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

Aufgabe 1

$$\Psi_{nlm}(r,\theta,\phi) = N_{nl}R_{nl}(r)Y_{lm}(\theta,\phi), \quad N_{nl} = \sqrt{\frac{8(n-l-1)!}{2n((n+l)!)^3(na_0)^3}}, \quad R_{nl} = -e^{-\frac{r}{na_0}}\left(\frac{2r}{na_0}\right)^l L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$$

$$\Psi_{300} = N_{30}R_{30}Y_{00} = \frac{a_0^{-3/2}}{27\sqrt{3}}e^{-\frac{r}{3a_0}}L_3^1\left(\frac{2r}{3a_0}\right)\frac{1}{\sqrt{4\pi}} = \frac{a_0^{-3/2}}{27\sqrt{3}}e^{-\frac{r}{3a_0}}\left(-3\left(\frac{2r}{3a_0}\right)^2 + 18\frac{2r}{3a_0} - 18\right)\frac{1}{\sqrt{4\pi}} = ...$$

analog:
$\Psi_{310} = N_{31}R_{31}Y_{10}$
$\Psi_{31\pm1} = N_{31}R_{31}Y_{1\pm1}$
$\Psi_{320} = N_{32}R_{32}Y_{20}$
$\Psi_{32\pm1} = N_{32}R_{32}Y_{2\pm1}$
$\Psi_{32\pm2} = N_{32}R_{32}Y_{2\pm2}$

Aufgabe 2

$$\Psi_{21\pm1} = N_{21}R_{21}Y_{1\pm1} = \frac{a_0^{-3/2}}{12\sqrt{6}}e^{-\frac{r}{2a_0}}\left(\frac{r}{a_0}\right)L_3^3\left(\frac{r}{a_0}\right)\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi} = \frac{a_0^{-3/2}}{8\sqrt{\pi}}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}\sin\theta e^{\pm i\phi}$$

$$\begin{aligned}\Psi_{32\pm1} &= N_{32}R_{32}Y_{2\pm1} = \frac{a_0^{-3/2}}{5\cdot 2^3\cdot 3^3\sqrt{30}}e^{-\frac{r}{3a_0}}\left(\frac{2r}{3a_0}\right)^2 L_5^5\left(\frac{2r}{3a_0}\right)3\sqrt{\frac{5}{24\pi}}\sin\theta\cos\theta e^{\pm i\phi}\\ &= \frac{a_0^{-3/2}}{81\sqrt{\pi}}\left(\frac{2r}{3a_0}\right)^2 e^{-\frac{r}{3a_0}}\sin\theta\cos\theta e^{\pm i\phi}\end{aligned}$$

$$\begin{aligned}\Psi_{32\pm2} &= N_{32}R_{32}Y_{2\pm2} = \frac{a_0^{-3/2}}{5\cdot 2^3\cdot 3^3\sqrt{30}}e^{-\frac{r}{3a_0}}\left(\frac{2r}{3a_0}\right)^2 L_5^5\left(\frac{2r}{3a_0}\right)3\sqrt{\frac{5}{96\pi}}\\ &= \frac{a_0^{-3/2}}{162\sqrt{\pi}}\left(\frac{2r}{3a_0}\right)^2 e^{-\frac{r}{3a_0}}\sin^2\theta e^{\pm 2i\phi}\end{aligned}$$

$$\begin{aligned}\Psi_{2p_x} &= \frac{1}{\sqrt{2}}\left(\Psi_{211}+\Psi_{21-1}\right) = \frac{1}{\sqrt{2}}N_{21}R_{21}\left(Y_{11}+Y_{1-1}\right) = \frac{1}{\sqrt{2}}\frac{a_0^{-3/2}}{8\sqrt{\pi}}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}\sin\theta(e^{i\phi}+e^{-i\phi})\\ &= \frac{a_0^{-3/2}}{4\sqrt{2\pi}}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}\sin\theta\cos\phi\end{aligned}$$

$$\begin{aligned}\Psi_{3d_{xz}} &= \frac{1}{\sqrt{2}}\left(\Psi_{321}+\Psi_{32-1}\right) = \frac{1}{\sqrt{2}}N_{32}R_{32}\left(Y_{21}+Y_{2-1}\right) = \frac{1}{\sqrt{2}}\frac{a_0^{-3/2}}{81\sqrt{\pi}}\left(\frac{2r}{3a_0}\right)^2 e^{-\frac{r}{3a_0}}\sin\theta\cos\theta(e^{i\phi}+e^{-i\phi})\\ &= \frac{\sqrt{2}a_0^{-3/2}}{81\sqrt{\pi}}\left(\frac{2r}{3a_0}\right)^2 e^{-\frac{r}{3a_0}}\sin\theta\cos\theta\cos\phi\end{aligned}$$

$$
\begin{aligned}
\Psi_{3d_{xy}} &= \frac{-i}{\sqrt{2}}\left(\Psi_{322}-\Psi_{32-2}\right) = \frac{1}{\sqrt{2}}N_{32}R_{32}\left(Y_{22}-Y_{2-2}\right) = \frac{-i}{\sqrt{2}}\frac{a_0^{-3/2}}{162\sqrt{\pi}}\left(\frac{2r}{3a_0}\right)^2 e^{-\frac{r}{3a_0}}\sin^2\theta(e^{2i\phi}-e^{-2i\phi}) \\
&= \frac{a_0^{-3/2}}{81\sqrt{\pi}}\left(\frac{2r}{3a_0}\right)^2 e^{-\frac{r}{3a_0}}\sin^2\theta\sin(2\phi)
\end{aligned}
$$

etc...

Aufgabe 3

Normierung:

$$
1 = N^2\int \mathrm{d}x\mathrm{e}^{-2\alpha x^2} = N^2\sqrt{\pi/2\alpha}, \quad N = (2\alpha/\pi)^{1/4}
$$

$$
\begin{aligned}
E(\alpha) &= \left\langle\Phi\middle|\hat{H}\middle|\Phi\right\rangle = -\frac{\hbar^2}{2m}\left\langle\Phi\middle|\frac{\partial^2}{\partial x^2}\middle|\Phi\right\rangle + \frac{m\omega^2}{2}\left\langle\Phi\middle|x^2\middle|\Phi\right\rangle \\
\frac{\partial^2}{\partial x^2}\Phi(x) &= N\frac{\partial}{\partial x}\left(-2\alpha x\right)\mathrm{e}^{-\alpha x^2} = N\left(-2\alpha+4\alpha^2x^2\right)\mathrm{e}^{-\alpha x^2} \\
E(\alpha) &= -\frac{\hbar^2}{2m}N^2\left(-2\alpha\int\mathrm{e}^{-2\alpha x^2}\mathrm{d}x + 4\alpha^2\int x^2\mathrm{e}^{-2\alpha x^2}\mathrm{d}x\right) \\
&\quad +\frac{m\omega^2N^2}{2}\int x^2\mathrm{e}^{-2\alpha x^2}\mathrm{d}x \\
&= -\frac{\hbar^2}{2m}N^2\left(-2\alpha\sqrt{\frac{\pi}{2\alpha}} + 4\alpha^2\sqrt{\frac{\pi}{32\alpha^3}}\right) \\
&\quad +\frac{m\omega^2N^2}{2}\sqrt{\frac{\pi}{32\alpha^3}} \\
&= -\frac{\hbar^2}{2m}\sqrt{\frac{2\alpha}{\pi}}\left(-2\alpha\sqrt{\frac{\pi}{2\alpha}}+\alpha\sqrt{\frac{\pi}{2\alpha}}\right) \\
&\quad +\frac{m\omega^2}{2}\sqrt{\frac{2\alpha}{\pi}}\sqrt{\frac{\pi}{32\alpha^3}} \\
&= \frac{\hbar^2\alpha}{2m}+\frac{m\omega^2}{8\alpha}
\end{aligned}
$$

$$
\frac{\partial^2}{\partial x^2}\phi(x) = N\frac{\partial}{\partial x}\left(-2\alpha x\right)\mathrm{e}^{-\alpha x^2} = N\left(-2\alpha+4\alpha^2x^2\right)\mathrm{e}^{-\alpha x^2}
$$

Variation nach α:

$$
0 = \frac{\partial E}{\partial\alpha} = \frac{\hbar^2}{2m}-\frac{m\omega^2}{8\alpha^2}
$$

$$
\alpha = m\omega/2\hbar
$$

Einsetzen:

$$
E(\alpha) = \frac{\hbar^2}{2m}\frac{m\omega}{2\hbar}+\frac{m\omega^2}{8}2\hbar m\omega = \frac{\hbar\omega}{2} = E_{\text{exakt}}
$$

Aufgabe 4

$$
\Psi(x) = \frac{N}{\alpha^2+x^2}
$$

Normierung:

$$
\int_{-\infty}^{+\infty}\mathrm{d}x\frac{1}{(\alpha^2+x^2)^2} = \frac{\pi}{2\alpha^3} \quad\Rightarrow\quad N = \sqrt{\frac{2\alpha^3}{\pi}}
$$

$$
\begin{aligned}
\frac{\partial^2}{\partial x^2}\Psi(x) &= \frac{\partial}{\partial x}\left(-\frac{N2x}{(\alpha^2+x^2)^2}\right) \\
&= -\frac{2N}{(\alpha^2+x^2)^2}+\frac{8Nx^2}{(\alpha^2+x^2)^3} \\
&= \frac{8Nx^2-2N(\alpha^2+x^2)}{(\alpha^2+x^2)^3} \\
&= \frac{6Nx^2-2N\alpha^2}{(\alpha^2+x^2)^3}
\end{aligned}
$$

$$
\begin{aligned}
E(\alpha) &= -\frac{\hbar^2}{2m}\left\langle \Psi \left| \frac{\partial^2}{\partial x^2} \right| \Psi \right\rangle + \frac{1}{2}m\omega^2N^2\int \mathrm{d}x\frac{x^2}{(\alpha^2+x^2)^2} \\
&= -\frac{\hbar^2}{2m}N^2\left[-2\alpha^2\int \mathrm{d}x\frac{1}{(\alpha^2+x^2)^4}+6\int \mathrm{d}x\frac{x^2}{(\alpha^2+x^2)^4}\right] \\
&\quad +\frac{1}{2}m\omega^2N^2\int \mathrm{d}x\frac{x^2}{(\alpha^2+x^2)^2} \\
&= -\frac{\hbar^2}{2m}N^2\left(-2\alpha^2\frac{5\pi}{16\alpha^7}+6\frac{\pi}{16\alpha^5}\right)+\frac{1}{2}m\omega^2N^2\frac{\pi}{2\alpha} \\
&= N^2\left(\frac{\hbar^2}{2m}\frac{\pi}{4\alpha^5}+\frac{m\omega^2\pi}{4\alpha}\right) \\
&= \frac{\hbar^2\pi}{8m\alpha^5}\frac{2\alpha^3}{\pi}+\frac{m\omega^2\pi}{4\alpha}\frac{2\alpha^3}{\pi} \\
&= \frac{\hbar^2}{4\alpha^2m}+\frac{1}{2}m\omega^2\alpha^2
\end{aligned}
$$

Variation nach α:

$$0=\frac{\partial E}{\partial \alpha}=-\frac{\hbar^2}{2\alpha_0^3m}+m\omega_2\alpha_0$$

$$\Rightarrow \quad \frac{\hbar^2}{m}=2m\omega^2\alpha_0^4 \quad \Rightarrow \quad \alpha_0^2=\frac{\hbar}{\sqrt{2}m\omega}$$

Einsetzen:

$$
\begin{aligned}
E(\alpha_0) &= \frac{\hbar^2}{4m}\frac{\sqrt{2}m\omega}{\hbar}+\frac{1}{2}m\omega^2\frac{\hbar}{\sqrt{2}m\omega} \\
&= \frac{\sqrt{2}}{4}\hbar\omega+\frac{1}{2\sqrt{2}}\hbar\omega \\
&= \frac{\hbar\omega}{\sqrt{2}}
\end{aligned}
$$

Abweichung:

$$\frac{E(\alpha_0)-E_{\text{exakt}}}{E(\alpha_0)}=\frac{\sqrt{2}-1}{\sqrt{2}}=0.2929$$

Aufgabe 5

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+\frac{m\omega^2x^2}{2}+\frac{m^{3/2}\omega^{5/2}x^3}{2\sqrt{\hbar}}+\frac{m^2\omega^3x^4}{2\hbar}$$

$$\xi=x\sqrt{\frac{m\omega}{\hbar}} \quad x=\xi\sqrt{\frac{\hbar}{m\omega}} \quad \frac{\partial}{\partial x}=\sqrt{\frac{m\omega}{\hbar}}\frac{\partial}{\partial \xi}$$

$$\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}=\frac{\hbar^2}{2m}\frac{m\omega}{\hbar}\frac{\partial^2}{\partial \xi^2}=\frac{\hbar\omega}{2}\frac{\partial^2}{\partial \xi^2}$$

$$\frac{m\omega^2 x^2}{2} + \frac{m^{3/2}\omega^{5/2}x^3}{2\sqrt{\hbar}} + \frac{m^2\omega^3 x^4}{2\hbar} = \frac{\hbar\omega}{2}\left(\xi^2+\xi^3+\xi^4\right)$$

$$\hat{H} = \frac{\hbar\omega}{2}\left(-\frac{\partial^2}{\partial\xi^2}+\xi^2+\xi^3+\xi^4\right)$$

(b)

$$\hat{H} = \hat{H}_0 + \hat{H}_1$$

$$\hat{H}_0 = \frac{\hbar\omega}{2}\left(-\frac{\partial^2}{\partial\xi^2}+\xi^2\right) \qquad \text{harm. Oszillator}$$

$$\hat{H}_1 = \frac{\hbar\omega}{2}\left(\xi^3+\xi^4\right)$$

(c)

$$\left\langle \phi_m \left| \hat{H}_0 \right| \phi_n \right\rangle = \frac{\hbar\omega}{2}(2n+1)\left\langle \phi_m \mid \phi_n\right\rangle = \frac{\hbar\omega}{2}(2n+1)\,\delta_{mn}$$

$$\hat{H}_0 = \hbar\omega\begin{pmatrix} 1/2 & 0 \\ 0 & 3/2 \end{pmatrix}$$

(d)

$$\xi\phi_0 = \sqrt{1/2}\phi_1$$

$$\xi^2\phi_0 = \xi\xi\phi_0 = \sqrt{1/2}\xi\phi_1 = \sqrt{1/2}\left(\sqrt{1/2}\phi_0+\phi_2\right)$$

$$\xi^3\phi_0 = \xi\xi^2\phi_0 = 1/2\sqrt{1/2}\phi_1 + \sqrt{1/2}\phi_1 + \sqrt{3/2}\phi_3$$

$$\xi^4\phi_0 = \xi\xi^3\phi_0 = 3/4\phi_0 + 3/2\sqrt{3/2}\phi_2 + 3/2\phi_2 + \sqrt{3}\phi_4$$

$$\xi^3\phi_1 = \xi^2\left(\sqrt{1/2}\phi_0+\phi_2\right) = 2/3\sqrt{1/2}\phi_0 + 1/2\phi_2 + \phi_2 + 3/2\phi_2 + \sqrt{3}\phi_4$$

$$\xi^4\phi_1 = \xi\xi^3\phi_1 = 9/4\phi_1 + \left(3\sqrt{3}/2+\sqrt{2\cdot 3}\right)\phi_3 + \sqrt{3\cdot 5/2}\phi_5$$

$$\left\langle \phi_0 \left| \xi^3 \right| \phi_0 \right\rangle = 0$$

$$\left\langle \phi_0 \left| \xi^3 \right| \phi_1 \right\rangle = \frac{3}{2}\sqrt{\frac{1}{2}}$$

$$\left\langle \phi_1 \left| \xi^3 \right| \phi_0 \right\rangle = \frac{3}{2}\sqrt{\frac{1}{2}}$$

$$\left\langle \phi_1 \left| \xi^3 \right| \phi_1 \right\rangle = 0$$

$$\left\langle \phi_0 \left| \xi^4 \right| \phi_0 \right\rangle = \frac{3}{4}$$

$$\left\langle \phi_0 \left| \xi^4 \right| \phi_1 \right\rangle = 0$$

$$\left\langle \phi_1 \left| \xi^4 \right| \phi_0 \right\rangle = 0$$

$$\left\langle \phi_1 \left| \xi^4 \right| \phi_1 \right\rangle = \frac{9}{4}$$

(e)

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_1 = \frac{\hbar\omega}{2}\begin{pmatrix} 7/4 & 3\sqrt{2}/4 \\ 3\sqrt{2}/4 & 27/4 \end{pmatrix}$$

(f) Eigenwerte:

$$\begin{vmatrix} h_{11}-\lambda & h_{12} \\ h_{12} & h_{22}-\lambda \end{vmatrix} = 0$$

$$(h_{11}-\lambda)(h_{22}-\lambda)-h_{12}^2=0$$
$$\lambda^2-\lambda(h_{11}+h_{22})+h_{11}h_{22}-h_{12}^2=0$$

$$\begin{aligned}\lambda_{1/2} &= \frac{1}{2}\left[h_{11}+h_{22}\pm\sqrt{(h_{11}+h_{22})^2-4(h_{11}h_{22}-h_{12}^2)}\right]\\ &= \frac{1}{2}\left[h_{11}+h_{22}\pm\sqrt{(h_{11}-h_{22})^2+4h_{12}^2}\right]\\ &= \hbar\omega\left(\frac{17}{8}\pm\sqrt{\frac{59}{32}}\right)\end{aligned}$$

mit
$$h_{11}+h_{22}=17\hbar\omega/4 \quad h_{11}-h_{22}=-5\hbar\omega/2$$

Aufgabe 6

$$\left\langle\psi_{100}\middle|\hat{H}\middle|\psi_{100}\right\rangle=-\frac{e^2Z^2}{8\pi\epsilon_0\alpha_0} \quad \Rightarrow \quad \frac{\partial}{\partial Z}\left\langle\psi_{100}\middle|\hat{H}\middle|\psi_{100}\right\rangle=-\frac{e^2Z}{4\pi\epsilon_0\alpha_0}$$
$$\frac{\partial\hat{H}}{\partial Z}=\frac{\partial}{\partial Z}\left(\hat{T}-\frac{e^2Z}{4\pi\epsilon_0 r}\right)=-\frac{e^2}{4\pi\epsilon_0 r} \quad \Rightarrow$$

$$\begin{aligned}\left\langle\psi_{100}\middle|\frac{\partial\hat{H}}{\partial Z}\middle|\psi_{100}\right\rangle &= -\frac{e^2}{4\pi\epsilon_0}\left\langle\psi_{100}\middle|\frac{1}{r}\middle|\psi_{100}\right\rangle\\ &= -\frac{e^2}{4\pi\epsilon_0}\frac{1}{\pi}\left(\frac{Z}{a_0}\right)^3\int_0^{+\infty}\mathrm{d}r r^2\int_{-1}^{+1}\mathrm{d}\cos\theta\int_0^{2\pi}\mathrm{d}\phi\frac{1}{r}\mathrm{e}^{-2Zr/a_0}\\ &= -\frac{e^2}{\pi\epsilon_0}\left(\frac{Z}{a_0}\right)^3\int_0^{+\infty}\mathrm{d}r r\mathrm{e}^{-2Zr/a_0}\\ &= -\frac{e^2Z}{4\pi\epsilon_0\alpha_0}\end{aligned}$$