Linear Combination of atomic orbital (LCAO)

Principle :-

The wave function describing a molecular orbital may be obtained by LCAO method. suppose two atom A and B have atomic orbital described by wave function $\Psi(A)$ and Ψ_B : when two atom approach together then electron cloud of these two atoms overlap then the wave function for molecular orbital $\Psi(AB)$ can be obtained by linear combination of . atomic orbital $\Psi(A)$ and $\Psi(B)$.

$$\Psi(AB) = N(c_1\Psi(A) + c_2\Psi(B))$$

N = normalizing constant

c_1 & c_2 are constants chosen to give a minimum energy for $\Psi(AB)$. If atom A and B are similar then value of $c_1 = c_2$

The Probability of finding an electron in a volume of space dv is $\Psi^2 dv$, so the probability density for the combination of two atoms as above is related to the wave function squared.

$$\Psi^2(AB) = (\underbrace{c_1^2\Psi^2(A)}_{1} + \underbrace{2c_1c_2\Psi(A)\Psi(B)}_{2} + \underbrace{c_2^2\Psi^2(B)}_{3})$$

1- describes the probability of finding an electron on atom A if A is an isolated atom.

3- Describes the probability of finding an electron on atom B if B is an isolated atom.

2- This term is called overlap integral because overlap between two atomic orbital increases. Larger the term stronger the bond.

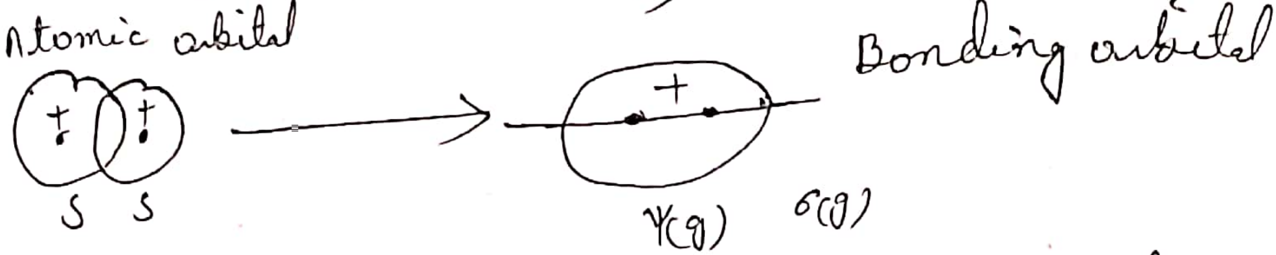
S-S combinations of orbitals :-

Suppose wave function of two 1S atomic orbital A & B of two hydrogen atom is Ψ(A) and Ψ(B). Then two combination of wave function Ψ(A) and Ψ(B) are possible.

① The signs of the two wave functions are the same
2) The signs of two wave functions are different.

① same sign wave functions are in phase, combined to give a larger resultant wave.

$$\Psi(g) = N(\Psi(A) + \Psi(B))$$



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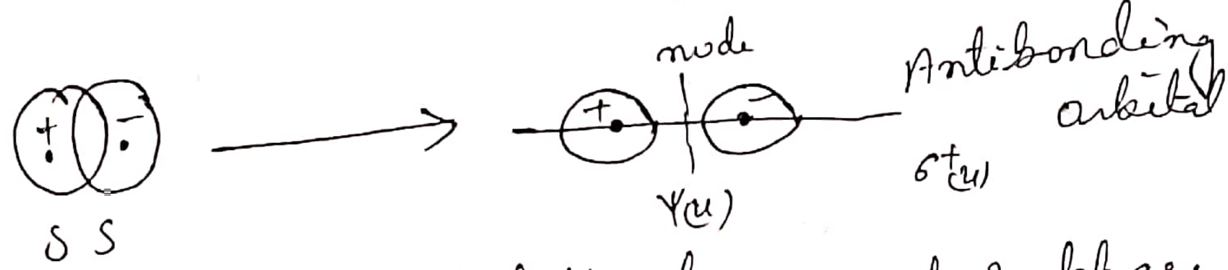

wave function of different sign out of phase cancel each other by destructive interference.

$$\Psi(u) = N\{\Psi(A) + [-\Psi(B)]\} = N\{\Psi(A) - \Psi(B)\}$$

Ψ(g) — g stands for gerade even wave function of molecular orbital, Ψg leads to increase electron density between nuclei and is bonding molecular orbital.

Ψ(u) — u stands for ungerade (odd) two lobes of opposite ~~side~~ sign cancelling and given zero electron density between nuclei. This is antibonding molecular orbital having higher energy.

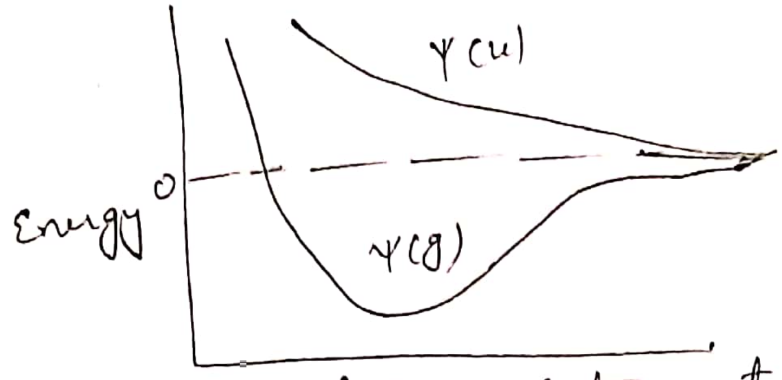

Fig ① distance between atom

Energy of ψ(g) and ψ(u) molecular orbital.

g and u refer to the symmetry of the orbital about its centre. 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 orbital is gerade. If the sign of lobes remain the same, the orbital is gerade, If the sign changes the orbital is ungerade.

—x—

From fig(1) It is observed that Energy of bonding molecular orbital (ψg) passes through a minimum and the distance between the atom corresponding to the internuclear distance between the atoms when they form bond bonding molecular orbital ψ(g) and antibonding molecular orbital ψ(u).

The energy of the bonding molecular orbital is lower than that of the atomic orbitals by an amount Δ. This is known as the stabilization energy.