- Delocalized Approach \( \Rightarrow \hat{H} \Phi = \mathcal{E} \Phi \)

\[ \Phi = c_1 \Phi_1 + c_2 \Phi_2 \]

\( \leq \text{Linear Combination of Atomic orbitals} \)

- Hartree–Fock Theory

- Localized Approach \( \Rightarrow \) Valence Bond Theory

\[ \text{AOs} \rightarrow \text{Hybridization} \]
THE HÜCKEL MODEL

conjugated or aromatic molecules:

\[ \text{H} = \text{C} = \text{C} = \text{H} \]

A delocalized model must be used.

\[ \text{H} - \text{C} - \text{C} - \text{H} \]

Butadiene

Single bond length: 147 pm
Double bond length: 134 pm

\[ \Rightarrow \text{a delocalized } \pi \text{ network is formed} \]

\[ \text{sp}^2 \text{- hybridized carbon atoms in a } \sigma \text{ bonded backbone} \]
The formation of the \( \pi \) network is reducing the total energy and also it is responsible for the reduced reactivity.

Aromatic Molecules \( \Rightarrow \) ring structure
\( \Rightarrow \) “Closed circuit” of mobile electrons

\( \Rightarrow \) bonding cannot be explained by electron pairing in localized bonds.
Erich Hückel

A qualitative MO theory to calculate energy levels of delocalized $\pi$ electrons in conjugated and aromatic molecules

- The Hückel model is a simple model however, it correctly predicts the stabilization that arises from delocalization and predicts which of many possible cyclic polyenes will be aromatic.

- In the model, the $\pi$ network of MOs can be treated separately from the $\sigma$ network of carbon backbone.

- The model uses hybridization and localized valence bond model to describe the $\sigma$ bonded skeleton and MO theory to describe the delocalized $\pi$ electrons.
The \( \pi \) molecular orbital

\[ H_{\pi} = c_1 \phi_{2p_z1} + c_2 \phi_{2p_z2} + c_3 \phi_{2p_z3} + c_4 \phi_{2p_z4} \]

\[ \Rightarrow \] secular eqns. w/ variational principle

\[
\begin{pmatrix}
H_{11} - \varepsilon S_{11} & H_{12} - \varepsilon S_{12} & H_{13} - \varepsilon S_{13} & H_{14} - \varepsilon S_{14} \\
H_{21} - \varepsilon S_{21} & H_{22} - \varepsilon S_{22} & H_{23} - \varepsilon S_{23} & H_{24} - \varepsilon S_{24} \\
H_{31} - \varepsilon S_{31} & H_{32} - \varepsilon S_{32} & H_{33} - \varepsilon S_{33} & H_{34} - \varepsilon S_{34} \\
H_{41} - \varepsilon S_{41} & H_{42} - \varepsilon S_{42} & H_{43} - \varepsilon S_{43} & H_{44} - \varepsilon S_{44}
\end{pmatrix}
\]

\( H_{11} \leq H_{22} \leq H_{33} \leq H_{44} \)
* The Coulomb Integrals ($H_{aa}$), the resonance integrals ($H_{ab}$) are assumed to be the same for all hydrocarbons and are given the symbols of $\alpha$ and $\beta$.

* It relies on both theory and experiments

\[ S_{ii} = 1, \quad S_{ij} = 0 \quad \text{if} \quad i \neq j \]

\[ H_{ij} = \begin{cases} \alpha & \text{if} \quad i = j \pm 1 \\ \beta & \text{otherwise} \end{cases} \]
\[
\begin{vmatrix}
\alpha - \varepsilon & \beta & 0 & 0 \\
\beta & \alpha - \varepsilon & \beta & 0 \\
0 & \beta & \alpha - \varepsilon & \beta \\
0 & 0 & \beta & \alpha - \varepsilon
\end{vmatrix} = 0
\]

\[\Rightarrow 4 \text{ solutions} \Rightarrow \]

\[\varepsilon = \alpha \pm 1.62\beta \]

\[\varepsilon = \alpha \pm 0.62\beta \]

\(\Leftarrow\) for butadiene
benzene
DENSITY FUNCTIONAL THEORY

The Hartree-Fock Energy

$E_{HF} = E_T + E_V + E_J$

Density Functional Theory

$E_{DFT} = E_T + E_V + E_J + E_{Exc}$

- Kinetic energy
- Electron-nuclear exchange
- Coulomb energy
- Exchange
- Correlation energy
Kohn-Sham's Eqns.

\[ E_{\text{DFT}} = E_{\text{DFT}} [\rho(r)] \]

Energy = functional of charge density

\[
\begin{aligned}
\left\{-\frac{1}{2}\sum_{i=1}^{\text{occ.}} \nabla_i^2 + \int \frac{2\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{\text{ext}}(r) + V_{\text{xc}}[\rho]\right\} \varphi_i &= \varepsilon_i \varphi_i \\
\rho(r) &= e \sum_{i=1}^{\text{occ.}} |\varphi_i|^2
\end{aligned}
\]
GAUSSIAN BASIS SETS

Early numerical calculations:

\[ \phi(r, \theta, \phi) = \frac{(2\zeta/a_0)^{n+1/2}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r/a_0} Y_l^m(\theta, \phi) \]

* Atomic Orbitals expanded in terms of Gaussian Functions

\[ g_{ijk}(r) = N x^i y^j z^k e^{-\alpha r^2} \]

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$S$-type: $\Psi_{2s}$

$p$-type: $\Psi_{2p}$

$d$-type: $\Psi_{3d}$

$i = j = k = 0$ (Zeroth order Gaussian)

$i = 1$, $j = 0$, $k = 0$

$i = 0$, $j = 1$, $k = 0$

$i = 0$, $j = 0$, $k = 1$ (first order Gaussian)

$i + j + k = 2$

Combinations (second order Gaussian)
Minimal Basis Sets

There is a minimal number for the number of functions: The number to hold all the electrons while maintaining atom's spherical structure.

H, He: one function (1s)

Li → Ne: five functions (1s, 2s, 2px, 2py, 2pz)

* Widely used: STO-3G Basis set

⇒ each basis function expanded by 3 Gaussian functions.
Minimal Basis Set: two shortcomings

Split-Valence Basis Sets

\[ P_{\sigma} = \sigma_{\text{inner}} \rightarrow \sigma_{\text{outer}} \]

\[ P_{\pi} = \pi_{\text{inner}} \rightarrow \pi_{\text{outer}} \]

to sets of valence basis sets
Polarization Basis Sets

* core atomic orbitals by one set of functions

* valence atomic orbitals by two sets of functions

$3 - 21G$, $6 - 31G^*$

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