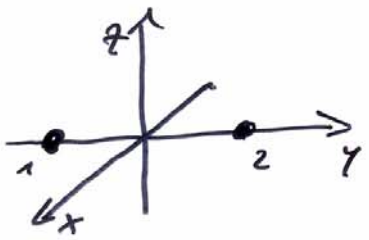
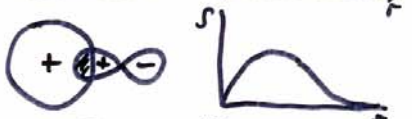
Überlappungsintegral S



φ_1 φ_2

AO vom Typ		S(r)	Bindungstyp
φ_1	φ_2		
s	s		σ (s,s)
s	p_y		σ (s, p_y)
s	p_x }		—
oder s	p_z }		
p_y	p_y		σ (p_y, p_y)
p_z	p_y }		—
p_x	p_y }		
p_z	p_z		$\overline{\pi}$ (p_z, p_z)
p_x	p_x		$\overline{\pi}$ (p_x, p_x)
p_z	p_x		—

Wechselwirkung zweier Orbitale φ_i, φ_m:

$$\int \varphi_i \, H \, \varphi_m \, d\tau = \beta_{im} = \begin{cases} \beta & \text{für } |i-m| = 1 \\ 0 & \text{sonst} \quad (i \neq m) \end{cases}$$

β = Resonanzintegral

$$\int \varphi_i \, \varphi_m \, d\tau = S_{im} = \begin{cases} 1 & \text{für } l = m \\ 0 & \text{sonst} \end{cases}$$

S = Überlappungsintegral

$\hat{=}$ Grad der Überlappung der Orbitale φ_i, φ_m

LCAO-Ansatz zur Berechnung von π-Systemen

$$\pi MO\ \psi_i = \sum_{k=1}^{n} c_{ik}\,\varphi_k \qquad \text{mit } i = 1 \dots n$$

Koeffizient c_{ik}: Beitrag des AO_k zum πMO_i

$$\Rightarrow E_i = \frac{\int \psi_i^* H \psi_i \, d\tau}{\int \psi_i^* \psi_i \, d\tau} = \frac{\int (\Sigma c_{ik} \varphi_k^* | H (\Sigma c_{ik} \varphi_k) \, d\tau}{\int (\Sigma c_{ik} \varphi_k^*)(\Sigma c_{ik} \varphi_k) \, d\tau}$$

HMO-Näherung: σ-π-Separation

$\alpha_i = \alpha$ für alle C

$\beta_{ij} = \beta$ für $|i-j| = 1$

$= 0$ sonst

$S_{ij} = 1$ für $i=j$

0 sonst

Suche nach energetischem Minimum

$\frac{\partial E_i}{\partial c_{ik}} = 0$ für alle c_{ik} ⇒ k „Säkulargleichungen"

homogenes, lineares Gleichungssystem

Lösung: Bildung und Ausmultiplizieren der „Säkulardeterminante"

$$|\alpha, \beta, S| = 0$$

Beispiel: Allylsystem 

$\varphi_1\ \varphi_2\ \varphi_3$

$k = 1, 2, 3$

$$\psi_i = \sum_{k=1}^{3} c_{ik}\,\varphi_k \qquad \text{LCAO}$$

$$\int \psi_i^* H \psi_i \, d\tau = E_i \int \psi_i^* \psi_i \, d\tau$$

$$= \int (c_{i1}\varphi_1 + c_{i2}\varphi_2 + c_{i3}\varphi_3)\, H\, (c_{i1}\varphi_1 + c_{i2}\varphi_2 + c_{i3}\varphi_3)\, d\tau$$

$$= \int (c_{i1}^2 \varphi_1^* H \varphi_1 + c_{i1}\varphi_1 H c_{i2}\varphi_2 + c_{i1}\varphi_1 H c_{i3}\varphi_3 +$$

$$+ c_{i2}\varphi_2^* H c_{i1}\varphi_1 + c_{i2}\varphi_2^* H c_{i2}\varphi_2 + c_{i2}\varphi_2^* H c_{i3}\varphi_3$$

$$+ c_{i3}\varphi_3^* H c_{i1}\varphi_1 + c_{i3}\varphi_3^* H c_{i2}\varphi_2 + c_{i3}\varphi_3 H c_{i3}\varphi_3)\, d\tau$$

$$E_i \int \psi_i^* \psi_i \, d\tau = c_{i1}^2 \alpha + c_{i1} c_{i2} \beta + 0$$

Hückel-Näherung $+ c_{i2} c_{i1} \beta + c_{i2}^2 \alpha + c_{i2} c_{i3} \beta$

$$+ 0 + c_{i2} c_{i3} \beta + c_{i3}^2 \alpha$$

$$= c_{i1}^2 \alpha + 2 c_{i1} c_{i2} \beta + c_{i2}^2 \alpha + 2 c_{i2} c_{i3} \beta + c_{i3}^2 \alpha$$

$$= E_i \sum c_{ik}^2 = E_i (c_{i1}^2 + c_{i2}^2 + c_{i3}^2)$$

wegen $\int \varphi_i \varphi_k = 0$ bei $i \neq k$

$$\Rightarrow \frac{\partial}{\partial c_{i1}}: \quad 2 c_{i1} E_i + \underbrace{\frac{\partial E_i}{\partial c_{i1}}}_{=0: \text{Minimum!}} (c_{i1}^2 + c_{i2}^2 + c_{i3}^2) = 2 c_{i1} \alpha + 2 c_{i2} \beta$$

$$\Rightarrow \quad 2 c_{i1} E_i = 2 c_{i1} \alpha + 2 c_{i2} \beta$$

$$\Rightarrow \quad 0 = (\alpha - E) c_{i1} + \beta c_{i2} + 0 c_{i3}$$

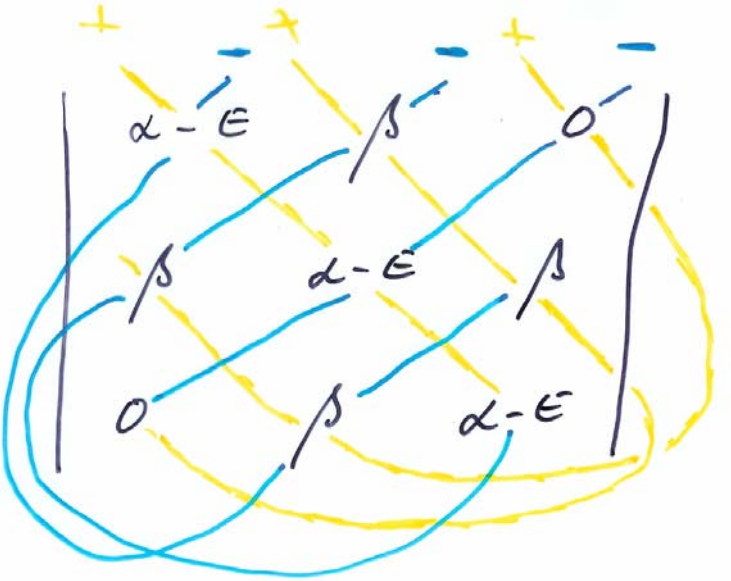
analog $\quad 0 = \beta c_{i1} + (\alpha - E) c_{i2} + \beta c_{i3}$

und $\quad 0 = 0 c_{i1} + \beta c_{i2} + (\alpha - E) c_{i3}$

Säkulargleichungen

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

Säkulardeterminante



$= 0$

$$\Rightarrow \quad 0 = (\alpha-\epsilon)^3 + 0\cdot\beta^2 + 0\beta^2 - (\alpha-\epsilon)\beta^2 - (\alpha-\epsilon)\beta^2 - 0(\alpha-\epsilon)$$

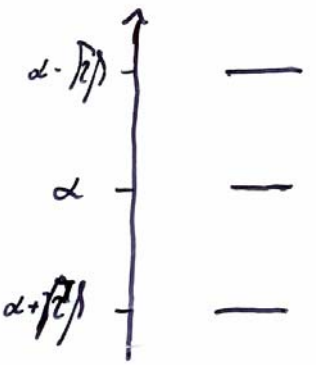
$$= (\alpha-\epsilon)^3 - 2(\alpha-\epsilon)\beta^2$$

$$= (\alpha-\epsilon)\left((\alpha-\epsilon)^2 - 2\beta^2\right)$$

1. Lösung: $\alpha - \epsilon = 0 \qquad \epsilon = \alpha$

2.+3. Lösung: $(\alpha-\epsilon)^2 = 2\beta^2 \Rightarrow \alpha - \epsilon = \pm\sqrt{2}\beta \qquad \epsilon = \alpha \pm \sqrt{2}\beta$

Energieschema:



lineare, unverzweigte Polyene (yl)e:

$E_i = \alpha + 2\beta \cos \frac{i\pi}{n+1}$ $\quad c_{iv} = \sqrt{\frac{2}{n+1}} \sin \frac{iv\pi}{n+1}$

Beispiel Butadien

Säkulardeterminante

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} \xrightarrow{:\beta,\ \frac{\alpha-E}{\beta}=x} 0 = \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = x \cdot \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1 \cdot \begin{vmatrix} \end{vmatrix}$$

$= x(x^3 - 2x) - (x^2 - 1) = x^4 - 3x^2 + 1$ $\quad$ via $y = x^2$

$\Rightarrow y(y-3) =$

Nullstellen: $x = \pm\sqrt{2{,}62}\ ;\ \pm\sqrt{0.382}$

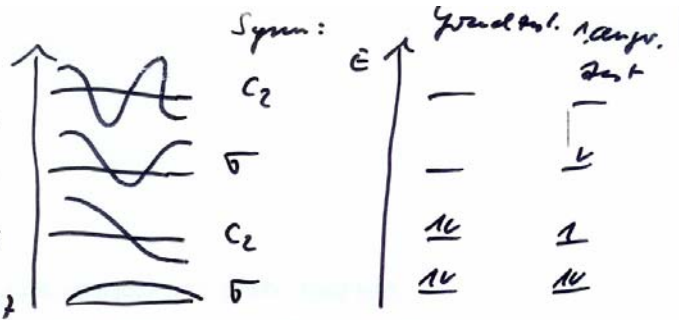
$= \pm 1{,}618 \quad \pm 0.6181$

$\Rightarrow E_{1,4} = \alpha \pm 1.618\beta \qquad E_{2,3} = \alpha \pm 0.618\beta$

mit $E_i = \alpha + 2\beta \cos \frac{i\pi}{} = \alpha + 1.618\beta \quad \pm$

Butadien

ψ_4	0.37	−0.6	0.6	−0.37
ψ_3	0.6	−0.37	−0.37	0.6
ψ_2	0.6	0.37	−0.37	0.6
ψ_1	0.37	0.6	0.6	0.37



π-Bindungsordnung $P_{\mu\nu} = \sum_{i=1}^{n} b_i \, c_{i\mu} \, c_{i\nu}$ μ,ν: Benachbarte Atome

$P_{1,2} = 2 \times 0.37 \cdot 0.6 + 2 \times 0.6 \times 0.37 = 0.88 = P_{3,4}$

$P_{2,3} = 2 \times 0.6 \times 0.6 + 2 \times 0.37 \cdot (-0.37) = 0.447$

π-Ladungsdichte $P_\nu = \sum b_i \, c_{i\nu}^2$

$P_1 = 2 \times 0.37^2 + 2 \times 0.6^2 = 0.994$

$P_2 = 2 \times 0.6^2 + 2 \times 0.37^2 = 0.994$

Freie Valenz $F_\nu = \sqrt{3} - \sum P_{\mu\nu}$

$F_1 = \sqrt{3} - 0.88 = 0.85$

$F_2 = \sqrt{3} - 0.88 - 0.447 = 0.40$

1. angr. Zustand:

$P_{1,2} = 2 \times 0.37 \times 0.6 + 1 \times 0.6 \times 0.37 + 1 \times 0.6 \times (-0.37) = 0.444$

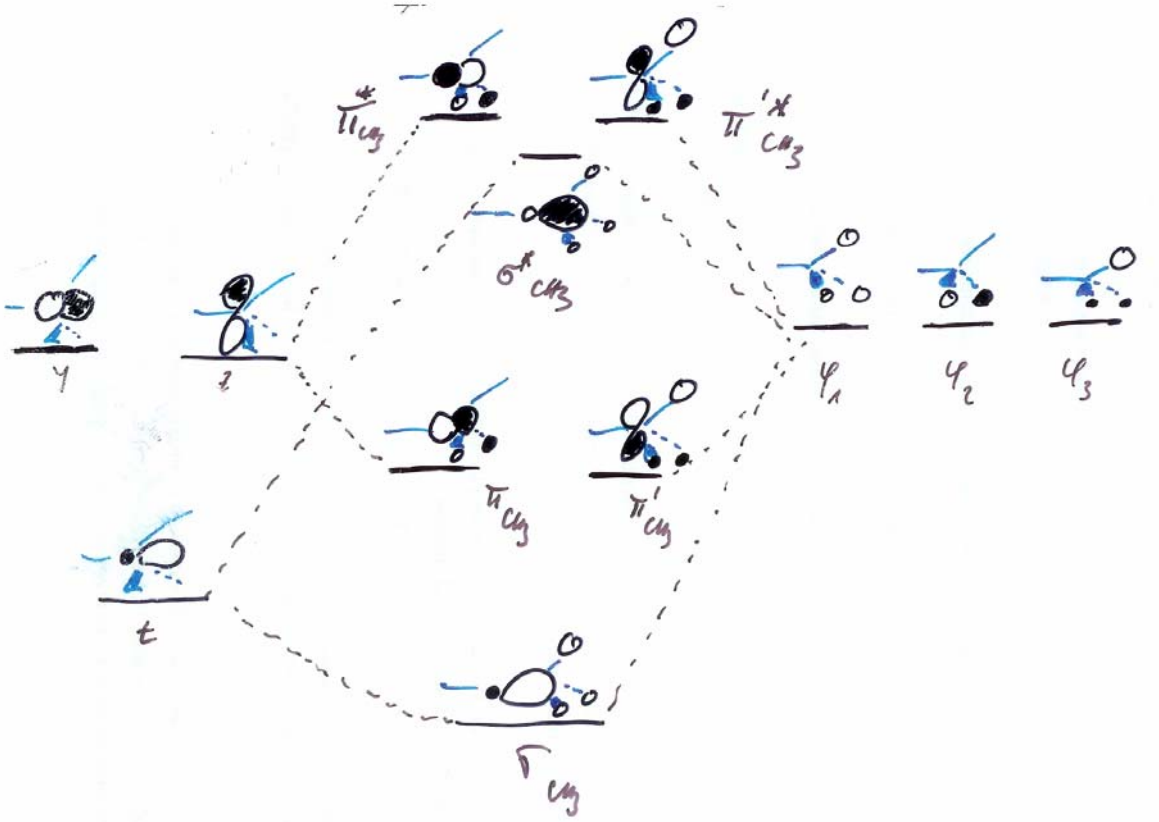
$P_{2,3} = 2 \times (0.6)^2 - 1 \times (0.37)^2 + 1 \times (0.37)^2 = 0.72$

$P_1 = 2 \times (0.37)^2 + 0.6^2 + 0.6^2 = 0.99$

$P_2 = 2 \times 0.6^2 + 0.37^2 + 0.37^2 = 0.99$

$F_1 = \sqrt{3} - 0.444 = 1.28$

$F_2 = \sqrt{3} - 0.444 - 0.72 = 0.56$



Gruppenorbitale der CH_3-Gruppe

AOs: 1s (H), 2py 2pz, Hybridorbital t (C)

C_3-Symmetrieadaptierte Kombinationen