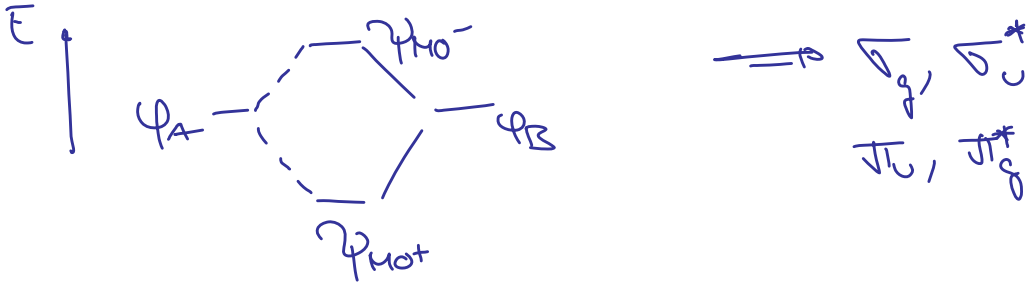
Note Title

HÜCKEL (HMO, LCAO)

$\psi_{MO\pm} = N(\varphi_A \pm \varphi_B)$

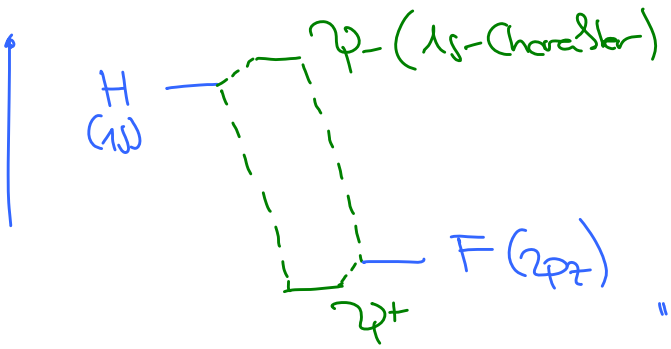
BORN (CE-Diche)

$\psi^2 = N^2(\varphi_A^2 + \varphi_B^2 + \underbrace{2\varphi_A\varphi_B}_{\triangleq S_{AB}})$



heteroatomar: $\psi_{MO} = c_A\varphi_A + c_B\varphi_B$

Bsp. HF



$\longrightarrow \psi_{MO} = \sum_{i=1}^{N} c_i\varphi_i$

"1s + 1s" "1s − 1s"

SALC, am Bsp. H_2O: $\Gamma(2H) = A_1 + B_2$

$\Gamma(O, n=2) = 2A_1 + B_1 + B_2$

↳ Auswahlregel: $\Gamma(\psi_d) \times \Gamma(\vec{\mu}_{x,y,z}) \times \Gamma(\psi_1) \stackrel{!}{=} A_1$

c. Variationsprinzip → Ziel: MO-Energien berechnen

$\hat{H}\psi = E\psi \;/\cdot \psi^*$, links

$\psi^*\hat{H}\psi = \psi^* E\psi$

↳ $\boxed{E = \frac{\int \psi^*\hat{H}\psi \, d\tau}{\int \psi^*\psi \, d\tau} = \langle\hat{H}\rangle}$ #

Da falls $\tilde{\psi}$ nicht die SGL löst, gilt: $\boxed{E(\tilde{\psi}) > \langle \hat{H} \rangle}$

"Variationsansatz" mit Probefunktion $\tilde{\psi} = \sum c_j \varphi_j$

gesucht: $\frac{\partial E}{\partial c_j} \stackrel{!}{=} 0$

2-atomig $\psi = c_A \varphi_A + c_B \varphi_B$ $\quad | \psi = \psi^*$

(i) $\int \psi_{MO}^2 \, d\tau = c_A^2 \underbrace{\int \varphi_A^2 \, d\tau}_{=1} + c_B^2 \underbrace{\int \varphi_B^2 \, d\tau}_{=1} + 2 c_A c_B \underbrace{\int \varphi_A \varphi_B \, d\tau}_{\text{Überlappintegral } S_{AB}}$

(Nenner von #) $\quad (= S_{AA}) \quad (= S_{BB})$

(ii) $\int \psi \hat{H} \psi \, d\tau = \int (c_A \varphi_A + c_B \varphi_B) \hat{H} (c_A \varphi_A + c_B \varphi_B) \, d\tau$

$= c_A^2 \underbrace{\int \varphi_A \hat{H} \varphi_A \, d\tau}_{\alpha_A} + c_B^2 \underbrace{\int \varphi_B \hat{H} \varphi_B \, d\tau}_{\alpha_B} + 2 c_A c_B \underbrace{\int \varphi_A \hat{H} \varphi_B \, d\tau}_{\beta}$

H_{AA} $\quad H_{BB}$ $\quad H_{AB}$

$\alpha_A \rightarrow$ Coulomb-Integrale

($\triangleq$ Ionisierungsenergie, z.B. $-13.6\,eV$ für 1S-H)

β Resonanzintegral

$\beta = 0 \ldots -3\,eV$

$\Rightarrow \quad \boxed{E = \frac{c_A^2 \alpha_A + c_B^2 \alpha_B + 2 c_A c_B \beta}{c_A^2 + c_B^2 + 2 c_A c_B S_{AB}}} \quad \#\#$

$\rightarrow \quad \frac{\partial E}{\partial c_j} \stackrel{!}{=} 0$

$\Rightarrow \quad \frac{\partial E}{\partial c_A} = (\alpha_A - E) \cdot c_A + (\beta - E S_{AB}) c_B \stackrel{!}{=} 0$

$\frac{\partial E}{c_B} = (\beta - E S_{AB}) \cdot c_A + (\alpha_B - E) \cdot c_B \stackrel{!}{=} 0$

Säkular-determinante $\begin{vmatrix} (\alpha_A - E) & (\beta - E S_{AB}) \\ (\beta - E S_{AB}) & (\alpha_B - E) \end{vmatrix} = 0 \; - \; \boxed{(\alpha_A - E)(\alpha_B - E) - (\beta - E S_{AB})^2}$

A = B $\quad \varphi_A = \varphi_B \;,\; \alpha_A = \alpha_B$

↳ $(\alpha - E)^2 - (\beta - ES)^2 = 0$ $\quad \beta < 0$

① Energie / MO:

$$E_+ = \frac{\alpha + \beta}{1+S}$$

$$E_- = \frac{\alpha - \beta}{1+S}$$

für H_2: $S(1s_1, 1s_2) \approx 0.6$

② Koeffizienten c_A / c_B: (aus ##) $\quad E = (c_A^2 + c_B^2)\cdot\alpha + 2c_A c_B \cdot \beta$

$$E_+ = \alpha \cdot \left(\frac{1}{1+S}\right) + \beta \cdot \left(\frac{1}{1+S}\right)$$

↳ $(c_A^2 + c_B^2) = \left(\frac{1}{1+S}\right)$ und $2c_A c_B = \left(\frac{1}{1+S}\right)$

⟶ $\boxed{c_A = \frac{1}{\sqrt{2(1+S)}} \;,\; c_B = c_A}$

③ WF: $\quad \boxed{\psi_{MO\pm} = \frac{1}{\sqrt{2(1\pm S)}} (\varphi_A \pm \varphi_B)}$

A ≠ B $\quad$ Annahme: $S_{AB} \approx 0$

↳ $0 = (\alpha_A - E)(\alpha_B - E) - \beta^2$

⟹ $\boxed{E_{+/-} = \frac{1}{2}(\alpha_A + \alpha_B) \pm \frac{1}{2}\left[(\alpha_A - \alpha_B)^2 + 4\beta^2\right]^{1/2}}$ … $c_A, c_B, \psi_{MO\pm}$

Bsp.: HF

$\beta = -1.0\,eV$

$\alpha_{1s,H} = -13.6\,eV$ ← 1s(H)

$\alpha_{2p_z,F} = -17.4\,eV$ ← $2p_z$(F)

↳ $E_+ = -17.6\,eV$

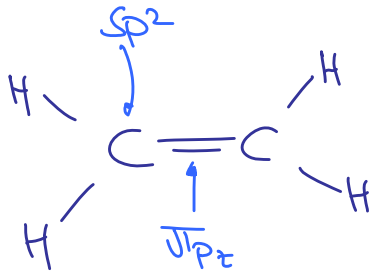
$E_- = -13.4\,eV$

$\psi_+ = 0.24 \cdot \varphi_{1s,H} + 0.97\,\varphi_{2p_z,F}$

$\psi_- = 0.97\,\varphi_{1s,H} - 0.24\,\varphi_{2p_z,F}$

D. Hückel-Näherung

am Bsp. Ethen:



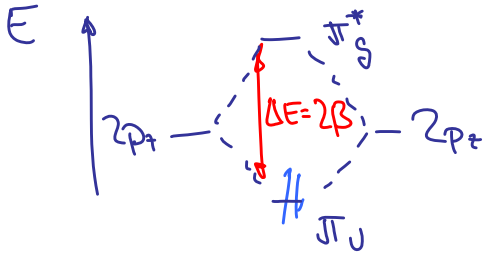
① nur π-Elektronen

② alle $\alpha_i = \alpha_j$

③ $S_{ij} := 0$

↳ $\begin{vmatrix} \alpha-E & \beta \\ \beta & \alpha-E \end{vmatrix} = (\alpha-E)^2 - \beta^2 \stackrel{!}{=} 0$

↳ $E_{+/-} = \alpha \pm \beta$



 , Butadien

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

← Resonanzintegral β nur für benachbarte Atome

↳ $(\alpha-E)^4 - 3(\alpha-E)^2\beta^2 + \beta^4 = 0$

→ $E_{1\ldots4} = \alpha \pm \sqrt{\frac{1}{2}\left(3 \pm \sqrt{5}\right)}\,\beta$

E	E_4	
LUMO	$E_3 = \alpha - 0.62\beta$	$\Delta E = 1.24\beta$
HOMO	$E_2 = \alpha + 0.62\beta$	
	$E_1 = \alpha + 1.62\beta$	

S. Frost-Reis