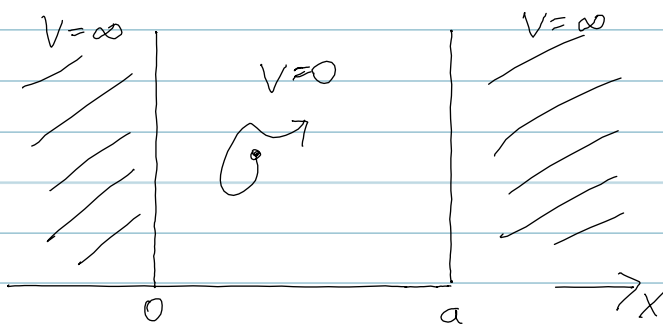


Vorlesung 21.11.2013

2.4 Beispiele

b) Teilchen in einem 1-dim. Kasten

Anwendung: π - e^- in konjug. Systemen



$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + V(x) \psi = E \psi}$$

außerh. des Kastens: $V = \infty$

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + \infty \psi = E \psi$$

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + \infty \psi = 0$$

↳ nur triviale Lsg: $\psi = 0 \rightarrow \psi^2 = 0$

↳ Teilchen ist innerhalb
des Kastens!

innerhalb des Kastens $V=0$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + 0\psi = E\psi$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

$$\boxed{\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2} \psi}$$

Lösungsansatz: $\psi = A \cdot \sin \alpha x$
 $\psi' = \alpha A \cdot \cos \alpha x$
 $\psi'' = -\alpha^2 \underbrace{A \sin \alpha x}_{\psi}$

$$\psi'' = -\alpha^2 \psi$$

$$\hookrightarrow \boxed{\alpha^2 = \frac{2mE}{\hbar^2}} \quad \text{jede Energie ^{ist} möglich!}$$

Randbed.: $\psi(0) = \psi(a) = 0$

$$\psi(0) = A \sin \alpha \cdot 0 = 0$$

$$\psi(a) = A \sin \alpha \cdot a = 0$$

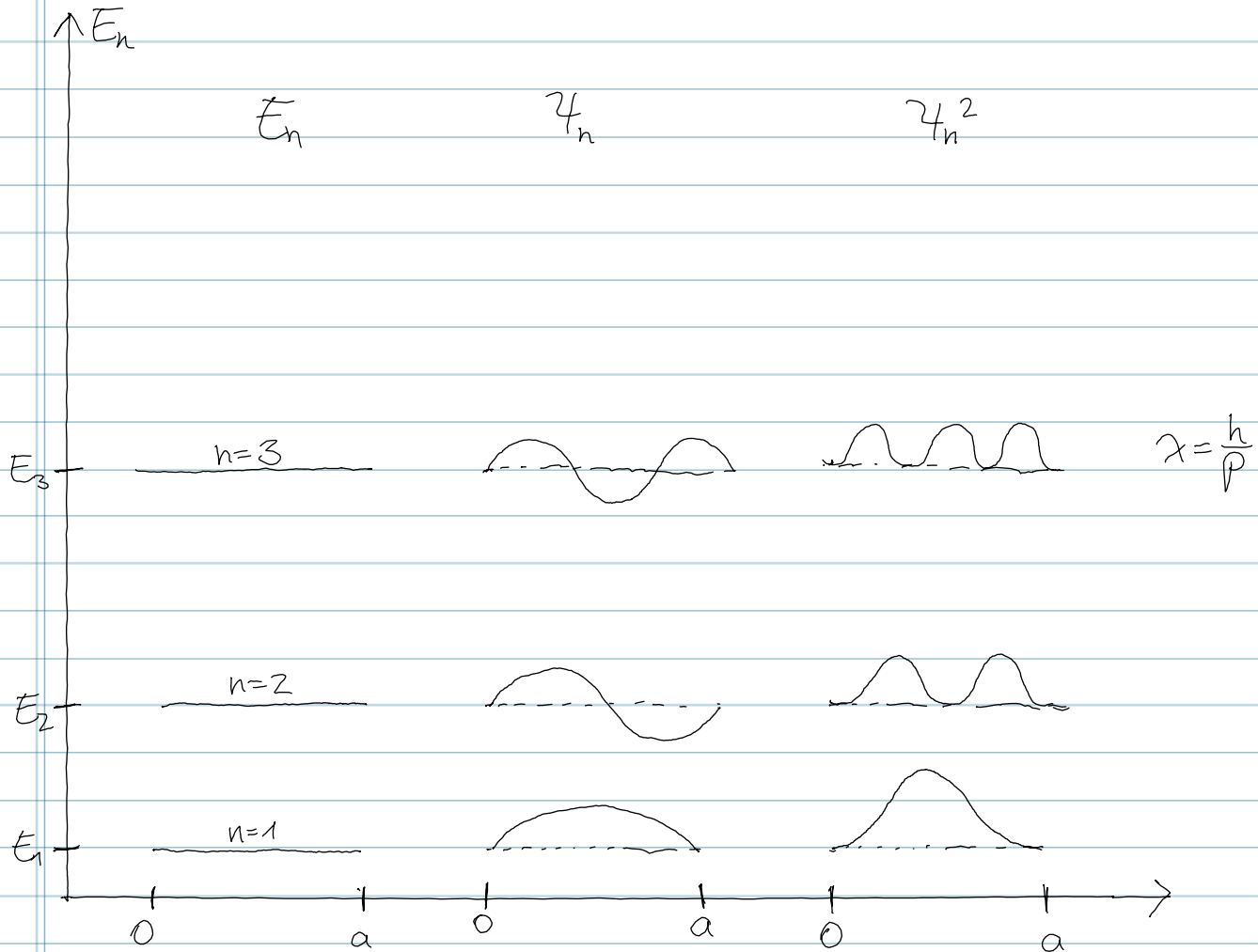
$$\alpha \cdot a = n\pi \quad n = 1, 2, 3, \dots$$

$$\rightarrow \alpha = \frac{n\pi}{a}$$

$$\hookrightarrow \alpha^2 = \frac{n^2\pi^2}{a^2}$$


↳ Energieeigenwerte $E_n = \frac{h^2 \pi^2 n^2}{2ma^2} = \frac{n^2 h^2}{8ma^2}$

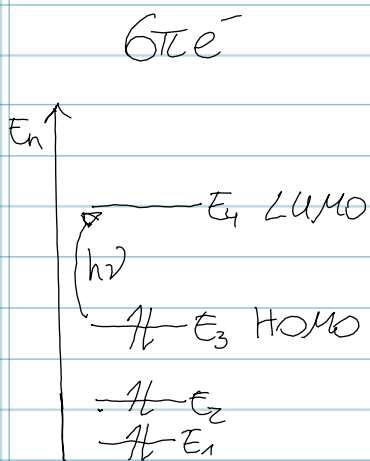
↳ Eigenfunktionen $\psi_n = A \sin \frac{n\pi}{a} \cdot x$



Masse m u. Länge a groß \rightarrow Energieniveaus dicht (Kontinuum)

" " klein \rightarrow Quantelung

Bsp: πe^- in Hexatrien 



$$\Delta E = \frac{h^2}{8m^2ca^2} \underbrace{(n_{LUMO}^2 - n_{HOMO}^2)}_7$$

$$a = 3 \times 135 \text{ pm} + 2 \times 154 \text{ pm} = 713 \text{ pm}$$

$$\Delta E = h\nu = h \frac{c}{\lambda}$$

$$\rightarrow \lambda = \frac{hc}{\Delta E} = 240 \text{ nm} \quad (\text{exp. } 268 \text{ nm})$$

Eigenschaften der Wellenfunktion

$$\psi_n(x) = A \sin \frac{n\pi}{a} x$$

Normierung: $\int_0^a \psi_n^2 dx = 1$

$$A^2 \int_0^a \sin^2 \frac{n\pi}{a} x dx$$

Subst.: $y = \frac{n\pi}{a} x \quad \frac{dy}{dx} = \frac{n\pi}{a}$

$$\frac{a}{n\pi} A^2 \int_0^{n\pi} \sin^2 y dy = \frac{a}{n\pi} A^2 \left(\frac{n\pi}{2} \right) = 1$$

$$\frac{a}{2} A^2 = 1 \rightarrow A = \sqrt{\frac{2}{a}}$$

$$\boxed{\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x} \quad n = 1, 2, 3, \dots$$

Orthogonalität: φ_1, φ_2

$$\int_0^a \varphi_1 \varphi_2 dx = 0 = \langle \varphi_1 | \varphi_2 \rangle$$

$$\varphi_1 = \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \quad \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \varphi_1$$

$$\varphi_2 = \sqrt{\frac{2}{a}} \sin \frac{2\pi x}{a} \quad \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \varphi_2$$

$$\langle \varphi_1 | \varphi_2 \rangle = \frac{2}{a} \int_0^a \sin \frac{\pi x}{a} \sin \frac{2\pi x}{a} dx$$

$$\sin 2\varphi = 2 \sin \varphi \cos \varphi$$

$$\begin{aligned} \langle \varphi_1 | \varphi_2 \rangle &= \frac{2 \cdot 2}{a} \int_0^a \sin^2 \frac{\pi x}{a} \cos \frac{\pi x}{a} dx \\ &= \frac{4}{a} \left(\frac{a}{3\pi} \sin^3 \frac{\pi}{a} x \right) \Big|_0^a = 0 \end{aligned}$$

$$\langle \varphi_1 | \varphi_2 \rangle = 0 \quad \begin{array}{c} \text{---} \\ \text{---} \\ \text{---} \end{array} \varphi_1 \cdot \varphi_2$$

$$\langle \varphi_1 | \varphi_3 \rangle = 0 \quad \langle \varphi_1 | \varphi_1 \rangle = 1$$

$$\langle \varphi_2 | \varphi_3 \rangle = 0 \quad \langle \varphi_2 | \varphi_2 \rangle = 1$$

⋮

⋮

allg.

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij}$$

↑
Kronecker-Symbol

$$\delta_{ij} \begin{cases} = 1 & \text{für } i=j \\ = 0 & \text{für } i \neq j \end{cases}$$

Orthonormalsystem

1) Wellenfkt sind normiert

2) Wellenfkt ψ_n, ψ_m sind paarweise orthogonal

Impuls

x-Komp. Impuls, ψ_1

$$\hat{p}_{x,1} \psi_1 = -i\hbar \frac{d}{dx} \left(\sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \right) = -i\hbar \sqrt{\frac{2}{a}} \cdot \frac{\pi}{a} \cos \frac{\pi x}{a}$$

↳ ψ_1 ist keine Eigenfkt von $\hat{p}_{x,1}$

Mittelwertbildung

$$\bar{p}_{x,1} = \int_0^a \psi_1 \hat{p}_{x,1} \psi_1 dx \quad \underbrace{\int_0^a \psi_1^2 dx}_1$$

$$\bar{p}_{x,1} = \int_0^a \sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} (-i\hbar) \sqrt{\frac{2}{a}} \frac{\pi}{a} \cos \frac{\pi x}{a} dx$$

$$\bar{p}_{x,1} = \frac{2}{a} (-i\hbar) \frac{\pi}{a} \int_0^a \sin \frac{\pi x}{a} \cdot \cos \frac{\pi x}{a} dx$$

$$\bar{p}_{x,1} = -i\hbar \frac{2\pi}{a^2} \left(\frac{1}{2} \sin^2 \frac{\pi x}{a} \right) \Big|_0^a = \underline{0}$$

Quadrat x-Komp. Impuls, Zustand ψ_1

$$\hat{p}_{x,1}^2 \psi_1 = -\hbar^2 \frac{d^2}{dx^2} \left(\sqrt{\frac{2}{a}} \sin \frac{\pi x}{a} \right) = +\hbar^2 \frac{\pi^2}{a^2} \underbrace{\sqrt{\frac{2}{a}} \sin \frac{\pi x}{a}}_{\psi_1}$$

$\hat{p}_{x,1}^2 \psi_1 = p_{x,1}^2 \psi_1$ ↳ ψ_1 ist eine Eigenfkt. von $\hat{p}_{x,1}^2$

$$p_{x,1}^2 = \frac{\hbar^2 \pi^2}{a^2} = 2mE_1$$

$$E_{kin} = \frac{p^2}{2m}$$

$$p_{x,1} = \pm \sqrt{2mE_1}$$

Genauigkeit: $2\sqrt{2mE_1}$