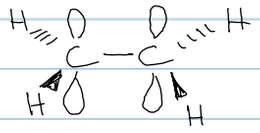
PC III 22.04.

1.3 Hückel-Theorie

Bindungen in ungesättigten Kohlenwasserstoffen
- σ-Bindungen: Grundgerüst
- π-Bindungen: delokalisiert MO's

z.B. Ethen



$$\psi = c_1 2p_{z,A} + c_2 2p_{z,B}$$

Lsg.: Säkulardeterminante

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

Wie kommt man darauf?

Variationsmethode

Grundzustand $\hat{H}\psi_0 = E_0\psi_0$

$$\frac{\int \psi_0^* \hat{H} \psi_0 \, d\tau}{\psi_0^* \psi_0 \, d\tau} = E_0$$

angeregter Zustand $\dfrac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} = E_\phi$ (1)

$E_\phi \geq E_0$ Variationsprinzip

lineare Kombination: $\Phi = c_1 2p_{z,A} + c_2 2p_{z,B}$

$= c_1 f_1 + c_2 f_2$ (c_n f_n reell)

$$\int \Phi \hat{H} \Phi \, d\tau = \int (c_1 f_1 + c_2 f_2) \hat{H} (c_1 f_1 + c_2 f_2) \, d\tau$$

$$= c_1^2 \underbrace{\int f_1 \hat{H} f_1 \, d\tau}_{H_{11}} + c_1 c_2 \underbrace{\int f_1 \hat{H} f_2 \, d\tau}_{H_{12}}$$

$$+ c_2 c_1 \underbrace{\int f_2 \hat{H} f_1 \, d\tau}_{H_{21}} + c_2^2 \underbrace{\int f_2 \hat{H} f_2 \, d\tau}_{H_{22}}$$

Hermitizität: $\int f_1 \hat{H} f_2 \, d\tau = \int f_2 \hat{H} f_1 \, d\tau$

also $H_{12} = H_{21}$

$$\boxed{\int \Phi \hat{H} \Phi \, d\tau = c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22} \quad (2)}$$

$$\boxed{\text{analog.} \quad \int \Phi \Phi \, d\tau = c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22} \quad (3)}$$

(2), (3) in (1)

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

$$\boxed{E(c_1, c_2) \cdot (c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22}) = c_1^2 H_{11} + 2 c_1 c_2 H_{12} + c_2^2 H_{22} \quad (4)}$$

(4) nach c_1 ableiten

$$(2 c_1 S_{11} + 2 c_2 S_{12}) E + \underbrace{\frac{\partial E}{\partial c_1}}_{=0} (c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22}) = 2 c_1 H_{11} + 2 c_2 H_{12}$$

umsortieren:

(a) $c_1 (H_{11} - E S_{11}) + c_2 (H_{12} - E S_{12}) = 0$

homogenes Gleichungssystem von (a) und (b)

(4) nach c_2 auflösen, umsortieren

(b) $\quad c_1 (H_{21} - E S_{21}) + c_2 (H_{22} - E S_{22}) = 0$

nichttriviale Lösung:

$$\begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} \\ H_{21} - E S_{21} & H_{22} - E S_{22} \end{vmatrix} = 0 \qquad \text{(siehe oben)}$$

Näherungen : Hückel, 1930

1) $S_{ij} = 1 \quad$ für $i = j$ } Überlappintegrale
$= 0 \quad$ für $i \neq j$ }

2) $H_{ii} = \alpha \quad$ alle gleich (gleiches Orbital) — hat nichts mit Wechselwirkung zu tun

3) $H_{ij} = \beta \quad$ für Atome i,j benachbart
$= 0 \quad$ für Atome i,j nicht benachbart

Anwendung: Ethen

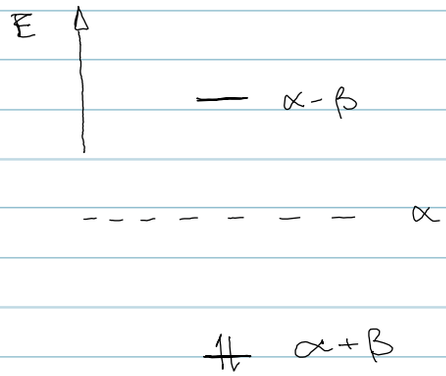
$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

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

$$E^2 - 2\alpha E + \alpha^2 - \beta^2 = 0$$

$$E_{1,2} = \alpha \pm \sqrt{\alpha^2 - \alpha^2 + \beta^2} = \alpha \pm \beta$$

exp.: $\beta \simeq -75 \frac{kJ}{mol}$



Grundzustand: $E_\pi = 2\alpha + 2\beta$

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

Koeffizient c_1, c_2?

$c_1(\alpha - E) + c_2\beta = 0$
$c_1\beta + c_2(\alpha - E) = 0$

a) für $E = \alpha + \beta$: $c_1 = c_2$

$\psi_\pi = c_1(2p_{z,A} + 2p_{z,B})$

Normieren:

$c_1^2(1 + \underbrace{2S}_{=0} + 1) = 1$

$c_1^2 \cdot 2 = 1 \longrightarrow c_1 = \frac{1}{\sqrt{2}}$

$$\boxed{\psi_1 = \frac{1}{\sqrt{2}}(2p_{z,A} + 2p_{z,B})}$$

b) für $E = \alpha - \beta$: $c_1 = -c_2$

$\psi_\pi = c_1(2p_{z,A} - 2p_{z,B})$

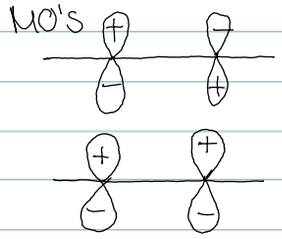
Normieren:

$c_1^2(1 - \underbrace{2S}_{=0} + 1) = 1$

$c_1^2 \cdot 2 = 1 \longleftrightarrow c_1 = \frac{1}{\sqrt{2}}$

$$\boxed{\psi_2 = \frac{1}{\sqrt{2}}(2p_{z,A} - 2p_{z,B})}$$

MO's



ψ_2 $\quad E = \alpha - \beta$

ψ_1 $\quad E = \alpha + \beta$

Anwendung: Benzol

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

β faktorisieren, substituieren $x = \frac{\alpha - E}{\beta}$

$$\beta^6 \begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

1. Zeile streichen, dann nacheinander alle Spalten

$\longrightarrow$ Determinante entwickeln

$$x \begin{vmatrix} x & 1 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 & 0 & 0 & 0 \\ 0 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 1 & x \end{vmatrix} - 1 \ldots$$

$$x^6 - 6x^4 - 9x^2 - 4 = 0$$

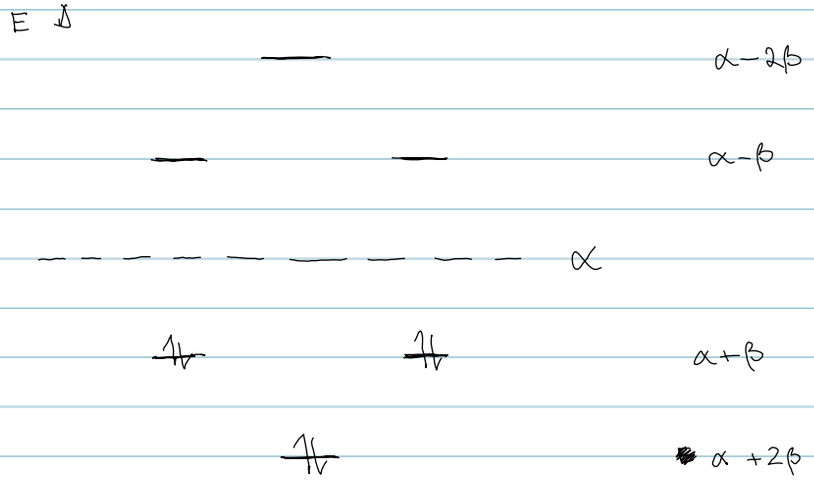
$$x = \pm 1 ; \pm 1 ; \pm 2$$

$E_1 = \alpha + 2\beta$

$E_2 = E_3 = \alpha + \beta$

$E_4 = E_5 = \alpha - \beta$

$E_6 = \alpha - 2\beta$



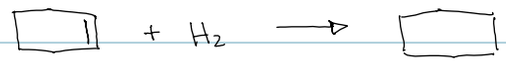
Grundzustand:

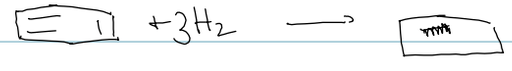
$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta)$

$= 6\alpha + 8\beta$

vgl.: $3 \cdot E_\pi(\text{Ethen}) = 6\alpha + 6\beta$

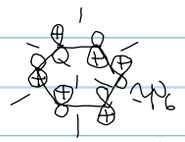
Delokalisierungsenergie $E_{delok} = 2\beta \simeq -150 \frac{kJ}{mol}$

exp.:  $\Delta H = -119 \frac{kJ}{mol}$

 $\Delta H = -207 \frac{kJ}{mol}$

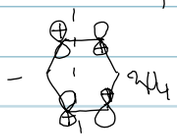
$\longrightarrow 2\beta \simeq -150 \frac{kJ}{mol}$

MO's Benzol

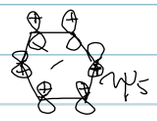


ψ_6 $\quad E = \alpha - 2\beta$

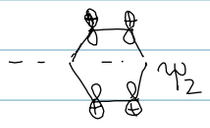
gestrichelt: Knotenebenen



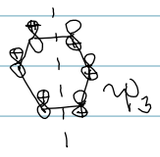
ψ_4



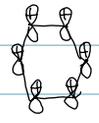
ψ_5 $\quad E = \alpha - \beta$



ψ_2



ψ_3 $\quad E = \alpha + \beta$



ψ_1 $\quad E = \alpha + 2\beta$

der Übersicht halber: nur positives Ende gekennzeichnet