axis of Ψ_2 and the z-axis, the angle between the axes of Ψ_1&Ψ_2 is $90° + 19°28' = 109°28'$.

The spatial arrangement of the four hybrid angles is tetrahedral.

Shape of the hybrid orbitals

Is given in the following diagram.