



Hückel MO theory: Is it still useful?

Brno, May 2012


Erich Hückel (09.08.1896 Berlin - 16.02.1980 Marburg)
 Postdoc with Max Born in Göttingen and Peter Debye in Zürich (Debye-Hückel theory, Habilitation 1925)

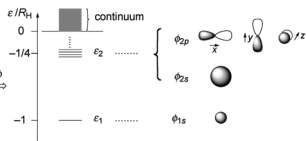
The HMO-Model and its applications: Basis and Manipulation,
 E. Heilbronner and H. Bock, English translation, 1976, Verlag Chemie
 (P. Klán and J.W., Photochemistry of Organic Compounds)

- Father Armand (MD) inherited – decided to go for private research (smallpox) in Göttingen, where his son Erich visited school and studied physics
- P. Debye, liq. crystals PhD 1921 (Debye -> ETH)
- Ass. D. Hilbert, M. Born
- 1922: Zürich Debye (electrolytes), hab. 1925
- 1929 Leipzig N. Bohr (QM double bond)
- 1931 hab. Benzene (MO vs VB) [L. Pauling "Nature chem. bond: VB, "resonance"] $4n + 2$
- 1937 a.o. Prof. Marburg
- 1962 emer.

Schrödinger equation

$$\hat{H}\psi = E\psi$$





Born-Oppenheimer Approximation for molecules: $\Psi = \Psi_{el}(q_{el}, Q_{nuc}) \chi(Q_{nuc})$


Trial wavefunction for molecules: product of MO's $\psi = \Pi \psi_i$
 Rayleigh's variation theorem for trial wavefunctions Φ

$$\frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \langle E_1 \rangle \geq \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = E_1$$

Molecular orbitals cannot (adequately) describe many-electron systems:

Born interpretation: $\Psi_{el}^2(1-el)dv =$ probability of finding e in volume element dv

2-electron wavefunction as a product of MO wavefunctions:
 $\Psi_{el}(2-el.) = \psi_{a_1}(e_1)\psi_{b_1}(e_2)$
 then: $\Psi_{el}^2(2-el.) = \psi_{a_1}^2(e_1)\psi_{b_1}^2(e_2)$
 i.e.: the probability of finding e_1 in a given volume element dv is assumed to be *independent* of the position of e_2



$P[(d_1 = 1) \text{ and } (d_2 = 4)] = P(d_1 = 1) \times P(d_2 = 4)$
 $= 1/6 \times 1/6 = 1/36$

Boiling down QM (HMO)

- Only electronic wavefunction (B-O approximation)
- Product wavefunction of MO's (correlation)
- Consider only π -electrons (highest in energy, frozen core)
- Neglect electronic interactions altogether (!)
- HMO's constructed as linear combinations of $2p_z$ -AOs (LCAO):

$$\Psi_j = c_{j,1}\phi_1 + c_{j,2}\phi_2 + c_{j,3}\phi_3 + \dots + c_{j,\omega}\phi_\omega = \sum_{\mu=1}^{\omega} c_{j,\mu}\phi_\mu$$
- Treat matrix elements H as parameters
- No physics left, only topology (connectivity) as input

$$H_{\mu\mu} = \langle \phi_\mu | \hat{H}^{HMO} | \phi_\mu \rangle = \alpha$$

(a constant value for carbon atoms C_μ)

$$H_{\mu\nu} = \langle \phi_\mu | \hat{H}^{HMO} | \phi_\nu \rangle = \begin{cases} \beta & \text{for } \mu \text{ bound to } \nu \\ 0 & \text{else} \end{cases}$$

Determination of LCAO-coefficients (e.g., cyclobutadiene)

$\mu=4$
 $\mu=3$

$\mu=1$
 $\mu=2$

\backslash
 ν

	1	2	3	4
1	$\alpha - \epsilon$	β	0	β
2	β	$\alpha - \epsilon$	β	0
3	0	β	$\alpha - \epsilon$	β
4	β	0	β	$\alpha - \epsilon$

$\| \dots \| = 0$

Divide all elements by β and take $x_j = \frac{\alpha - \epsilon_j}{\beta}$ as reference: $x_j = \frac{\alpha - \epsilon_j}{\beta} = 0$

HMO of cyclobutadiene

Pauli principle, Hund's 1st rule

The Fermi "hole": electronic interaction as an afterthought

Electronic configurations

Calculate: C=C C#C ...

The "physical" basis of "bow-and-arrow" chemistry

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 18, NUMBER 3 MARCH, 1950

Some Studies in Molecular Orbital Theory
I. Resonance Structures and Molecular Orbitals in Unsaturated Hydrocarbons*

H. C. LONGBOTTOM-HIGGINS
Department of Physics, University of Chicago, Chicago, Illinois
(Received June 13, 1949)

The predictions of qualitative resonance theory, as to the electronic structures of unsaturated hydrocarbons, are analyzed in terms of LCAO molecular orbital theory. The following results are proved for "alternant" hydrocarbons, that is, hydrocarbons containing no odd-membered unsaturated rings:

- (1) The number of unpaired electrons present in the ground state is at least as great as the number of carbon atoms having a deficiency of valence bonds in any principal resonance structure.
- (2) With a few special exceptions, these odd electrons are distributed over just those atoms which have a deficiency of valence bonds in one or more of the principal resonance structures.
- (3) In singly charged hydrocarbon anions or cations the ionic charge is located on just those atoms which bear charges in the various principal resonance structures.

It follows that enumeration of the principal resonance structures of a hydrocarbon molecule or ion gives much valuable information as to its electronic structure, and in particular, an alternant hydrocarbon possessing no normal Kekulé-type structure must have a paramagnetic ground state, and behave as a radical or multiradical.

These results do not depend on the neglect of overlap, or the assumption of a constant carbon-carbon resonance integral.

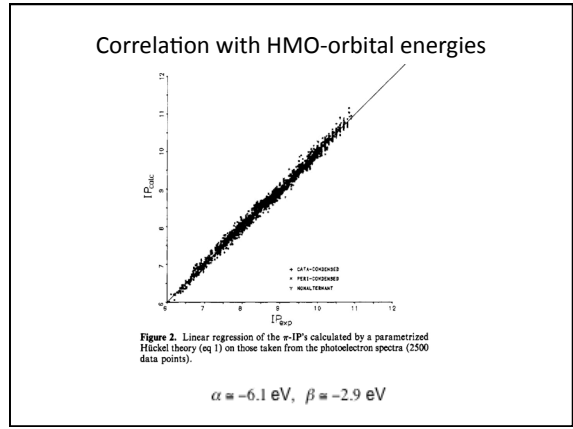
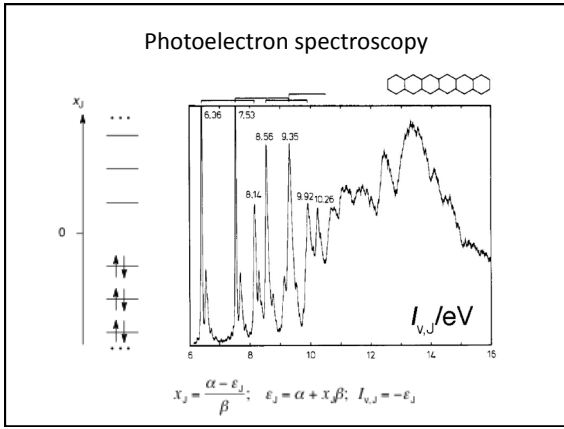
"Resonance" theory

Heilbronner, *Helv. Chim. Acta* 45, 1962, 1722.

The complete set of unexcited VB structures that can be written for an even π -electron-system containing only six-membered rings and/or linear chains of orbitals, defines a matrix which is the inverse of the Hückel-matrix of the same system

See also:
Herndon, *Tetrahedron*, 29, 1973, 3.
Dewar, Longuet-Higgins, *Proc. Roy. Soc.* A214, 1952, 482

Aromaticity (4n+2)



J. Am. Chem. Soc. **1981**, *103*, 1320–1328

Photoelectron Spectra of Polynuclear Aromatics. 6. Applications to Structural Elucidation: "Circumanthracene"^{1a†}

E. Clar,^{1b} J. M. Robertson,^{1b} R. Schlögl,^{1c} and W. Schmidt^{*1c}

C38H16, $M = 472$

Perturbation theory for HMO's

$$\frac{\partial \epsilon_J}{\partial \alpha_\mu} = C_{J\mu}^2; \quad \frac{\partial \epsilon_J}{\partial \beta_{\mu\nu}} = 2C_{J\mu}C_{J\nu}$$

First - order perturbations are additive:

$$\partial \epsilon_J = \sum_{\mu} C_{J\mu}^2 \partial \alpha_\mu + 2 \sum_{\mu-\nu} C_{J\mu}C_{J\nu} \partial \beta_{\mu\nu}$$

Total π -energy:

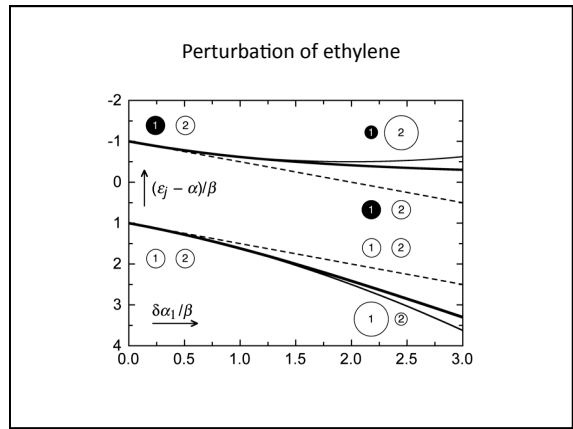
$$\partial E_\pi = \sum_{\mu} p_{\mu\mu} \partial \alpha_\mu + 2 \sum_{\mu-\nu} p_{\mu\nu} \partial \beta_{\mu\nu}$$

where $p_{\mu\nu} = \sum_J^{\text{occ.}} b_J C_{J\mu} C_{J\nu}; \quad b_J = 0, 1, 2 \text{ (occ. nrs)}$

HMO Heteroparameters

Parameters for heteroatoms after Steinhilber
 $s_x = \alpha + h_x \beta$
 $f_{xy} = k_{xy} \beta$

atom	bond	example	h_x	k_{xy}
C	C=C	<chem>C=C</chem> (1, -4.0 β)	$h_C = 0.0$	$k_{C=C} = 1.0$
	C=C	<chem>C=C</chem> (1, -3.4 β)	$h_C = 0.0$	$k_{C=C} = 1.1$
	C=C	<chem>C=C</chem> (1, -4.7 β)	$h_C = 0.0$	$k_{C=C} = 0.9$
B	C=B		$h_B = -1.0$	$k_{C=B} = 0.7$
N	C=N	<chem>C=N</chem>	$h_N = 0.5$	$k_{C=N} = 1.0$
	C=N	<chem>C=N</chem>	$h_N = 1.5$	$k_{C=N} = 0.8$
	C=N	<chem>C=N</chem>	$h_N = 2.0$	$k_{C=N} = 1.0$
	C=N	<chem>C=N</chem>	$h_N = 2.0$	$k_{C=N} = 0.8$
O	C=O	<chem>C=O</chem>	$h_O = 1.0$	$k_{C=O} = 1.0$
	C=O	<chem>C=O</chem>	$h_O = 2.0$	$k_{C=O} = 0.8$
F	C-F	<chem>C-F</chem>	$h_F = 3.0$	$k_{C-F} = 0.7$
	C-F	<chem>C-F</chem>	$h_F = 2.0$	$k_{C-F} = 0.4$



1st-Order perturbation of degenerate orbitals

Need to use symmetry-adapted LCMOs (any LC is equally valid)

Pairing theorems

Coulson–Rushbrooke theorems for alternant hydrocarbons (AHs)
(Hold also for π -SCF calculations (PPP))

Pairing theorems

- HMOs with $x_j \neq 0$ occur in pairs of energies $\epsilon_{\pm j} = \pm x_j \beta$
The coefficients $c_{j\mu}$ of paired MO's are the same, but the sign is changed in one set: $c_{j\mu}^{\circ} = c_{-j\mu}^{\circ}$, $c_{j\mu}^* = -c_{-j\mu}^*$.
- The number of nonbonding orbitals ($x_j = 0$) is at least equal to the [difference] between the number of atoms in each set. Thus odd AHs have at least one NBMO.
- NBMOs are 'self-paired': $c_{j\mu}^* = -c_{j\mu}^*$ requires that $c_{j\mu}^* = 0$.
- $q_{\mu\mu} = 1$ on all atoms μ for neutral AHs.
- $q_{\mu}^{\circ} q_{\nu}^{\circ} = q_{\mu}^* q_{\nu}^* = 0$ between atoms of the same set for neutral AHs.

Back-of-envelope NBMO's

The NBMO coefficients* on all atoms attached to an atom with $c_{\text{NBMO}}^{\circ} = 0$ must add up to 0 (always choose * for the larger set):

Charge densities $q_{\mu} = \rho_{\text{H}\mu}$ of odd AH anions: $q_{\mu} = 1 + c_{\text{NBMO},\mu}^2$

$$q_{\mu} = \rho_{\text{H}\mu} = \sum_j^{\text{occ}} b_j^{\text{anion}} c_{j\mu}^2 = \sum_j^{\text{occ}} b_j^{\text{neutral}} c_{j\mu}^2 + c_{\text{NBMO},\mu}^2 = 1 + c_{\text{NBMO},\mu}^2$$

Fused systems: Perinaphthenyl

$\#* - \#^{\circ} = 7 - 6 = 1$

Perinaphthenyl anion has no excess charge in the center!

Biradicals: Singlet or triplet ground state?

Borden, Davidson, JACS 99, 1977, 4587

Can the NBMOs, if necessary by appropriate LC, be confined to different sets of atoms ("disjoint")?

Cyclobutadiene: disjoint (singlet GS)

Trimethylenemethane: non-disjoint (triplet GS)

Calculate:

