Note Title

$$\sum_{i,j} (H_{ij} - E S_{ij}) c_j = 0$$ Säkulargleichung

$H_{AA} = \alpha_A$ $\quad S_{AA} = S_{BB} = 1$

$H_{AB} = \beta$ $\quad S_{AB}$

↳ Säkulardeterminante → E_{MO}, c_j, Ψ_{MO}'s

⟹ HMO

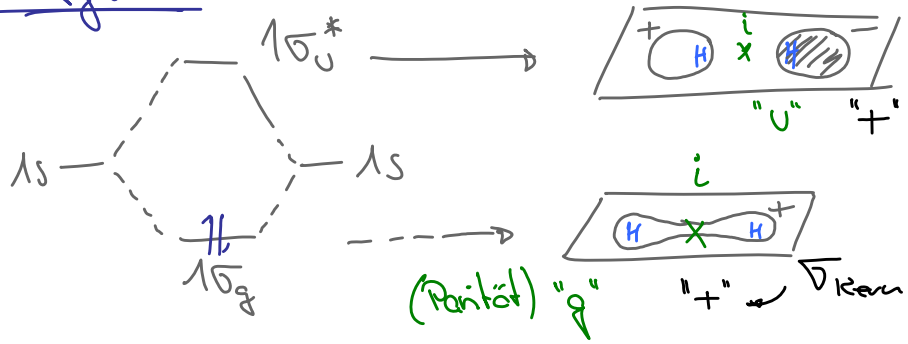
"Strategie": (i) LCAO / SALC ⟸ Auswahlregeln

(ii) E_{MO} ← QM

(iii) Termsymbole/Moleküle ⇒ Auswahlregeln

E. Termsymbole

H_2 (GZ)

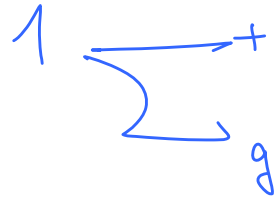


$(1\sigma_g^+)^2$ $\quad S=0,\ 2S+1=1$

⟹ $\Lambda = 0+0 = 0 \Rightarrow \Sigma$

Parität: "g" × "g" = g

σ_{Rem}: "+" × "+" = +



H_2 angeregt: $(1\sigma_g^+)^1 (1\sigma_u^{*(+)})^1$

σ^* ↑ $\quad$ $^1\Sigma_u^+$ $\quad$ ↑

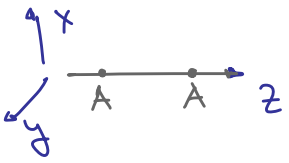
σ ↑ $\quad$ ↑

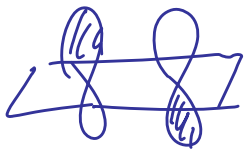
$(2S+1)$ $\quad S = \frac{1}{2}+\frac{1}{2} = 1$

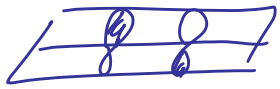
$(1\sigma_g^+)^1 (2p_z\sigma_g^+)^1$, e^- gepaart $\longrightarrow$ ${}^1\Pi_g^{(+)}$

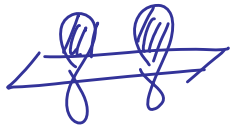
$(\Lambda = 0 + 1)$

π-Orbitale



$2p_x\pi_g^{*-}$ 

$2p_y\pi_g^{*+}$ 

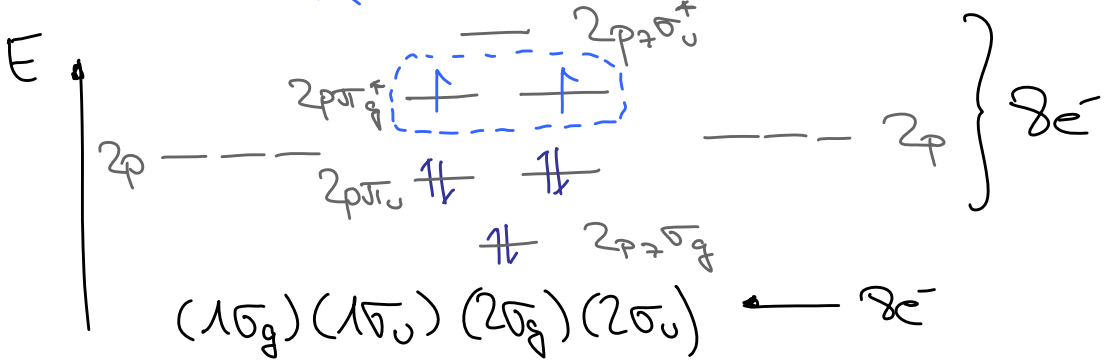
$2p_x\pi_u^-$ 

$2p_y\pi_u^+$ 

$\lambda = +1$

$\lambda = -1$

$\longrightarrow O_2$ (GZ)



$\hookrightarrow {}^3\Sigma_g^-$

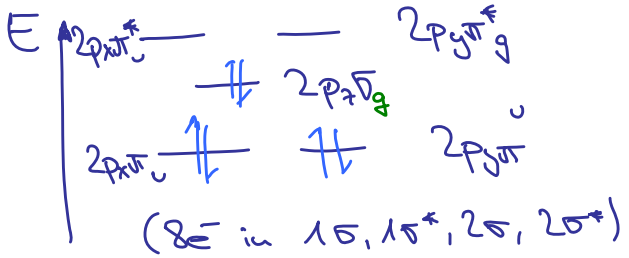
O_2 angeregt: (1) $(2p_y\pi_g^{*+})^2$ bzw. $(2p_x\pi_g^{*-})^2$

$\Lambda = |1 + 1| = (p_x\pi^*)$

$= |-1 - 1| = (p_y\pi^*)$

$\longrightarrow {}^1\Delta_g \leftarrow g \times g$

N_2 GZ



$S = 0 \rightarrow (2S+1) = 1$

$\Lambda = |(\underbrace{0+0}_{2p_z\sigma} \underbrace{+1+1}_{2p_x\pi_u} \underbrace{-1-1}_{2p_y\pi_u})|$

Parität: $(g \times g) \times (u \times u) \times (u \times u) = g$

$1 \rightarrow {}^+\Sigma_g$

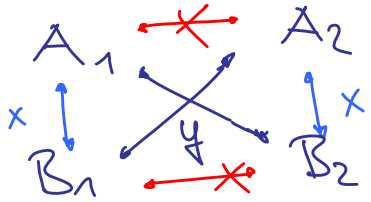
⇒ Auswahlregeln (allg.) für Molekülspektroskopie

① SYMMETRIE ← "ausführlich"

GDH: $\Gamma(\psi_0) \times \Gamma(\mu_{x,y,z}) \times \Gamma(\psi_1) = A_{1g}$

Bsp.: a_1 — LUMO
b_1 ⇅ HOMO ⇒ μ_x-Polarisation

allg. zu C_{2v}:

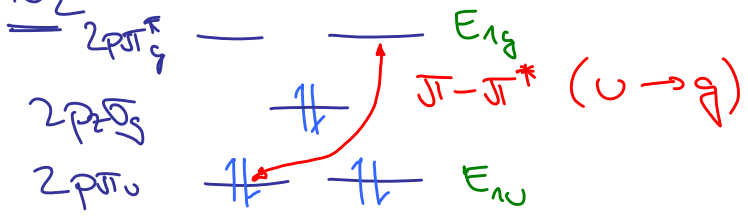


sowie: $\Gamma(\psi_0) = \Gamma(\psi_1)$
⇒ z-polarisiert (A_1)

② Parität, "LaPorte-Regel"

nur $u \leftrightarrow g$ – Übergänge erlaubt
(⇒ $\mu_{x,y,z}$ ist "ungerade")

N_2



$^1\Sigma_g^+ \longrightarrow {}^1\Sigma_u^+$

$(E_{1u} \longrightarrow E_{1g})$

⟶ A_{1u} (z-polarisiert)

③ $\Sigma^{+/-}$?

nur $\Sigma^+ \to \Sigma^+$ / $\Sigma^- \to \Sigma^-$ erlaubt

④ Drehimpuls

(i) Spin: $\Delta S = 0$

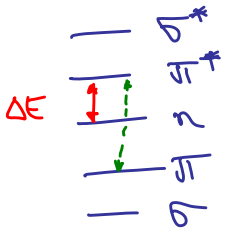
(ii) $\Delta\Lambda = 0, \pm 1$: $\Sigma \leftrightarrow \Sigma/\Pi$

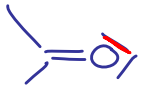
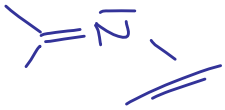
$\Sigma \not\leftrightarrow \Delta$

6. Elektronische Übergänge in Molekülen

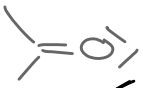
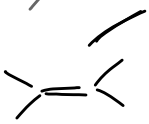
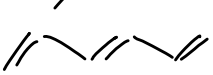
$\sigma \rightarrow \sigma^*$ $\quad CH_4$, $\lambda = 122\,nm$

$n \rightarrow \pi^*$ $\quad$ nicht-bindende e^-



		$\varepsilon / \frac{L}{mol \cdot cm}$
	280 nm	10–20
	"	~20
H_2O $(b_1 \rightarrow a_1)$ $n \rightarrow \sigma^*$	170 nm	7000

$\pi_u \rightarrow \pi_g^*$ $\quad \varepsilon_{max} \sim 10 \ldots 10^5 \; \frac{L}{M \cdot cm}$

	190 nm	$\varepsilon \sim 1000$
	170 nm	16.000
	260 nm	35.000 etc.