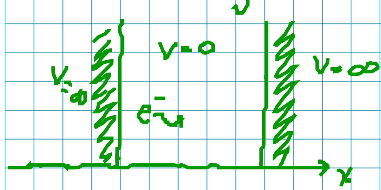
Physikalische Chemie II — 23.11.18 Freitag

Wiederholung:

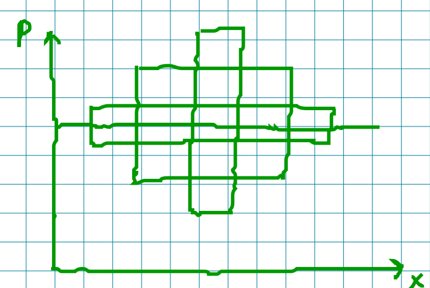


$E_N = \frac{n^2 h^2}{8ma^2}$ $n = 1, 2, 3.$

Ort + Impuls simultan messbar?

$\Delta x \Delta p_x = a \cdot 2\sqrt{2mE_1} = a\, 2 \frac{\pi\hbar}{a} = h$

„Heisenbergsche Unschärferelation"



$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$

$\Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2}$

$\langle x \rangle = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) x \sin\left(\frac{n\pi a}{a}\right) dx$

$= \frac{2}{a} \int_0^a x \sin^2\left(\frac{n\pi a}{a}\right) dx = \frac{a}{2}$

$\langle x^2 \rangle = \frac{2}{a} \int_0^a x^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2}$

$\langle p_x \rangle = 0$ (siehe VL 7)

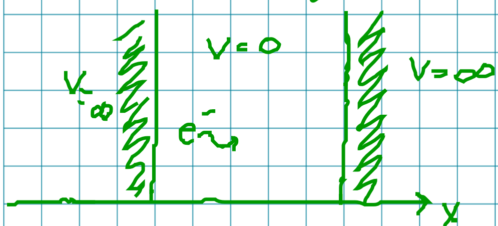
$\langle p_x^2 \rangle = \frac{2}{a} \int_0^a \sin\left(\frac{n\pi x}{a}\right)\left(-\hbar^2 \frac{d}{dx^2} \sin\left(\frac{n\pi x}{a}\right)\right) dx$

$= \frac{2}{a} \hbar^2 \frac{n^2\pi^2}{a^2} \int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{n^2\pi^2\hbar^2}{a}$

Physikalische Chemie II

28.11.18
Freitag

Wiederholung:



$$E_N = \frac{n^2 h^2}{8ma^2} \qquad n = 1, 2, 3$$

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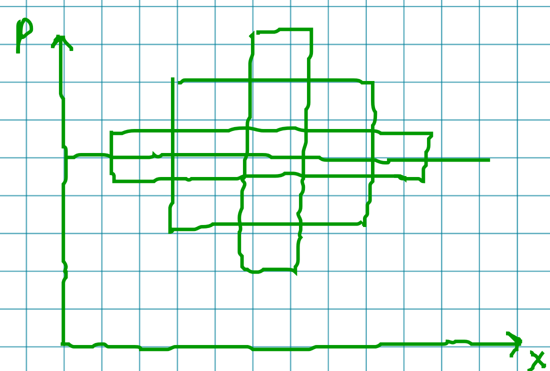


$$\Delta x \equiv \sqrt{\langle x^2\rangle - \langle x\rangle^2}$$

$$\Delta p_x = \sqrt{\langle p_x^2\rangle - \langle p_x\rangle^2}$$

$$\langle x\rangle = \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) x \sin\left(\frac{n\pi a}{a}\right) dx$$

$$= \frac{2}{a}\int_0^a x \sin^2\left(\frac{n\pi a}{a}\right) dx = \frac{a}{2}$$

$$\langle x^2\rangle = \frac{2}{a}\int_0^a x^2 \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2}$$

$\langle p_x\rangle = 0$ (siehe VL 7)

$$\langle p_x^2\rangle = \frac{2}{a}\int_0^a \sin\left(\frac{n\pi x}{a}\right)\left(-\hbar^2 \frac{d}{dx^2} \sin\left(\frac{n\pi x}{a}\right)\right) dx$$

$$= \frac{2}{a}\hbar^2 \frac{n^2\pi^2}{a^2}\int_0^a \sin^2\left(\frac{n\pi x}{a}\right) dx = \frac{n^2\pi^2\hbar^2}{a}$$

$$\Delta x \Delta p_x = \left(\frac{a^2}{3} - \frac{a^2}{2n^2\pi^2} - \frac{a^2}{4} \right)^{1/2} \left(\frac{n^2\hbar^2\pi^2}{a^2} - 0 \right)^{1/2}$$

$$= n\pi\hbar \left(\frac{1}{3} - \frac{1}{2n^2\pi^2} - \frac{1}{4} \right)^{1/2}$$

$$= \frac{\hbar}{2} \underbrace{\left(\frac{n^2\pi^2}{3} - 2 \right)^{1/2}}_{>1}$$

$$\boxed{\Delta x \Delta p_x > \frac{\hbar}{2}}$$

c) Teilchen im 3dim Kasten

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi}$$ d.h. $$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{2mE}{\hbar^2} \psi$$

Lösung?

Ansatz: $\psi = X(x)\,Y(y)\,Z(z) = XYZ$

$$YZ \frac{\partial^2 X}{\partial x^2} + XZ \frac{\partial^2 Y}{\partial y^2} + XY \frac{\partial^2 Z}{\partial z^2} = -\frac{2mE}{\hbar^2} XYZ \quad | : XYZ$$

$$\Leftrightarrow \frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = -\frac{2mE}{\hbar^2}$$

$$\underbrace{-\text{"}- + -\text{"}- + \frac{2mE}{\hbar^2}}_{\text{const}} = \underbrace{-\frac{1}{Z} \frac{\partial^2 Z}{\partial z^2}}_{\text{const.}}$$

$$-\frac{1}{Z} \frac{\partial^2 Z}{\partial z^2} = \text{konst.} = \frac{2mE_z}{\hbar^2} \longrightarrow \text{1 dim siehe VL 7.}$$

analoges Verfahren für X, Y

$$\frac{2mE}{\hbar^2} = \frac{2mE_z}{\hbar^2} + \frac{2mE_y}{\hbar^2} + \frac{2m_eE_x}{\hbar^2}$$

Produktansatz: $\psi = X(x)\,Y(y)\,Z(z)$

$$\psi = \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}$$

Energieeigenwerte

$$E = E_x + E_y + E_z$$

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

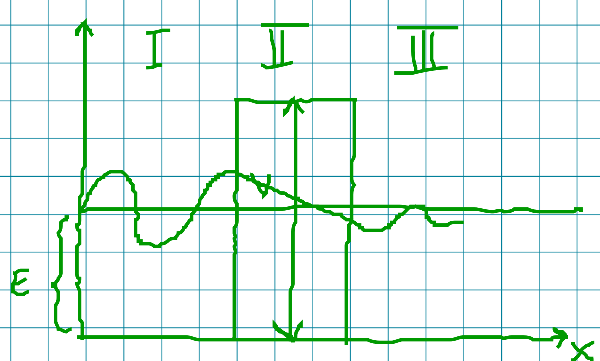
Bsp. Teilchen im Würfel $a = b = c$

$$E = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad n_x = 2 \quad n_y = 1 \quad n_z = 1$$

$$\hookrightarrow E = \frac{h^2}{8ma^2}\,6 = E(2,1,1)$$

$$\underbrace{E(2,1,1) = E(1,2,1) = E(1,1,2)}_{\text{3 fach entartet}}$$ „Entartung"

d| Tunneleffekt



$E < V$
$V =$ endlich } Tunneln!

Berech I: $V = 0$

$$\Psi = \left(e^{i\alpha x} + \ldots\right) e^{i\alpha x}$$

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{p_x^2}{\hbar^2}} = \frac{p_x}{\hbar}$$

$$e^{i\alpha x} = \cos\alpha x + i\sin\alpha x$$ (alle Lsg!)

Bereich II: V endlich

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

$$\psi = Ee^{\kappa x} + Fe^{-\kappa x} \qquad \kappa = \sqrt{\frac{2m(V-E)}{\hbar^2}}$$

Bereich III $V=0$

$$\psi = c' e^{i\alpha x}$$

Ziel: Transmissionswahrscheinlichkeit T Tunnel

$$T = \frac{|c'|^2}{|c|^2}$$

Randbed. → Koeff.

$\kappa a \gg 1$

$$T = \frac{16E(V-E)}{V^2} e^{-2\kappa a}$$

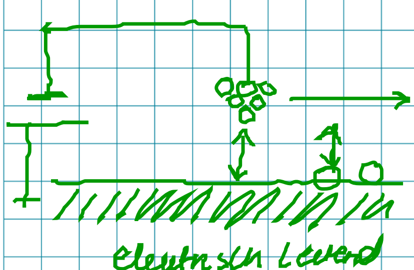
$$\kappa = \sqrt{\frac{2m(V-E)}{\hbar^2}}$$

leichte Teilchen tunneln leichter

z. B. e^-, Protonen

2.5 Anwendungen

Rastertunnelmikroskopie (STM)



Bsp. Änderung von $a = 0{,}5$ auf $0{,}6$ nm

$(V-E = 2\,eV)$

$$\frac{I(a_2)}{I(a_1)} = \frac{T(a_2)}{T(a_1)} = e^{-2\kappa(a_2-a_1)} = 0{,}23$$