Prof. D. Egorova

SS 2011
Blatt 2 (Teil I)
27.04.2011

Lösungen zur Übungen zur Vorlesung Theoretische Chemie, Teil I: Quantenmechanik

Aufgabe 1

(a)

(Weil $\hat{A}$ und $\hat{B}$ beide lineare Operatoren sind,)

$$\begin{aligned}
\left\langle x \mid \left(\hat{A}+\hat{B}\right)^{\dagger} y\right\rangle &= \left\langle \left(\hat{A}+\hat{B}\right) x \mid y\right\rangle \\
&= \left\langle \hat{A}x \mid y\right\rangle + \left\langle \hat{B}x \mid y\right\rangle \\
&= \left\langle x \mid \hat{A}^{\dagger} y\right\rangle + \left\langle x \mid \hat{B}^{\dagger} y\right\rangle
\end{aligned}$$

$$\Longrightarrow \quad \left(\hat{A}+\hat{B}\right)^{\dagger} = \hat{A}^{\dagger} + \hat{B}^{\dagger}$$

(b)

$$\left\langle \hat{A}x \right| = \langle x| \, \hat{A}^{\dagger}$$

$$\begin{aligned}
\left\langle \left(\hat{A}\hat{B}\right)^{\dagger} x \mid y\right\rangle &= \left\langle x \mid \hat{A}\hat{B} y\right\rangle \\
&= \left\langle \hat{A}^{\dagger} x \mid \hat{B} y\right\rangle \\
&= \left\langle \hat{B} y \mid \hat{A}^{\dagger} x\right\rangle^{*} \\
&= \left\langle y \mid \hat{B}^{\dagger}\hat{A}^{\dagger} x\right\rangle^{*} \\
&= \left\langle \hat{B}^{\dagger}\hat{A}^{\dagger} x \mid y\right\rangle
\end{aligned}$$

$$\Longrightarrow \quad \left(\hat{A}\hat{B}\right)^{\dagger} = \hat{B}^{\dagger}\hat{A}^{\dagger}$$

(c)

$$\begin{aligned}
\left\langle x \mid \left(\alpha\hat{A}\right)^{\dagger} y\right\rangle &= \left\langle \alpha\hat{A} x \mid y\right\rangle \\
&= \left\langle y \mid \alpha\hat{A} x\right\rangle^{*} \\
&= \alpha^{*} \left\langle y \mid \hat{A} x\right\rangle^{*} \\
&= \alpha^{*} \left\langle \hat{A} x \mid y\right\rangle \\
&= \alpha^{*} \left\langle x \mid \hat{A}^{\dagger} y\right\rangle \\
&= \left\langle x \mid \alpha^{*}\hat{A}^{\dagger} y\right\rangle
\end{aligned}$$

$$\Longrightarrow \quad \left(\alpha\hat{A}\right)^\dagger = \alpha^*\hat{A}^\dagger$$

(d)

$$\left\langle x \mid \left(\hat{A}^\dagger\right)^\dagger y\right\rangle = \left\langle \hat{A}^\dagger x \mid y\right\rangle = \left\langle y \mid \hat{A}^\dagger x\right\rangle^* = \left\langle \hat{A} y \mid x\right\rangle^* = \left\langle x \mid \hat{A} y\right\rangle \quad \Rightarrow \quad \left(\hat{A}^\dagger\right)^\dagger = \hat{A}$$

Aufgabe 2

(a)

$$\left(\hat{E}+\hat{F}\right)^\dagger = \hat{E}^\dagger + \hat{F}^\dagger = \hat{E}+\hat{F}$$

(b)

$$\left(\hat{E}\hat{E}\right)^\dagger = \hat{E}^\dagger\hat{E}^\dagger = \hat{E}\hat{E}$$

(c)

$$\left(\hat{E}\hat{F}\right)^\dagger = \hat{F}^\dagger\hat{E}^\dagger = \hat{F}\hat{E} \neq \hat{E}\hat{F}$$

wenn $\left[\hat{E},\hat{F}\right] \neq 0$

(d)

Wenn $\left[\hat{E},\hat{F}\right] = 0$, $\hat{E}\hat{F}$ ist hermitesch.

Aufgabe 3

(a)

$$\frac{\mathrm{d}}{\mathrm{d}x} f_1 = 0, \quad \frac{\mathrm{d}}{\mathrm{d}x} f_2 = \sqrt{\frac{3}{2}}, \quad \frac{\mathrm{d}}{\mathrm{d}x} f_3 = 3\sqrt{\frac{5}{2}}x$$

$$\begin{aligned}
\left\langle \Psi \left| \hat{A} \right| \Psi \right\rangle &= \int_{-1}^{1} \mathrm{d}x\, \Psi^* \hat{A}\, \Psi \\
&= \int_{-1}^{1} \mathrm{d}x\, \Psi^* \frac{\mathrm{d}}{\mathrm{d}x}\, \Psi \\
&= \int_{-1}^{1} \mathrm{d}x \left(c_1^* f_1^* + c_2^* f_2^* + c_3^* f_3^*\right) \frac{\mathrm{d}}{\mathrm{d}x} \left(c_1 f_1 + c_2 f_2 + c_3 f_3\right) \\
&= c_1^* c_1 \left\langle f_1 \mid f_1' \right\rangle + c_1^* c_2 \left\langle f_1 \mid f_2' \right\rangle + c_1^* c_3 \left\langle f_1 \mid f_3' \right\rangle \\
&\quad + c_2^* c_1 \left\langle f_1 \mid f_1' \right\rangle + c_2^* c_2 \left\langle f_1 \mid f_2' \right\rangle + c_2^* c_3 \left\langle f_1 \mid f_3' \right\rangle \\
&\quad + c_3^* c_1 \left\langle f_1 \mid f_1' \right\rangle + c_3^* c_2 \left\langle f_1 \mid f_2' \right\rangle + c_3^* c_3 \left\langle f_1 \mid f_3' \right\rangle \\
&= 0 + c_1^* c_2 \frac{\sqrt{3}}{2} \int_{-1}^{1} \mathrm{d}x + c_1^* c_3 \sqrt{\frac{45}{2}} \int_{-1}^{1} x\mathrm{d}x \\
&\quad + 0 + c_2^* c_2 \frac{3}{2} \int_{-1}^{1} x\mathrm{d}x + c_2^* c_3 \frac{\sqrt{135}}{2} \int_{-1}^{1} x^2\mathrm{d}x \\
&\quad + 0 + c_3 2^* c_2 \frac{\sqrt{15}}{4} \int_{-1}^{1} \mathrm{d}x \left(3x^2 - 1\right) + c_3 2^* c_3 \frac{15}{4} \int_{-1}^{1} \mathrm{d}x \left(3x^3 - x\right) \\
&= c_1^* c_2 \sqrt{3} + c_2^* c_3 \sqrt{15}
\end{aligned}$$

(b)

$$\mathbf{A} = \begin{pmatrix} 0 & \sqrt{3} & 0 \\ 0 & 0 & \sqrt{15} \\ 0 & 0 & 0 \end{pmatrix}; \quad \mathbf{c} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix}; \quad \mathbf{c}^\dagger = \begin{pmatrix} c1^* & c2^* & c3^* \end{pmatrix}$$

$$\mathbf{A}\cdot\mathbf{c}=\begin{pmatrix}0 & \sqrt{3} & 0\\ 0 & 0 & \sqrt{15}\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}c_1\\ c_2\\ c_3\end{pmatrix}=\begin{pmatrix}\sqrt{3}c_2\\ \sqrt{15}c_3\\ 0\end{pmatrix}$$

$$\mathbf{c}^\dagger\cdot\mathbf{A}\cdot\mathbf{c}=\begin{pmatrix}c_1^* & c_2^* & c_3^*\end{pmatrix}\begin{pmatrix}\sqrt{3}c_2\\ \sqrt{15}c_3\\ 0\end{pmatrix}=c_1^*c_2\sqrt{3}+c_2^*c_3\sqrt{15}$$

(c)

$$\left\langle\hat{A}\right\rangle=2\mathrm{e}^{-\mathrm{i}\pi}\frac{1}{\sqrt{3}}\sqrt{3}+\frac{1}{\sqrt{3}}\mathrm{e}^{-\mathrm{i}\pi}\frac{1}{\sqrt{5}}\mathrm{e}^{\mathrm{i}\pi/2}\sqrt{15}=2+\mathrm{e}^{-\mathrm{i}\pi/2}=2-\mathrm{i}$$

(d)

$\hat{A}$ ist nicht hermitesch, weil $\left\langle\hat{A}\right\rangle$ komplex ist, und $\hat{A}$ bzw. $\mathbf{A}$ nicht selbst-adjungiert ist.

Aufgabe 4

(a)

$$n=1,\psi(x)=\sqrt{\frac{2}{L}}\sin\frac{\pi x}{L}$$

(b)

$$\begin{aligned}\langle\psi\,|x|\,\psi\rangle &= \frac{2}{L}\int_0^L \mathrm{d}x x\sin^2\frac{\pi x}{L}\\ &= \frac{2}{L}\frac{L^2}{\pi^2}\int_0^L \mathrm{d}\left(\frac{\pi x}{L}\right)\frac{\pi x}{L}\sin^2\frac{\pi x}{L}\\ &= \frac{2L}{\pi^2}\frac{\pi^2}{4}\\ &= \frac{L}{2}\end{aligned}$$

(c)

$$\begin{aligned}\left\langle x^2\right\rangle &= \frac{2}{L}\int_0^L \mathrm{d}x x^2\sin^2\frac{\pi x}{L}\\ &= \frac{2}{L}\frac{L^3}{\pi^3}\int_0^L \mathrm{d}\left(\frac{\pi x}{L}\right)\frac{\pi^2x^2}{L^2}\sin^2\frac{\pi x}{L}\\ &= \frac{2L^2}{\pi^3}\left(\frac{\pi^3}{6}-\frac{\pi}{4}\right)\\ &= \frac{L^2}{3}-\frac{L^2}{2\pi^2}\end{aligned}$$

$$\Delta x=\sqrt{\left\langle x^2\right\rangle-\left\langle x\right\rangle^2}=\sqrt{L^2\left(\frac{1}{3}-\frac{1}{2\pi^2}-\frac{1}{4}\right)}=L\sqrt{\frac{1}{12}-\frac{1}{2\pi^2}}$$

(d)

$$\langle p\rangle=\frac{2}{L}\frac{\hbar}{\mathrm{i}}\int_0^L \mathrm{d}x\sin\frac{\pi x}{L}\frac{\mathrm{d}}{\mathrm{d}x}\sin\frac{\pi x}{L}=\frac{2}{L}\frac{\hbar}{\mathrm{i}}\frac{\sin^2\frac{\pi x}{L}}{2}\Bigg|_0^L=0$$

(e)

$$\begin{aligned}
\langle p^2\rangle &= \frac{2}{L}\left(-\hbar^2\right)\int_0^L \mathrm{d}x \sin\frac{\pi x}{L}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\sin\frac{\pi x}{L} \\
&= \frac{2\hbar^2}{L}\frac{\pi^2}{L^2}\int_0^L \mathrm{d}x \sin^2\frac{\pi x}{L} \\
&= \frac{2\hbar^2}{L}\frac{\pi}{L}\frac{\pi}{2} \\
&= \frac{\hbar^2\pi^2}{L}
\end{aligned}$$

$$\Delta p = \frac{\hbar\pi}{L}$$

(f)

$$\Delta x\Delta p = \hbar\pi\sqrt{\frac{\pi^2-6}{12\pi^2}} = \hbar\sqrt{\frac{\pi^2-6}{12}} > \hbar\sqrt{\frac{9-6}{12}} = \frac{\hbar}{2} \quad (\pi = 3.14.., \pi^2 > 9)$$

$$\Delta x\Delta p > \frac{\hbar}{2}$$

Aufgabe 5

$$\int \mathrm{d}y \sin^2(y) = \int \frac{1-\cos(2y)}{2}$$

(a) Grundzustand: $n = 1$

$$\begin{aligned}
W_1 = \frac{2}{L}\int_0^{L/4}\mathrm{d}x \sin^2\left(\frac{\pi x}{L}\right) &= \frac{2}{L}\frac{L}{\pi}\int_0^{L/4}\mathrm{d}\left(\frac{\pi x}{L}\right)\sin^2\left(\frac{\pi x}{L}\right) \\
&= \frac{2}{\pi}\int_0^{L/4}\mathrm{d}\left(\frac{\pi x}{L}\right)\frac{1-\cos\left(2\pi x/L\right)}{2} \\
&= \frac{2}{\pi}\frac{1}{2}\left(\left.\frac{\pi x}{L}\right|_0^{L/4} - \frac{1}{2}\sin\left(2\pi x/L\right)\Big|_0^{L/4}\right) \\
&= \frac{1}{4} - \frac{1}{2\pi}
\end{aligned}$$

(b) Erster angeregter Zustand: $n = 2$

$$\begin{aligned}
W_2 = \frac{2}{L}\int_0^{L/4}\mathrm{d}x \sin^2\left(\frac{2\pi x}{L}\right) &= \frac{1}{\pi}\int_0^{L/4}\mathrm{d}\left(\frac{2\pi x}{L}\right)\frac{1-\cos\left(4\pi x/L\right)}{2} \\
&= \frac{1}{\pi}\frac{1}{2}\left(\left.\frac{2\pi x}{L}\right|_0^{L/4} - \frac{1}{2}\sin\left(4\pi x/L\right)\Big|_0^{L/4}\right) \\
&= \frac{1}{4}
\end{aligned}$$

(d)

$$\begin{aligned}
W_n = \frac{2}{L}\int_0^{L/4}\mathrm{d}x \sin^2\left(\frac{n\pi x}{L}\right) &= \frac{2}{n\pi}\int_0^{L/4}\mathrm{d}\left(\frac{n\pi x}{L}\right)\frac{1-\cos\left(2n\pi x/L\right)}{2} \\
&= \left.\frac{2n\pi x}{2n\pi L}\right|_0^{L/4} - \frac{1}{n\pi}\frac{1}{2}\sin\left(2n\pi x/L\right)\Big|_0^{L/4} \\
&= \frac{1}{4} - \frac{1}{2n\pi}\sin\left(\frac{n\pi}{2}\right)
\end{aligned}$$

(c)

$$\sin(ax)\sin(bx) = \frac{1}{2}(\cos((a-b)x) - \cos((a+b)x))$$

$$\begin{aligned}
W_\Psi = \int_0^{L/4} \mathrm{d}x\, \Psi^*(x)\, \Psi(x) \\
&= |c_1|^2 W_1 + |c_2|^2 W_2 + |c_3|^2 W_3 \\
&+ (c_1^* c_2 + c_2^* c_1)\frac{2}{L}\int_0^{L/4} \mathrm{d}x \sin(\frac{\pi x}{L})\sin(2\frac{\pi x}{L}) \\
&+ (c_1^* c_3 + c_3^* c_1)\frac{2}{L}\int_0^{L/4} \mathrm{d}x \sin(\frac{\pi x}{L})\sin(3\frac{\pi x}{L}) \\
&+ (c_2^* c_3 + c_3^* c_2)\frac{2}{L}\int_0^{L/4} \mathrm{d}x \sin(2\frac{\pi x}{L})\sin(3\frac{\pi x}{L}) \\
&= |c_1|^2\left(\frac{1}{4} - \frac{1}{2\pi}\right) + |c_2|^2\left(\frac{1}{4}\right) + |c_3|^2\left(\frac{1}{4} + \frac{1}{6\pi}\right) \\
&+ (c_1^* c_2 + c_2^* c_1)\frac{2}{L}\frac{1}{3\sqrt{2}} \\
&+ (c_1^* c_3 + c_3^* c_1)\frac{2}{L}\frac{1}{4} \\
&+ (c_2^* c_3 + c_3^* c_2)\frac{2}{L}\frac{3}{5\sqrt{2}}
\end{aligned}$$

Aufgabe 6

allgemeine Lösung:

$$\psi = A\sin kx + B\cos kx$$

Randbedingungen:

$$\psi(0) = 0 \quad \Rightarrow \quad \psi = A\sin kx$$

$$\psi\left(\frac{L}{2}\right) = 0 \quad \Rightarrow \quad A\sin\left(\frac{kL}{2}\right) = 0 \quad \Rightarrow \quad k = \frac{2n\pi}{L}$$

$$\Longrightarrow \quad \psi = A\sin\left(\frac{2n\pi}{L}x\right)$$

Normierung:

$$\begin{aligned}
\langle\psi\,|\,\psi\rangle &= A^2\int_0^{L/2} \mathrm{d}x \sin^2\left(\frac{2n\pi}{L}x\right) \\
&= A^2\frac{L}{2n\pi}\int_0^{L/2} \mathrm{d}\left(\frac{2n\pi}{L}x\right)\left(\frac{1-\cos\left(\frac{4n\pi}{L}x\right)}{2}\right) \\
&= A^2\frac{L}{4n\pi}\left(\frac{2n\pi x}{L}\bigg|_0^{L/2} - \frac{1}{2}\sin\left(\frac{4n\pi}{L}x\right)\bigg|_0^{L/2}\right) \\
&= A^2\frac{L}{4}
\end{aligned}$$

$$\Longrightarrow \quad A = \frac{2}{\sqrt{L}}$$

$$\Longrightarrow \quad \psi = \frac{2}{\sqrt{L}}\sin\left(\frac{2n\pi}{L}x\right)$$

die Eigenfunktionen ψ_2 und ψ_4 vom Teilchen in der Aufgabe 1 sind auch Eigenfunktionen für dieses Potential.