M.O. Treatment of Polyatomics

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

If the Hamiltonian is separated into a sum of one - electron operators, $\quad \hat{H} = -\frac{1}{2}\nabla^2 + V_{eff}$

a difficult problem involving n electrons can be rewritten as a set of simpler problems

each involving one electron. $\quad \hat{H}\sum_{i=1}^{n} c_i \phi_i = E\sum_{i=1}^{n} c_i \phi_i \quad$ one equation

$$\sum_{i=1}^{n} c_i \left\{ \left\langle \phi_j \left| \hat{H} \right| \phi_i \right\rangle - E \left\langle \phi_j \middle| \phi_i \right\rangle \right\} = 0 \quad j\text{th equation of } n$$

$$\sum_{i=1}^{n} c_i \left\{ \hat{H}_{ji} - E S_{ji} \right\} = 0 \quad \text{a set of } n \text{ secular equations}$$

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

For a non-trivial solution of

these n simultaneous equations, $\quad \left| \hat{H}_{ji} - E S_{ji} \right| = 0 \quad$ secular determinant

Expansion of the determinant gives an nth 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. $\qquad \Psi = \sum_{i=1}^{n} c_i \phi_i \qquad$ n 2p orbitals, one per C

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

Hückel Approximations $\qquad$ 1. $\quad S_{ij} = \delta_{ij} \quad$ Zero overlap for orbitals on different atoms.

2. $\quad H_{ii} = \alpha \quad$ Coulomb integrals are all equal.

3. $\quad H_{ij} = \beta \quad$ if atom i bonded to j, else $H_{ij} = 0$

Secular determinant

e.g. Ethene

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

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

$$\Rightarrow \quad (\alpha - E)^2 - \beta^2 = 0$$

$$\Rightarrow \quad E = \alpha \pm \beta$$

Hückel Calculation for Butadiene

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

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

$$x^4 - 3x^2 + 1 = 0 \implies x^2 = \tfrac{1}{2}(3 \pm \sqrt{5}) \implies x = \pm 1.62, \pm 0.62$$

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

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

$$\begin{pmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = 0$$
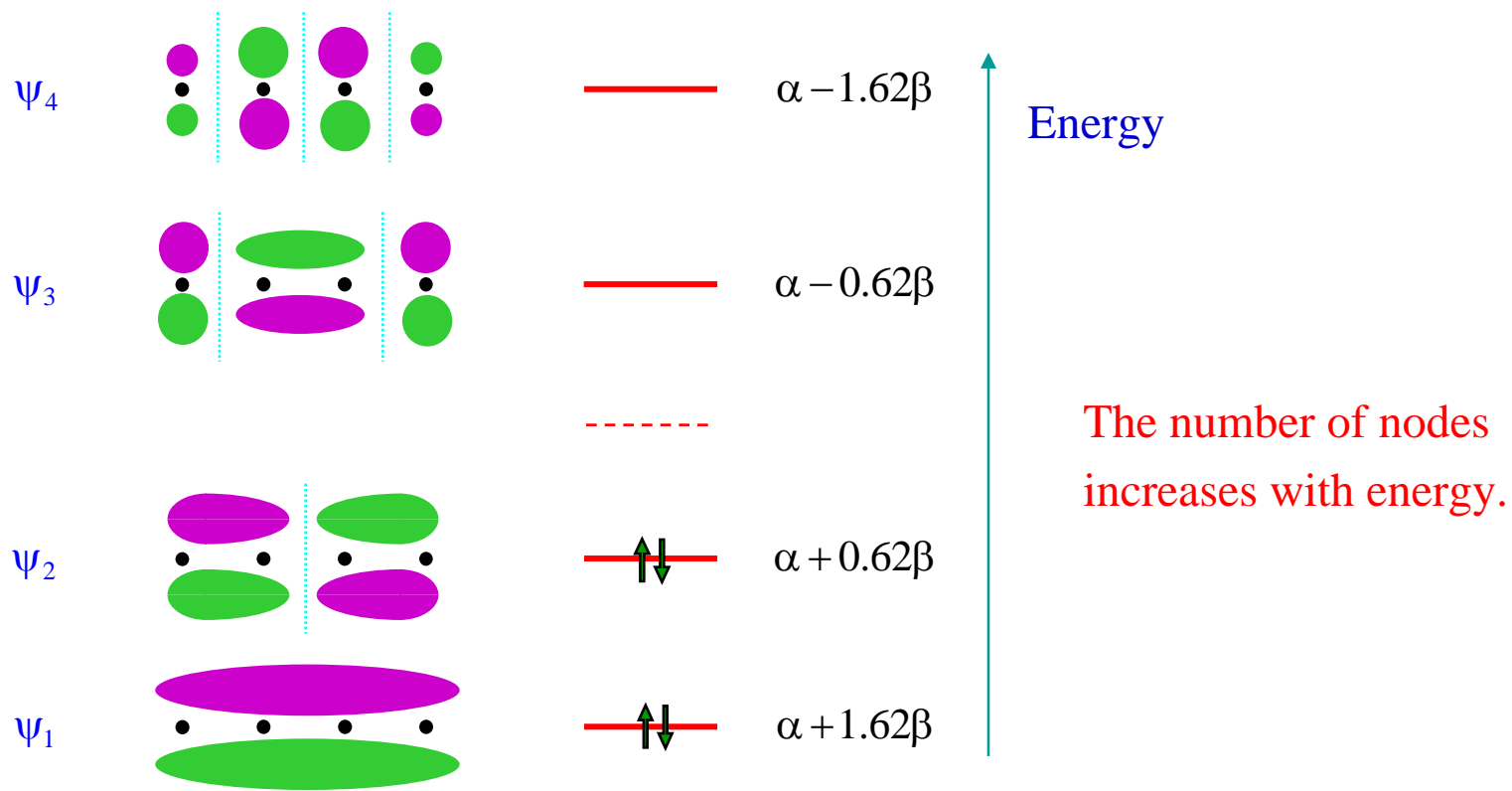
$$\begin{aligned} -1.62c_1 \quad +c_2 &= 0 \\ c_1 \quad -1.62c_2 \quad +c_3 &= 0 \\ c_2 \quad -1.62c_3 \quad +c_4 &= 0 \\ c_3 \quad -1.62c_4 &= 0 \end{aligned}$$

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

but $c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1$ for normalization $\implies$ $\underline{c_1 = c_4 = 0.37, \ c_2 = c_3 = 0.60}$ 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

ψ_4 $\alpha - 1.62\beta$

Energy

ψ_3 $\alpha - 0.62\beta$

The number of nodes
increases with energy.

ψ_2 $\alpha + 0.62\beta$

ψ_1 $\alpha + 1.62\beta$

Hückel Applications

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

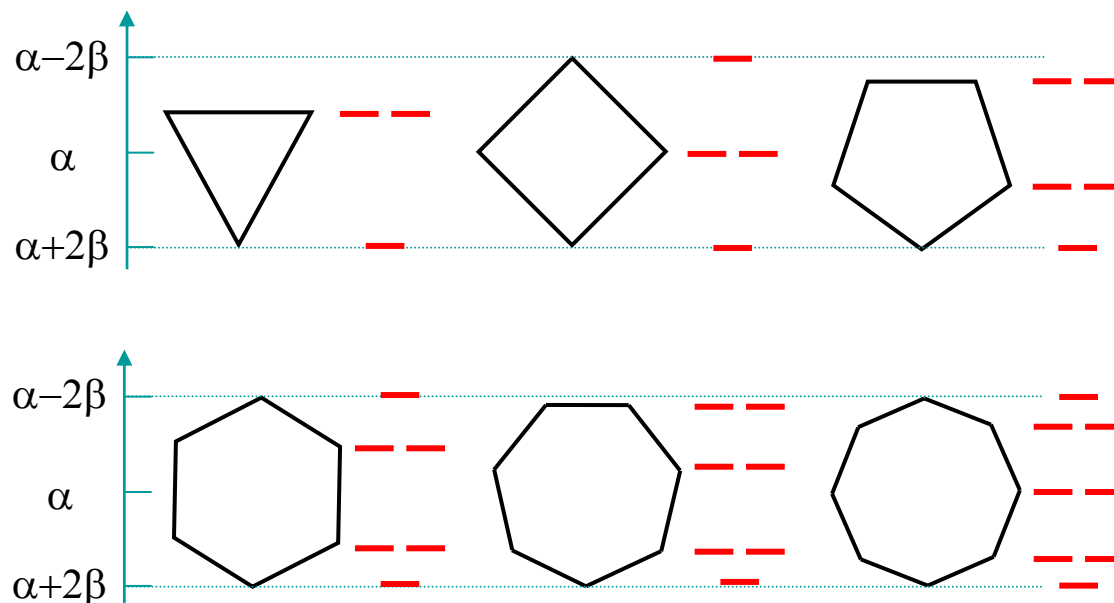e.g. for butadiene $\;\; E_{\text{tot}} = 4\alpha + 4.48\beta,\;$ for ethene $\;\; E_{\text{tot}} = 2\alpha + 2\beta$

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

resonance energy $\qquad\qquad$ e.g. for butadiene $\;\;$ D.E. $= 4\alpha + 4.48\beta - 2(2\alpha + 2\beta) = 0.48\beta$

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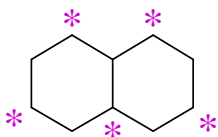

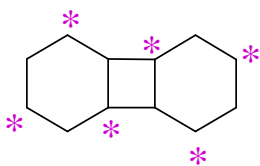$4n+2$ electrons is the most stable, e.g. $C_5H_5^-$ is better than C_5H_5.

Hückel Applications – 2

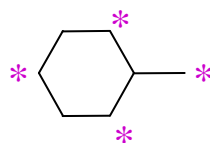**Alternant Hydrocarbons**   for conjugaged π systems

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.
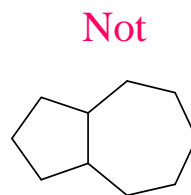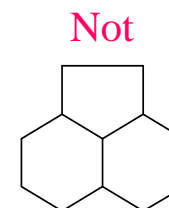
Not   Not

Naphthalene   Biphenylene   Benzyl radical   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, $P_{12} = 0.89$, $P_{23} = 0.45$.

Simplifying the Secular Determinant

$$\det\left|H_{ij} - E\, S_{ij}\right| = \begin{vmatrix} H_{11} - E\,S_{11} & H_{12} - E\,S_{12} & \ldots & H_{1n} - E\,S_{1n} \\ H_{21} - E\,S_{21} & H_{22} - E\,S_{22} & \ldots & H_{2n} - E\,S_{2n} \\ \vdots & \vdots & \ddots & \ldots \\ H_{n1} - E\,S_{n1} & H_{n2} - E\,S_{n2} & \ldots & H_{nn} - E\,S_{nn} \end{vmatrix} = 0$$

In principle, by manipulating rows and columns it is possible to achieve a diagonal form:

$$\begin{vmatrix} g_{11} - E & 0 & \ldots & 0 \\ 0 & g_{22} - E & \ldots & 0 \\ \vdots & \vdots & \ddots & \ldots \\ 0 & 0 & \ldots & g_{nn} - E \end{vmatrix} = 0$$

Evaluation of the determinant gives an equation of order n in E

$$(g_{11} - E)(g_{22} - E)\ldots(g_{nn} - E) = 0$$

which can be solved to give n eigenvalues, each corresponding to one of n eigenfunctions. These orthogonal eigenfunctions are linear combinations of the original basis set ψ.

Quantum chemistry programs utilize efficient computer algorithms to diagonalize matrices.

Computational Chemistry Methods and Programs

Molecular Mechanics

Geometry optimization using classical mechanics and parameterized force fields.
The most common force-field is MM2, which is used by HyperChem, Chem3D and many other chemical structure programs.

Semi-empirical M.O. Methods

LCAO applied to valence electrons only, with parameterized constants for the integrals.
The Hückel Method is simple enough to do with paper and pencil.
HyperChem uses the Extended Hückel Method.
More sophisticated methods include

CNDO, INDO, MNDO, MINDO, MINDO/3, AM1, PM3

They are often included in ab initio quantum chemistry packages and are useful for quick or approximate answers before applying the "big guns".

Ab initio M.O. Methods

Calculations start from scratch, in principle using all electrons and interactions but then have to invoke various approximations to make the problem tractable.
The best known programs are GAUSSIAN (commercial) and GAMESS (free).

The Self-consistent Field Method

Think of the probability distribution of an individual electron as its charge density.

Then the potential energy that electron 1 experiences at r_1 due to electron 2 is

$$V_1^{eff}(r_1) = \left\langle \phi^*(r_2) \left| \frac{1}{r_{12}} \right| \phi(r_2) \right\rangle$$

Define a one-electron Hamiltonian

$$\hat{H}_1^{eff}(r_1) = -\frac{1}{2}\nabla_1^2\psi - \frac{Z}{r_1}\psi + V_1^{eff}(r_1)$$

In principle, the Shrödinger equation can be solved to find the orbital energy ε_1 and the wave function ϕ.

$$\hat{H}_1^{eff}(r_1)\phi(r_1) = \varepsilon_1\phi(r_1)$$

Problem: We don't know the electrostatic potential because it depends on $\phi^*(r_2)\phi(r_2)$ (and others if more than 2 electrons).

Procedure: Guess the form of $\phi(r)$ and use it as an estimate of V_1.
Solve the Schrödinger equation to get $\phi_1(r)$ which can be used for V_2.
Solve the Schrödinger equation to get $\phi_2(r)$ which can be used for V_1.
Iterate until the $\phi(r)$ are self-consistent (i.e. input = output)

Such orbitals are Hartree-Fock orbitals.

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:

$$\Psi_{MO} \propto \left[a(1) \pm b(1)\right]\left[a(2) \pm b(2)\right] \qquad \Psi_{VB} \propto a(1)b(2) \pm b(1)a(2)$$

➢ 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; C.I. is used to correct this.

➢ V.B. wavefunctions naturally ignore ionic terms, but they can be added.

➢ In M.O., hybridization is simply L.C.A.O. on a single centre.

➢ V.B. needs hybridization to explain molecular shapes.

➢ M.O. uses SCF 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.