The extended Huckel theory:- The HMO theory is applicable to planer conjugated π-systems only. An extension to this emperical method was made by Hoffmann in which both σ and π e's are considered and can be applicable to both planer are non planer molecules ∴ This is known as EHT.

Both HMO and EH methods begin with the approximation that the complete Hamiltonion is a of i.e Hamiltonians ; $\hat{H} = \sum_i \hat{H}(i)$

But Hamiltonian is not specified ⇒ Schrodinger eq^n is not solved

The complete electronic wave function ψ is a simple product of i.e wave function ψ_i and total energy E is the sum of i.e molecular orbital energies E_i.

The molecular orbital are linear combination of atomic orbitals ϕ_r containing valence e's only.

$$\psi_i = \sum_r a_{ir} \phi_r$$

The atomic orbitals are of slater type (STO)

Linear variation method leads to secular eq^n

$$\sum [a_{ir} (H_{rs} - E_i S_{rs})] = 0$$

The secular determinant,

$$\det | H_{rs} - E_i S_{rs} | = 0$$

where $H_{rs} = \int \phi_r \hat{H}(i) \phi_s \, dt$

$S_{rs} = \int \phi_r \phi_s \, dt$

and E_i = Energy of the MO ψ_i

All this is similar to HMO theory. The diff lies in that now all valence atomic orbitals will be taken into the linear combination ; in addition all overlap integrals are evaluated. formulae for which are readily available

The diagonal elements, $H_{rr} = \int \phi_r \hat{H}(i) \phi_r d\tau$

H_{rr} = Average energy of one e^- in the AO. ϕ_r centred on the atom r in the molecule.

∴ H_{rr} = Orbital energy of AO,

ϕ_r = Ionization potential of the atom in its valence state (with opposite sign).

∴ The off diagonal element H_{rs} =>

$$H_{rs} = \frac{1}{2} K S_{rs} (H_{rr} + H_{ss})$$ Approximate formul

where K = Adjusted b/w 1 & 3

∴ H_{rr} and H_{ss} are -ve => H_{rs} = -ve ; if. S_{rs} is +ve.

If $S_{rs} = 0$ => $H_{rs} = 0$

∴ a_{ir} are obtained by substituting H_{rs} and S_{rs}

Total energy, $E = \sum E(i)$

from MOs, ψ ; known the electronic wave functi ψ is written as the slater determinant.