

M.O. Treatment of Polyatomics

L.C.A.O. $\Psi = \sum_{i=1}^n c_i \phi_i$ n atomic orbitals

If the Hamiltonian is separated into a sum of one - electron operators,

$$\hat{H} = -\frac{1}{2} \nabla^2 + V_{\text{eff}}$$

a difficult problem involving n electrons can be rewritten as a set of simpler problems each involving one electron.

$$\hat{H} \sum_{i=1}^n c_i \phi_i = E \sum_{i=1}^n c_i \phi_i$$

$$\sum_{i=1}^n c_i (\hat{H} - E) \phi_i = 0$$

one equation

$$\sum_{i=1}^n c_i \{ \langle \phi_j | \hat{H} | \phi_i \rangle - E \langle \phi_j | \phi_i \rangle \} = 0$$

j th equation of n

$$\sum_{i=1}^n c_i \{ \hat{H}_{ji} - E S_{ji} \} = 0$$

secular equations

In all, there are n molecular orbitals, each with n terms.

For a non-trivial solution of these n simultaneous equations,

$$|\hat{H}_{ji} - E S_{ji}| = 0$$

secular determinant

Expansion of the determinant gives an n th order equation, which has n roots, i.e. n possible values of E .

Substituting a value of E into the secular equations results in a set of simultaneous equations which can be solved for c_i .

Hückel M.O. Theory

Mostly used for carbon π electron systems; the σ electrons determine the molecular geometry (carbon skeleton).

L.C.A.O. $\Psi = \sum_{i=1}^n c_i \phi_i$ n 2p orbitals, one per C

Secular Equations $\sum_{i=1}^n c_i \{ \hat{H}_{ji} - E S_{ji} \} = 0$

Hückel Approximations

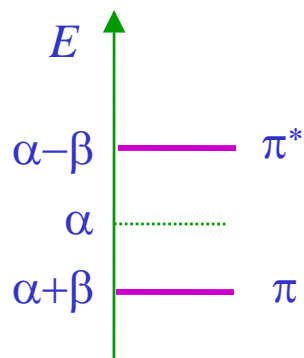
1. $S_{ij} = \delta_{ij}$ Zero overlap for orbitals on different atoms.
2. $H_{ii} = \alpha$ Coulomb integrals are all equal.
3. $H_{ij} = \beta$ if atom i bonded to j , else $H_{ij} = 0$

Secular Determinant

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & \dots \\ \beta & \alpha - E & \beta & 0 & \dots \\ 0 & \beta & \alpha - E & \beta & \dots \\ \dots & \dots & \dots & \dots & \dots \end{vmatrix} = 0$$

e.g. Ethene

$$\begin{aligned} & \begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \\ \Rightarrow & (\alpha - E)^2 - \beta^2 = 0 \\ \Rightarrow & E = \alpha \pm \beta \end{aligned}$$



Hückel Calculation for Butadiene

$$\begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0$$



$$x = \frac{\alpha - E}{\beta}$$

$$x^4 - 3x^2 + 1 = 0$$

$$x^2 = \frac{1}{2}(3 \pm \sqrt{5})$$

$$x = \pm 1.62, \pm 0.62$$

Energies: $E = \alpha - \beta x = \alpha \pm 1.62\beta, \alpha \pm 0.62\beta$

To Find Coefficients

solve the equations for each value of x

$$\begin{pmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$

e.g. for $x = -1.62$,

$$-1.62c_1 + c_2 = 0$$

$$c_1 - 1.62c_2 + c_3 = 0$$

$$c_2 - 1.62c_3 + c_4 = 0$$

$$c_3 - 1.62c_4 = 0$$

$$\Rightarrow c_2 = 1.62c_1 \quad c_3 = 1.62c_4 \quad c_1 = c_4 \quad c_2 = c_3$$

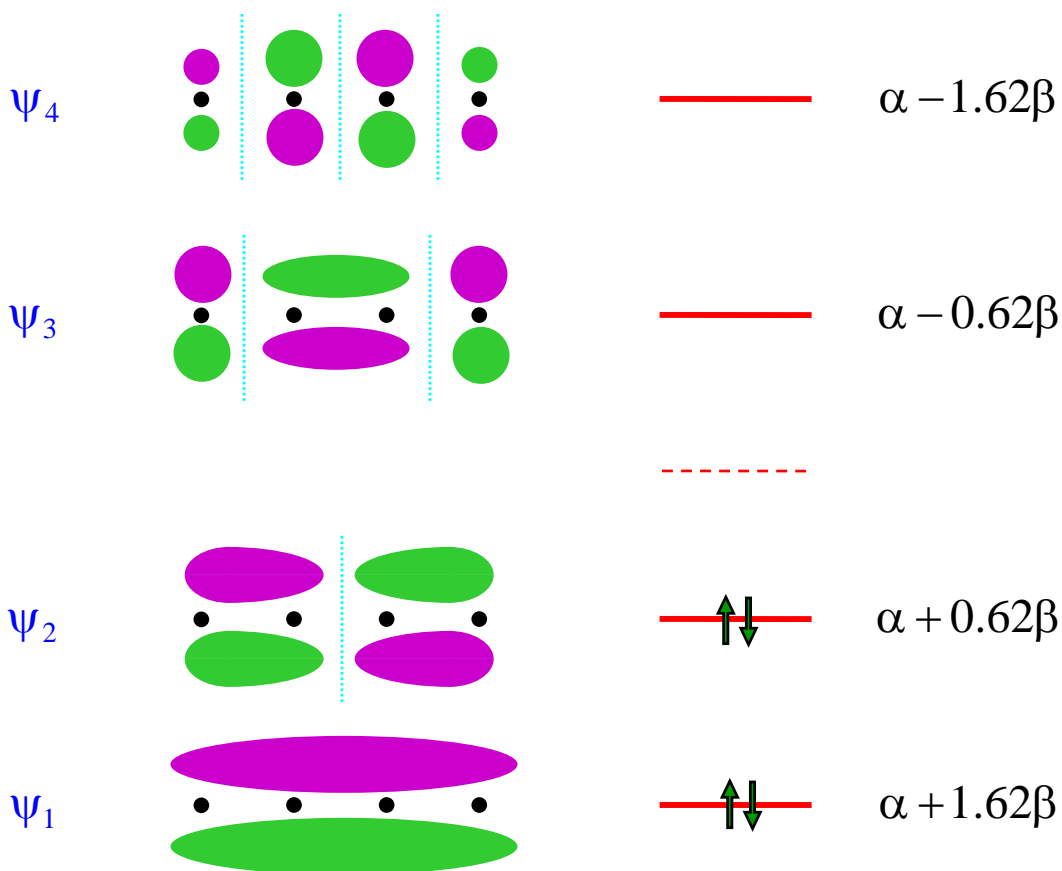
but $c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1$ for normalization

$$\Rightarrow \underline{c_1 = c_4 = 0.37, \quad c_2 = c_3 = 0.60} \quad \text{for } E = \alpha + 1.62\beta$$

Hückel Calculation for Butadiene – 2

	ϕ_1	ϕ_2	ϕ_3	ϕ_4	x	
ψ_1	0.37	0.60	0.60	0.37	-1.62	lowest energy
ψ_2	0.60	0.37	-0.37	-0.60	-0.62	
ψ_3	0.60	-0.37	-0.37	0.60	0.62	
ψ_4	0.37	-0.60	0.60	-0.37	1.62	highest energy

The number of nodes increases with energy.



Hückel Applications

Hückel Energy $E_{\text{total}} = \sum_{\text{el}} \varepsilon_i =$ sum of one-electron energies

e.g. for butadiene $E_{\text{tot}} = 4\alpha + 4.48\beta$, for ethene $E_{\text{tot}} = 2\alpha + 2\beta$

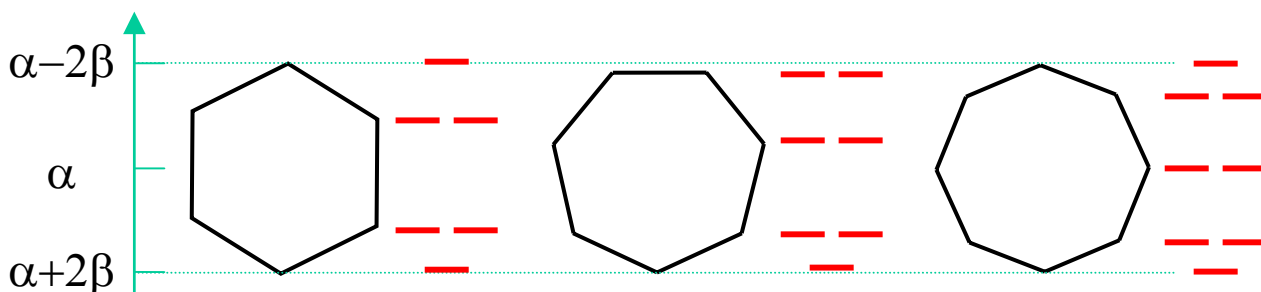
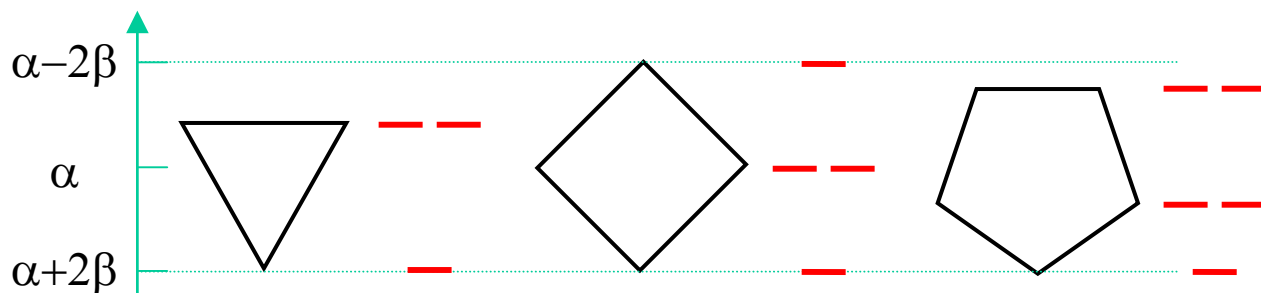
Delocalization Energy resonance energy

$$\text{D.E.} = E_{\text{tot}} - \sum E(\text{double bonds})$$

e.g. for butadiene $\text{D.E.} = 4\alpha + 4.48\beta - 2(2\alpha + 2\beta) = 0.48\beta$

Cyclic Polyenes

$$E = \alpha + 2\beta \cos(2\pi k / N) \quad k = 0, 1, 2, \dots \begin{cases} N/2 & N \text{ even} \\ (N-1)/2 & N \text{ odd} \end{cases}$$



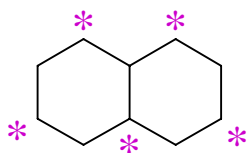
$4n+2$ electrons is the most stable, e.g. C_5H_5^- is better than C_5H_5 .

Hückel Applications – 2

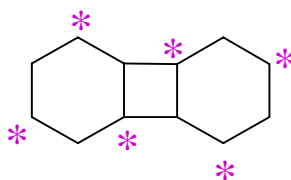
Alternant Hydrocarbons

for conjugated π systems

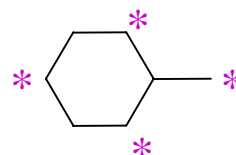
C atoms can be divided into two sets (e.g. with and without stars) such that no two members of the same set are bonded together.



Naphthalene

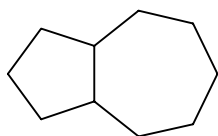


Biphenylene

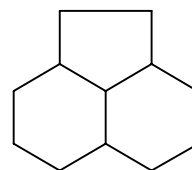


Benzyl radical

Not:



Azulene



Acenaphthylene

For alternant hydrocarbons, the energy levels of bonding and anti-bonding orbitals are arranged symmetrically about α .

The π -electron density is distributed equally over the carbons *in the ground state*, i.e. the molecules are non-polar.

π Electron Density

$$q_k = \sum_i c_{ik}^2 n_i$$

i molecular orbital
 k atom

π Bond Order

$$P_{ab} = \sum_i c_{ia} c_{ib} n_i$$

e.g. for butadiene, $P_{12} = 0.89$, $P_{23} = 0.45$.

Numerical Methods in Quantum Mechanics

Self-consistent field – Hartree and Fock

1. Start with orbital approximation for ψ but for each electron write the Schrödinger equation using a constant V_{ee} to represent the electron repulsion from all other electrons:

$$-\frac{1}{2}\nabla^2\psi_{3s} - \frac{Z}{r}\psi_{3s} + V_{ee}\psi_{3s} = E\psi_{3s}$$

Solve for ψ_{3s} .

2. Repeat for all other orbitals.
3. Redo ψ_{3s} problem (step 1) using the improved value of V_{ee} calculated using the solutions to step 2.
4. Do as many cycles as necessary until ψ_{3s} etc. are **consistent**.

Correlation Energy

Even a perfect **SCF-HF** calculation gives an answer too high by an amount called the correlation energy, because *local* e–e interactions are not considered, only *average* fields.

Configuration Interaction

Mixing in other electron configurations (excited states), using the Variation Principle.

Ab initio calculations start from scratch, consider all electrons and interactions... but then have to solve by approximation.

Semi-empirical calculations start with approximations so that the problem is relatively easy to handle.

Comparison of M.O. and V.B. Methods

- ❑ Both predict increased electron density between bound states.
- ❑ Both start with atomic orbitals but combine them in different ways:
$$\Psi_{\text{MO}} \propto [a(1) \pm b(1)][a(2) \pm b(2)]$$
$$\Psi_{\text{VB}} \propto a(1)b(2) \pm b(1)a(2)$$
- ❑ Both require paired electron spins in the bond (**Pauli Principle**).
- ❑ M.O. theory predicts states; electrons are then added (**Aufbau**).
V.B. starts with electron-pair bonds and builds up structures.
- ❑ M.O. electrons are naturally delocalized over a number of atoms, although a particular orbital may be localized.
V.B. uses resonant structures to achieve delocalization.
- ❑ M.O. wavefunctions overemphasize ionic terms; configuration interaction is used to correct this.
V.B. wavefunctions naturally ignore ionic terms, but ionic structures can be included.
- ❑ V.B. needs hybridization to explain molecular shapes.
In M.O., hybridization is simply L.C.A.O. on a single centre.
- ❑ M.O. uses the SCF method to accommodate orbital distortion as electrons are added to states – easily handled by computer.
V.B. calculations involve more complicated integrals, and a large number of resonant structures.