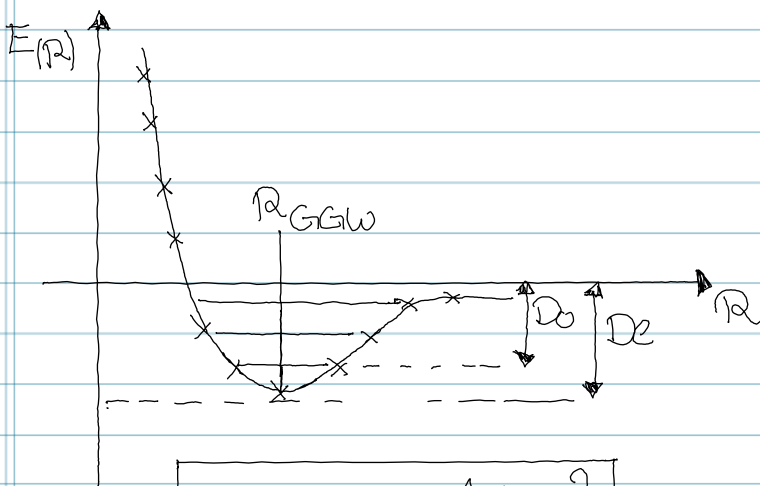
Vorlesung 19.12.2013

Wiederholung:

$H_2^{\oplus}$

Born-Oppenheimer-Näherung

$$\boxed{\hat{H}\,\Psi(R,r) = E_{(R)}\,\Psi(R,r)}$$ Schrödinger-Gleichung

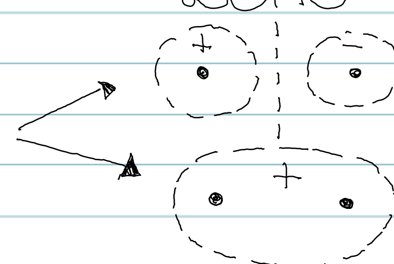


$$\boxed{D_e = D_0 + \frac{1}{2}h\nu}$$

Näherungslösung: MO-Theorie

LCAO → MO

$\overset{\oplus}{S}_{1s} \pm \overset{\oplus}{S}_{1s}$



σ_u^* antibindend

σ_g bindend

$$\boxed{\Psi = c\,(S_A \pm S_B)}$$

$|S_A + S_B|^2 = |S_A|^2 + |S_B|^2 + 2S_AS_B$ Erhöhung der $e^{\ominus}$-Dichte

$|S_A - S_B|^2 = |S_A|^2 + |S_B|^2 - 2S_AS_B$ Erniedrigung der $e^{\ominus}$-Dichte

Normierung der WF des Grundzustandsorbitals Ψ_0

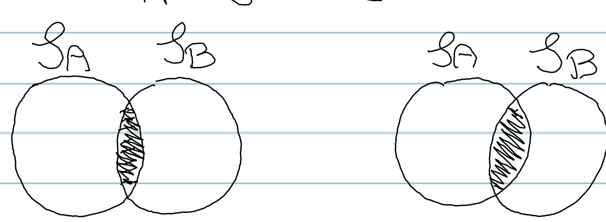
$$\boxed{\Psi_0 = c_0(\varphi_A + \varphi_B)}$$

$$\int |\Psi_0|^2 d\tau = 1 = \left[\overbrace{\int |\varphi_A|^2 d\tau}^{1} + \overbrace{\int |\varphi_B|^2 d\tau}^{1} + \int \varphi_A^* \varphi_B \, d\tau + \int \varphi_A \varphi_B^* \, d\tau\right] \cdot c_0^2$$

$$1 = c_0^2 \left(1 + 1 + \underbrace{\int \varphi_A^* \varphi_B \, d\tau}_{S_{AB}} + \int \varphi_A \varphi_B^* \, d\tau\right)$$

$$\boxed{S_{AB} \equiv \int \varphi_A^* \varphi_B \, d\tau} \qquad S_{AB}^* = \int \varphi_A \varphi_B^* \, d\tau$$

Überlappungsintegral



$$1 = c_0^2 (2 + S_{AB} + S_{AB}^*) = c_0^2 (2 + 2 S_{AB})$$

$S_{AB} = S_{AB}^*$ da 1s-Orbitale reale Funktionen sind

$$c_0 = \frac{1}{[2(1+S_{AB})]^{1/2}}$$

normierte WF des Grundzustands

$$\boxed{\Psi_0 = \frac{\varphi_A + \varphi_B}{[2(1+S_{AB})]^{1/2}}}$$

$$|\Psi_0|^2 = \frac{|\varphi_A|^2 + |\varphi_B|^2 + 2\varphi_A\varphi_B}{2(1+S_{AB})}$$ Erhöhung der $e^{\ominus}$-Dichte

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$$\boxed{\Psi_1 = \frac{\varphi_A - \varphi_B}{[2(1-S_{AB})]^{1/2}}}$$

<u>Berechnung der Energie E(R)</u>

Variationsprinzip $E = \int \Psi^* \hat{H} \Psi \, d\tau$

exakte WF → exakte ~~WF~~ Energien
LCAO-Näherung → höhere Energien

$$E_0(R) = \int \Psi_0^* \hat{H} \Psi_0 \, d\tau = \int (\varphi_A + \varphi_B)^* \hat{H} (\varphi_A + \varphi_B) \, d\tau / 2(1+S_{AB})$$

$$= \frac{\underbrace{\int \varphi_A^* \hat{H} \varphi_A \, d\tau}_{H_{AA}} + \underbrace{\int \varphi_A^* \hat{H} \varphi_B \, d\tau}_{H_{AB}} + \underbrace{\int \varphi_B^* \hat{H} \varphi_B \, d\tau}_{H_{BB}} + \underbrace{\int \varphi_B^* \hat{H} \varphi_A \, d\tau}_{H_{BA}}}{2(1+S_{AB})}$$

$$\boxed{H_{ij} = \int \varphi_i^* \hat{H} \varphi_j \, d\tau}$$

$$E_0(R) = \frac{H_{AA} + H_{AB} + H_{BB} + H_{BA}}{2(1+S_{AB})}$$

$$H_{AA} = H_{BB}$$
$$H_{AB} = H_{BA}$$

$$\boxed{E_0(R) = \frac{H_{AA} + H_{AB}}{1+S_{AB}}}$$

Auswertung der Integrale:

$$H_{AA} = \int \varphi_A^* \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_A}\right)\varphi_A \, d\tau + \frac{e^2}{R}\overbrace{\int \varphi_A^* \varphi_A \, d\tau}^{1}$$

Anziehung Kern A Abstoßung Kerne

$$- \int \frac{e^2}{r_B}\varphi_A \varphi_A^* \, d\tau$$

Anziehung Kern B

$$H_{AA} = \int \varphi_A^* E_H(1s)\, \varphi_A \, d\tau + \frac{e^2}{R} \underbrace{- \int \frac{e^2}{r_B}\varphi_A^* \varphi_A \, d\tau}_{J}$$

$$H_{AA} = E_H(1s) + \frac{e^2}{R} + J$$

$$\boxed{J \equiv - \int \frac{e^2}{r_B}\varphi_A^* \varphi_A \, d\tau}$$ Coulomb-Integral

$$H_{AB} = \int \varphi_A^* \left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{r_B}\right)\varphi_B \, d\tau + \frac{e^2}{R}\underbrace{\int \varphi_A^* \varphi_B \, d\tau}_{S_{AB}}$$

$$- \int \frac{e^2}{r_A}\varphi_A^* \varphi_B \, d\tau$$

$$H_{AB} = \int \varphi_A^* E_H(1s)\, \varphi_B \, d\tau - \frac{e^2}{R} S_{AB} + \underbrace{\int \frac{e^2}{r_A}\varphi_A^* \varphi_B \, d\tau}_{K}$$

$$\boxed{K = - \int \frac{e^2}{r_A}\varphi_A^* \varphi_B \, d\tau}$$ Austausch-Integral (Resonanz-Integral)

$$H_{AB} = E_H(1s) \cancel{+ \frac{e^2}{R}} S_{AB} + \frac{e^2}{R} S_{AB} + K$$

$$E_0(R) = E_H(1S) + \frac{e^2}{R} + \frac{J+K}{1+S_{AB}}$$ chemische Bindung

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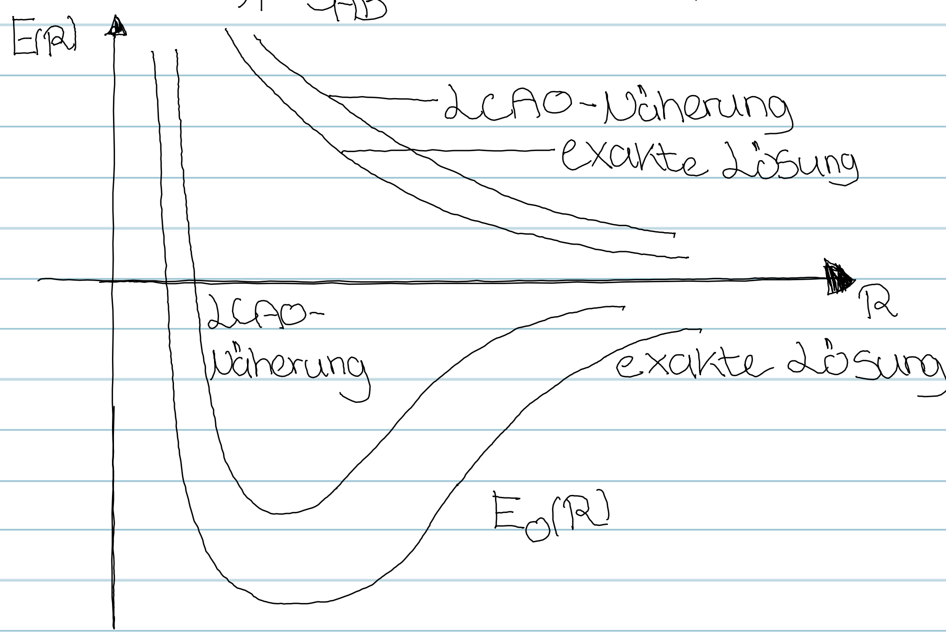
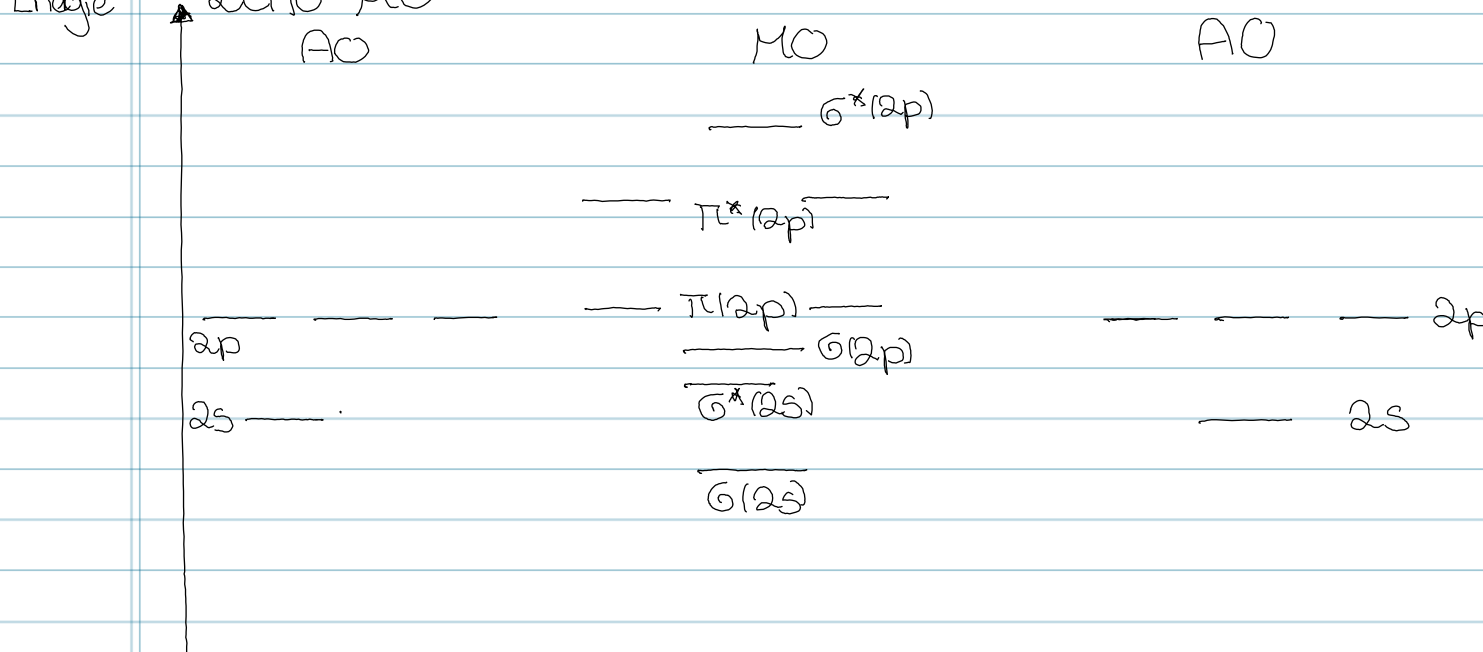
$$E_1(R) = \frac{H_{AA} - H_{AB}}{1-S_{AB}} = E_H(1s) + \frac{e^2}{R} + \frac{J-K}{1-S_{AB}}$$



exakt: $R_{GGW} = 1{,}06$ Å, $D_e = -2{,}79$ eV
LCAO: $R_{GGW} = 1{,}32$ Å, $D_e = -1{,}78$ eV

LCAO-MO



Mischen 2s - 2p