

Forms of Schrodinger wave equations:

There are two forms of Schrodinger wave equation. They are,

1) Time Independent wave equation

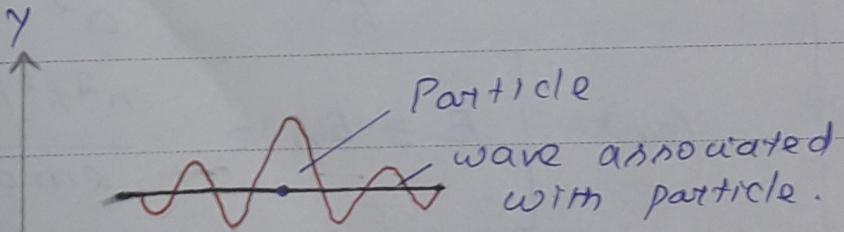
This is applicable only to steady state conditions in which, the wave function can have variation only with position but not with time. It does not involve the imaginary quantity 'i'.

2) Time dependent wave equation:

This takes care of both the position and time variations of the wave function.

It involves the imaginary quantity 'i'.

Derivation of Schrodinger Time Independent wave equation:



The classical differential equation for wave motion
is given by

$$\frac{d^2\varphi}{dx^2} + \frac{d^2\varphi}{dy^2} + \frac{d^2\varphi}{dz^2} = \frac{1}{v^2} \frac{d^2\varphi}{dt^2} \rightarrow \textcircled{1}$$

Eqn \textcircled{1} can be written as $(V \text{ is the velocity})$

$$V^2 \varphi = \frac{1}{v^2} \frac{d^2\varphi}{dt^2} \rightarrow \textcircled{2} \quad (V^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \text{ is the Laplacian's operator})$$

The solution of eqn \textcircled{2} gives φ as a periodic variations
in terms of time t ,

$$\varphi(x, y, z, t) = \varphi_0(x, y, z) e^{-i\omega t} \rightarrow \textcircled{3}$$

ω - angular velocity

Differentiating eqn \textcircled{3} with respect to t , we get

$$\frac{\partial \varphi}{\partial t} = -i\omega \varphi_0 e^{-i\omega t}$$

Again differentiating with respect to 't' we have

$$\frac{\partial^2 \varphi}{\partial t^2} = (-i\omega)(-i\omega) \varphi_0 e^{-i\omega t}.$$

$$(or) \quad \frac{\partial^2 \varphi}{\partial t^2} = i^2 \omega^2 \varphi_0 e^{-i\omega t} \quad \because i^2 = -1$$

$$\frac{\partial^2 \varphi}{\partial t^2} = -\omega^2 \varphi \rightarrow \textcircled{4} \quad (+\varphi = \varphi_0 e^{-i\omega t})$$

Substituting eqn 1. \textcircled{4} in \textcircled{2} we have

$$V^2 \varphi = \frac{1}{v^2} \times (-\omega^2 \varphi)$$

$$\frac{V^2 \varphi}{v^2} = -\frac{\omega^2}{v^2} \varphi$$

(or)

$$\nabla^2 \psi + \frac{\omega^2}{v^2} \psi = 0 \rightarrow ⑤$$

We know that angular frequency $\omega = 2\pi\nu = 2\pi \frac{v}{\lambda}$

Here ν is the frequency & v is the velocity.

$$\therefore \omega = 2\pi \frac{v}{\lambda}$$

$$(or) \quad \frac{\omega}{v} = \frac{2\pi}{\lambda} \rightarrow ⑥$$

Squaring the eqn. ⑥ on both sides, we get

$$\frac{\omega^2}{v^2} = \frac{4\pi^2}{\lambda^2} = \frac{4\pi^2}{\lambda^2} \rightarrow ⑦$$

Substituting eqn. ⑦ in ⑤ we get

$$\nabla^2 \psi + \frac{4\pi^2}{\lambda^2} \psi = 0 \rightarrow ⑧$$

On substituting $\lambda = \frac{\hbar}{mv}$ in eqn. ⑧, we get

$$\nabla^2 \psi + \frac{4\pi^2}{\frac{\hbar^2}{m^2 v^2}} \psi = 0$$

$$\nabla^2 \psi + \frac{4\pi^2 m^2 v^2}{\hbar^2} \psi = 0 \rightarrow ⑨$$

If E is the total energy of the particle,

V is the potential energy & $\frac{1}{2}mv^2$ is the kinetic energy, then,

Total Energy = Potential Energy + Kinetic Energy

$$E = V + \frac{1}{2}mv^2$$

$$(or) \quad E - V = \frac{1}{2}mv^2$$

$$(or) \quad 2(E - V) = mv^2$$

$$i.e. \quad mv^2 = 2(E - V)$$

Multiplying by ' m ' on both the sides, we get

$$m^2 v^2 = 2m(CE - V) \rightarrow \textcircled{10}$$

Substituting eqn. \textcircled{10} in eqn \textcircled{9} we get

$$\nabla^2 \psi + \frac{4\pi^2}{\hbar^2} \times 2m(CE - V)\psi = 0$$

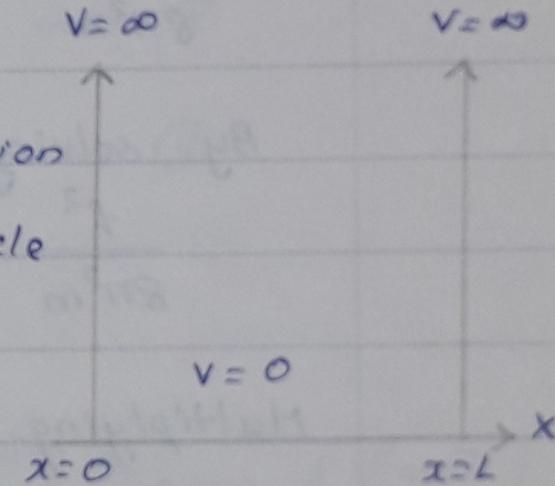
$$\left[\nabla^2 \psi + \frac{8\pi^2 m}{\hbar^2} (CE - V)\psi = 0 \right] \rightarrow \textcircled{11}$$

Eqn \textcircled{11} is known as Schrodinger time independent wave equation for three dimensions.

Particle in One Dimensional Box:

Consider a particle

constrained to move only in x direction from $x=0$ to $x=L$. As the particle is moving only inside the box, the probability of finding the particle outside the box is zero. As the particle is inside the box, the pot. energy of the particle is zero whereas at the boundary or outside the box, the pot. energy is infinity. ($V=\infty$)



The Schrodinger wave equation in the operator form

is $\hat{H} \psi = E \psi \rightarrow ①$

where \hat{H} - Hamiltonian operator in x direction)

\hat{H} is given by Schrodinger equation as,

$$\hat{H} = -\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2} + V \rightarrow ②$$

where V is the pot. energy & m - mass & \hbar - Planck's constant).

Substituting the value of \hat{H} in eqn. ①

$$-\frac{\hbar^2}{8\pi^2 m} \cdot \frac{d^2 \psi}{dx^2} + V \psi = E \psi \rightarrow ③$$

(or)

$$-\frac{\hbar^2}{8\pi^2 m} \cdot \frac{d^2 \psi}{dx^2} + V \psi - E \psi = 0 \rightarrow ④$$

By solving the above eqn. we get

$$\frac{\hbar^2}{8\pi^2 m} \cdot \frac{d^2 \psi}{dx^2} + (E - V) \psi = 0 \rightarrow ⑤$$

Multiplying throughout the eqn. by $\frac{8\pi^2 m}{\hbar^2}$ we get,

$$\frac{\hbar^2}{8\pi^2 m} \times \frac{8\pi^2 m}{\hbar^2} \cdot \frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{\hbar^2} (E - V) \psi = 0$$

$$\therefore \frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{\hbar^2} (E - V) \psi = 0 \rightarrow ⑥$$

Now, Here are two conditions.

1. Outside the box

2. Inside the box.

For outside the box, the pot. energy $V = \infty$.

Substituting the value of $V = \infty$ in the above eqn/.

we get,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{L^2} (E - \infty) \psi = 0. \rightarrow \textcircled{7}$$

This is possible only when $\psi = 0$, which means,
the particle is not outside the box.

For a particle inside the box, the eqn. is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{L^2} (E - 0) \psi = 0.$$

(or)

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{L^2} E \psi = 0 \rightarrow \textcircled{8}$$

$$\text{(or)} \quad \frac{d^2\psi}{dx^2} + \textcircled{8} k^2 \psi = 0 \rightarrow \textcircled{9}$$

i.e. $k^2 = \frac{2mE}{L^2}$ & $k = \frac{\lambda}{2\pi}$.

$$\therefore k^2 = \frac{2mE}{\frac{L^2}{4\pi^2}} \quad \text{(or)} \quad \frac{2mE}{L^2} \times \frac{4\pi^2}{\text{(or)}} \quad \frac{8\pi^2 m E}{L^2}$$

Wave function can be represented in terms of trigonometry functions.

$$\psi(x) = A \sin kx + B \cos kx. \rightarrow \textcircled{10}$$

where A & B - arbitrary constants.

When $x=0$, $\psi_{(0)} = 0$.

$$\therefore 0 = A \sin 0 + B \cos 0 \quad (\sin 0 = 0 \times \\ \cos 0 = 1)$$
$$\therefore 0 = 0 + B$$

$$(\text{or}) \quad B = 0.$$

When $x=L$ (This is the boundary condition where the probability of finding the e^- is 0)

When $x=L$ $\psi_{(L)} = 0$.

Substituting this value in eqn. ⑩ we get

$$0 = A \sin kL + 0.$$

$\sin kL = 0 \times kL = n\pi$ where n is an integer i.e $0, 2\pi, 3\pi, \dots$

$$A \sin kL = 0$$

$$(\text{or}) \quad kL = n\pi$$

$$k = \frac{n\pi}{L}$$

$$\text{but } k^2 = \frac{\omega m E}{\hbar^2}$$

$$(\text{or}) \quad \frac{n^2 \pi^2}{L^2} = \frac{\omega m E}{\hbar^2} \times 4\pi^2$$

By solving the eqn. we get,

$$E = \frac{n^2 \hbar^2}{8m L^2}$$

This is the formula which will give the energy of the particle in one dimensional box.

Molecular Orbital Theory :

(MO theory is another approach to explain the formation of covalent bonds in molecules or ions. This theory is also called as Hund - Mulliken theory. This theory is based on Linear combination of atomic orbitals (LCAO) of the atoms constituting the molecule and hence it is called LCAO theory.)

(According to this theory), all the e^- s in a given molecule or ion are considered to be present in molecular orbitals. Thus, these e^- s move under the influence of all the nuclei of all the constituent atoms making the molecule or ion.

Salient Features of MO theory (or) Rules for LCAO :

- When two isolated atomic orbitals (or wave functions) residing on two atoms having similar energy and same symmetry combine linearly with each other, by linear combination of atomic orbitals (LCAO method), two molecular orbitals are obtained.

It may be from homo nuclear diatomic molecule ($H_2, H_2^+, H_2^-, N_2, O_2, O_2^+, O_2^- \dots$) or from hetero nuclear

diatomic molecule ion (CO, CN, NO...)

(When three atomic orbitals of same energy & same symmetry combine with one another three MOs are obtained. Hence, we conclude that the number of MOs obtained is always equal to the number of atomic orbitals combining together.)

2. Two different ways of LCAO and formation of bonding & antibonding molecular orbitals:

Suppose the wave functions of two atomic orbitals on two atoms A and B of AB type molecule (hetero nuclear diatomic molecule) are represented as ψ_A & ψ_B respectively. There are two different ways in which ψ_A & ψ_B can combine linearly with each other. They are,

a) Additive (or) positive (or) + overlap and formation of bonding MO.

In this type of linear combination, the positive lobe (+) of ψ_A overlaps with the positive lobe of ψ_B (+) and a molecular orbital is formed. This MO has lower energy & results in a stable chemical bond formed by the attraction between the two

nuclei called bonding molecular orbital which is represented as ψ_b .

b) Subtractive overlap (or) negative lobe + overlap and formation of antibonding MO:

In this type of linear combination, the positive lobe of ψ_A overlaps with the negative lobe of ψ_B and a molecular orbital is formed. This MO has higher energy than each of the two atomic orbital, and the formation of MO produces repulsion between the two nuclei of A & B. Since, this MO opposes the formation of any bond between the nuclei, it is called antibonding MO which is represented as ψ^* .

(The + & - signs of the lobes are only geometric signs of AO wave function and not '+' & '-' charges)

(The formation of bonding MO wavefunction & anti-bonding MO wavefunction by the linear combination of two atomic orbital wave function can be represented as,

$$\psi_b = +\psi_A + \psi_B \quad (++ \text{ overlap}) \rightarrow 1$$

$$\psi^* = +\psi_A - \psi_B \quad (+- \text{ overlap}) \rightarrow 2$$

When we show the contributions made by

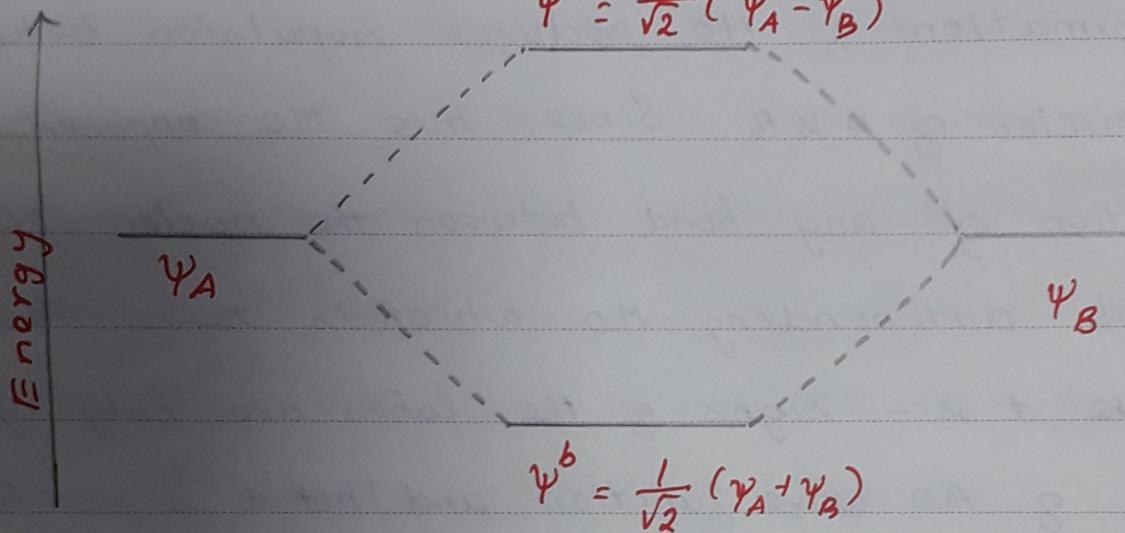
ψ_A & ψ_B in ψ^b & ψ^* MOs the above equations can be written as,

$$\psi^b = \frac{1}{\sqrt{2}} (\psi_A + \psi_B)$$

$$\psi^* = \frac{1}{\sqrt{2}} (\psi_A - \psi_B)$$

Obviously, the sum of the squares of ψ_A & ψ_B in MO wave function is equal to unity for both bonding & anti-bonding MO. $\left[\left(\frac{1}{\sqrt{2}} \right)^2 + \left(\frac{1}{\sqrt{2}} \right)^2 = 1 \right]$

$$\psi^* = \frac{1}{\sqrt{2}} (\psi_A - \psi_B)$$



Relative order of the energy of ψ_A , ψ_B , ψ^b & ψ^*

When two atomic orbitals of same energy and same symmetry combine together linearly, two molecular orbitals wave functions are obtained.

One of these MO wave function is bonding and another is antibonding. Bonding MO wave function has lower energy than anti-bonding MO wave function.

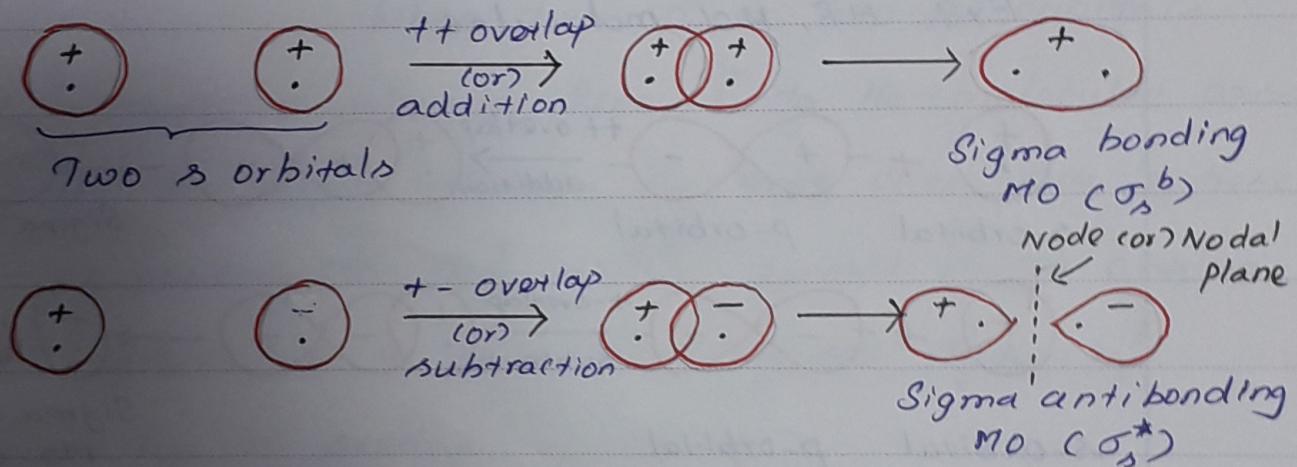
Molecular Orbitals formed by the combination 8

1. s-s orbital :

When two s-orbitals overlap with each other, two σ molecular orbitals are obtained.

1. Sigma bonding MO σ_s^b - when '+' lobe of one s orbital combine with '+' lobe of another s orbital. This is $++$ overlap or addition of orbital.

2. Sigma anti bonding MO σ_s^* - when '+' lobe of one s orbital combine with '-' lobe of another s orbital. This is $+-$ overlap or subtraction of orbitals.



In σ_s^b orbital, the e⁻ density between the nuclei of combining atoms is very high and hence a stable bond is formed. On the other hand,

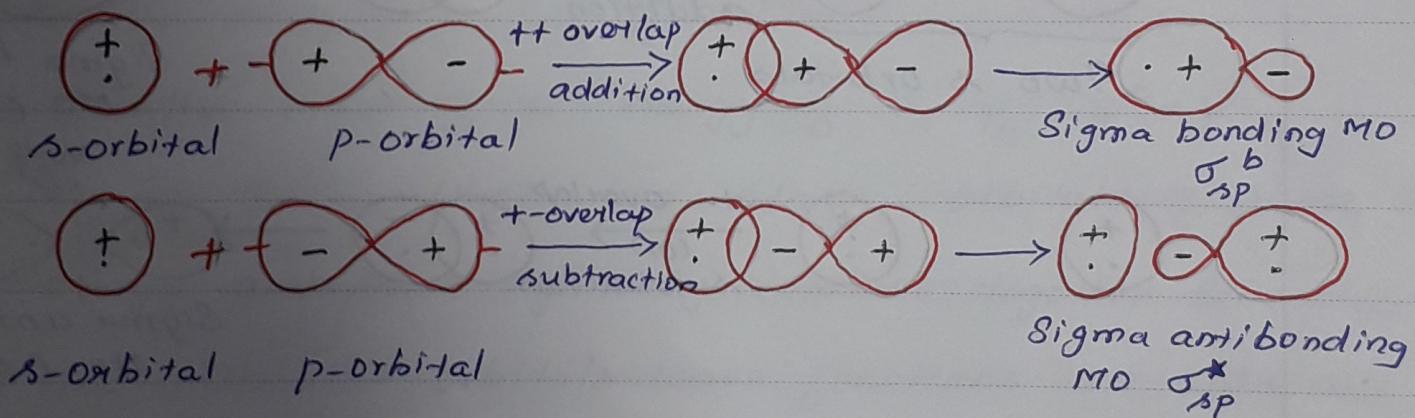
in σ_s^* orbital, the e⁻ density between the nuclei is negligible and hence the nuclei fly apart.

σ_{s^b} orbital has no node while σ_s^* orbital has one node.

2. S-P orbital:

If x-axis is assumed to be the molecular (or) internuclear axis, then the overlap of one s and one p orbital along x-axis gives rise to the formation of two molecular orbitals, one of which is sigma bonding MO σ_{sp}^b obtained by + overlap and another one is sigma antibonding MO σ_{sp}^* obtained by - overlap.

Ex: HF, HCl molecules.

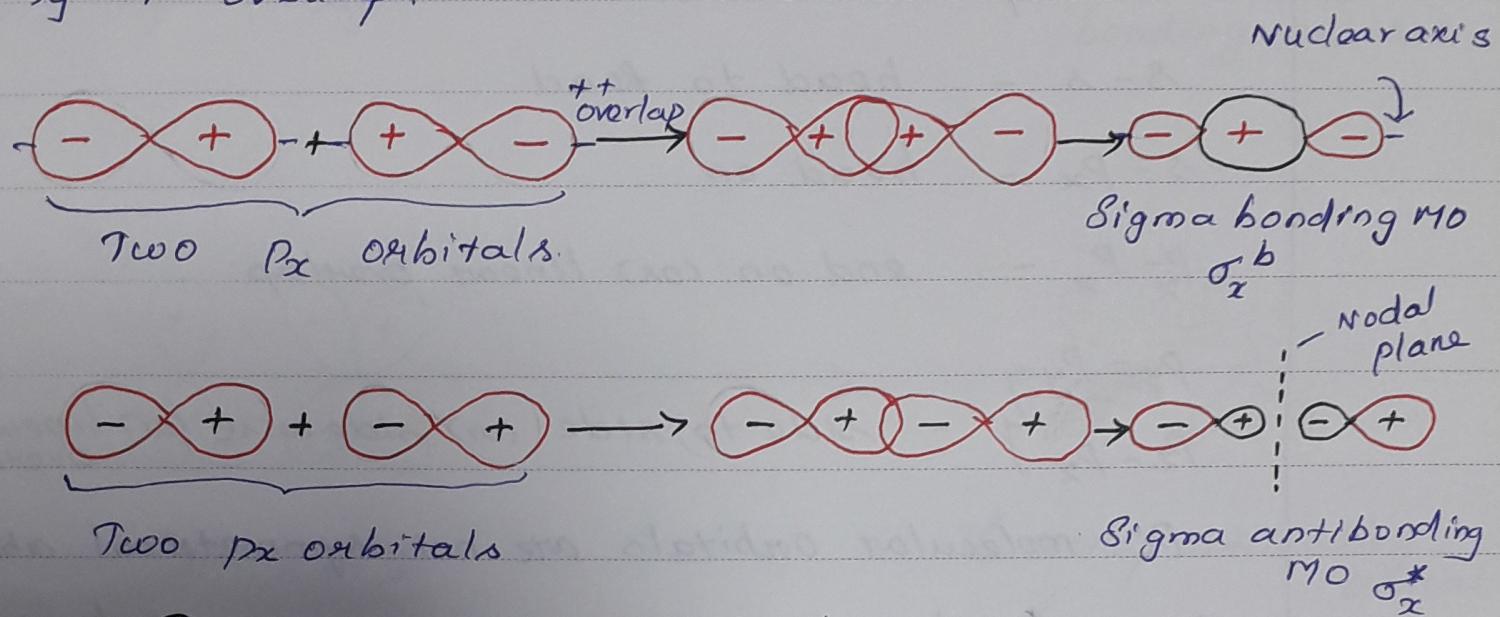


3. P-P orbitals:

i) Two p_x orbitals:

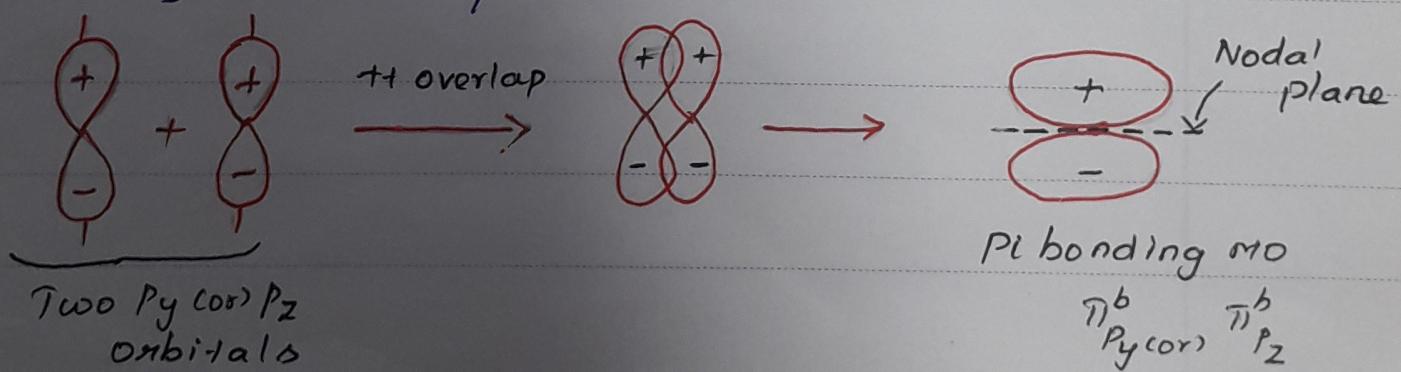
If x axis is assumed to be

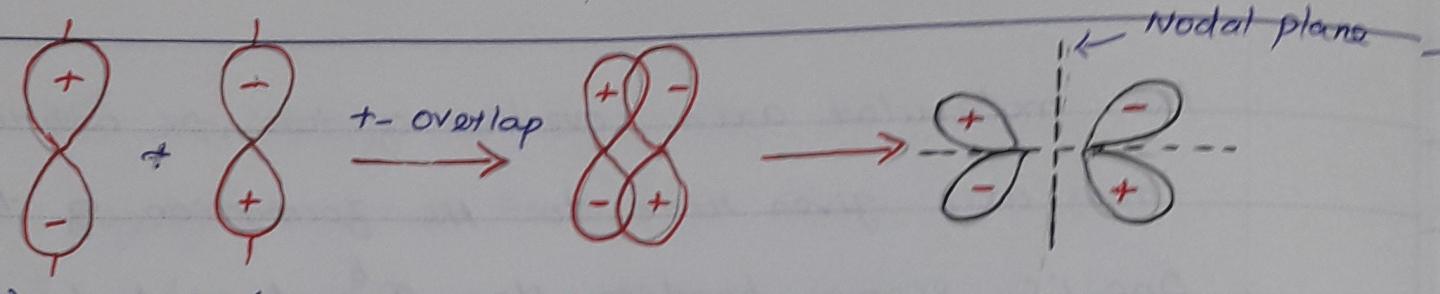
the molecular axis, overlap of two p_x orbitals along this axis gives rise to the formation of two G MOs. One is sigma bonding MO σ_x^b formed by $++$ overlap & another one is sigma antibonding MO σ_x^* formed by $+ -$ overlap.



(ii) Two p_y or Two p_z orbitals:

When two p_y or two p_z orbitals overlap together along a line \perp to the molecular axis, two pi MOs are formed in each case. One of these is pi bonding MO π_y^b (or) π_z^b formed by $++$ overlap and another one is pi antibonding MO π_y^* (or) π_z^* formed by $+ -$ overlap.





Two p_z orbitals

Overlap between

$s-s$ - head to head

$s-p_z$ - head on

$p_x-p_{z^*}$ - end on (or) linear overlap

p_y-p_y

p_z-p_z - side to side (or) sideways (or) linear overlap.

Pc molecular orbitals are not symmetrical about the molecular axis as the e⁻ density in $\text{p}_y^b \& \text{p}_z^b$ MO is zero on the nuclear axis and it is concentrated in the region above and below the nodal plane. $\text{p}_y^b \& \text{p}_z^b$ orbitals have the same energy & hence these are called degenerate orbitals.