

(b) The Hückel Method

(Erich Hückel, 1931)

This is an example of an independent electron approximation, in which the effect of electron-electron repulsion on the energy levels is ignored. (This does not mean e-e repulsion is assumed not to exist, only that it is assumed to be similar in the molecular orbitals and in the atomic orbitals from which they are constructed.)

It is considered an appropriate (crude) approach to the π electrons of conjugated and aromatic hydrocarbons. The σ electrons (lower in energy) are assumed to constitute a rigid bonding framework (i.e. it is assumed that π bonding involves no change in bond length), while the highest energy electrons lie in the π bonding and π^* antibonding orbitals.

In general, in LCAO theory we write $\Psi = c_A \Psi_A + c_B \Psi_B + c_C \Psi_C + \dots$

leading to e.g. $\Psi = c_A \Psi_A + c_B \Psi_B$ for ethene
or $\Psi = c_A \Psi_A + c_B \Psi_B + c_C \Psi_C + c_D \Psi_D$ for butadiene.



According to the variation principle the optimum coefficients are obtained when the secular determinant is zero, e.g. when for ethene

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

Additional approximations of the Hückel model:

- (1) All overlap integrals (S) are set to zero.
- (2) All non-nearest-neighbor resonance integrals β are set to zero.
- (3) All nearest-neighbor resonance integrals are set to the same value, β .

Ex. 1: Ethene

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad \text{leading to solutions}$$

$$E_+ = \alpha + \beta; \quad E_- = \alpha - \beta$$

(HOMO)

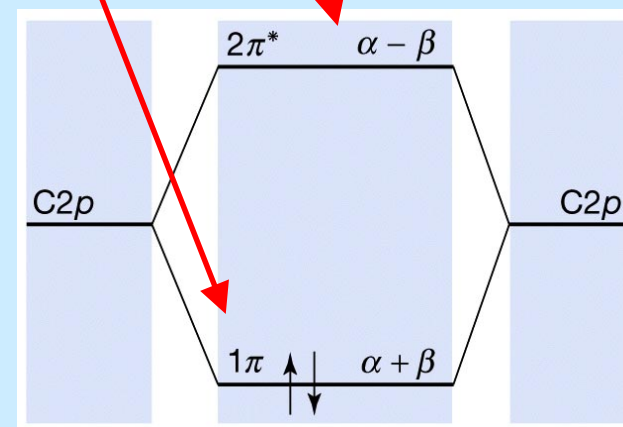
(LUMO)

We can substitute back into the secular equation to find the coefficients c_A and c_B (one set each for ψ_+ and ψ_-).

$$\psi_+ = \frac{1}{\sqrt{2}}(\psi_A + \psi_B)$$

$$\psi_- = \frac{1}{\sqrt{2}}(\psi_A - \psi_B)$$

Normalization constant



The normalization constants are obtained from the consideration that

$$\int \psi_+^2 d\tau = \int (\psi_A + \psi_B)^2 d\tau = \int \psi_A^2 d\tau + \int \psi_A \psi_B d\tau + \int \psi_B \psi_A d\tau + \int \psi_B^2 d\tau = 1 + 0 + 0 + 1 = 2$$

and multiplying the atomic orbitals by an appropriate factor to make this integral 1 rather than 2.

The HMO method can be used to calculate the total π -electron binding energy in a particular molecule (sum of the energies of all the electrons, i.e. weighted sum of orbital energies).

It can also be used to calculate the delocalization energy in a given system containing n double bonds by comparing that system with n individual double bond energies (ethene molecules).

See Examples 14.7 and 14.8 in Atkins, on pp414-415.

Matrix formulation of the HMO method

This is a useful formulation of the approach for treatment of larger systems.

Example: 2-center system:

$$\begin{aligned}(H_{AA} - ES_{AA})c_A + (H_{AB} - ES_{AB})c_B &= 0 \\ (H_{BA} - ES_{BA})c_A + (H_{BB} - ES_{BB})c_B &= 0\end{aligned}$$

Let $\mathbf{H} = \begin{bmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{bmatrix}$ $\mathbf{S} = \begin{bmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{bmatrix}$ and $\mathbf{c} = \begin{bmatrix} c_A \\ c_B \end{bmatrix}$

Then $(\mathbf{H} - E\mathbf{S})\mathbf{c} = 0$ or $\mathbf{H}\mathbf{c} = \mathbf{S}\mathbf{c}E$

In Hückel theory $S_{ij} = \delta_{ij}$ and so \mathbf{S} (the overlap matrix) is the unit matrix \mathbf{I} - in more sophisticated treatments \mathbf{S} will differ from \mathbf{I} .

For each eigenvalue E_i there will be a set of coefficients \mathbf{c}_i ; hence we can write a set of equations (one for each eigenvalue): $\mathbf{H}\mathbf{c}_i = \mathbf{S}\mathbf{c}_iE_i$

With (for our 2-center problem):

$$\mathbf{c} = \begin{bmatrix} c_{1A} & c_{2A} \\ c_{1B} & c_{2B} \end{bmatrix} \quad E = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix}$$

we have

$$\mathbf{HC} = \mathbf{SCE}$$

In the Hückel approximation $S=I$, so $\mathbf{HC} = \mathbf{CE}$

and we notice that $\mathbf{C}^{-1}\mathbf{HC} = \mathbf{E}$

i.e. to find the eigenvalues we need to find a *transformation* of \mathbf{H} that makes it *diagonal*.

The diagonal elements then correspond to the eigenvalues E_i and the columns of the diagonalizing matrix \mathbf{C} yield the coefficients of the molecular orbitals.

Hückel calculations are useful for obtaining qualitative information about π electrons, but once the size of the system increases past a certain point the calculations must be carried out numerically, by computer. This being the case, we are as well to use a more sophisticated model which includes electron-electron repulsion.

In general, such QM calculations are divided into two types:

Ab initio - These attempt to solve the Schrödinger equation without the use of any experimental parameters (except in construction of the basis sets). The only variables of the problem are (in principle) the Z values and positions of the nuclei, and the overall charge and spin state (which determines the number of electrons).

Semiempirical - Not all of the integrals in the secular determinant are calculated from first principles - some are included in the model as empirical parameters obtained from spectroscopic data or ionization energies.

(c) Semiempirical theories 1 - Extended Hückel Theory

Differences from Hückel theory:

1. Includes σ and π orbitals.
2. Calculates overlap integrals S .
3. Diagonal elements H_{ii} set equal to I (ionization energy) of that atom.
4. Off-diagonal elements H_{ij} are assumed to be proportional to overlap integrals S_{ij} . Specifically,

$$H_{ij} = \frac{1}{2}KS_{ij}(H_{ii} + H_{jj})$$

K is an empirical constant, often set equal to 1.75.

Whereas in Hückel theory we had $\mathbf{HC} = \mathbf{CE}$

Here we have $\mathbf{HC} = \mathbf{SCE}$ i.e. $\mathbf{S}^{-1}\mathbf{HC} = \mathbf{CE}$ i.e. $\mathbf{C}^{-1}(\mathbf{S}^{-1}\mathbf{H})\mathbf{C} = \mathbf{E}$

That is, now we diagonalize $\mathbf{S}^{-1}\mathbf{H}$ instead of \mathbf{H} itself.

(d) *Ab initio* theory 1 - self-consistent field (SCF) methods.

Typically based on the Hartree-Fock equations. Nobel prize 1998 went to John Pople and Walter Kohn for pioneering developments in these methods.

Consider a determinantal wavefunction

(standard notation for Slater determinants)

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a^\alpha(1) & \psi_a^\beta(1) & \dots & \psi_z^\beta(1) \\ \psi_a^\alpha(2) & \psi_a^\beta(2) & \dots & \psi_z^\beta(2) \\ \dots & \dots & \dots & \dots \\ \psi_a^\alpha(N) & \psi_a^\beta(N) & \dots & \psi_z^\beta(N) \end{vmatrix}$$

$$\equiv \frac{1}{\sqrt{N!}} \det|\psi_a^\alpha(1)\psi_a^\beta(2)\dots\psi_z^\beta(N)|$$

It can be shown that the variation principle implies that the best possible (lowest energy) single-determinant wavefunctions satisfy the Hartree-Fock equations:

$$f_1 \psi_{a,\sigma}(1) = \epsilon \psi_{a,\sigma}(1) \quad \sigma = \alpha, \beta$$

“Fock operator”

$$f_1 = h_1 + \sum_j \{2J_j(1) - K_j(1)\}$$

$$f_1 \psi_{a,\sigma}(1) = \epsilon \psi_{a,\sigma}(1)$$

$$\sigma = \alpha, \beta$$

“Fock operator”

f depends on the wavefunctions of *all* the electrons

$$f_1 = h_1 + \sum_j \{2J_j(1) - K_j(1)\}$$

“core hamiltonian”

“Exchange operator”

$$h_1 = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \sum_n \frac{Zne^2}{4\pi\epsilon_0 r_{n1}}$$

$$K_j(1)\psi_a(1) = \left\{ \int \psi_j^*(2)\psi_a(2) \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} \right) d\tau_2 \right\} \psi_j(1)$$

“Coulomb operator”

$$J_j(1)\psi_a(1) = \left\{ \int \psi_j^*(2)\psi_j(2) \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} \right) d\tau_2 \right\} \psi_a(1)$$

Steps (2), (3), and (4) are repeated until the energy and wavefunctions do not change (within some convergence criterion) on successive iterations.

Solved self-consistently

Guess initial wavefunctions

(1)

Generate improved wavefunctions

(4)

Form Coulomb and exchange operators

(3)

Solve H-F equations

(2)

Within the LCAO approach: $\psi_a = \sum_{i=1}^N c_{ia} \phi_i$ ← (atomic orbitals)

Substituting into the H-F equation: $f_1 \sum_{i=1}^N c_{ia} \phi_i(1) = \epsilon_a \sum_{i=1}^N c_{ia} \phi_i(1)$

Premultiply by $\phi_j^*(1)$ and integrate with respect to \mathbf{r}_1 :

$$\sum_{i=1}^N c_{ia} \int \phi_j^*(1) f_1 \phi_i(1) d\mathbf{r}_1 = \epsilon_a \sum_{i=1}^N c_{ia} \int \phi_j^*(1) \phi_i(1) d\mathbf{r}_1$$

F_{ji}
(integral of Fock operator)

S_{ji}
(overlap integral)

(Fock matrix)

(overlap matrix)

i.e. $\sum_{i=1}^N c_{ia} F_{ji} = \epsilon_a \sum_{i=1}^N c_{ia} S_{ji}$

or in matrix form,

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

This resembles the matrix form of the secular equations used in extended Hückel theory - F is however structurally complex, and takes into account the requirements of the Pauli principle.

(e) Density Functional Theory

Hartree-Fock theory yields reasonable results for many cases. However, it has limitations. The method does not consider *instantaneous* electrostatic interactions between electrons, nor does it correctly take account of QM effects on electron distributions, because it uses the *average* interaction from other electrons.

Various methods (CI, coupled-cluster, MCSCF) exist which attempt to address this problem of electron correlation. However, these have a considerable computational cost. While H-F has a cost approximately N^3 in the number of basis functions, in some higher-order methods this can rise to N^7 or N^8 . This makes these methods prohibitive for all but the smallest molecules.

An alternative method of cost similar to H-F is Density Functional Theory.

In DFT the energy is represented as a function of the electronic density, which in turn is a function of position; $E[\rho]$ is a functional of $\rho(\mathbf{r})$.

The ground state energy is

$$E[\rho] = E_K + E_{\rho;e,N} + E_{\rho;e,e} + E_{XC}[\rho]$$

Electronic KE

e-N and e-e PE

Exchange-correlation energy (inc. spin effects)

The method is usually (but not always) applied using an orbital-based approach, in which case the orbitals are used to construct the electron density according to

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2$$

The orbitals are solutions of the Kohn-Sham equations

$$\left\{ \underbrace{-\frac{\hbar^2}{2m_e} \nabla_1^2}_{\text{KE}} - \underbrace{\sum_{j=1}^N \frac{Z_j e^2}{4\pi\epsilon_0 r_{ji}}}_{\text{e-n PE}} + \underbrace{\int \frac{\rho(\mathbf{r}_2) e^2}{4\pi\epsilon_0 r_{12}} d\mathbf{r}_2}_{\text{e-e PE}} + \underbrace{V_{xc}(\mathbf{r}_1)}_{\text{“Exchange-correlation potential”}} \right\} \psi_i(\mathbf{r}_1) = \epsilon_i \psi_i(\mathbf{r}_1)$$

$$V_{xc}[\rho] = \frac{\delta E_{xc}[\rho]}{\delta \rho}$$

Like the H-F equations, the K-S equations are then solved iteratively to self-consistency.