Método Variacional

$$\hat{H}\Psi_o = E_o\Psi_o$$

estado fundamental

Uma função teste ϕ com parâmetros a serem otimizados.

ϕ **não** é auto-função de $\hat{H}$

$$E_\phi = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau}$$

Princípio variacional

$$E_\phi \geq E_o$$

depende de parâmetros variacionais

Aplicação do Método Variacional em LCAO-MO

Por exemplo, $\Psi = c_1\psi_1 + c_2\psi_2$

$$E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \longrightarrow E = \frac{\int (c_1\psi_1 + c_2\psi_2)^* \hat{H} (c_1\psi_1 + c_2\psi_2) d\tau}{\int (c_1\psi_1 + c_2\psi_2)^* (c_1\psi_1 + c_2\psi_2) d\tau}$$

Notação com elementos matriciais: $H_{ij} \equiv \int \psi_i^* \hat{H} \psi_j d\tau$ $S_{ij} \equiv \int \psi_i^* \psi_j d\tau$

$$E = \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

$$E(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}$$

Aplicação do Método Variacional em LCAO-MO

$$E(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) = c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}$$

Método variacional: $\frac{\partial E}{\partial c_1} = 0$ $\frac{\partial E}{\partial c_2} = 0$

$$\frac{\partial E}{\partial c_1}(\dots) + E\frac{\partial(\dots)}{\partial c_1} = E\frac{\partial}{\partial c_1}(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22})$$

$\frac{\partial E}{\partial c_1} \rightarrow 0$

$$E\frac{\partial}{\partial c_1}(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) = \frac{\partial}{\partial c_1}(c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22})$$

Aplicação do Método Variacional em LCAO-MO

$$E\frac{\partial}{\partial c_1}(c_1^2S_{11} + 2c_1c_2S_{12} + c_2^2S_{22}) = \frac{\partial}{\partial c_1}(c_1^2H_{11} + 2c_1c_2H_{12} + c_2^2H_{22})$$

$$E(2c_1S_{11} + 2c_2S_{12}) = 2c_1H_{11} + 2c_2H_{12}$$

$$E(c_1S_{11} + c_2S_{12}) = c_1H_{11} + c_2H_{12}$$

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

$$c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$$

Aplicação do Método Variacional em LCAO-MO

Equações Seculares:

$$\begin{cases} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0 \end{cases}$$

$$\begin{cases} ax + by = 0 \\ cx + dy = 0 \end{cases} \quad \text{Solução não trivial quando} \Longrightarrow \quad \begin{vmatrix} a & b \\ c & d \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

equação de segundo grau em *E*

⇓

duas raízes: E_1 e E_2

Substitui E_1 no sistema de equação e obtém os parâmetros (c_1, c_2) do orbital molecular Ψ_1.

Depois substitui E_2 para obter (c_1, c_2) do orbital molecular Ψ_2.

$$\Psi = \sum_{i=1}^{N} c_i \psi_i$$

$$\begin{aligned}
c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{21}) + \cdots + c_N(H_{1N} - ES_{1N}) &= 0 \\
c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) + \cdots + c_N(H_{2N} - ES_{2N}) &= 0 \\
\vdots \qquad\qquad\qquad \vdots \qquad\qquad\qquad & \vdots \\
c_1(H_{1N} - ES_{1N}) + c_2(H_{2N} - ES_{2N}) + \cdots + c_N(H_{NN} - ES_{NN}) &= 0
\end{aligned}$$

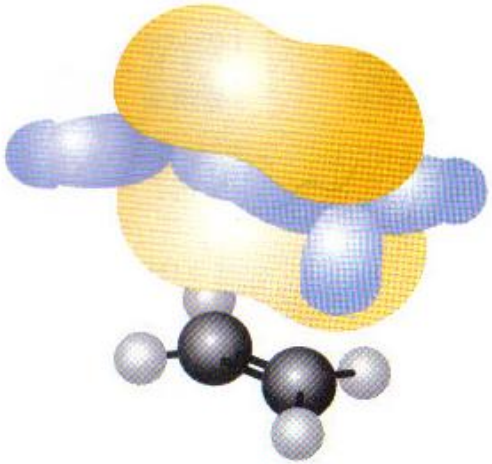
$$\Psi_m = \sum_{i=1}^{N} c_{im} \psi_i$$

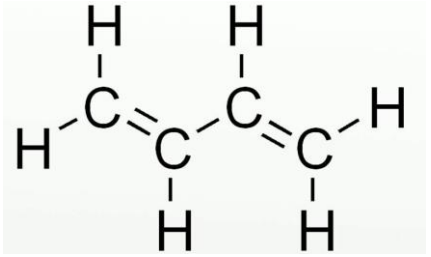
$$\begin{vmatrix}
H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\
H_{12} - ES_{12} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\
\vdots & \vdots & & \vdots \\
H_{1N} - ES_{1N} & H_{2N} - ES_{2N} & \cdots & H_{NN} - ES_{NN}
\end{vmatrix} = 0$$

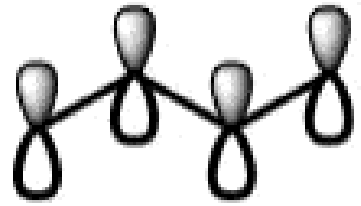
Combinação linear de *N* orbitais atômicos

N orbitais moleculares de energias E_1, E_2,...E_N. Cada MO descrito pelo seu conjunto de parâmetros.

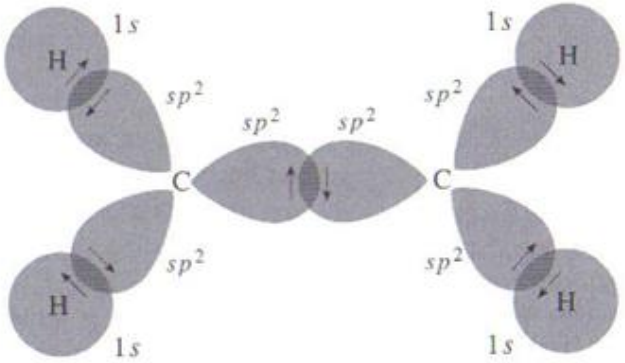
Aplicação do Método Variacional em Sistemas Conjugados
Aproximação de elétrons-π: Teoria de Hückel



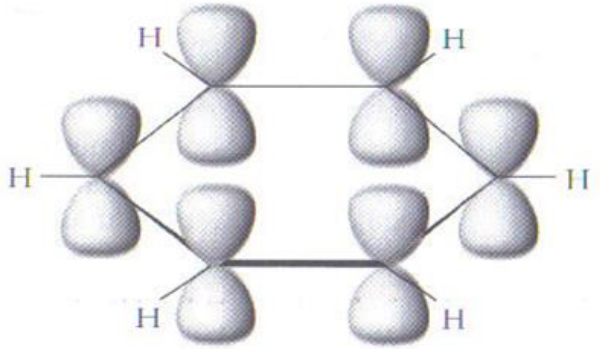


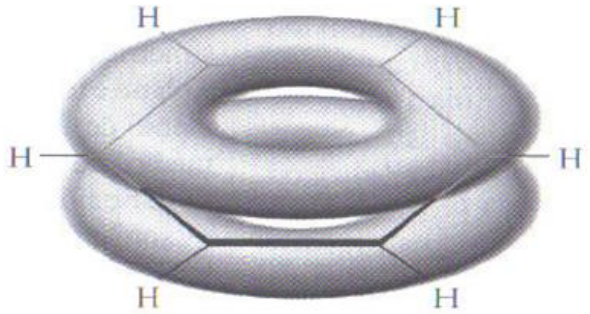


butadieno



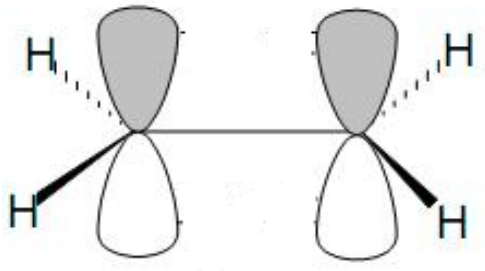
eteno





benzeno

Aproximação de elétrons-π: Teoria de Hückel



$$\psi_\pi = c_1 2p_{z\mathrm{A}} + c_2 2p_{z\mathrm{B}}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$H_{ij} \equiv \int \psi_i^* \hat{H} \psi_j d\tau \qquad S_{ij} \equiv \int \psi_i^* \psi_j d\tau$$

Aproximações: $S_{ij} = 0$, $S_{ii} = 1$

$H_{11} = H_{22} = \alpha$ (energia de $2p_z$ isolado)

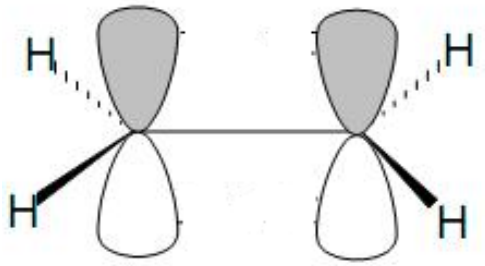
$H_{12} = \beta$ (parâmetro empírico, $\beta \sim$ -75 kJ/mol)

$H_{12} = 0$ se (i,j) não são vizinhos

Determinante secular:

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

Aproximação de elétrons-π: Teoria de Hückel



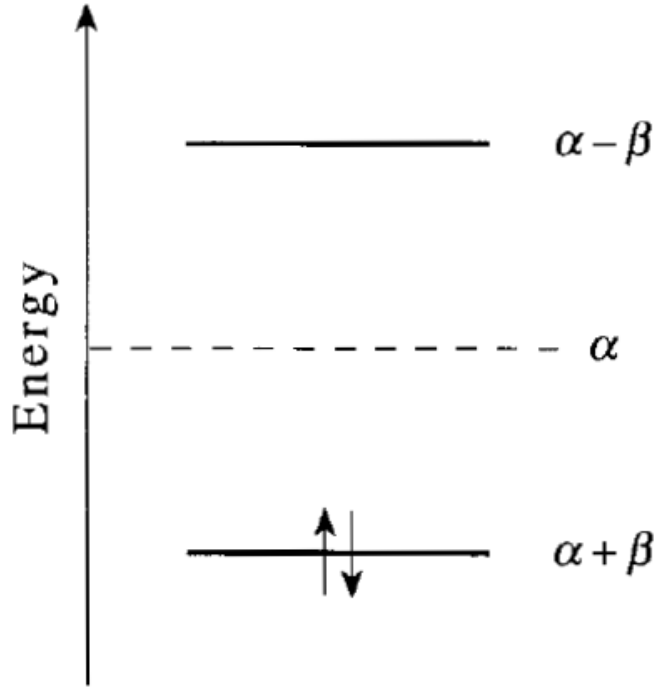
$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

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

$$(\alpha - E)^2 = \beta^2$$

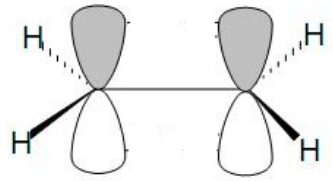
$$\boxed{E_{\pm} = \alpha \pm \beta}$$

$\beta \sim$ -75 kJ/mol



Aproximação de elétrons-π: Teoria de Hückel

$$\psi_\pi = c_1 2p_{z\mathrm{A}} + c_2 2p_{z\mathrm{B}}$$



$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \quad \Rightarrow \quad \boxed{E_\pm = \alpha \pm \beta}$$

$$\begin{cases} c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0 \end{cases}$$

$$\begin{cases} c_1(\alpha - E) + c_2\beta = 0 \\ c_1\beta + c_2(\alpha - E) = 0 \end{cases}$$

Substituir nas equações seculares $E_+ = \alpha + \beta$

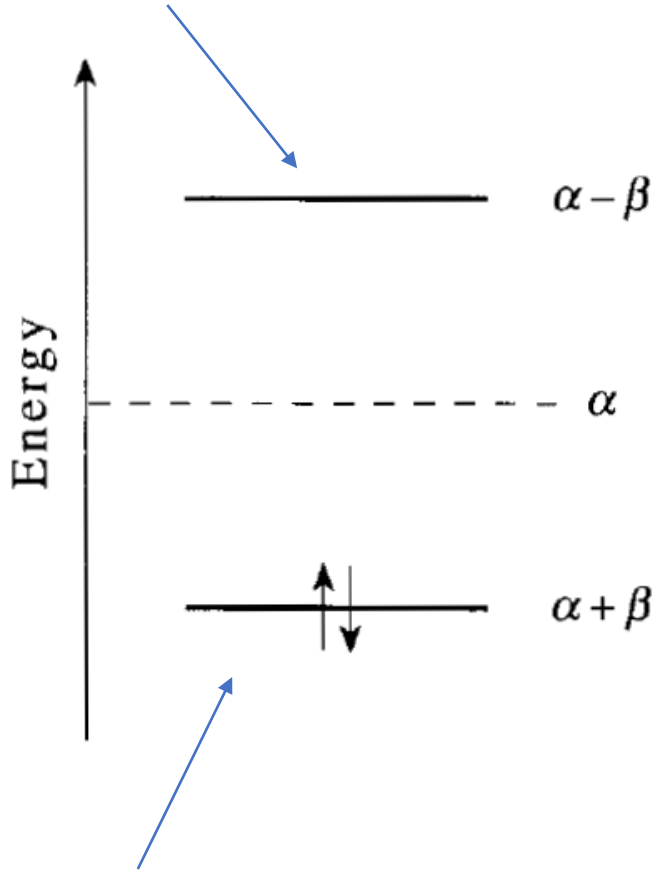
$$\begin{cases} -c_1\beta + c_2\beta = 0 \\ c_1\beta - c_2\beta = 0 \end{cases} \quad \Rightarrow \quad c_1 = c_2$$

Substituir nas equações seculares $E_- = \alpha - \beta$

$$\begin{cases} c_1\beta + c_2\beta = 0 \\ c_1\beta + c_2\beta = 0 \end{cases} \quad \Rightarrow \quad c_1 = -c_2$$

Aproximação de elétrons-π: Teoria de Hückel

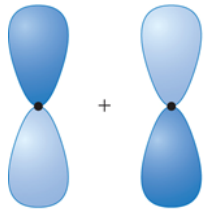
LUMO, *lowest unoccupied molecular orbital*

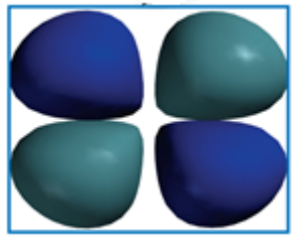


HOMO, *highest occupied molecular orbital*

orbital molecular π* (anti-ligante)

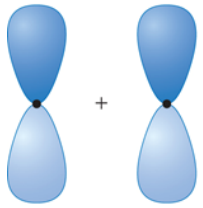
$$\Psi_{\pi^*} = 2p_{zA} - 2p_{zB}$$



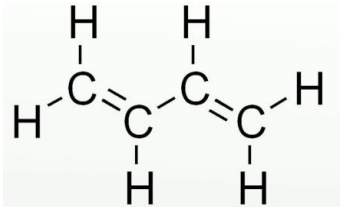


orbital molecular π (ligante)

$$\Psi_{\pi} = 2p_{zA} + 2p_{zB}$$



$$\psi_i = \sum_{j=1}^{4} c_{ij} 2p_{zj}$$

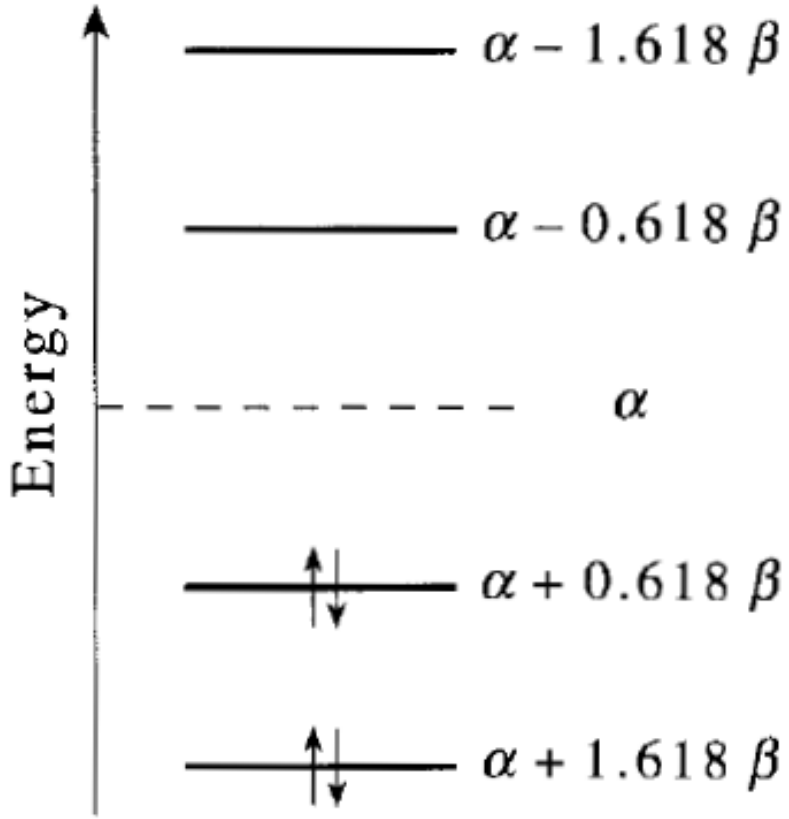


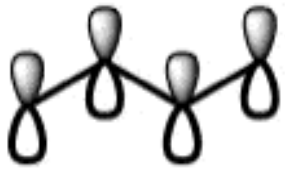
butadieno

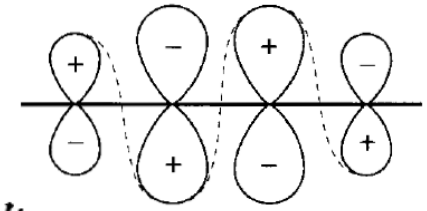
$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

E_1, E_2, E_3, E_4

$\beta \sim$ -75 kJ/mol



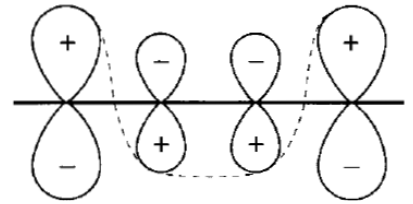




$$\psi_4 = 0.3717 \cdot 2p_{z1} - 0.6015 \cdot 2p_{z2} + 0.6015 \cdot 2p_{z3} - 0.3717 \cdot 2p_{z4}$$

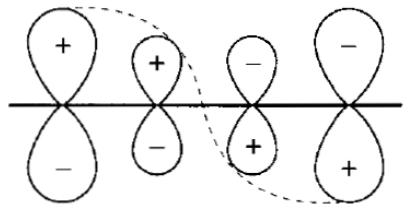
Energy

$\alpha - 1.618\,\beta$



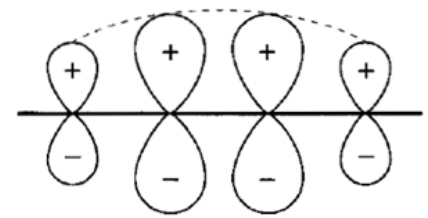
$\alpha - 0.618\,\beta$ $\quad \psi_3 = 0.6015 \cdot 2p_{z1} - 0.3717 \cdot 2p_{z2} - 0.3717 \cdot 2p_{z3} + 0.6015 \cdot 2p_{z4}$

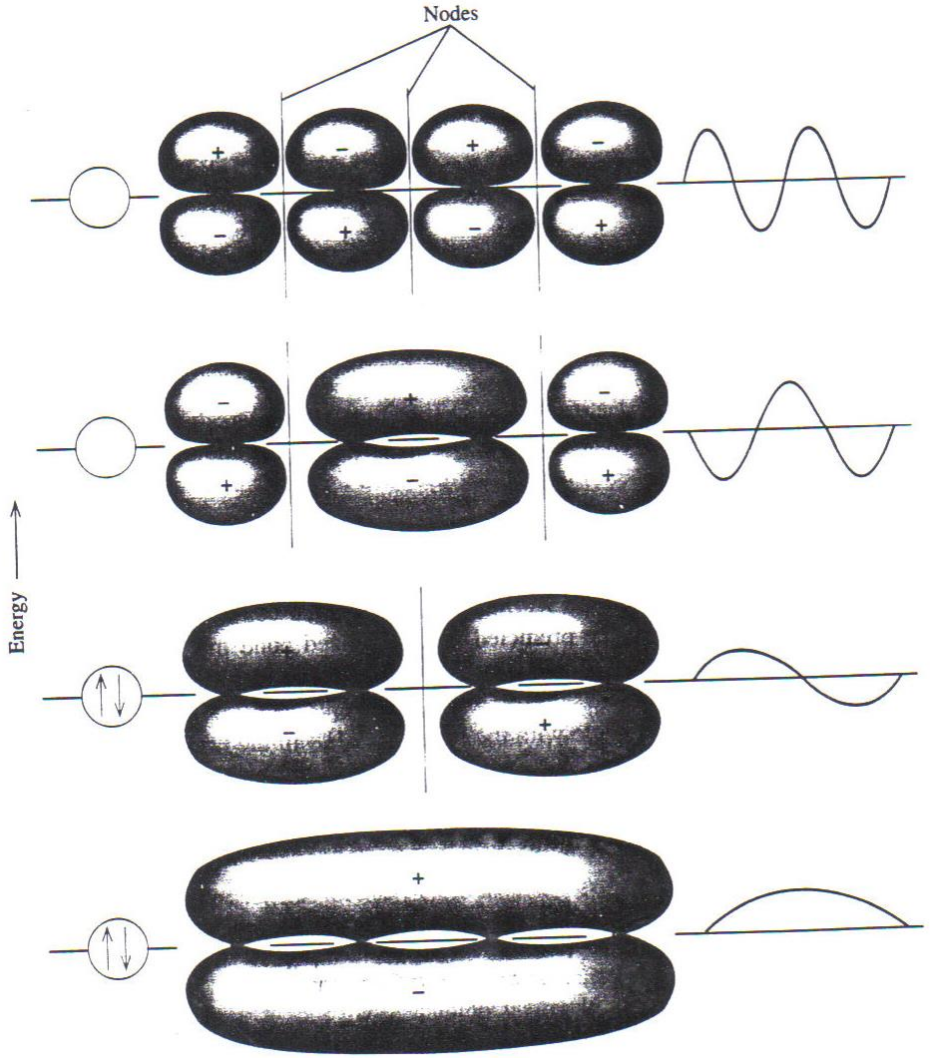
α



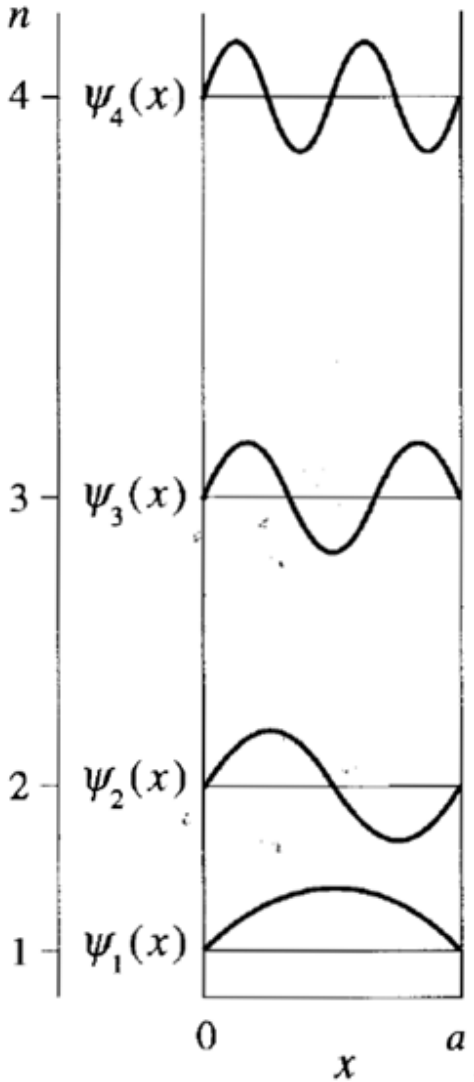
$\alpha + 0.618\,\beta$ $\quad \psi_2 = 0.6015 \cdot 2p_{z1} + 0.3717 \cdot 2p_{z2} - 0.3717 \cdot 2p_{z3} - 0.6015 \cdot 2p_{z4}$

$\alpha + 1.618\,\beta$ $\quad \psi_1 = 0.3717 \cdot 2p_{z1} + 0.6015 \cdot 2p_{z2} + 0.6015 \cdot 2p_{z3} + 0.3717 \cdot 2p_{z4}$

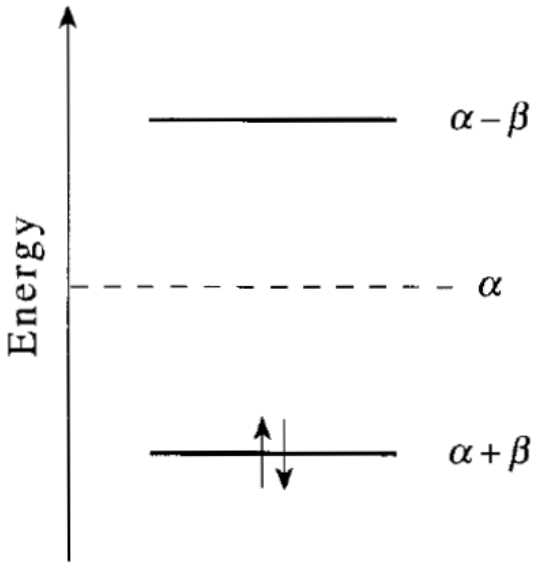




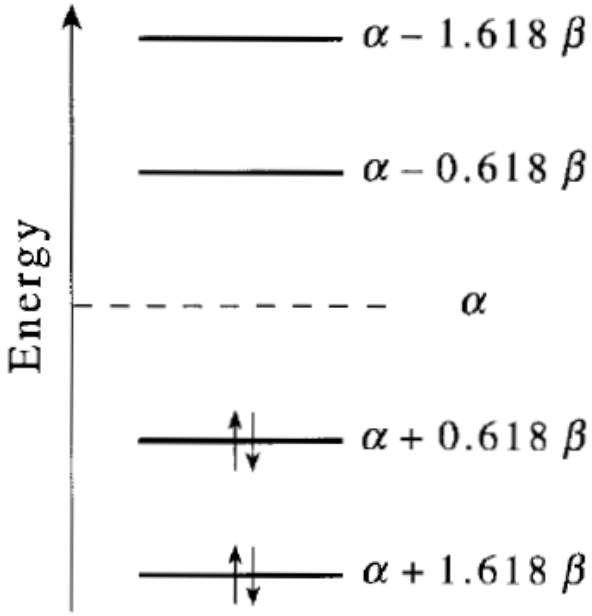
orbitais moleculares do butadieno na aproximação de elétrons π



partícula na caixa



$E_{eteno} = 2(\alpha + \beta)$



$E_{butadieno} = 2(\alpha + 1{,}62\beta) + 2(\alpha + 0{,}62\beta)$

$= 4\alpha + 4{,}48\beta$

Energia de deslocalização

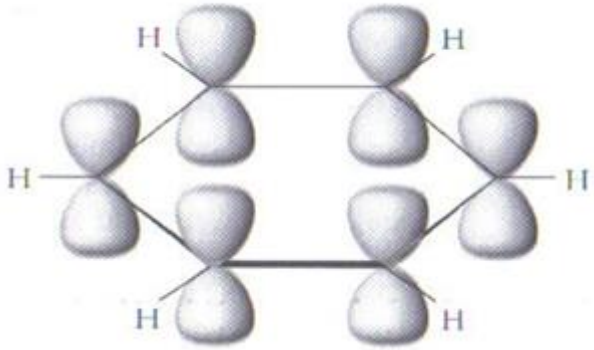
$E_{desloc.} = E_{butadieno} - 2.E_{eteno}$

$E_{desloc.} = 0{,}48\beta$

$\beta \sim$ -75 kJ/mol

$E_{desloc.} \approx$ -36 kJ/mol

Benzeno



$S_{ij} = 0$, $S_{ii} = 1$

$H_{ii} = \alpha$ $\quad$ $H_{ij} = \beta$

$H_{ij} = 0$ se (i,j) não são vizinhos

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

$$E_1 = \alpha + 2\beta$$

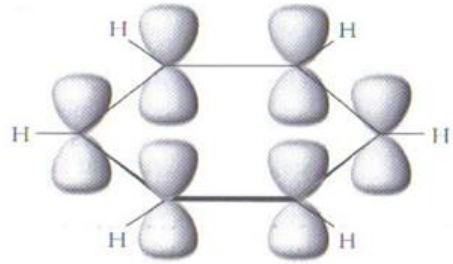
$$E_2 = \alpha + \beta$$

$$E_3 = \alpha + \beta$$

$$E_4 = \alpha - \beta$$

$$E_5 = \alpha - \beta$$

$$E_6 = \alpha - 2\beta$$



$$\psi_1 = \tfrac{1}{\sqrt{6}}(2p_{z1} + 2p_{z2} + 2p_{z3} + 2p_{z4} + 2p_{z5} + 2p_{z6}) \qquad E_1 = \alpha + 2\beta$$

$$\psi_2 = \tfrac{1}{\sqrt{4}}(2p_{z2} + 2p_{z3} - 2p_{z5} - 2p_{z6}) \qquad E_2 = \alpha + \beta$$

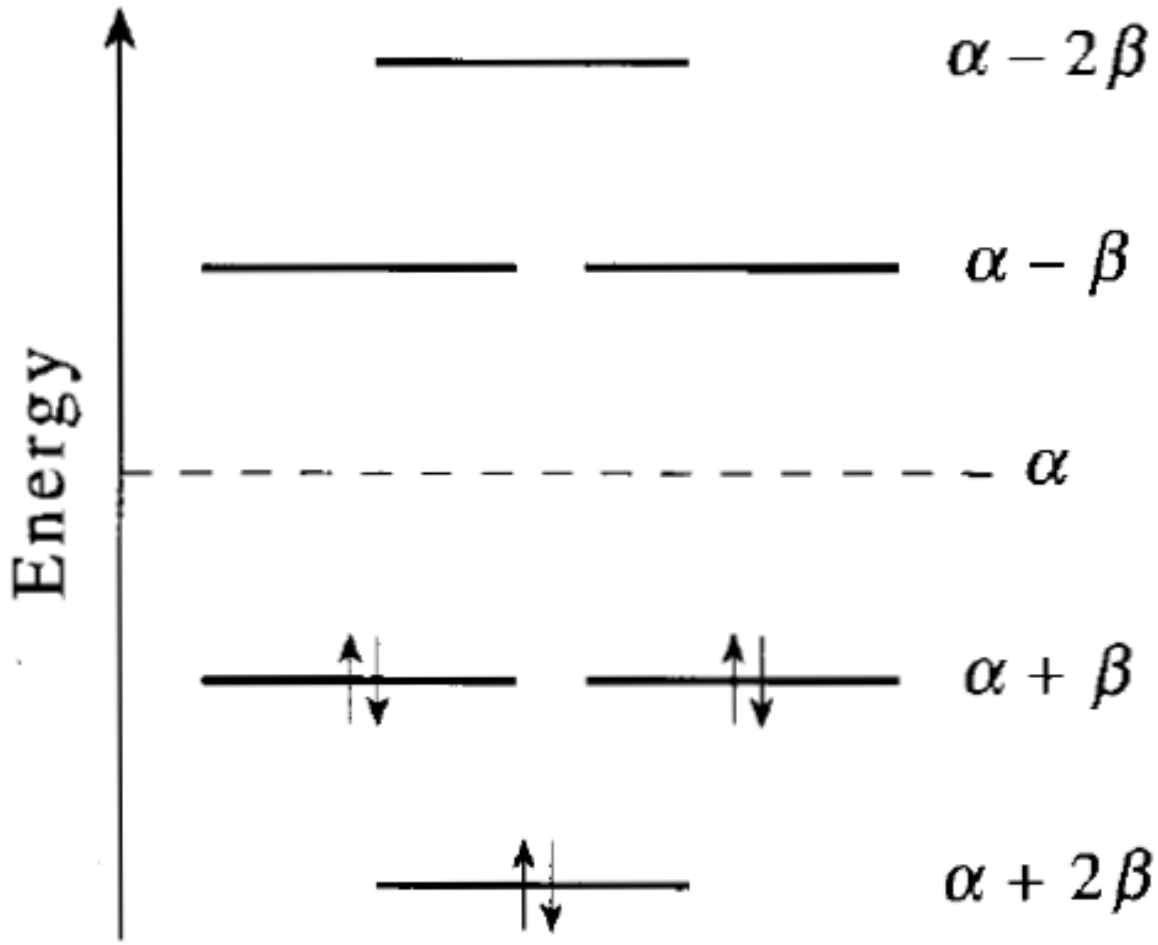
$$\psi_3 = \tfrac{1}{\sqrt{3}}(2p_{z1} + \tfrac{1}{2}2p_{z2} - \tfrac{1}{2}2p_{z3} - 2p_{z4} - \tfrac{1}{2}2p_{z5} + \tfrac{1}{2}2p_{z6}) \qquad E_3 = \alpha + \beta$$

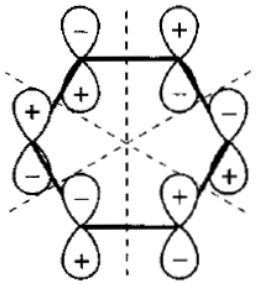
$$\psi_4 = \tfrac{1}{\sqrt{4}}(2p_{z2} - 2p_{z3} + 2p_{z5} - 2p_{z6}) \qquad E_4 = \alpha - \beta$$

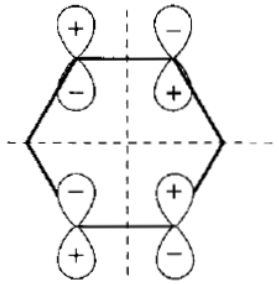
$$\psi_5 = \tfrac{1}{\sqrt{3}}(2p_{z1} - \tfrac{1}{2}2p_{z2} - \tfrac{1}{2}2p_{z3} + 2p_{z4} - \tfrac{1}{2}2p_{z5} - \tfrac{1}{2}2p_{z6}) \qquad E_5 = \alpha - \beta$$

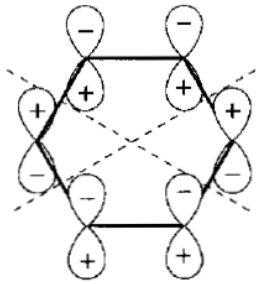
$$\psi_6 = \tfrac{1}{\sqrt{6}}(2p_{z1} - 2p_{z2} + 2p_{z3} - 2p_{z4} + 2p_{z5} - 2p_{z6}) \qquad E_6 = \alpha - 2\beta$$

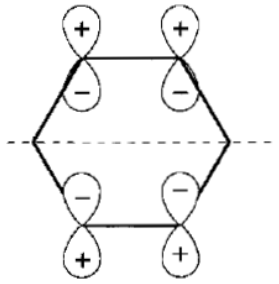
Benzeno

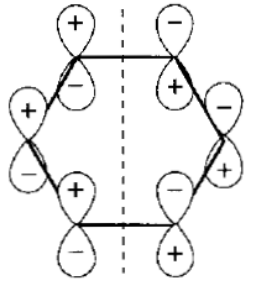

Energy
$\alpha - 2\beta$
$\alpha - \beta$
α
$\alpha + \beta$
$\alpha + 2\beta$

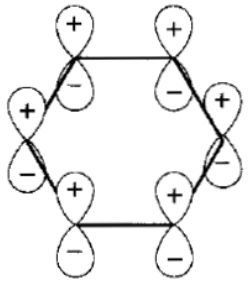

ψ_6


ψ_4

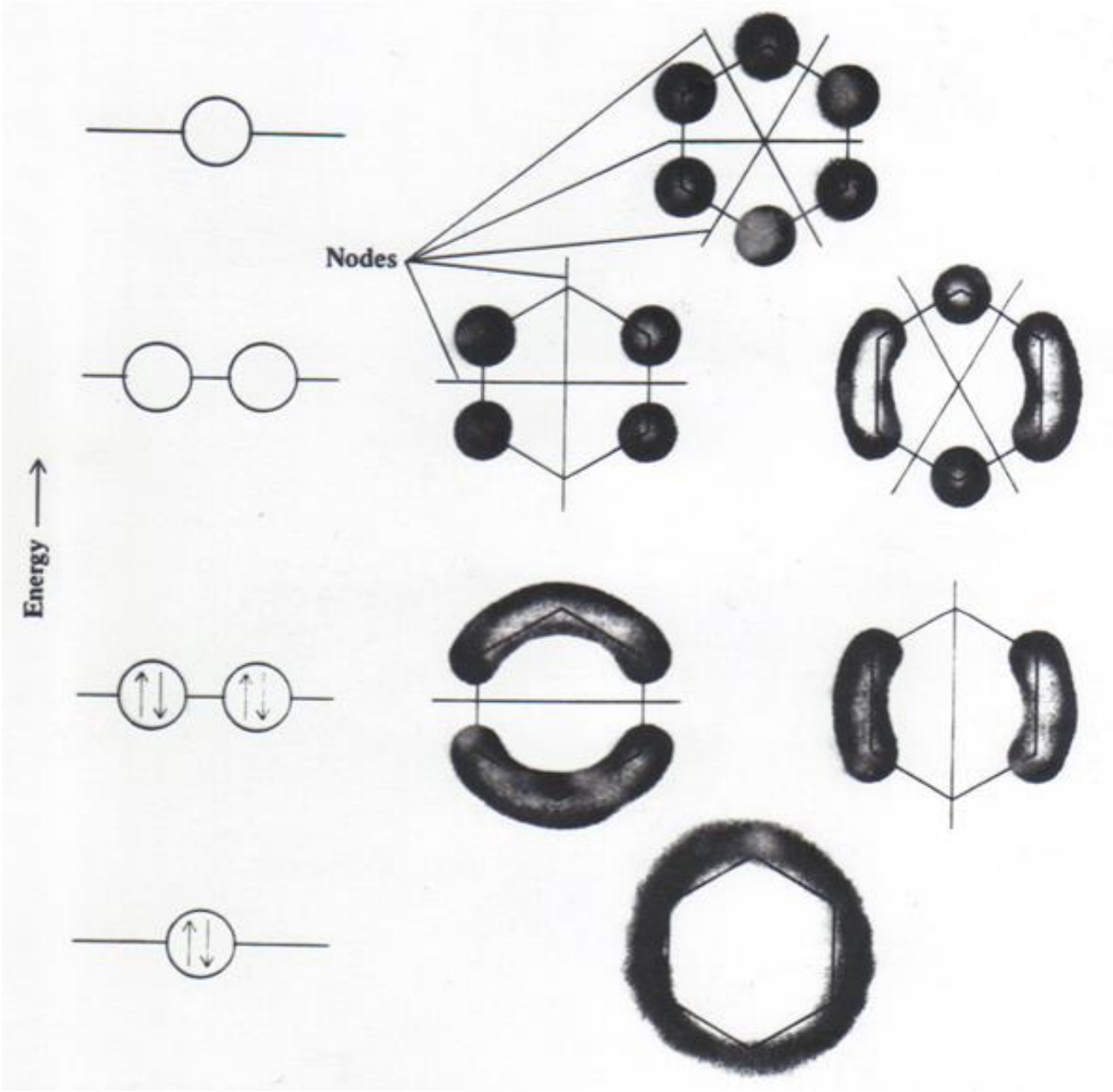

ψ_5

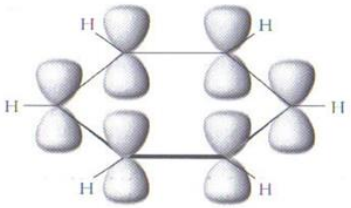

ψ_2


ψ_3


ψ_1

Benzeno





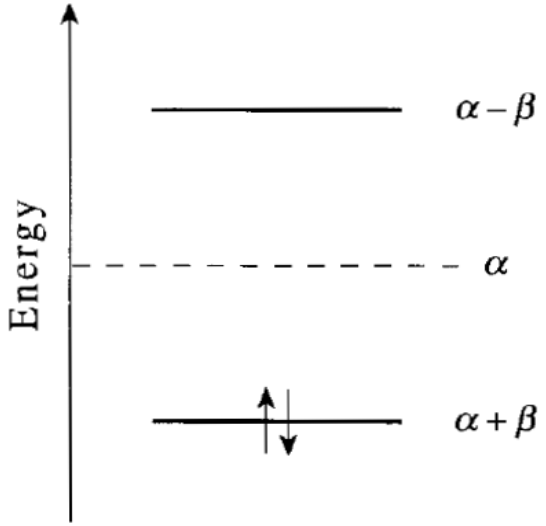
Energia de deslocalização

$$E_{\text{desloc.}} = E_{\text{benzeno}} - 3.E_{\text{eteno}}$$

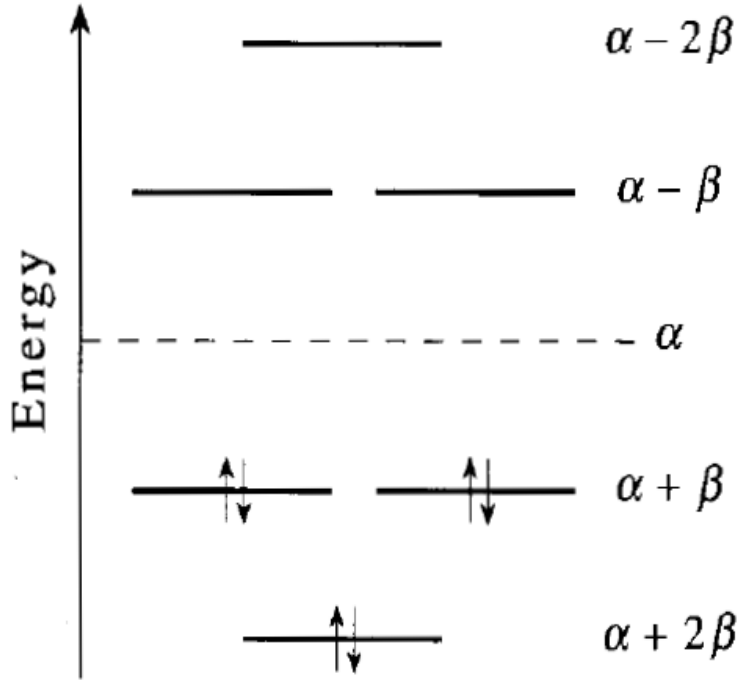
$$E_{\text{desloc.}} = 2\beta$$

$\beta \sim$ -75 kJ/mol

$$E_{\text{desloc.}} \approx \text{-150 kJ/mol}$$



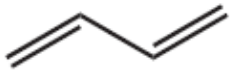
$$E_{\text{eteno}} = 2(\alpha + \beta)$$



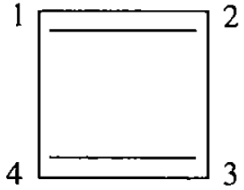
$$E_{\text{benzeno}} = 2(\alpha + 2\beta) + 4(\alpha + \beta)$$

$$= 6\alpha + 8\beta$$

butadieno



ciclobutadieno



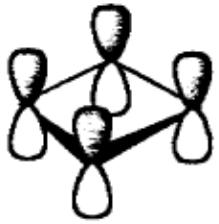
$$\begin{vmatrix} \alpha - E & \beta & 0 & \boldsymbol{\beta} \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \boldsymbol{\beta} & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

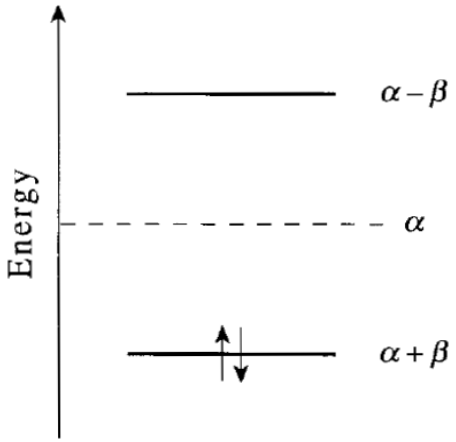
$$E_1 = \alpha + 2\beta$$

$$E_2 = \alpha$$

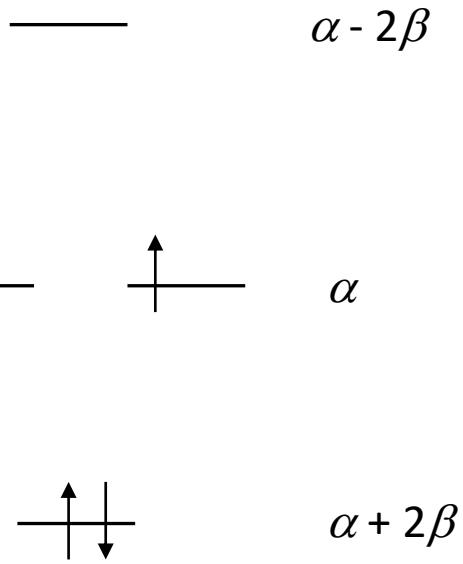
$$E_3 = \alpha$$

$$E_4 = \alpha - 2\beta$$





$E_{\text{eteno}} = 2(\alpha + \beta)$

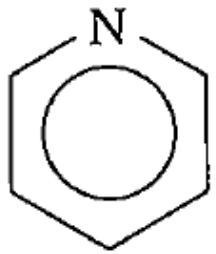


$E_{\text{ciclobutadieno}} = 4\alpha + 4\beta$

Energia de deslocalização

$E_{\text{desloc.}} = E_{\text{ciclobutadieno}} - 2.E_{\text{eteno}}$

$E_{\text{desloc.}} = 0$



piridina

$S_{ij} = 0$, $S_{ii} = 1$

$H_{ii} = \alpha \longrightarrow (\alpha_C , \alpha_N)$ $\qquad$ $H_{ij} = \beta \longrightarrow (\beta_{CC} , \beta_{CN})$

$H_{ij} = 0$ se (i,j) não são vizinhos

$$\begin{vmatrix} \alpha_N - E & \beta_{CN} & 0 & 0 & 0 & \beta_{CN} \\ \beta_{CN} & \alpha_C - E & \beta_{CC} & 0 & 0 & 0 \\ 0 & \beta_{CC} & \alpha_C - E & \beta_{CC} & 0 & 0 \\ 0 & 0 & \beta_{CC} & \alpha_C - E & \beta_{CC} & 0 \\ 0 & 0 & 0 & \beta_{CC} & \alpha_C - E & \beta_{CC} \\ \beta_{CN} & 0 & 0 & 0 & \beta_{CC} & \alpha_C - E \end{vmatrix} = 0$$