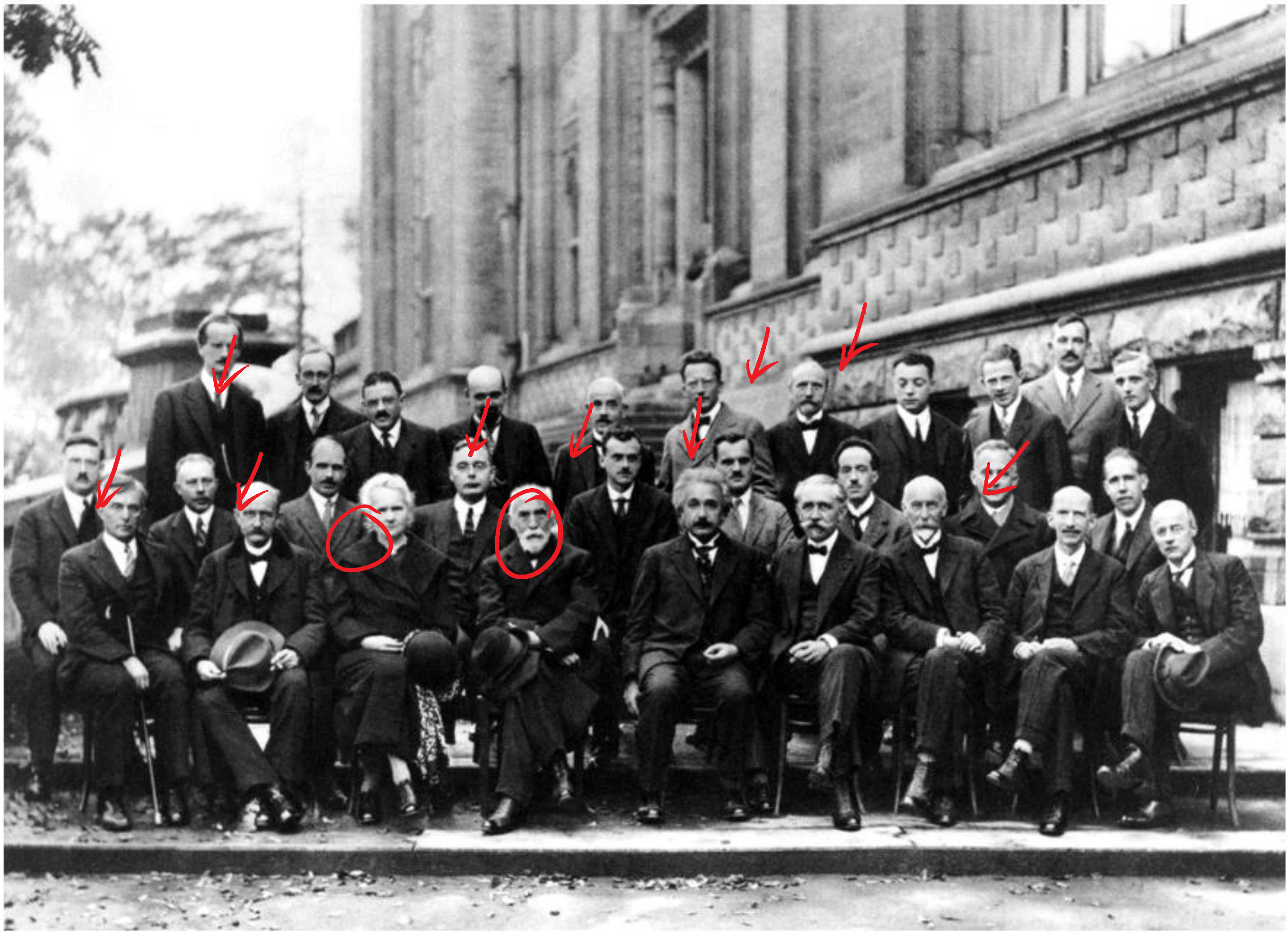
5. Solvay Kongress 1927



① $\underline{\psi(\vec{x},t)}$ ② $\langle x\rangle = \int_{-\infty}^{+\infty} \psi^* x \psi \, dx$

$\langle p_x\rangle = \int_{-\infty}^{+\infty} \psi^* \left(-i\hbar \frac{\partial}{\partial x} \psi\right) dx$

$$\langle E_{ges}\rangle = \langle E_{kin}\rangle + \langle E_{pot}\rangle \begin{cases} \langle E_{kin}\rangle = \int \psi^* \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi\right) dx \\ \langle E_{pot}\rangle = \int \psi^* V(x) \psi \, dx \end{cases}$$

Schrödinger Gleichung $\boxed{\hat{\mathcal{H}}\psi = E\psi}$ Eigenwert-Gleichung

$\hat{\mathcal{H}}$ = E-Operator = $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$ 1-Dimensional

$$\hat{\mathcal{H}} = E\text{-Operator} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \quad \text{1-Dimensional}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} + V(x,y,z)\right)$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + \underline{V(x)}\,\psi(x) = \boxed{E}\,\psi(x)$$

Eigenenergie

Welche Funktionen $\psi(x)$ erfüllen obige Gleichg ?

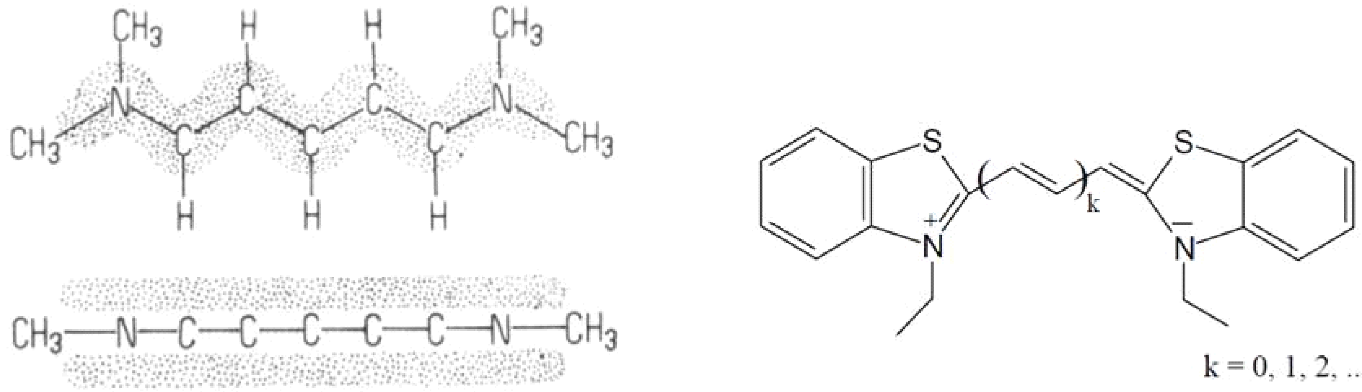


Abb. 1: Links: π-Elektronenwolken im Kerngerüst eines Polymethincyaninfarbstoffs (Farbstoff-Kation, oben: Ansicht von oben; unten: Ansicht von der Seite.
Rechts: Strukturformel der im Versuch verwendeten Cyaninfarbstoffe, Gegenion ist Iodid.

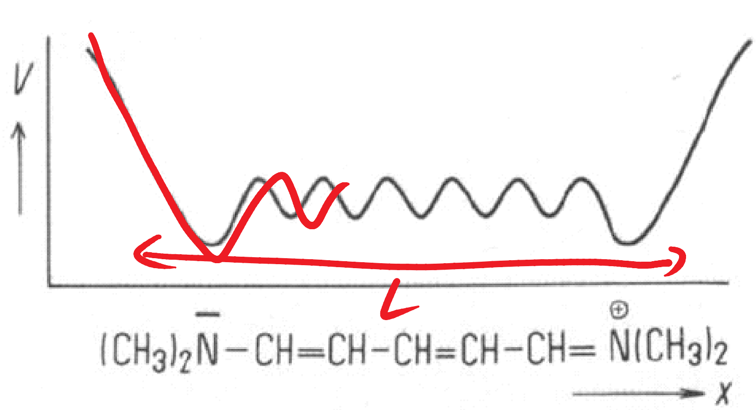


Abb. 2: Potentielle Energie V eines Elektrons längs der Kohlenstoffkette.

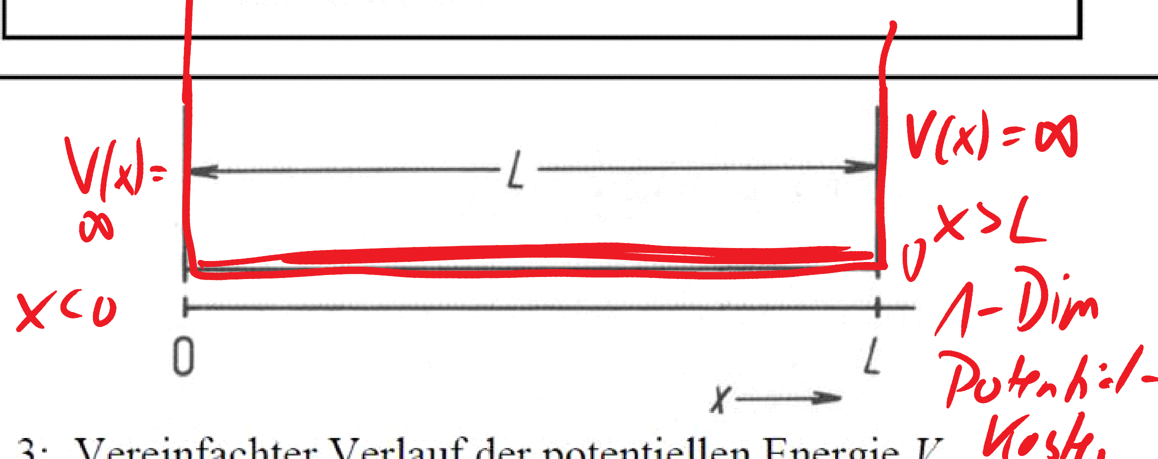
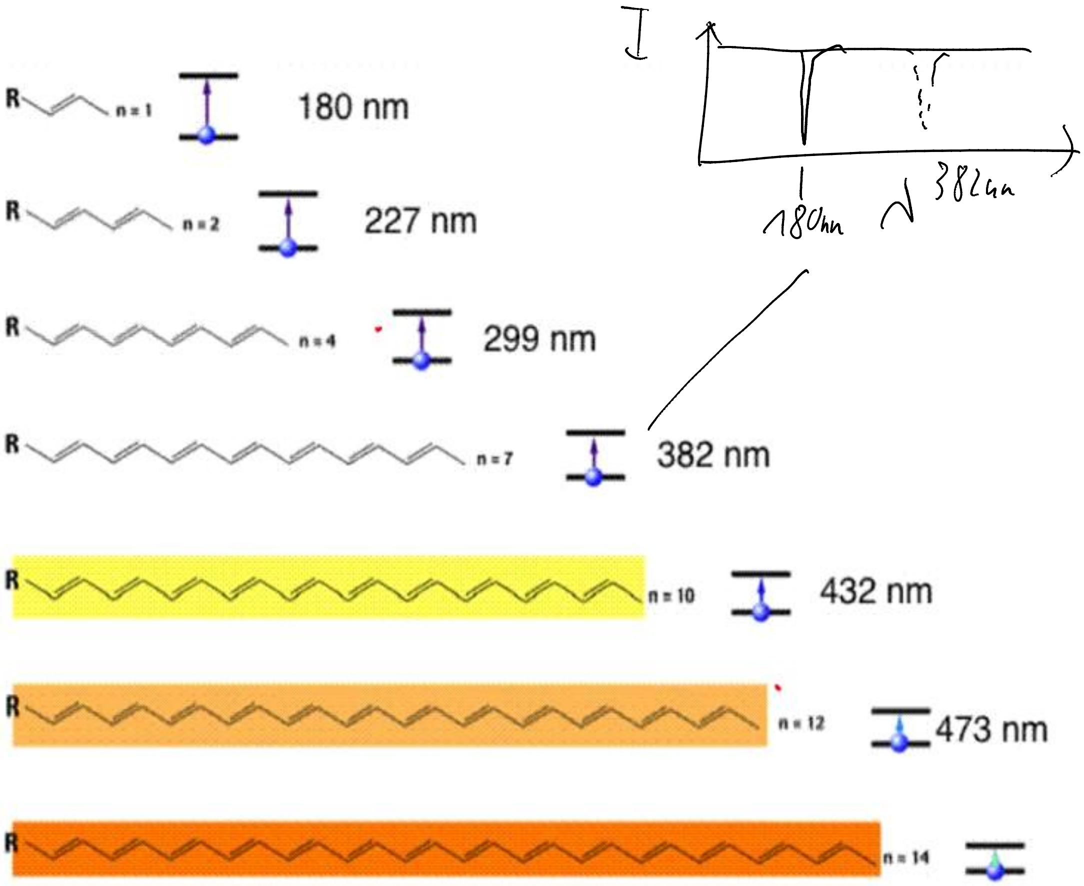
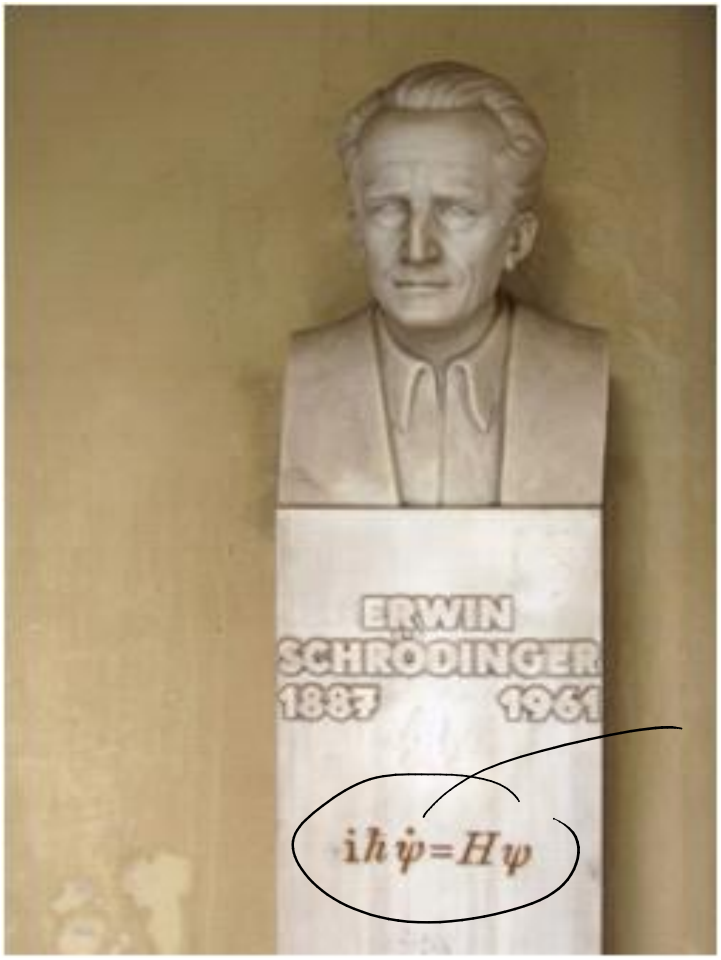
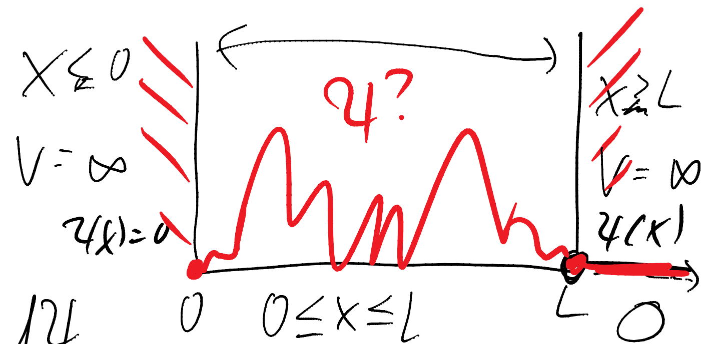


Abb. 3: Vereinfachter Verlauf der potentiellen Energie V
(L = Längsausdehnung des π-Elektronensystems in Abb. 2).


I
180nm
382nm
R
n = 1
180 nm
n = 2
227 nm
n = 4
299 nm
n = 7
382 nm
n = 10
432 nm
n = 12
473 nm
n = 14





$$\frac{d\psi}{dt}$$

$V(x)=0$

Born'schen Wahrscheinlichkeits-Interpretation

$$\left.\begin{array}{l} x<0 \\ x>L \end{array}\right\} \psi^2(x)=0 \longrightarrow \psi(x)=0$$

$$0 \leq x \leq L \quad \boxed{-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x^2}\psi(x) = E\,\psi(x)}$$

$$+\underbrace{V(x)\cdot\psi(x)}_{=0}$$

$$e^{ikx} \longleftrightarrow (\sin kx\,,\ \cos kx)$$

$e^{i\varphi} = \cos\varphi + i\sin\varphi$

Ansatz für Wellenfunktion $\psi(x) = A \cdot \cos kx + B \sin kx$

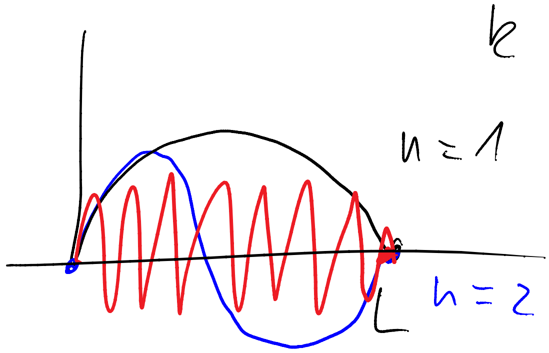
Randbedingung 1: $\boxed{\psi(0) = 0 \stackrel{!}{=} A}$ + B·0

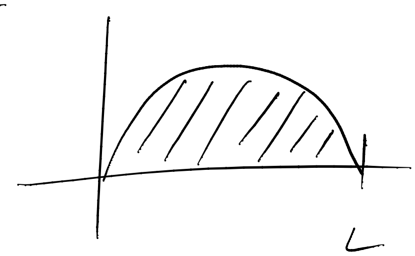
folgt aus Beding. ψ stetig

Randbedingung 2: $\psi(L) = 0 = B \cdot \sin k \cdot L$

Bedingung für k: $\boxed{k \cdot L = n \cdot \pi}$ $n = 1, 2, 3, 4, 5$

$$k = \frac{n \cdot \pi}{L}$$





$$\psi_n(x) = B \cdot \sin\left(\frac{n \cdot \pi}{L} \cdot x\right)$$

$$\int_0^L \psi_n^*(x) \cdot \psi(x)\, dx \stackrel{!}{=} 1$$

$$\int_0^L B \cdot \sin\left(\frac{n\pi}{L} \cdot x\right) \cdot B \cdot \sin\left(\frac{n\pi}{L} \cdot x\right) dx = 1$$

$$\int_0^L B\cdot \sin\left(\frac{n\pi}{L}\cdot x\right)\cdot B\cdot \sin\left(\frac{n\pi}{L}\cdot x\right) dx = 1$$

$\sin^2(ax) = \sin(ax)\cdot \sin(ax)$

$f \quad g$

$f\cdot g = \int f' g + \int f g'$

$$B^2 \cdot \underbrace{\int_0^L \sin^2\left(\frac{n\pi}{L}x\right) dx}_{\frac{L}{2}} \overset{!}{=} 1$$

$$B^2 = \frac{2}{L} \rightarrow B = \sqrt{\frac{2}{L}}$$

Lösungen sind $\boxed{\psi_n = \sqrt{\frac{2}{L}}\cdot \sin\left(\frac{n\pi}{L}\cdot x\right)}$

Einsetzen in SG:

$$\frac{\partial}{\partial x}\psi_n(x) = \sqrt{\frac{2}{L}}\cdot \cos\left(\frac{n\pi}{L}\cdot x\right)\cdot \frac{n\pi}{L}$$

$$\frac{\partial^2}{\partial x^2}\psi_n(x) = \sqrt{\frac{2}{L}}\cdot \frac{n^2\pi^2}{L^2}\left\{-\sin\left(\frac{n\pi}{L}x\right)\right\}\cdot$$

$$\mathcal{H}\cdot\psi_n = +\frac{\hbar^2}{2m_e}\cdot\sqrt{\frac{2}{L}}\cdot\frac{n^2\pi^2}{L^2}\cdot \sin\left(\frac{n\pi}{L}x\right)$$

$\hbar = \frac{h}{2\pi}$

$\hbar^2 = \frac{h^2}{4\pi^2}$

$$= \underbrace{\frac{\hbar^2 n^2 \pi^2}{2 m_e L^2}}_{\frac{h^2 n^2}{\ldots}}\cdot\left\{\sqrt{\frac{2}{L}}\cdot \sin\left(\frac{n\pi}{L}\cdot x\right)\right\}$$

$\psi_n(x)$ ☺

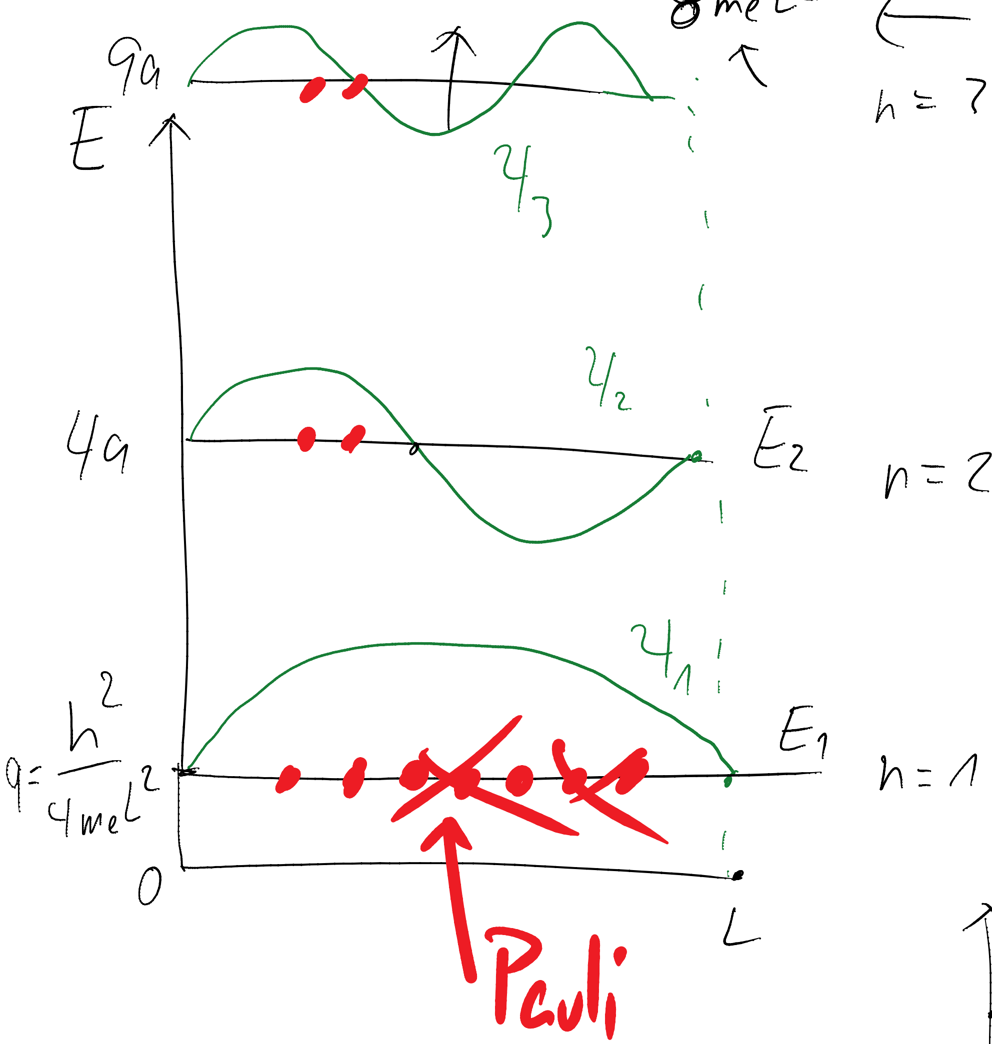
$$\frac{h^2 n^2}{8 m_e L^2} \rightarrow E_n$$

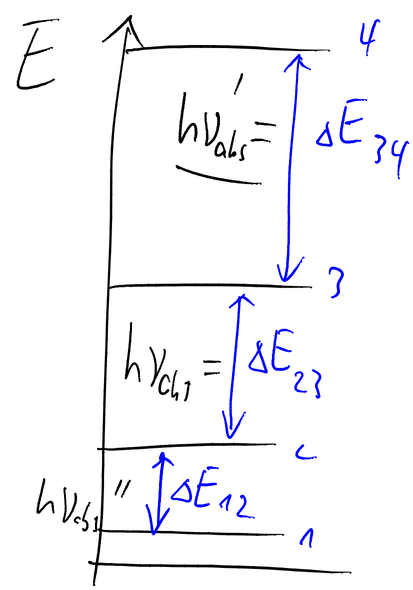
$\psi_n(x)$ ☺

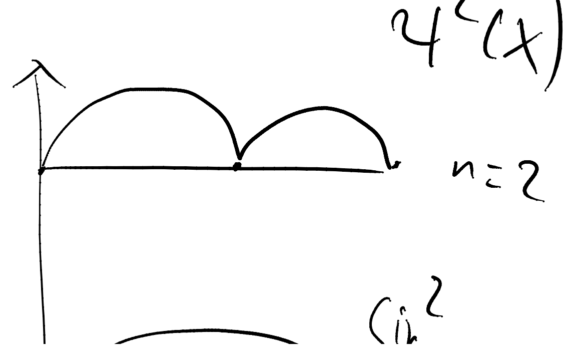
Lösung für π-e^- in Polyenen:

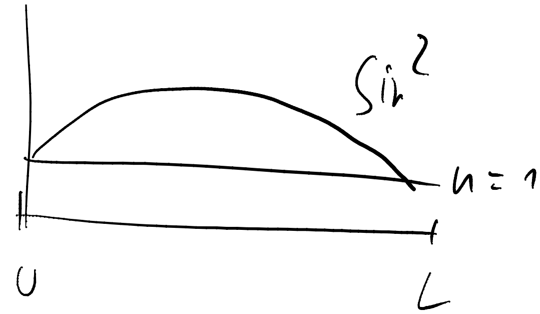
$$\psi_n(x) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi}{L} \cdot x\right)$$

$$E_n = \frac{h^2 n^2}{8 m_e L^2} \quad \leftarrow \quad n \in \{1, 2, 3, 4, \ldots$$









sin²
n = 1
0
L

$$(CH_3)_2\overset{+}{N}=C-C=C-C=C-C=C-\ddot{N}(CH_3)_2$$

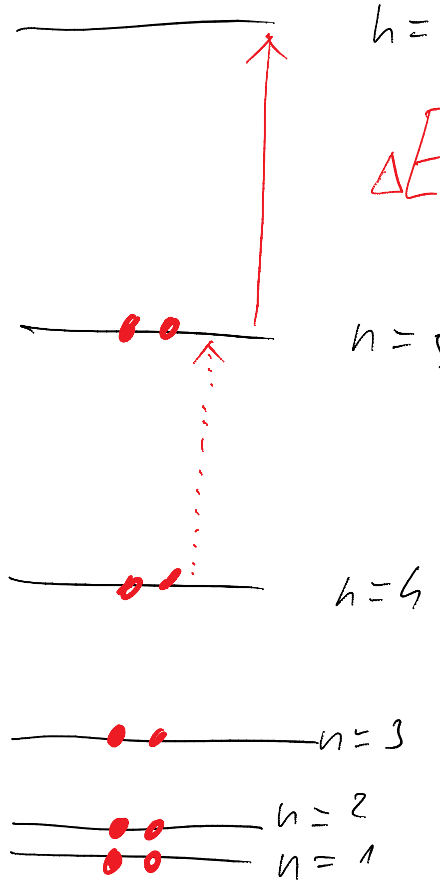
$$\longleftrightarrow$$

Länge L

4 ~~pro~~ konj. Doppelbindungen $\rightarrow$ $8\,\pi\, e^-$

2 π-Elektronen von $\ddot{N}$ $\rightarrow$ $2\,\pi\, e^-$

10 freie π-Elektronen



LUMO

$$\Delta E_{\cancel{LUMO}} = E_{LUMO} - E_{HOMO} = h\nu_{abs}$$

HOMO

$$n_{HOMO} = \frac{N}{2} = 5$$

$$n_{LUMO} = \frac{N}{2} + 1 = 6$$

$$E_n = \frac{h^2 n^2}{8 m_e L^2}$$

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

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

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

$$L = N \cdot d_0 \qquad (d_0 = 140\,pm)$$

$$h \cdot \nu_{abs} = \Delta E = \frac{h^2}{8 m_e d_0^2 \cdot N^2} \cdot (N+1)$$

$$\lambda_{abs} = \frac{c}{\nu_{abs}} = \frac{c \cdot h}{\Delta E} = \frac{8 m_e d_0^2}{h} \cdot \frac{N^2}{(N+1)}$$

$$N >> 1 \qquad \sim N$$

N	λ_{calc} [nm]	λ_{exp}		Farbe
6	332	393	uv	gelb
8	459	416	v	
10	587	516	g	rot
12	716	625	o	blau
14	844	735	r	grün
16	973	848	ir	

Vorgehensweise:

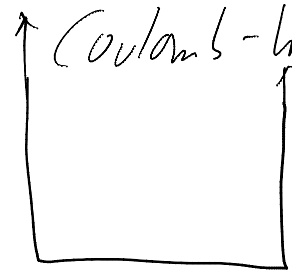
(1) Welche Art von Q-Teilchen?

e^-, H, ^{12}C, ^{60}C, CH_3

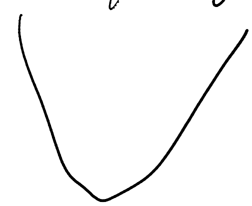
m_e

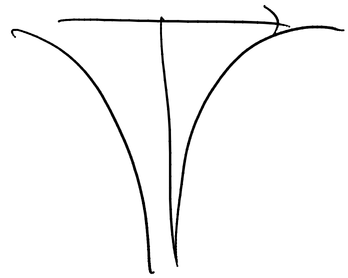
(2) Wie sieht das Potential $V(x,y,z)$ aus?

Coulomb-WW, Bindungsenergie...



V=0





(3) Schreibe SG und "rate" ψ

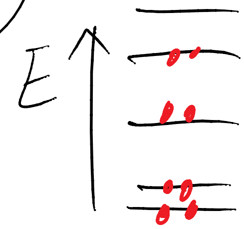
$$\mathcal{H}\cdot\psi = E\cdot\psi$$

(4) Überprüfe ψ durch Einsetzen

↳ Bestimme E_n

(5) Zeichne E-Diagramm für Q-Teilch

5 Zeichne E-Diagramm für Q-Teilch und besetze nach QM-Regeln



6 Berechne $\Delta E = E_{LUMO} - E_{HOMO}$

$\rightarrow \nu_{abs}$