Molecular orbital Theory ÷

According to VBT, a molecule is considered ~~made up~~ to be made up of atoms. Electrons in atoms occupy atomic orbitals.

These may or may not be hybridised. If they are hybridized, atomic orbitals from the same atom combine to produce hybrid orbitals which can overlap more effectively with orbitals from other atoms, thus producing stronger bonds. Thus the atomic orbitals (or the hybrid orbitals) are thought to remain even when the atom is chemically bonded in a molecule.

→ In the MOT, the valency electrons are considered to be associated with all the nuclei in the molecule. Thus the atomic orbitals from different atoms must be combined to produce molecular orbitals.

→ Functioning of molecular orbitals may be obtained by two methods.

1. Linear combination of atomic orbitals (LCAO)
2. United atom method.

LCAO Method :-

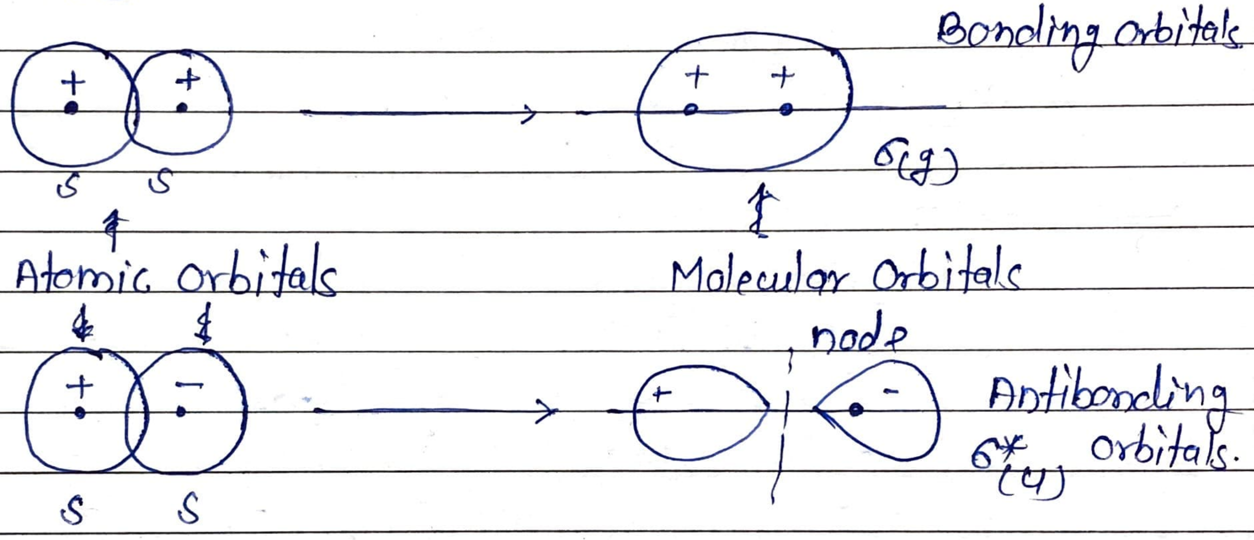
1. s-s combination of orbitals :-

Two possible combination.

i) when the sign of the two wavefunctions are the same

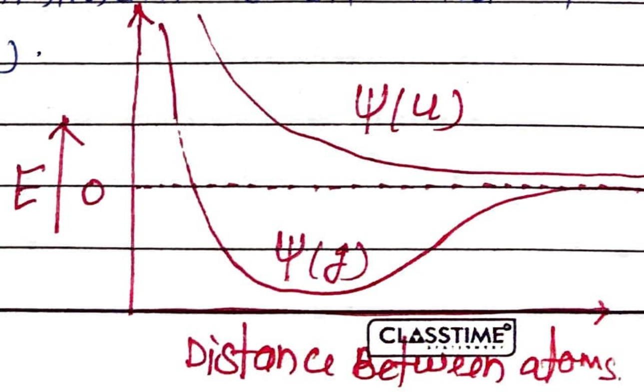
ii) when the sign of the two wave functions are different.

when a pair of atomic orbitals ψ_A and ψ_B combine they give rise to a pair of molecular orbitals $\psi_{(g)}$ and $\psi_{(u)}$



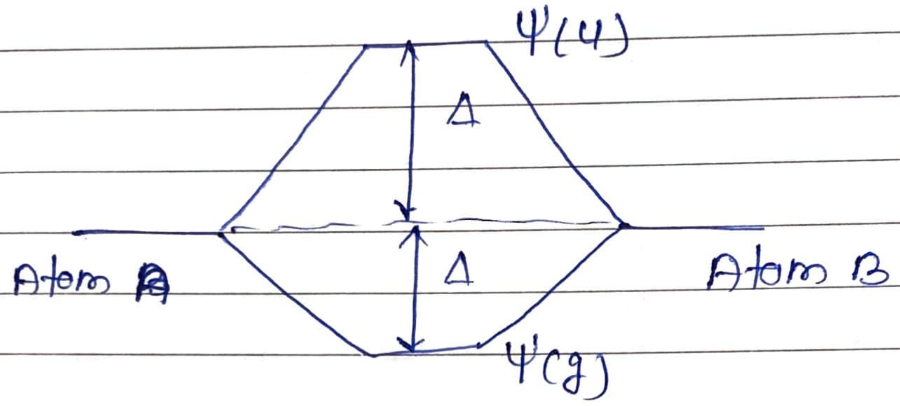
Gerade (g) and ungerade (u) wavefunctions :-
If the sign of the wave function is unchanged when the orbital is reflected about its centre (i.e. x, y and z are replaced by -x, -y and -z) the orbitals is gerade and if the sign of the wavefunction is changed then its called as ungerade wavefunction.

→ The energy of $\psi_{(g)}$ is minimum while that of $\psi_{(u)}$ is more than $\psi_{(g)}$.



Energy of s-s combination of orbitals:-

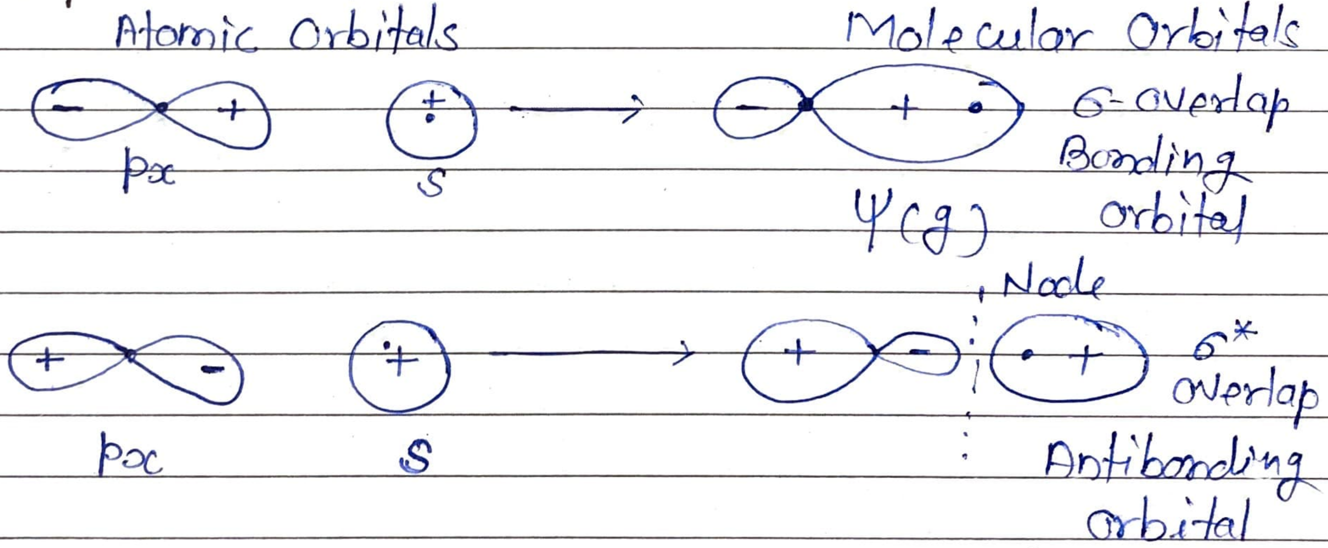
When s orbitals of two H atom combine they produces two molecular orbitals one is $\Psi(g)$ and other one is $\Psi(u)$



Δ = stablization energy

If Δ → Negative → molecule form
→ Zero ┐
→ Positive ┘ → molecule does not exist

s-p Combination of orbitals:-

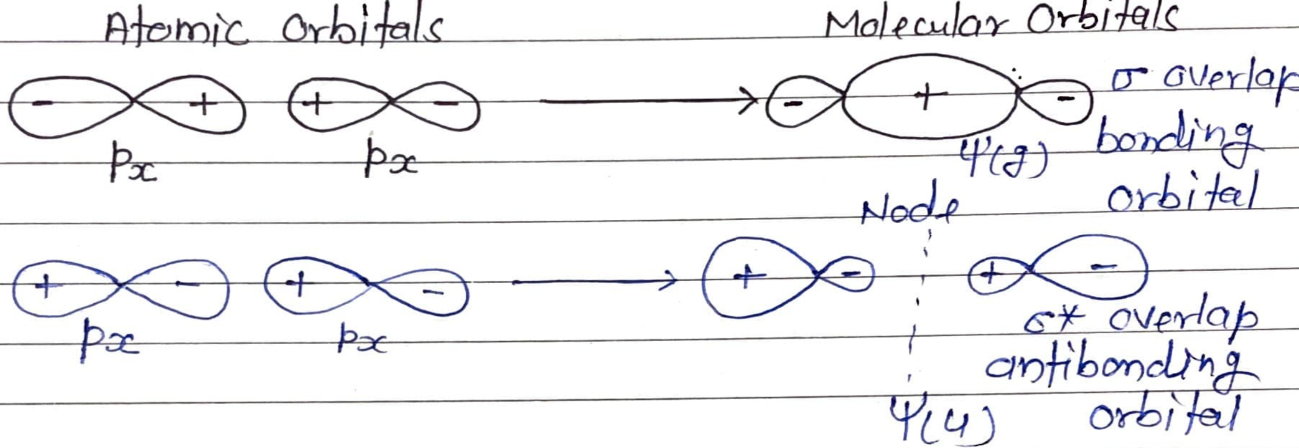


Node:- Region in atom/molecule where the electron density is zero.

p-p Combination of orbitals÷

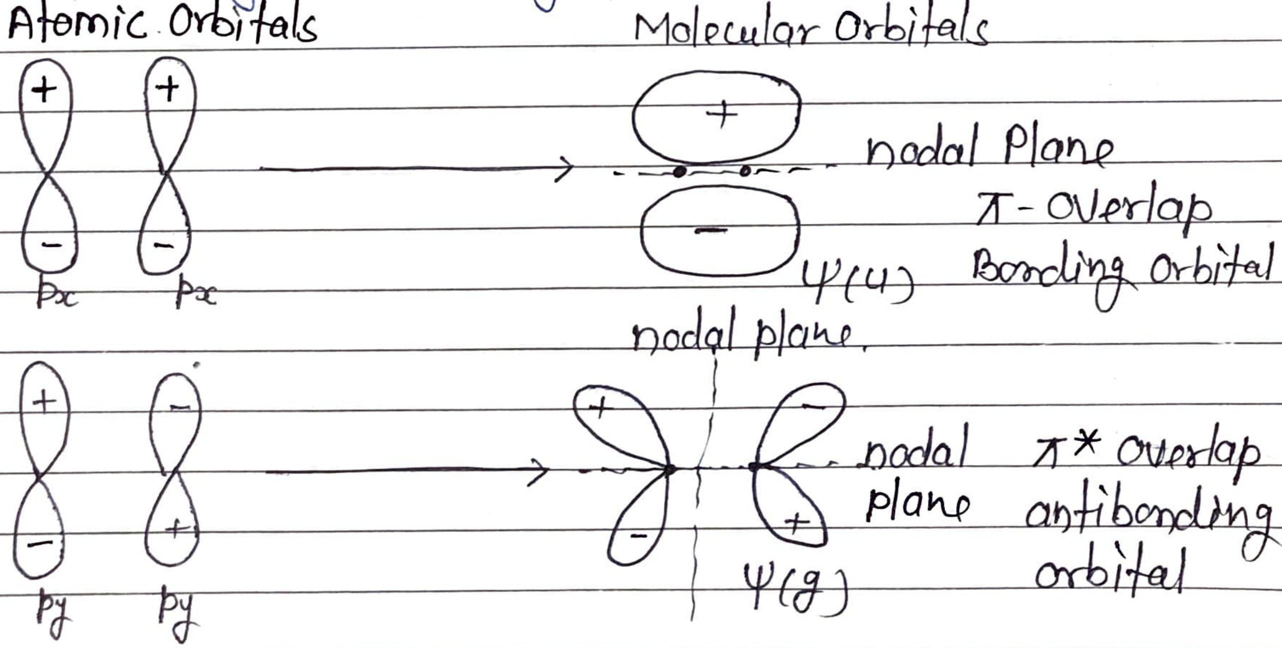
Three cases

σ-Bonding Case I÷ when ~~a~~ both p orbitals have lobes pointing along the axis joining the nuclei. Both a bonding molecular orbital (BMO) and an antibonding molecular orbital (ABMO) are produced.



Case II - π- Bonding ÷

When both the p-orbitals have lobes perpendicular to the axis joining the nuclei, lateral overlap of orbitals will occur, resulting in π bonding and π* antibonding MOs being produced.



Difference Between π overlap and σ-overlap :-

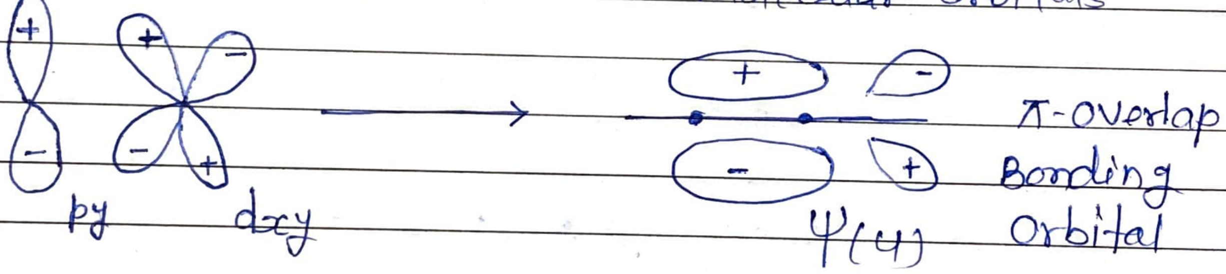
1. For π-overlap the lobes of the atomic orbitals are perpendicular to the line joining the nuclei, whilst for σ overlap the lobes point along the line joining the two nuclei.

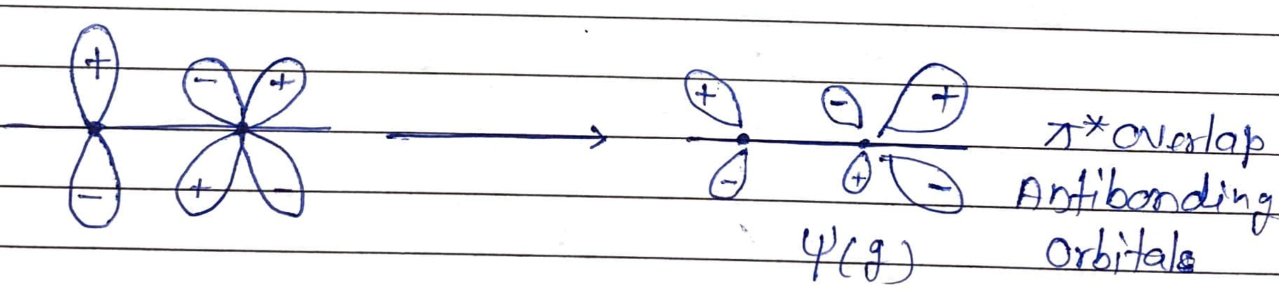
2. For π molecular orbitals, ψ is zero along the internuclear line and consequently the electron density ψ^2 is also zero. This is contrast to σ orbitals.

3. The symmetry of π molecular orbitals is different from that shown by σ orbitals.

p-d Combination of Orbitals :-

Atomic Orbitals   Molecular Orbitals





Non-Bonding Combination of Orbitals :-

Any stablization which occurs from overlapping + with + is destalized by an equal amount of overlap of + and -. There is no overall change in energy and this situation is termed as non-bonding. eg. s-p_y Combination, p_x-d_{yz} combination.

Rules for LCAOs :-

Rule 1:- The atomic orbitals must be roughly of the same energy.

Rule2:- The orbitals must overlap one another as much as possible.

Rule3:- In order to produce bonding and antibonding MOs either the symmetry of the two atomic orbitals must remain unchanged when rotated about the internuclear line, or both atomic orbitals must change symmetry in an identical manner.

Rules for filling electrons in MOs :-

1. The principal quantum number n has the same significance as in atomic orbitals.
2. The subsidiary quantum number l also has the same significance as in atomic orbitals.
3. The magnetic quantum number of atomic orbitals is replaced by a new quantum number λ.

   λ = Quantization of angular momentum

   $\lambda = -l$ to $+l$

   If $\lambda = 0$ σ orbitals

   $= \pm 1$ π orbitals

   $= \pm 2$ δ orbitals.
4. The spin quantum number is the same as for atomic orbitals and may have values of $\pm \frac{1}{2}$.

Rules for filling electron in Homonuclear lighter molecules upto N_2 :-

$$\sigma 1s, \sigma^* 1s, \sigma 2s, \sigma^* 2s, \begin{cases} \pi 2p_y \\ \pi 2p_z \end{cases} \sigma 2p_x \; \sigma^* 2p_x \begin{cases} \pi^* 2p_y \\ \pi^* 2p_z \end{cases}$$

$$\xrightarrow[\uparrow E]{\hspace{10cm}}$$