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

Aufgabe 1

(a)

$$\hat{p} = \frac{\hbar}{\mathrm{i}}\nabla, \quad \nabla = \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix}$$

$$\hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}, \quad \hat{p}_y = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial y}, \quad \hat{p}_z = \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial z}$$

$$T = \frac{p^2}{2m}, \quad \hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\Delta$$

$$\Delta = \begin{pmatrix} \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{pmatrix} \begin{pmatrix} \frac{\partial}{\partial x} \\ \frac{\partial}{\partial y} \\ \frac{\partial}{\partial z} \end{pmatrix} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\hat{T}_x = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \quad \hat{T}_y = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}, \quad \hat{T}_z = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}$$

(b)

$$[\hat{p}_z, \hat{z}] = \hat{p}_z\hat{z} - \hat{z}\hat{p}_z = \frac{\hbar}{\mathrm{i}}\left(\frac{\partial}{\partial z}z - z\frac{\partial}{\partial z}\right)$$

$$[\hat{p}_z, \hat{z}]\,\psi = \frac{\hbar}{\mathrm{i}}\left(\frac{\partial}{\partial z}z - z\frac{\partial}{\partial z}\right)\psi = \frac{\hbar}{\mathrm{i}}\left(\psi + z\frac{\partial \psi}{\partial z} - z\frac{\partial \psi}{\partial z}\right) = \frac{\hbar}{\mathrm{i}}\psi$$

$$\Rightarrow [\hat{p}_z, \hat{z}] = \frac{\hbar}{\mathrm{i}}$$

(gilt auch für $[\hat{p}_x, \hat{x}]$ und $[\hat{p}_y, \hat{y}]$)

$$[\hat{p}_x, \hat{y}]\,\psi = \frac{\hbar}{\mathrm{i}}\left(\frac{\partial}{\partial x}y\psi - y\frac{\partial \psi}{\partial x}\right) = \frac{\hbar}{\mathrm{i}}\left(y\frac{\partial \psi}{\partial x} - y\frac{\partial \psi}{\partial x}\right) = 0$$

$$[\hat{p}_x, \hat{y}] = [\hat{p}_y, \hat{x}] = [\hat{p}_y, \hat{z}] = [\hat{p}_z, \hat{y}] = [\hat{p}_z, \hat{x}] = [\hat{p}_x, \hat{z}] = 0$$

$$\left[\hat{T}_x, \hat{p}_x\right]\psi = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\frac{\hbar}{\mathrm{i}}\frac{\partial \psi}{\partial x} + \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} = -\frac{\hbar^3}{2m\mathrm{i}}\frac{\partial^3 \psi}{\partial x^3} + \frac{\hbar^3}{2m\mathrm{i}}\frac{\partial^3 \psi}{\partial x^3} = 0$$

$$\Rightarrow \left[\hat{T}_x, \hat{p}_x\right] = 0$$

$\left[\hat{A},\hat{B}\right]=0 \Rightarrow$gleichzeitig meßbar

$$\begin{aligned}
\left[\hat{T}_y,\hat{y}\right]\psi &= \left(\hat{T}_y\hat{y}-\hat{y}\hat{T}_y\right)\psi \\
&= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}y\psi+y\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}\psi \\
&= \frac{\hbar^2}{2m}\left(-\frac{\partial}{\partial y}\left(\psi+y\frac{\partial\psi}{\partial y}\right)+y\frac{\partial^2}{\partial y^2}\psi\right) \\
&= \frac{\hbar^2}{2m}\left(-\frac{\partial\psi}{\partial y}-\frac{\partial\psi}{\partial y}-y\frac{\partial^2\psi}{\partial y^2}+y\frac{\partial^2\psi}{\partial y^2}\right) \\
&= -\frac{\hbar^2}{2m}\left(2\frac{\partial\psi}{\partial y}\right) \\
&= -\frac{\hbar^2}{m}\frac{\partial\psi}{\partial y}
\end{aligned}$$

$$\Longrightarrow \qquad \left[\hat{T}_x,\hat{x}\right]=-\frac{\hbar^2}{m}\frac{\partial}{\partial x}$$

Aufgabe 2

(a)

$$\hat{H}=\hat{T}+\hat{V}, \quad \hat{T}(x)=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \quad \hat{V}(x)=0$$

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

(b)

$$\hat{T}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \quad \hat{V}(x)=V(x)=\frac{kx^2}{2}$$

$$\hat{H}=\hat{T}+\hat{V}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{kx^2}{2}$$

Aufgabe 3

$$\frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\phi_i=p_{x_i}\phi_i$$

$$\frac{\partial}{\partial x}\phi_i=\frac{\mathrm{i}}{\hbar}p_{x_i}\phi_i$$

$$\lambda=\frac{\mathrm{i}}{\hbar}p_{x_i}, \phi_i=A_i\mathrm{e}^{\frac{\mathrm{i}p_{x_i}}{\hbar}x}$$

$$\text{freies Teilchen: } p_{x_i}\in\{-\infty,+\infty\}\Rightarrow\phi=A\mathrm{e}^{\frac{\mathrm{i}}{\hbar}p_x x}$$

Aufgabe 4

Orthonormalbasis: $\langle f_i \mid f_j\rangle=\delta_{ij}$
Orthogonalität: $\langle f_i \mid f_j\rangle=0, i\neq j$; Normierung: $\langle f_i \mid f_i\rangle=1$
$f_i=c_iP_i$

$$\text{Normierung: } i=j, \quad \langle f_i \mid f_i\rangle=c_i^*c_i\langle P_i \mid P_i\rangle=1 \quad \Longrightarrow \quad c_i^*c_i=\frac{1}{\langle P_i \mid P_i\rangle}$$

$$\langle P_1 \mid P_1\rangle=\int_{-1}^{1}x^2\mathrm{d}x=\left.\frac{x^3}{3}\right|_{-1}^{1}=\frac{2}{3}$$

$$\Longrightarrow \quad f_1 = \sqrt{\frac{3}{2}} P_1 = \sqrt{\frac{3}{2}} x$$

$$\begin{aligned}
\langle P_2 \mid P_2 \rangle &= \frac{1}{4} \int_{-1}^{1} \mathrm{d}x \left(3x^2 - 1\right)^2 \\
&= \frac{1}{4} \int_{-1}^{1} \mathrm{d}x \left(9x^4 - 6x^2 + 1\right) \\
&= \frac{9}{4} \left. \frac{x^5}{5} \right|_{-1}^{1} - \frac{6}{4} \left. \frac{x^3}{3} \right|_{-1}^{1} + \frac{1}{4} \left. x \right|_{-1}^{1} \\
&= \frac{9}{10} - 1 + \frac{1}{2} \\
&= \frac{2}{5}
\end{aligned}$$

$$\Longrightarrow \quad f_2 = \sqrt{\frac{5}{2}} P_2 = \sqrt{\frac{5}{8}} \left(3x^2 - 1\right)$$

$$\begin{aligned}
\langle P_3 \mid P_3 \rangle &= \frac{1}{4} \int_{-1}^{1} \mathrm{d}x \left(5x^3 - 3x\right)^2 \\
&= \frac{1}{4} \int_{-1}^{1} \mathrm{d}x \left(25x^6 - 30x^4 + 9x^2\right) \\
&= \frac{25}{4} \left. \frac{x^7}{7} \right|_{-1}^{1} - \frac{30}{4} \left. \frac{x^5}{5} \right|_{-1}^{1} + \frac{9}{4} \left. \frac{x^3}{3} \right|_{-1}^{1} \\
&= \frac{25}{14} - 3 + \frac{3}{2} \\
&= \frac{2}{7}
\end{aligned}$$

$$\Longrightarrow \quad f_3 = \sqrt{\frac{7}{2}} P_3 = \sqrt{\frac{7}{8}} \left(5x^3 - 3x\right)$$

Orthogonalität: $i \neq j, \quad \langle f_1 \mid f_2 \rangle = \langle f_1 \mid f_3 \rangle = \langle f_2 \mid f_3 \rangle \stackrel{!}{=} 0 \Longrightarrow \quad \langle P_1 \mid P_2 \rangle = \langle P_1 \mid P_3 \rangle = \langle P_2 \mid P_3 \rangle \stackrel{!}{=} 0$

$$\begin{aligned}
\langle P_1 \mid P_2 \rangle &= \int_{-1}^{1} x \frac{1}{2} \left(3x^2 - 1\right) \mathrm{d}x \\
&= \frac{1}{2} \left(\int_{-1}^{1} 3x^3 \mathrm{d}x - \int_{-1}^{1} x \mathrm{d}x \right) \\
&= \frac{3}{2} \left. \frac{x^4}{4} \right|_{-1}^{1} - \frac{1}{2} \left. \frac{x^2}{2} \right|_{-1}^{1} \\
&= 0 - 0 \\
&= 0
\end{aligned}$$

$$\begin{aligned}
\langle P_1 \mid P_3 \rangle &= \int_{-1}^{1} x \frac{1}{2} \left(5x^3 - 3x\right) \mathrm{d}x \\
&= \frac{1}{2} \left. \frac{x^5}{5} \right|_{-1}^{1} - \frac{1}{2} \left. \frac{x^3}{3} \right|_{-1}^{1} \\
&= \frac{1}{2} \left(1 + 1 - 1 - 1\right) \\
&= 0
\end{aligned}$$

$$
\begin{aligned}
\langle P_2 \mid P_3\rangle &= \int_{-1}^{1} \frac{1}{2}\left(3x^2-1\right)\frac{1}{2}\left(5x^3-3x\right)\mathrm{d}x \\
&= \frac{15}{4}\int_{-1}^{1} x^5 \mathrm{d}x - \frac{9}{4}\int_{-1}^{1} x^3 \mathrm{d}x - \frac{5}{4}\int_{-1}^{1} x^3 \mathrm{d}x + \frac{3}{4}\int_{-1}^{1} x \mathrm{d}x \\
&= 0
\end{aligned}
$$

(b)

$$
\begin{aligned}
\langle f_1 \mid g\rangle &= \sqrt{\frac{3}{2}}\left(5\left\langle x \mid x^3\right\rangle + \mathrm{i}\frac{3}{2}\left\langle x \mid x^2\right\rangle + \left(\sqrt{6}-3\right)\langle x \mid x\rangle - \mathrm{i}\frac{1}{2}\langle x \mid 1\rangle\right) \\
&= \sqrt{\frac{3}{2}}\left(2 + \mathrm{i}0 - \left(\sqrt{6}-3\right)\frac{2}{3} - \mathrm{i}0\right) \\
&= 2
\end{aligned}
$$

$$
\begin{aligned}
\langle f_2 \mid g\rangle &= \sqrt{\frac{5}{8}}\left(5\cdot 3\left\langle x^2 \mid x^3\right\rangle + \mathrm{i}\frac{3}{2}\cdot 3\left\langle x^2 \mid x^2\right\rangle + \left(\sqrt{6}-3\right)3\left\langle x^2 \mid x\right\rangle - \mathrm{i}\frac{1}{2}\cdot 3\left\langle x^2 \mid 1\right\rangle\right. \\
&\qquad \left. -5\left\langle 1 \mid x^3\right\rangle - \mathrm{i}\frac{3}{2}\left\langle 1 \mid x^2\right\rangle + \left(\sqrt{6}-3\right)\langle 1 \mid x\rangle + \mathrm{i}\frac{1}{2}\langle 1 \mid 1\rangle\right) \\
&= \sqrt{\frac{5}{8}}\left(0 + \mathrm{i}\frac{3}{2}\cdot 3\cdot\frac{2}{5} + 0 - \mathrm{i}\frac{1}{2}\cdot 3\cdot\frac{2}{3} - 0 - \mathrm{i}\frac{3}{2}\cdot\frac{2}{3} - 0 + \mathrm{i}\frac{1}{2}\cdot 2\right) \\
&= \sqrt{\frac{5}{8}}\mathrm{i}\left(\frac{9}{5} - 1 - 1 + 1\right) \\
&= \sqrt{\frac{2}{5}}\mathrm{i}
\end{aligned}
$$

$$
\begin{aligned}
\langle f_3 \mid g\rangle &= \sqrt{\frac{7}{8}}\left(5\cdot 5\left\langle x^3 \mid x^3\right\rangle + \mathrm{i}\frac{3}{2}\cdot 5\left\langle x^3 \mid x^2\right\rangle + \left(\sqrt{6}-3\right)5\left\langle x^3 \mid x\right\rangle - \mathrm{i}\frac{1}{2}\cdot 5\left\langle x^3 \mid 1\right\rangle\right. \\
&\qquad \left. -5\cdot 3\left\langle x \mid x^3\right\rangle - \mathrm{i}\frac{3}{2}\cdot 3\left\langle x \mid x^2\right\rangle + \left(\sqrt{6}-3\right)\cdot 3\langle x \mid x\rangle + \mathrm{i}\frac{1}{2}\cdot 3\langle x \mid 1\rangle\right) \\
&= \sqrt{\frac{7}{8}}\left(\frac{50}{7} + \mathrm{i}0 + \left(\sqrt{6}-3\right)\cdot 2 - \mathrm{i}0 - 6 - \mathrm{i}0 - \left(\sqrt{6}-3\right)\cdot 2 + \mathrm{i}0\right) \\
&= \sqrt{\frac{7}{8}}\cdot\frac{8}{7} \\
&= 2\sqrt{\frac{2}{7}}
\end{aligned}
$$

$$
g(x) = 2f_1 + i\sqrt{\frac{2}{5}}f_2 + 2\sqrt{\frac{2}{7}}f_3
$$

Alternativ

$$
\begin{aligned}
g(x) &= 5x^3 + \mathrm{i}\frac{3}{2}x^2 + \sqrt{6}x - 3x - \frac{\mathrm{i}}{2} \\
&= \left\{\left(5x^3 - 3x\right)\right\} + \left\{\sqrt{6}x\right\} + \left\{\frac{\mathrm{i}}{2}\left(3x^2-1\right)\right\} \\
&= 2P_3 + \sqrt{6}P_1 + \mathrm{i}P_2 \\
&= \sqrt{6}\sqrt{\frac{2}{3}}f_1 + \mathrm{i}\sqrt{\frac{2}{5}}f_2 + 2\sqrt{\frac{2}{7}}f_3 \\
&= 2f_1 + \mathrm{i}\sqrt{\frac{2}{5}}f_2 + 2\sqrt{\frac{2}{7}}f_3
\end{aligned}
$$

Aufgabe 5

$$\hat{H}\psi = E\psi, \quad E > 0, \quad \hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\lambda^2 = E \quad \Rightarrow \quad \lambda = \pm\frac{\mathrm{i}}{\hbar}\sqrt{2mE}$$

$$\psi = A_1 \mathrm{e}^{\mathrm{i}\sqrt{2mE}x/\hbar} + A_2 \mathrm{e}^{-\mathrm{i}\sqrt{2mE}x/\hbar}$$

$$E = \frac{p^2}{2m}, \quad \sqrt{2mE} = p; \quad k = \frac{p}{\hbar}$$

$$\begin{aligned}\psi &= A_1\mathrm{e}^{\mathrm{i}kx} + A_2\mathrm{e}^{-\mathrm{i}kx} \\ &= (A_1 + A_2)\cos kx + \mathrm{i}\,(A_1 - A_2)\sin kx \\ &= \tilde{A}_1\cos kx + \tilde{A}_2\sin kx\end{aligned}$$

Eigenfunktionen des Impulsoperators:

$$\phi = A\mathrm{e}^{\mathrm{i}p_x x/\hbar} = A\mathrm{e}^{\mathrm{i}kx}$$

falls $A_2 = 0$,

$$\psi = A_1\mathrm{e}^{\mathrm{i}kx}$$

ist auch Eigenfunktion von $\hat{p}_x$.

Aufgabe 6

(a)

$$p = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}$$

$$\hat{p}f_1 = 0, \quad \hat{p}f_2 = \frac{\hbar}{\mathrm{i}}kf_3, \quad \hat{p}f_3 = -\frac{\hbar}{\mathrm{i}}kf_2$$

$$\begin{aligned} & p_{11} = 0 \quad p_{12} = 0 \quad p_{13} = 0 \\ \Rightarrow\ & p_{21} = 0 \quad p_{22} = 0 \quad p_{23} = -\frac{\hbar}{\mathrm{i}}k \\ & p_{31} = 0 \quad p_{32} = \frac{\hbar}{\mathrm{i}}k \quad p_{33} = 0 \end{aligned}$$

$$\hat{\mathbf{p}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -\frac{\hbar}{\mathrm{i}}k \\ 0 & \frac{\hbar}{\mathrm{i}}k & 0 \end{pmatrix}$$

(b)

$$\det(\hat{\mathbf{p}} - \mathbf{E}\lambda) = \begin{vmatrix} -\lambda & 0 & 0 \\ 0 & -\lambda & -\frac{\hbar}{\mathrm{i}}k \\ 0 & \frac{\hbar}{\mathrm{i}}k & -\lambda \end{vmatrix} = 0$$

$$-\lambda^3 + \hbar^2k^2 = 0$$

Eigenwerte:

$$\lambda_1 = 0, \quad \lambda_2 = \hbar k, \quad \lambda_3 = -\hbar k$$

Eigenvektoren:
zu $\lambda_1 = 0$:

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \mathrm{i}\hbar k \\ 0 & -\mathrm{i}\hbar k & 0 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = 0 \Rightarrow \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

zu $\lambda_2 = \hbar k$:

$$x_1 = 0$$

$$\begin{matrix} \mathrm{i}\hbar k x_3 = \hbar k x_2 \\ -\mathrm{i}\hbar k x_2 = \hbar k x_3 \end{matrix} \Rightarrow \begin{matrix} x_2 = \mathrm{i} \\ x_3 = 1 \end{matrix}$$

$$\Rightarrow \begin{pmatrix} 0 \\ \mathrm{i} \\ 1 \end{pmatrix}$$

zu $\lambda_3 = \hbar k$:

$$x_1 = 0$$

$$\begin{matrix} \mathrm{i}\hbar k x_3 = -\hbar k x_2 \\ -\mathrm{i}\hbar k x_2 = -\hbar k x_3 \end{matrix} \Rightarrow \begin{matrix} x_2 = -\mathrm{i} \\ x_3 = 1 \end{matrix}$$

$$\Rightarrow \begin{pmatrix} 0 \\ -\mathrm{i} \\ 1 \end{pmatrix}$$

Eigenfunktionen:

$$\psi_1 = \frac{1}{\sqrt{2\pi}}$$

$$\psi_2 = \mathrm{i} f_2 + f_3 = \frac{1}{\sqrt{\pi}} (\mathrm{i} \sin kx + \cos kx) = \frac{1}{\sqrt{\pi}} \mathrm{e}^{\mathrm{i}kx}$$

$$\psi_3 = -\mathrm{i} f_2 + f_3 = \frac{1}{\sqrt{\pi}} \mathrm{e}^{-\mathrm{i}kx}$$

(c) $\hat{p}$ ist hermitisch, da die Eigenwerte reel sind