

Hückel MO-Theorie

Elektronische Anregung in konjugierten Polymeren und Aromaten $\pi \rightarrow \pi^*$

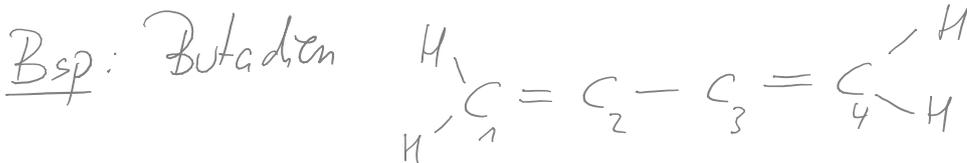
Hückel-Approximation

$$\det |\tilde{H} - E\tilde{S}| = 0$$

Wähle π -Orbitale (p_x, p_y) als AO
 Setze $S_{ij} = \delta_{ij}$ (kein Überlapp!)

Setze $H_{ii} = \alpha$ für alle i

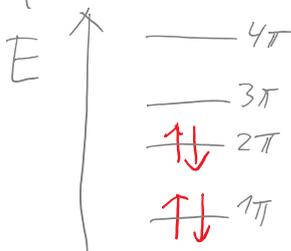
Setze $H_{ij} = \beta$ wenn $j = i \pm 1$
 sonst 0



α, β negativ

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

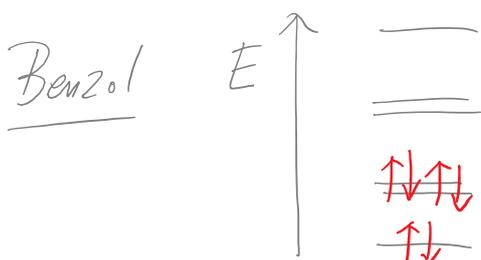
$\rightarrow E_1, E_2, E_3, E_4$
 $\rightarrow C_1 \dots C_4$ for ψ_1
 $C_1 \dots C_4$ for ψ_2
 \vdots



Elektronen-Konfiguration $1\pi^2 2\pi^2$

Beispiel Cyclisches Polyene $C_N H_N$

$$\tilde{H} = \begin{pmatrix} \alpha & \beta & & & \beta \\ \beta & \alpha & \beta & & \\ & \beta & \alpha & \beta & \\ \vdots & & \beta & \alpha & \beta \\ & & & \beta & \alpha & \beta \\ \beta & & & & \beta & \alpha \end{pmatrix}$$



$$E_k = \alpha + 2\beta \cos\left(\frac{2\pi k}{N}\right)$$

$$k = 0, \pm 1, \pm 2, \dots, \pm \frac{(N-1)}{2}$$

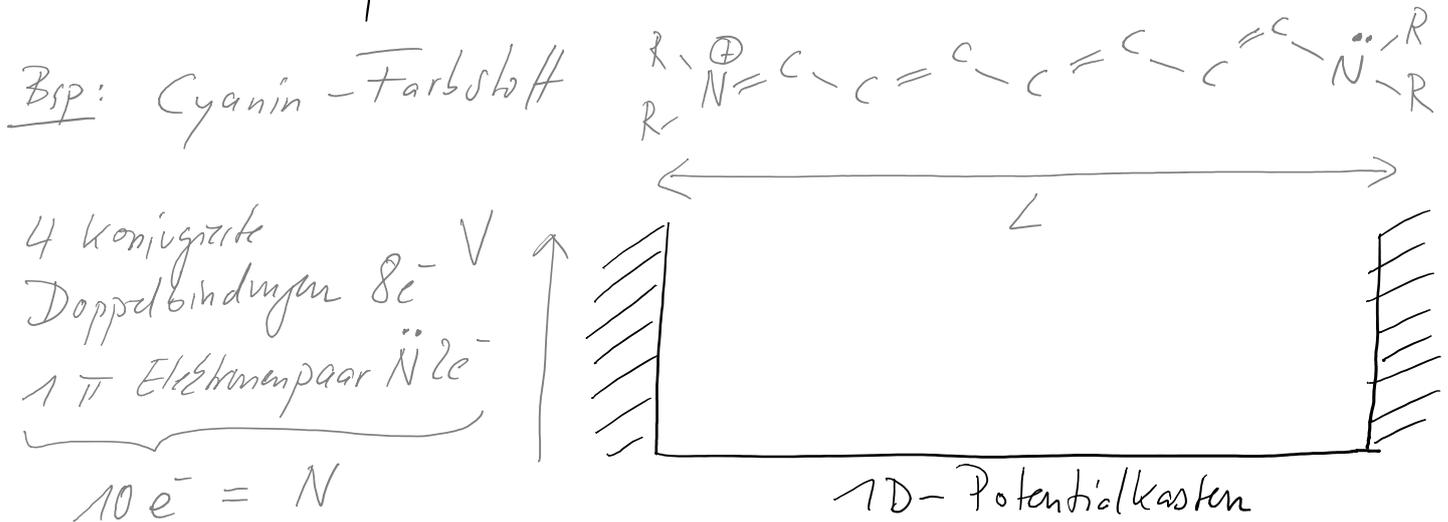
wenn N ungerade

$$k = 0, \pm 1, \pm 2, \dots, \pm \frac{N}{2}$$

wenn N gerade

1D Kastenmodell

Noch einfacher können die delokalisierten π -Elektronen von konjugierten Polymeren und Aromaten über Kastenpotential beschrieben werden



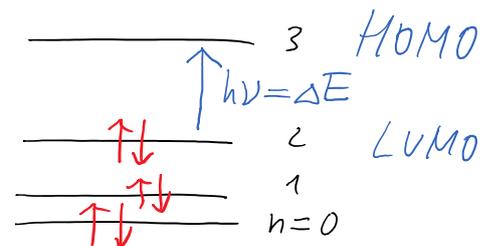
Eigenenergien für 1D-Potentialkasten

$$E_n = \frac{h^2 n^2}{8m_e L^2} \quad n \in \{0, 1, 2, \dots\}$$

$$n_{LUMO} = \frac{N}{2}, \quad n_{HOMO} = \frac{N}{2} + 1$$

$$\Delta E = \frac{h^2}{8m_e L^2} (N+1)$$

$$h \cdot \nu_{ex} = \Delta E \quad \lambda_{ex} = \frac{c}{\nu_{ex}} = \frac{ch}{\Delta E} = \frac{c}{h} \frac{8m_e N^2 d_0^2}{(N+1)} \approx \frac{c}{h} \frac{8m_e d_0^2}{N} \quad \text{falls } N \gg 1$$



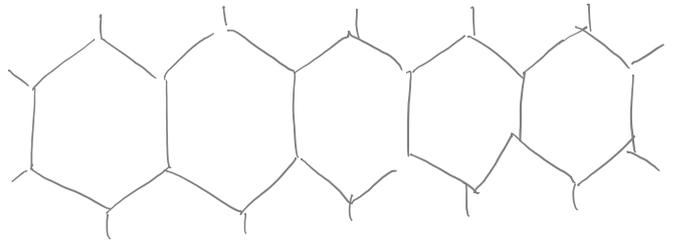
$$L = N \cdot d_0 \quad \text{mit } d_0 = 140 \text{ pm}$$

$\Rightarrow \lambda_{ex} \sim N$ (Kettenlänge)

N	λ_{ex} [1D-Kasten]	λ_{ex} [Exp]	Farbe
6	332	313 UV	—
8	459	416 V	Yellow
10	587	516 g	Red
12	716	625 o	Blue
14	844	735 r	Green
16	973	848 ir	—

2D-Kasten

Beispiel: Pentacene

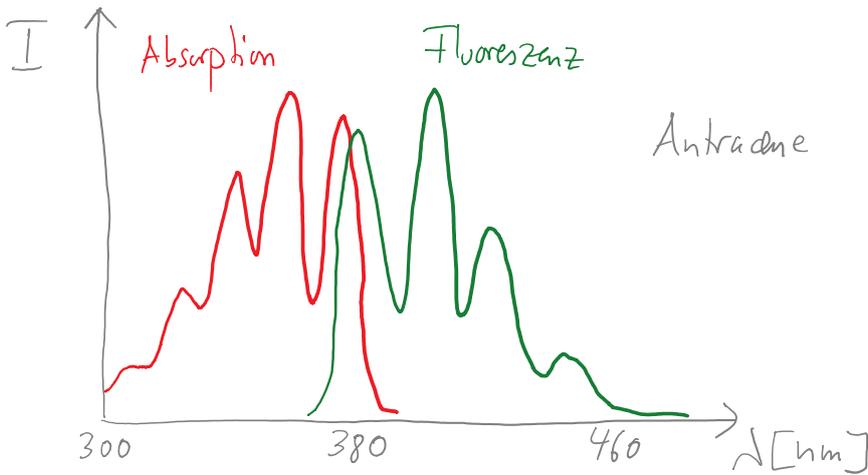


$$E_{n,m} = E_n + E_m$$

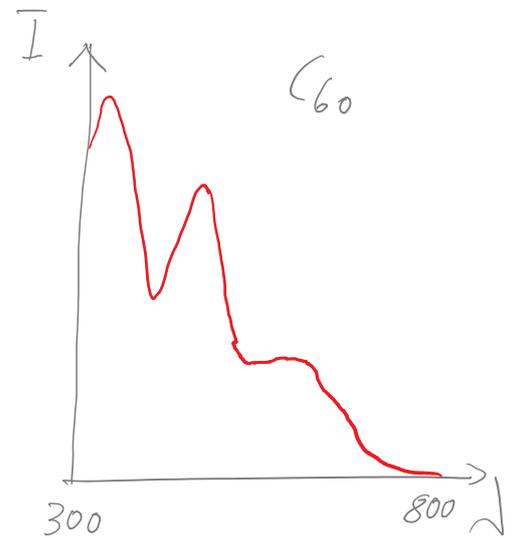
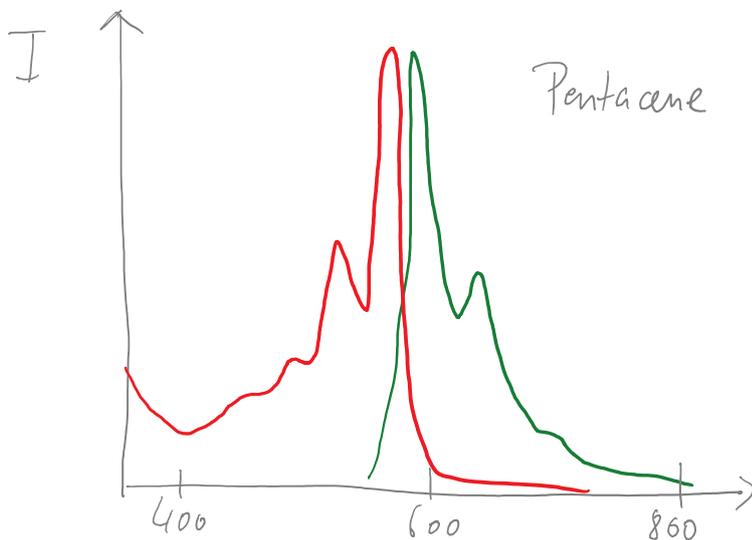
$$n, m \in \{0, 1, \dots\}$$

$$(\psi_{n,m} = \psi_n \cdot \psi_m)$$

2D-Potentialkasten L_2
 L_1



N	λ_{abs} [nm]
1	255
2	315
3	380
4	480
5	580



Delokalisiertes e^- auf Kugeloberfläche

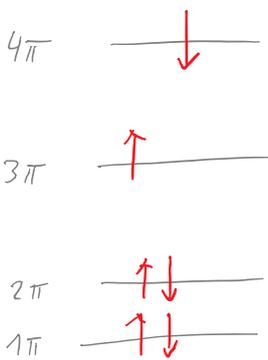
Triplet/Singulett



Grundzustand
 $1\pi^2 2\pi^2 3\pi^2 \quad S=0$

Betrachte letzten $2e^-$:
 antisymmetrische Spin- $\chi = \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \beta(1)\alpha(2))$

symmetrische Orbital- $\psi = \phi_3(1) \cdot \phi_3(2)$



angeregter Zustand {Singulett}

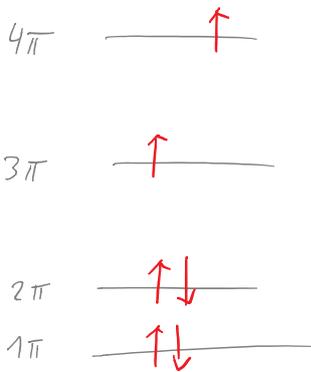
$$\psi_S = \frac{1}{\sqrt{2}} \{ \phi_3(1)\phi_4(2) + \phi_4(1)\phi_3(2) \}$$

symmetrisch

Spinwellenfunktion ($S=0$)

$$\chi = \frac{1}{\sqrt{2}} \{ \alpha(1)\beta(2) - \beta(1)\alpha(2) \}$$

antisymmetrisch



angeregter Triplet-Zustand $S=1$

$$\psi_T = \frac{1}{\sqrt{2}} \{ \phi_3(1)\phi_4(2) - \phi_4(1)\phi_3(2) \}$$

antisymmetrisch

$$\chi_T = \begin{cases} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) + \beta(1)\alpha(2)) \end{cases}$$

$$E(\text{Grundzustand}) = \frac{h^2}{8m_e L^2} (3^2 + 3^2) = 7.69 \cdot 10^{-19} \text{ J}$$

$$E(\text{angeregte Zustände}) = \frac{h^2}{8m_e L^2} (3^2 + 4^2) = 13.66 \cdot 10^{-19} \text{ J}$$

mit $e^- - e^-$ WW:

$$\iint \psi_6^* \frac{e^2}{4\pi \epsilon_0 r_{12}} \psi_6 dx_1 dx_2 = 4 \cdot 10^{-19} \text{ J} \quad \text{Grundzustand}$$

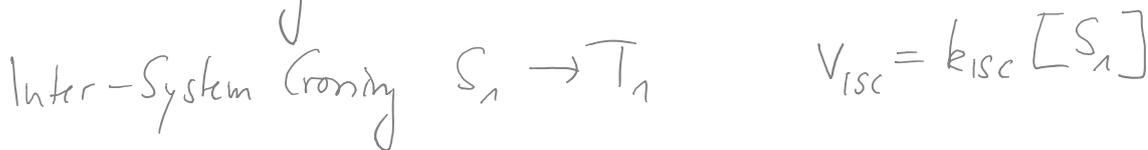
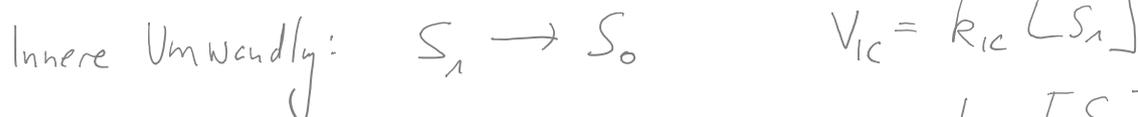
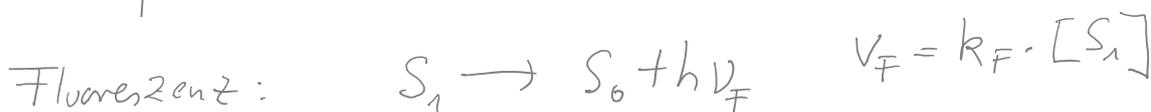
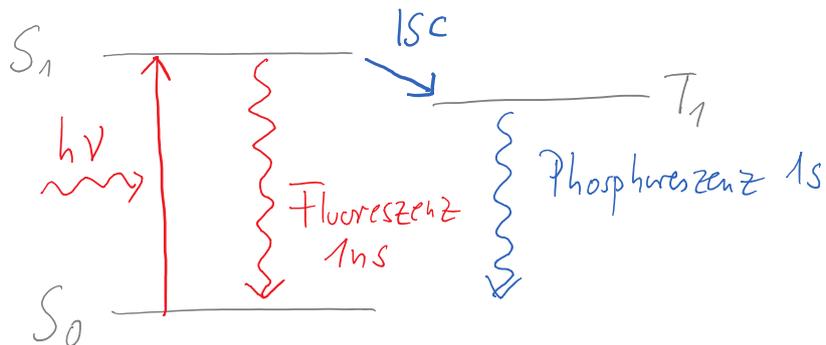
$$\iint \psi_5^* \frac{e^2}{4\pi \epsilon_0 r_{12}} \psi_5 dx_1 dx_2 = 4.8 \cdot 10^{-19} \text{ J} \quad \text{Singulett-} \\ \text{Angeregterzustand}$$

$$\iint \psi_T^* \frac{e^2}{4\pi \epsilon_0 r_{12}} \psi_T dx_1 dx_2 = 3.1 \cdot 10^{-19} \text{ J} \quad \text{Triplet-} \\ \text{Angeregterzustand}$$

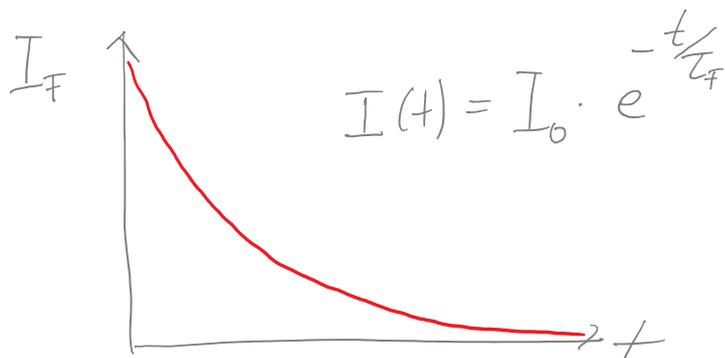
Quantenausbeute

mit $\phi_3(1) = \sqrt{\frac{2}{L}} \sin \frac{3\pi x_1}{L}$ $\phi_4(2) = \sqrt{\frac{2}{L}} \sin \frac{4\pi x_2}{L}$

$x_{12} = x_1 - x_2$



nach Einstrahl: $\frac{d[S_1]}{dt} = - (k_F + k_{isc} + k_{ic}) [S_1]$ 1. Ordnung Reaktion



$\tau_F = \frac{1}{k_F + k_{isc} + k_{ic}}$
Fluoreszenz-Lebensdauer

kontinuierliche Einstrahlung mit kleiner Lichtintensität:

$0 \stackrel{!}{=} \frac{d[S_1]}{dt} = I_{abs} - (k_F + k_{isc} + k_{ic}) [S_1]$

$\rightarrow I_{abs} = (k_F + k_{isc} + k_{ic}) [S_1]$

Fluoreszenz-Quantenausbeute $\phi = \frac{V_F}{V_{abs}} = \frac{k_F \cdot [S_1]}{(k_F + k_{isc} + k_{ic}) [S_1]}$

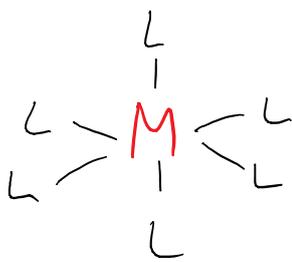
Ligandenfeldtheorie

Im Atom sind d-Orbitale der Übergangsmetalle Energie-entartet.

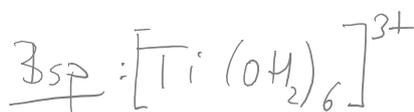
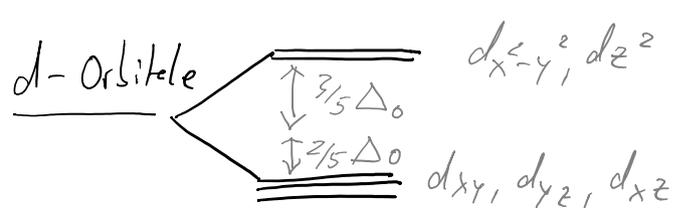
Im Komplex mit Liganden wird diese sphärische Symmetrie aufgehoben.

Ligandenfeld-Theorie beschreibt diese Aufspaltung abhängig von Liganden-Symmetrie und Art der Liganden

Oktahedrale Geometrie



Ligandenfeld



Anregung von d-Elektron $\Delta_o \approx 2.5 \text{ eV}$
 Absorptionsbande bei $\tilde{\nu} \approx 20000 \text{ cm}^{-1}$

Bsp: Oktaedrale Fe-Komplexe

