Lösungen des Übungsblattes 9 zur Vorlesung Theoretische Chemie I
WS 2018/19 – Übungsblatt 9

1. **Die Schrödingergleichung des Wasserstoffatoms**

$$\left(-\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x_e^2}-\frac{\hbar^2}{2m_N}\frac{\partial^2}{\partial x_N^2}-\frac{e^2}{4\pi\epsilon_0|x_e-x_N|}\right)\Psi(x_e,x_N)=E\Psi(x_e,x_N) \tag{1}$$

$$X=\frac{m_e}{M}x_e+\frac{m_N}{M}x_N \tag{2}$$

$$r=x_e-x_N \tag{3}$$

a) **(Referenz: Abschnitt 3.2 „Reduced mass“in Further Information, Kapitel 3, *Molecular Quantum Mechanics*, 5th ed., Peter Atkins und Ronald Friedman)**
Verwenden der Kettenregel

$$\begin{aligned}\frac{\partial\psi}{\partial x_e}&=\left(\frac{\partial\psi}{\partial X}\right)\left(\frac{\partial X}{\partial x_e}\right)+\left(\frac{\partial\psi}{\partial r}\right)\left(\frac{\partial r}{\partial x_e}\right)=\frac{\partial\psi}{\partial X}\cdot\frac{m_e}{M}+\frac{\partial\psi}{\partial r}\cdot 1\\&=\frac{m_e}{M}\frac{\partial\psi}{\partial X}+\frac{\partial\psi}{\partial r}\end{aligned}$$

$$\begin{aligned}\frac{\partial^2\psi}{\partial x_e^2}&=\frac{\partial}{\partial x_e}\frac{\partial\psi}{\partial x_e}=\frac{m_e}{M}\frac{\partial}{\partial X}\left(\frac{m_e}{M}\cdot\frac{\partial\psi}{\partial X}+\frac{\partial\psi}{\partial r}\right)+\frac{\partial}{\partial r}\left(\frac{m_e}{M}\cdot\frac{\partial\psi}{\partial X}+\frac{\partial\psi}{\partial r}\right)\\&=\frac{m_e^2}{M^2}\frac{\partial^2\psi}{\partial X^2}+\frac{m_e}{M}\frac{\partial^2\psi}{\partial X\partial r}+\frac{m_e}{M}\frac{\partial^2\psi}{\partial r\partial X}+\frac{\partial^2\psi}{\partial r^2}\end{aligned}$$

$$\implies\frac{\partial^2}{\partial x_e^2}=\frac{m_e^2}{M^2}\frac{\partial^2}{\partial X^2}+\frac{2m_e}{M}\frac{\partial^2}{\partial X\partial r}+\frac{\partial^2}{\partial r^2} \tag{4}$$

$$\begin{aligned}\frac{\partial\psi}{\partial x_N}&=\left(\frac{\partial\psi}{\partial X}\right)\left(\frac{\partial X}{\partial x_N}\right)+\left(\frac{\partial\psi}{\partial r}\right)\left(\frac{\partial r}{\partial x_N}\right)=\frac{\partial\psi}{\partial X}\cdot\frac{m_N}{M}+\frac{\partial\psi}{\partial r}\cdot(-1)\\&=\frac{m_N}{M}\frac{\partial\psi}{\partial X}-\frac{\partial\psi}{\partial r}\end{aligned}$$

$$\begin{aligned}\frac{\partial^2\psi}{\partial x_N^2}&=\frac{\partial}{\partial x_N}\frac{\partial\psi}{\partial x_N}=\frac{m_N}{M}\cdot\frac{\partial}{\partial X}\left(\frac{m_N}{M}\frac{\partial\psi}{\partial X}-\frac{\partial\psi}{\partial r}\right)-\frac{\partial}{\partial r}\left(\frac{m_N}{M}\frac{\partial\psi}{\partial X}-\frac{\partial\psi}{\partial r}\right)\\&=\frac{m_N^2}{M^2}\frac{\partial^2\psi}{\partial X^2}-\frac{m_N}{M}\frac{\partial^2\psi}{\partial X\partial r}-\frac{m_N}{M}\frac{\partial^2\psi}{\partial r\partial X}+\frac{\partial^2\psi}{\partial r^2}\end{aligned}$$

$$\implies\frac{\partial^2}{\partial x_N^2}=\frac{m_N^2}{M^2}\frac{\partial^2}{\partial X^2}-\frac{2m_N}{M}\frac{\partial^2}{\partial X\partial r}+\frac{\partial^2}{\partial r^2} \tag{5}$$

b)

$$\hat{H} = -\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial x_e^2} - \frac{\hbar^2}{2m_N}\frac{\partial^2}{\partial x_N^2} - \frac{e^2}{4\pi\epsilon_0 \underbrace{|x_e - x_N|}_{=|r|}}$$

$$= -\frac{\hbar^2}{2m_e}\left(\frac{m_e^2}{M^2}\frac{\partial^2}{\partial X^2} + \frac{2m_e}{M}\frac{\partial^2}{\partial X \partial r} + \frac{\partial^2}{\partial r^2}\right) - \frac{\hbar^2}{2m_N}\left(\frac{m_N^2}{M^2}\frac{\partial^2}{\partial X^2} - \frac{2m_N}{M}\frac{\partial^2}{\partial X \partial r} + \frac{\partial^2}{\partial r^2}\right)$$

$$- \frac{e^2}{4\pi\epsilon_0 |r|}$$

$$= -\frac{\hbar^2 m_e}{2M^2}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{M}\frac{\partial^2}{\partial X \partial r} - \frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2 m_N}{2M^2}\frac{\partial^2}{\partial X^2} + \frac{\hbar^2}{M}\frac{\partial^2}{\partial X \partial r} - \frac{\hbar^2}{2m_N}\frac{\partial^2}{\partial r^2}$$

$$- \frac{e^2}{4\pi\epsilon_0 |r|}$$

$$= -\frac{\hbar^2}{2M^2}\underbrace{(m_e + m_N)}_{=M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2}\underbrace{\left(\frac{1}{m_e} + \frac{1}{m_n}\right)}_{=\frac{1}{\mu}}\frac{\partial^2}{\partial r^2} - \frac{e^2}{4\pi\epsilon_0 |r|}$$

$$= -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} - \frac{e^2}{4\pi\epsilon_0 |r|} \tag{6}$$

c) Setzen den Produktansatz $\Psi(X, r) = \xi(X)\psi(r)$ in die Schrödingergleichung(6)

$$\hat{H}\xi(X)\psi(r) = E\xi(X)\psi(r)$$

$$-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X^2}\xi(X)\psi(r) - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}\xi(X)\psi(r) - \frac{e^2}{4\pi\epsilon_0 |r|}\xi(X)\psi(r) = E\xi(X)\psi(r) \tag{7}$$

$$-\frac{\hbar^2}{2M}\psi(r)\frac{\mathrm{d}^2}{\mathrm{d}X^2}\xi(X) - \frac{\hbar^2}{2\mu}\xi(X)\frac{\mathrm{d}^2}{\mathrm{d}r^2}\psi(r) - \xi(X)\frac{e^2}{4\pi\epsilon_0 |r|}\psi(r) = E\xi(X)\psi(r) \tag{8}$$

Beide Seiten durch $\xi(X)\psi(r)$ teilen

$$\frac{1}{\xi(X)} \cdot \left(-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}X^2}\xi(X)\right) + \frac{1}{\psi(r)} \cdot \left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2}\psi(r)\right) + \frac{1}{\psi(r)}\left(-\frac{e^2}{4\pi\epsilon_0 |r|}\psi(r)\right) = E$$

$$\underbrace{\frac{1}{\xi(X)}\left(-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}X^2}\xi(X)\right)}_{=E_X} + \underbrace{\frac{1}{\psi(r)}\left[\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{e^2}{4\pi\epsilon_0 |r|}\right)\psi(r)\right]}_{=E_r} = E$$

$$\implies -\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}X^2}\xi(X) = E_X\xi(X) \tag{9}$$

und

$$\left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{e^2}{4\pi\epsilon_0 |r|}\right)\psi(r) = E_r\psi(r) \tag{10}$$

d) $M \approx m_N$ und $\mu \approx m_e$ weil $m_N \gg m_e$.

2. **Das Teilchen im Zentralpotential**

$$\left(\left(\frac{\hat{p}_r^2}{2\mu} + \frac{\hat{l}^2}{2\mu r^2}\right) + V(r)\right)\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi) \tag{11}$$

$$\hat{p}_r = -\mathrm{i}\hbar\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)$$

a) Einsetzen den Separationsansatz $\Psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m_l}(\theta,\phi)$ in die Schrödingergleichung (11)

$$\left[\frac{\hat{p}_r^2}{2\mu} + \frac{\hat{l}^2}{2\mu r^2} + V(r)\right] R_{n,l}(r)Y_{l,m_l}(\theta,\phi) = ER_{n,l}(r)Y_{l,m_l}(\theta,\phi) \tag{12}$$

$$Y_{l,m_l}(\theta,\phi)\frac{\hat{p}_r^2}{2\mu}R_{n,l}(r)+R_{n,l}(r)\frac{\hat{l}^2}{2\mu r^2}Y_{l,m_l}(\theta,\phi)+Y_{l,m_l}(\theta,\phi)V(r)R_{n,l}(r) = ER_{n,l}(r)Y_{l,m_l}(\theta,\phi) \tag{13}$$

Lösung des Winkelanteils bekannt: $\hat{l}^2 Y_{l,m_l}(\theta,\phi) = \hbar^2 l(l+1)Y_{l,m_l}(\theta,\phi)$

$$Y_{l,m_l}(\theta,\phi)\frac{\hat{p}_r^2}{2\mu}R_{n,l}(r)+R_{n,l}(r)\frac{\hbar^2 l(l+1)}{2\mu r^2}Y_{l,m_l}(\theta,\phi)+Y_{l,m_l}(\theta,\phi)V(r)R_{n,l}(r) = ER_{n,l}(r)Y_{l,m_l}(\theta,\phi) \tag{14}$$

Multiplizieren beide Seiten der Gleichung mit $Y^*_{l,m_l}(\theta,\phi)$ und integrieren zwischen den Grenzen

$$\because \int_0^\pi \int_0^{2\pi} Y^*_{l,m_l}(\theta,\phi)Y_{l,m_l}(\theta,\phi)\,\mathrm{d}\theta\,\mathrm{d}\phi = 1$$

Die Gleichung für den Radianteil $R_{n,l}(r)$ ergibt

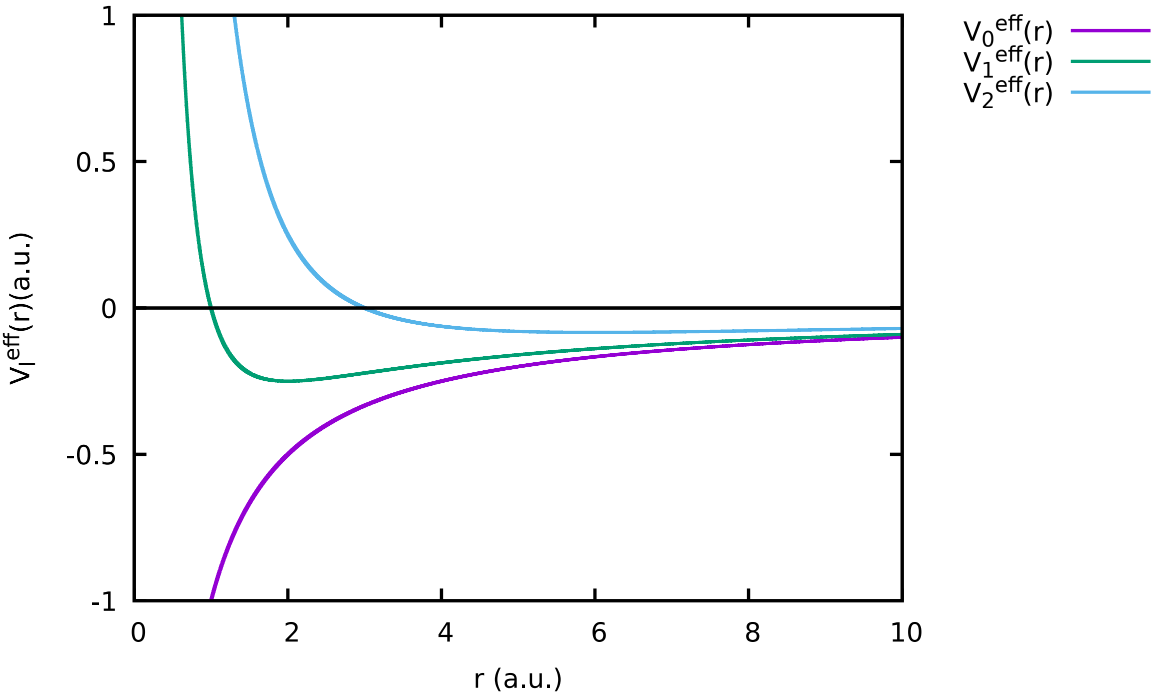
$$\frac{\hat{p}_r^2}{2\mu}R_{n,l}(r) + \frac{\hbar^2}{2\mu r^2}l(l+1)R_{n,l}(r) + V(r)R_{n,l}(r) = ER_{n,l}(r) \tag{15}$$

$$\therefore \left(\frac{\hat{p}_r^2}{2\mu} + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)\right)R_{n,l}(r) = ER_{n,l}(r) \tag{16}$$

b)

$$V_l^{eff}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}$$

In atomaren Einheiten, $e = 1, \frac{1}{4\pi\epsilon_0} = 1, \hbar = 1, \mu \approx 1$



c)

$$\Psi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)Y_{l,m_l}(\theta,\phi) \implies |\Psi_{n,l,m_l}(r,\theta,\phi)|^2 = |R_{n,l}(r)|^2|Y_{l,m_l}(\theta,\phi)|^2$$

$$R_{n=1,l=0}(r) = \frac{2}{a_0^{\frac{3}{2}}}e^{-\frac{r}{a_0}} \implies |R_{n=1,l=0}(r)|^2 = \frac{4}{a_0^3}e^{-\frac{2r}{a_0}} \tag{17}$$

$$Y_{l=0,m_l=0}(\theta,\phi) = \frac{1}{2\sqrt{\pi}} \implies |Y_{l=0,m_l=0}(\theta,\phi)|^2 = \frac{1}{4\pi} \tag{18}$$

(**Referenz**: Tabelle 3.2, Kapitel 3, *Molecular Quantum Mechanics*, 5th ed., Peter

Atkins und Ronald Friedman)

$$
\begin{aligned}
P &= \int_0^{r'}\int_0^{\pi}\int_0^{2\pi} r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi |\Psi_{n,l,m_l}(r,\theta,\phi)|^2 \\
&= \int_0^{r'}\int_0^{\pi}\int_0^{2\pi} r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi |R_{n=1,l=0}(r)|^2 |Y_{l=0,m_l=0}(\theta,\phi)|^2 \\
&= \frac{1}{4\pi}\int_0^{r'} \frac{4}{a_0^3} e^{-\frac{2r}{a_0}} r^2 \,\mathrm{d}r \int_0^{\pi} \sin\theta \,\mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \\
&= \frac{1}{\pi a_0^3}\int_0^{r'} r^2 e^{-\frac{2r}{a_0}} \,\mathrm{d}r \cdot [-\cos\theta]_0^{\pi} \cdot [\phi]_0^{2\pi} \\
&= \frac{1}{\pi a_0^3} \cdot 2 \cdot 2\pi \int_0^{r'} r^2 e^{-\frac{2r}{a_0}} \,\mathrm{d}r = \frac{4}{a_0^3}\int_0^{r'} r^2 e^{-\frac{2r}{a_0}} \,\mathrm{d}r \\
&= \frac{4}{a_0^3}\left[\frac{r^2 e^{-\frac{2r}{a_0}}}{-\frac{2}{a_0}}\right]_0^{r'} - \frac{4}{a_0^3}\int_0^{r'} \frac{2re^{-\frac{2r}{a_0}}}{-\frac{2}{a_0}} \,\mathrm{d}r \\
&= -\frac{a_0}{2}\cdot\frac{4}{a_0^3}\left(r'^2 e^{-\frac{2r'}{a_0}} - 0\right) + \frac{4}{a_0^2}\int_0^{r'} re^{-\frac{2r}{a_0}} \,\mathrm{d}r \\
&= -\frac{2}{a_0^2} r'^2 e^{-\frac{2r'}{a_0}} + \frac{4}{a_0^2}\left[\frac{re^{-\frac{2r}{a_0}}}{-\frac{2}{a_0}} - \frac{e^{-\frac{2r}{a_0}}}{\frac{4}{a_0^2}}\right]_0^{r'} \\
&= -\frac{2}{a_0^2} r'^2 e^{-\frac{2r'}{a_0}} + \frac{4}{a_0^2}\left[\frac{r'e^{-\frac{2r'}{a_0}}}{-\frac{2}{a_0}} - \frac{e^{-\frac{2r'}{a_0}}}{\frac{4}{a_0^2}} - 0 + \frac{e^0}{\frac{4}{a_0^2}}\right] \\
&= -\frac{2}{a_0^2} r'^2 e^{-\frac{2r'}{a_0}} + \frac{4}{a_0^2}\left[-\frac{a_0 r' e^{-\frac{2r'}{a_0}}}{2} - \frac{a_0^2 e^{-\frac{2r'}{a_0}}}{4} + \frac{a_0^2}{4}\right]
\end{aligned}
\tag{19}
$$

Für den Fall $r' = 2a_0$

$$
\begin{aligned}
P &= -\frac{2}{a_0^2}\cdot 4a_0^2 e^{-4} + \frac{4}{a_0^2}\left[\frac{2a_0^2 e^{-4}}{2} - \frac{a_0^2 e^{-4}}{4} + \frac{a_0^2}{4}\right] \\
&= 1 - 13e^{-4} = 0.76
\end{aligned}
$$

Dies ist das 1s-Orbital des Wasserstoffatoms. Die Aufenthaltswahrscheinlichkeit P ist unabhängig von den Winkelvariabeln (θ, ϕ), da die sphärischen Harmonischen für das 1s-Orbital konstant sind.