Lösungen des Übungsblattes 6 zur Vorlesung Theoretische Chemie I
WS 2018/19 – Übungsblatt 6

1.

$$\varphi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad , \quad n \in \mathbb{N} \tag{1}$$

$$E_n = \frac{h^2\pi^2 n^2}{2mL^2} \quad , \quad n \in \mathbb{N} \tag{2}$$

a)

$$\psi_n(x,t) = \varphi_n(x) e^{-\mathrm{i}\frac{E_n}{\hbar}t}$$

Die zeitabhängige Schrödingergleichung für Teilchen in einer Box lautet:

$$\hat{H}\psi_n(x,t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_n(x,t) + V(x)\psi_n(x,t) = \mathrm{i}\hbar\frac{\partial}{\partial t}\psi_n(x,t) \tag{3}$$

Innerhalb der Box ist $V(x) = 0$.

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi_n(x,t) = \mathrm{i}\hbar\frac{\partial}{\partial t}\psi_n(x,t) \tag{4}$$

Beide Seiten der Gleichung getrennt lösen,

$$\begin{aligned}
\text{LHS} &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\varphi_n(x)e^{-\frac{\mathrm{i}}{\hbar}E_n t} \\
&= -\frac{\hbar^2}{2m}e^{-\frac{\mathrm{i}}{\hbar}E_n t}\frac{\partial^2}{\partial x^2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \\
&= -\frac{\hbar^2}{2m}e^{-\frac{\mathrm{i}}{\hbar}E_n t}\cdot\sqrt{\frac{2}{L}}\cdot\frac{\partial}{\partial x}\cos\left(\frac{n\pi x}{L}\right)\cdot\frac{n\pi}{L} \\
&= -\frac{\hbar^2}{2m}e^{-\frac{\mathrm{i}}{\hbar}E_n t}\cdot\sqrt{\frac{2}{L}}\cdot\frac{n^2\pi^2}{L^2}\left(-\sin\left(\frac{n\pi x}{L}\right)\right) \\
&= \frac{\hbar^2}{2m}\frac{n^2\pi^2}{L^2}\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)e^{-\frac{\mathrm{i}}{\hbar}E_n t} \\
&= \frac{\hbar^2\pi^2 n^2}{2mL^2}\varphi_n(x)e^{-\frac{\mathrm{i}}{\hbar}E_n t} \\
&= E_n\psi_n(x,t)
\end{aligned}$$

$$\begin{aligned}
\text{RHS} &= \mathrm{i}\hbar\frac{\partial}{\partial t}\varphi_n(x)e^{-\frac{\mathrm{i}}{\hbar}E_n t} = \mathrm{i}\hbar\varphi_n(x)\frac{\partial}{\partial t}e^{-\frac{\mathrm{i}}{\hbar}E_n t} \\
&= \mathrm{i}\hbar\varphi_n(x)\cdot\left(-\frac{\mathrm{i}}{\hbar}\right)E_n e^{-\frac{\mathrm{i}}{\hbar}E_n t} \\
&= \varphi_n(x)E_n e^{-\frac{\mathrm{i}}{\hbar}E_n t} = E_n\varphi_n(x)e^{-\frac{\mathrm{i}}{\hbar}E_n t} \\
&= E_n\psi_n(x,t)
\end{aligned}$$

$\therefore$ LHS = RHS. Daher erfüllt $\psi_n(x,t)$ die zeitabhängig Schrödingergleichung des Teilchens im Kasten.

b)

$$\begin{aligned}\Psi(x,t) &= c_1\psi_1(x,t) + c_2\psi_2(x,t) \\ &= c_1\varphi_1(x)e^{-\mathrm{i}\frac{E_1}{\hbar}t} + c_2\varphi_2(x)e^{-\mathrm{i}\frac{E_2}{\hbar}t} \\ &= c_1\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)e^{-\mathrm{i}\frac{E_1}{\hbar}t} + c_2\sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)e^{-\mathrm{i}\frac{E_2}{\hbar}t}\end{aligned} \tag{5}$$

$$\begin{aligned}|\Psi(x,t)|^2 &= \Psi^*(x,t)\Psi(x,t) \\ &= \left[c_1\varphi_1(x)e^{-\mathrm{i}\frac{E_1}{\hbar}t} + c_2\varphi_2(x)e^{-\mathrm{i}\frac{E_2}{\hbar}t}\right]^* \left[c_1\varphi_1(x)e^{-\mathrm{i}\frac{E_1}{\hbar}t} + c_2\varphi_2(x)e^{-\mathrm{i}\frac{E_2}{\hbar}t}\right] \\ &= \left[c_1^*\varphi_1^*(x)e^{\mathrm{i}\frac{E_1}{\hbar}t} + c_2^*\varphi_2^*(x)e^{\mathrm{i}\frac{E_2}{\hbar}t}\right] \left[c_1\varphi_1(x)e^{-\mathrm{i}\frac{E_1}{\hbar}t} + c_2\varphi_2(x)e^{-\mathrm{i}\frac{E_2}{\hbar}t}\right] \\ &= c_1^*\varphi_1^*(x)e^{\mathrm{i}\frac{E_1}{\hbar}t}c_1\varphi_1(x)e^{-\mathrm{i}\frac{E_1}{\hbar}t} + c_1^*\varphi_1^*(x)e^{\mathrm{i}\frac{E_1}{\hbar}t}c_2\varphi_2(x)e^{-\mathrm{i}\frac{E_2}{\hbar}t} \\ &+ c_2^*\varphi_2^*(x)e^{\mathrm{i}\frac{E_2}{\hbar}t}c_1\varphi_1(x)e^{-\mathrm{i}\frac{E_1}{\hbar}t} + c_2^*\varphi_2^*(x)e^{\mathrm{i}\frac{E_2}{\hbar}t}c_2\varphi_2(x)e^{-\mathrm{i}\frac{E_2}{\hbar}t} \\ &= |c_1|^2|\varphi_1(x)|^2 + |c_2|^2|\varphi_2(x)|^2 + c_1^*c_2\varphi_1^*(x)\varphi_2(x)e^{\mathrm{i}\left(\frac{E_1-E_2}{\hbar}\right)t} \\ &+ c_2^*c_1\varphi_2^*(x)\varphi_1(x)e^{\mathrm{i}\left(\frac{E_2-E_1}{\hbar}\right)t}\end{aligned} \tag{6}$$

$c_1^* = c_1$ und $c_2^* = c_2 \quad \because c_1, c_2 \in \mathbb{R}$

$$\begin{aligned}|\Psi(x,t)|^2 &= c_1^2\varphi_1^2(x) + c_2^2\varphi_2^2(x) + c_1c_2\varphi_1(x)\varphi_2(x)\left[e^{\mathrm{i}\left(\frac{E_2-E_1}{\hbar}\right)t} + e^{-\mathrm{i}\left(\frac{E_2-E_1}{\hbar}\right)t}\right] \\ &= c_1^2\varphi_1^2(x) + c_2^2\varphi_2^2(x) + 2c_1c_2\varphi_1(x)\varphi_2(x)\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right]\end{aligned} \tag{7}$$

Die Aufenthaltswahrscheinlichkeitsdichte ist nicht zeitlich konstant. Sie schwingt mit dem Frequenz, die der Differenz zwischen den Energieniveaus $\frac{E_2-E_1}{\hbar}$ entspricht. Im Falle $c_1 = c_2 = \frac{1}{\sqrt{2}}$,

$$\begin{aligned}\Psi(x,t) &= c_1\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)e^{-\mathrm{i}\frac{E_1}{\hbar}t} + c_2\sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)e^{-\mathrm{i}\frac{E_2}{\hbar}t} \\ &= \frac{1}{\sqrt{2}}\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)e^{-\mathrm{i}\frac{E_1}{\hbar}t} + \frac{1}{\sqrt{2}}\sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)e^{-\mathrm{i}\frac{E_2}{\hbar}t} \\ &= \frac{1}{\sqrt{L}}\sin\left(\frac{\pi x}{L}\right)e^{-\mathrm{i}\frac{E_1}{\hbar}t} + \frac{1}{\sqrt{L}}\sin\left(\frac{2\pi x}{L}\right)e^{-\mathrm{i}\frac{E_2}{\hbar}t}\end{aligned}$$

$$\begin{aligned}|\Psi(x,t)|^2 &= \frac{1}{2}\varphi_1^2(x) + \frac{1}{2}\varphi_2^2(x) + 2\cdot\frac{1}{\sqrt{2}}\cdot\frac{1}{\sqrt{2}}\varphi_1(x)\varphi_2(x)\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right] \\ &= \frac{1}{2}\varphi_1^2(x) + \frac{1}{2}\varphi_2^2(x) + \varphi_1(x)\varphi_2(x)\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right]\end{aligned}$$

c)

$$\langle\hat{x}\rangle = \int_0^L \chi^*(x,t)\hat{x}\chi(x,t)\,\mathrm{d}x \tag{8}$$

Für die erste Eigenfunktion, $\chi(x,t) = \psi_1(x,t)$,

$$\begin{aligned}
\langle \hat{x} \rangle &= \int\limits_0^L \varphi_1^*(x) e^{\mathrm{i}\frac{E_1}{\hbar}t} x \varphi_1(x) e^{-\mathrm{i}\frac{E_1}{\hbar}t}\,\mathrm{d}x = \int\limits_0^L x\varphi_1^2(x)\,\mathrm{d}x = \frac{2}{L}\int\limits_0^L x\sin^2\left(\frac{\pi x}{L}\right)\,\mathrm{d}x \\
&= \frac{2}{L}\left[\frac{2L^2\cdot\frac{\pi^2}{L^2} - 2L\cdot\frac{\pi}{L}\sin\left(2L\cdot\frac{\pi}{L}\right) - \cos\left(2L\cdot\frac{\pi}{L}\right) + 1}{8\frac{\pi^2}{L^2}}\right] \\
&= \frac{2}{L}\left[\frac{2\pi^2 - 2\pi\sin 2\pi - \cos 2\pi + 1}{\frac{8\pi^2}{L^2}}\right] = \frac{2}{L}\cdot\frac{L^2}{8\pi^2}\left[2\pi^2 - 0 - 1 + 1\right] \\
&= \frac{L}{4\pi^2}\cdot 2\pi^2 = \frac{L}{2}
\end{aligned} \tag{9}$$

Für die Superposition aus Aufgabenteil b), $\chi(x,t) = \Psi(x,t)$:

$$\begin{aligned}
\langle \hat{x} \rangle &= \int\limits_0^L \Psi^*(x,t)\hat{x}\Psi(x,t)\,\mathrm{d}x = \int\limits_0^L x|\Psi(x,t)|^2\,\mathrm{d}x \\
&= \int\limits_0^L x\left\{c_1^2\varphi_1^2(x) + c_2^2\varphi_2^2(x) + 2c_1c_2\varphi_1(x)\varphi_2(x)\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right]\right\}\,\mathrm{d}x \\
&= c_1^2\underbrace{\int\limits_0^L x\varphi_1^2(x)\,\mathrm{d}x}_{\mathrm{I}} + c_2^2\underbrace{\int\limits_0^L x\varphi_2^2(x)\,\mathrm{d}x}_{\mathrm{II}} + 2c_1c_2\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right]\underbrace{\int\limits_0^L x\varphi_1(x)\varphi_2(x)\,\mathrm{d}x}_{\mathrm{III}}
\end{aligned} \tag{10}$$

Die Begriffe getrennt lösen,

$$\mathrm{I} = \frac{L}{2} \quad \text{aus Gl.(9)}$$

$$\begin{aligned}
\mathrm{II} &= \frac{2}{L}\int\limits_0^L x\sin^2\left(\frac{2\pi x}{L}\right)\,\mathrm{d}x = \frac{2}{L}\left[\frac{2L^2\cdot\frac{4\pi^2}{L^2} - 2L\cdot\frac{2\pi}{L}\sin\left(2L\cdot\frac{2\pi}{L}\right) - \cos\left(2L\cdot\frac{2\pi}{L}\right) + 1}{8\cdot\frac{4\pi^2}{L^2}}\right] \\
&= \frac{2}{L}\left[\frac{8\pi^2 - 4\pi\sin 4\pi - \cos 4\pi + 1}{\frac{32\pi^2}{L^2}}\right] = \frac{2}{L}\cdot\frac{L^2}{32\pi^2}\left[8\pi^2 - 0 - 1 + 1\right] \\
&= \frac{L}{16\pi^2}\cdot 8\pi^2 = \frac{L}{2}
\end{aligned}$$

$$
\begin{aligned}
\mathrm{III} &= \int_0^L x\sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)\sqrt{\frac{2}{L}}\sin\left(\frac{2\pi x}{L}\right)\,\mathrm{d}x = \frac{2}{L}\int_0^L x\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{2\pi x}{L}\right)\,\mathrm{d}x \\
&= \frac{2}{L}\cdot\frac{1}{2}\int_0^L x\left[\cos\left(\frac{\pi x}{L}-\frac{2\pi x}{L}\right)-\cos\left(\frac{\pi x}{L}+\frac{2\pi x}{L}\right)\right]\mathrm{d}x \\
&= \frac{1}{L}\int_0^L x\left[\cos\left(-\frac{\pi x}{L}\right)-\cos\left(\frac{3\pi x}{L}\right)\right]\mathrm{d}x \\
&= \frac{1}{L}\int_0^L x\cos\left(\frac{\pi x}{L}\right)\mathrm{d}x - \frac{1}{L}\int_0^L x\cos\left(\frac{3\pi x}{L}\right)\mathrm{d}x \\
&= \frac{1}{L}\left[\frac{x\sin\left(\frac{\pi x}{L}\right)}{\frac{\pi}{L}}+\frac{\cos\left(\frac{\pi x}{L}\right)}{\left(\frac{\pi}{L}\right)^2}\right]_0^L - \frac{1}{L}\left[\frac{x\sin\left(\frac{3\pi x}{L}\right)}{\frac{3\pi}{L}}+\frac{\cos\left(\frac{3\pi x}{L}\right)}{\left(\frac{3\pi}{L}\right)^2}\right]_0^L \\
&= \frac{1}{L}\left[\frac{L\sin\pi}{\frac{\pi}{L}}+\frac{\cos\pi}{\frac{\pi^2}{L^2}}-0-\frac{\cos 0}{\frac{\pi^2}{L^2}}\right] - \frac{1}{L}\left[\frac{L\sin 3\pi}{\frac{3\pi}{L}}+\frac{\cos 3\pi}{\frac{9\pi^2}{L^2}}-0-\frac{\cos 0}{\frac{9\pi^2}{L^2}}\right] \\
&= \frac{1}{L}\left[0-\frac{1}{\frac{\pi^2}{L^2}}-0-\frac{1}{\frac{\pi^2}{L^2}}\right] - \frac{1}{L}\left[0-\frac{1}{\frac{9\pi^2}{L^2}}-0-\frac{1}{\frac{9\pi^2}{L^2}}\right] \\
&= \frac{1}{L}\cdot\frac{L^2}{\pi^2}\cdot(-2) - \frac{1}{L}\cdot\frac{L^2}{9\pi^2}\cdot(-2) = -\frac{2L}{\pi^2}+\frac{2L}{9\pi^2} \\
&= \frac{-18L+2L}{9\pi^2} = -\frac{16L}{9\pi^2}
\end{aligned}
$$

$$
\begin{aligned}
\therefore \langle\hat{x}\rangle &= c_1^2\frac{L}{2}+c_2^2\frac{L}{2}+2c_1c_2\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right]\left(-\frac{16L}{9\pi^2}\right) \\
&= \frac{L}{2}\left(c_1^2+c_2^2\right)-\frac{32L}{9\pi^2}c_1c_2\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right] \qquad (11) \\
&= \frac{L}{2}-\frac{32L}{9\pi^2}c_1c_2\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right]
\end{aligned}
$$

Im Falle $c_1 = c_2 = \frac{1}{\sqrt{2}}$,

$$
\begin{aligned}
\langle\hat{x}\rangle &= \frac{1}{2}\cdot\frac{L}{2}+\frac{1}{2}\cdot\frac{L}{2}+2\cdot\frac{1}{\sqrt{2}}\cdot\frac{1}{\sqrt{2}}\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right]\left(-\frac{16L}{9\pi^2}\right) \\
&= \frac{L}{4}+\frac{L}{4}-\frac{16L}{9\pi^2}\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right] \qquad (12) \\
&= \frac{L}{2}-\frac{16L}{9\pi^2}\cos\left[\left(\frac{E_2-E_1}{\hbar}\right)t\right]
\end{aligned}
$$