Prof. D. Egorova

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

Aufgabe 1

$$\hat{A}\,|\phi_n\rangle = a_n\,|\phi_n\rangle$$

$$\mathrm{e}^{\hat{A}}\,|\phi_n\rangle = \sum_{k=0}^{+\infty}\frac{1}{k!}\hat{A}^k\,|\phi_n\rangle = \sum_{k=0}^{+\infty}\frac{1}{k!}a_n^k\,|\phi_n\rangle = \mathrm{e}^{a_n}\,|\phi_n\rangle$$

Aufgabe 2

$$\begin{aligned}\left[\mathrm{e}^{\mathrm{i}x}, p_x\right]\psi &= \mathrm{e}^{\mathrm{i}x}p_x\psi - p_x\mathrm{e}^{\mathrm{i}x}\psi \\ &= \mathrm{e}^{\mathrm{i}x}\frac{\hbar}{\mathrm{i}}\frac{\partial\psi}{\partial x} - \frac{\hbar}{\mathrm{i}}\frac{\partial}{\partial x}\left(\mathrm{e}^{\mathrm{i}x}\psi\right) \\ &= \mathrm{e}^{\mathrm{i}x}\frac{\hbar}{\mathrm{i}}\frac{\partial\psi}{\partial x} - \hbar\mathrm{e}^{\mathrm{i}x}\psi - \frac{\hbar}{\mathrm{i}}\mathrm{e}^{\mathrm{i}x}\frac{\partial\psi}{\partial x} \\ &= \hbar\mathrm{e}^{\mathrm{i}x}\psi\end{aligned}$$

d.h. $\left[\mathrm{e}^{\mathrm{i}x}, p_x\right] = -\hbar\mathrm{e}^{\mathrm{i}x}$

Aufgabe 3

(a)

$$\hat{L}_x = y\hat{p}_z - z\hat{p}_y \quad \hat{p}_x = -\mathrm{i}\hbar\partial/\partial x$$

$$\hat{L}_y = z\hat{p}_x - x\hat{p}_z \quad \hat{p}_y = -\mathrm{i}\hbar\partial/\partial y$$

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x \quad \hat{p}_z = -\mathrm{i}\hbar\partial/\partial z$$

$$\begin{aligned}\left[\hat{L}_x, \hat{L}_y\right] &= \left(y\hat{p}_z - z\hat{p}_y\right)\left(z\hat{p}_x - x\hat{p}_z\right) - \left(z\hat{p}_x - x\hat{p}_z\right)\left(y\hat{p}_z - z\hat{p}_y\right) \\ &= y\hat{p}_z z\hat{p}_x - yx\hat{p}_z^2 - z^2\hat{p}_y\hat{p}_x + z\hat{p}_y x\hat{p}_z \\ &\quad - z\hat{p}_x y\hat{p}_z + z^2\hat{p}_x\hat{p}_y - x\hat{p}_z z\hat{p}_y + xy\hat{p}_z^2 \\ &= y\hat{p}_x\hat{p}_z z - xy\hat{p}_z^2 - z^2\hat{p}_x\hat{p}_y + x\hat{p}_y z\hat{p}_z \\ &\quad - y\hat{p}_x z\hat{p}_z + z^2\hat{p}_x\hat{p}_y - x\hat{p}_y\hat{p}_z z + xy\hat{p}_z^2 \\ &= y\hat{p}_x\hat{p}_z z - x\hat{p}_y\hat{p}_z z - y\hat{p}_x z\hat{p}_z + x\hat{p}_y z\hat{p}_z \\ &= \left(x\hat{p}_y - y\hat{p}_x\right)\left(z\hat{p}_z - \hat{p}_z z\right) \\ &= \hat{L}_z\left[z, \hat{p}_z\right] = i\hbar\hat{L}_z\end{aligned}$$

analog:

$$\left[\hat{L}_y, \hat{L}_z\right] = \mathrm{i}\hbar\hat{L}_x$$

$$\left[\hat{L}_z, \hat{L}_x\right] = \mathrm{i}\hbar \hat{L}_y$$

(b)

$$\begin{aligned}
\left[L^2, L_x\right] &= \left[L_x^2, L_x\right] + \left[L_y^2, L_x\right] + \left[L_z^2, L_x\right] \\
&= L_y\left[L_y, L_x\right] + \left[L_y, L_x\right] L_y + L_z\left[L_z, L_x\right] + \left[L_z, L_x\right] L_z \\
&= -L_y\left[L_x, L_y\right] - \left[L_x, L_y\right] L_y + L_z\left[L_z, L_x\right] + \left[L_z, L_x\right] L_z \\
&= \mathrm{i}\hbar\left(-L_y L_z - L_z L_y + L_z L_y + L_y L_z\right) \\
&= 0
\end{aligned}$$

analog:

$$\left[L^2, L_y\right] = \left[L^2, L_z\right] = 0$$

Aufgabe 4

(a)

$$\begin{aligned}
\left[L_z, L_+\right] &= \left[L_z, L_x\right] + \mathrm{i}\left[L_z, L_y\right] \\
&= \mathrm{i}\hbar L_y + \mathrm{i}\left(-\mathrm{i}\hbar L_x\right) \\
&= \hbar\left(\mathrm{i}L_y + L_x\right) \\
&= \hbar L_+
\end{aligned}$$

$$\begin{aligned}
\left[L_z, L_-\right] &= \left[L_z, L_x\right] - \mathrm{i}\left[L_z, L_y\right] \\
&= \mathrm{i}\hbar L_y - \mathrm{i}\left(-\mathrm{i}\hbar L_x\right) \\
&= \hbar\left(\mathrm{i}L_y - L_x\right) \\
&= -\hbar L_-
\end{aligned}$$

$$\begin{aligned}
\left[L_+, L_-\right] &= \left[L_x, L_x\right] + \mathrm{i}\left[L_y, L_x\right] - \mathrm{i}\left[L_x, L_y\right] + \left[L_y, L_y\right] \\
&= \mathrm{i}\left(-\mathrm{i}\hbar L_z\right) - \mathrm{i}\mathrm{i}\hbar L_z \\
&= 2\hbar L_z
\end{aligned}$$

(b)

$$L_z \Psi = \hbar m \Psi$$

$$L_z L_+ - L_+ L_z = \hbar L_+ \quad \Rightarrow \quad L_z L_+ = \hbar L_+ + L_+ L_z$$

$$\begin{aligned}
L_z\left(L_+\Psi\right) &= \hbar\left(L_+\Psi\right) + L_+ L_z \Psi \\
&= \hbar\left(L_+\Psi\right) + \hbar m L_+ \Psi \\
&= \hbar\left(m+1\right)\left(L_+\Psi\right)
\end{aligned}$$

$$L_z L_- - L_- L_z = -\hbar L_- \quad \Rightarrow \quad L_z L_- = -\hbar L_- + L_- L_z$$

$$\begin{aligned}
L_z\left(L_-\Psi\right) &= -\hbar\left(L_-\Psi\right) + L_- L_z \Psi \\
&= -\hbar\left(L_-\Psi\right) + \hbar m L_- \Psi \\
&= \hbar\left(m-1\right)\left(L_-\Psi\right)
\end{aligned}$$

Aufgabe 5

(a) $\left[L_x, L_z\right] \neq 0$ und $\left[L_y, L_z\right] \neq 0$: keine Information über L_x, L_y

(b)

$$L^2 \left|lm\right\rangle = l\left(l+1\right)\left|lm\right\rangle = 12\hbar^2 \left|lm\right\rangle$$

$$l\left(l+1\right) = 12 \quad \Rightarrow \quad l = 3, m = 0, \pm 1, \pm 2, \pm 3$$

L_z-Eigenwerte: $0, \pm\hbar, \pm 2\hbar, \pm 3\hbar$

(c) $L_+\psi_m$ ($L_-\psi_m$) ergibt einen Zustand indem L_z den Wert $\hbar(m+1)$ ($\hbar(m-1)$) hat (siehe auch Aufgabe 4b)

Aufgabe 6

(a)

$$E_n = -\frac{Z^2 E_\mathrm{R}}{n^2}$$

mit $Z = 1$ für das H-atom

$$h\nu_{nm} = E_n - E_m = -E_\mathrm{R}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \quad \Rightarrow \quad \nu_{nm} = \frac{E_\mathrm{R}}{h}\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

(b)
$2s$, $2p$: $n = 2$, $\Delta E = 0$ (entartet)
$1s$, $4d$: $E_n = \frac{Z^2 E_\mathrm{R}}{n^2}$ hier mit $Z = 1$

$$\Rightarrow \quad \Delta E_{1s,4d} = -\frac{E_\mathrm{R}}{4^2} - \left(-\frac{E_\mathrm{R}}{1^2}\right) = \frac{15}{16}E_\mathrm{R}$$

(c)

n	l	m_l	Orbital
3	0	0	$3s$
3	1	$-1, 0, +1$	$3p$
3	2	$-2, -1, 0, +1, +2$	$3d$

Aufgabe 7

(a)

$$1 = \langle \Psi_{nlm} | \Psi_{nlm} \rangle = \int_0^\infty r^2 \mathrm{d}r \int_0^\pi \sin\theta \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \left|\Psi_{nlm}(r,\theta,\phi)\right|^2$$

$$\Psi_{nlm}(r,\theta,\phi) = N_{nl}R_{nl}(r)Y_{lm}(\theta,\phi); \quad \int_0^\pi \sin\theta \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \left|Y_{lm}(\theta,\phi)\right|^2 = \langle Y_{lm}|Y_{lm}\rangle = 1;$$

$$\langle \Psi_{nlm}|\Psi_{nlm}\rangle = N_{nl}^2 \langle R_{nl}|R_{nl}\rangle\langle Y_{lm}|Y_{lm}\rangle; \quad N_{nl}^2 = 1/\langle R_{nl}|R_{nl}\rangle$$

$1s$:

$$\Psi_{100}(r,\theta,\phi) = N_{10}R_{10}(r)Y_{00}(\theta,\phi) = N_{10}\mathrm{e}^{-r/a_0}Y_{00}(\theta,\phi), \quad Y_{00}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$$

$$\begin{aligned} 1 &= N_{10}^2\langle R_{10}|R_{10}\rangle = N_{10}^2 \int r^2 \mathrm{d}r \mathrm{e}^{-2r/a_0} \\ &= N_{10}^2 \left(a_0/2\right)^3 \int (2r/a_0)^2 \mathrm{d}(2r/a_0)\mathrm{e}^{-2r/a_0} \\ &= N_{10}^2 \left(a_0/2\right)^3 2! \\ &= N_{10}^2 \frac{a_0^3}{4} \end{aligned}$$

$$N_{10} = 2a_0^{-3/2}$$

$$\Psi_{100} = \frac{1}{\sqrt{\pi}} a_0^{-3/2} \mathrm{e}^{-r/a_0}$$

$2s$:

$$\Psi_{200} = N_{20}R_{20}(r)Y_{00}(\theta,\phi) = N_{20} 2\left(r/a_0 - 2\right)\mathrm{e}^{-r/2a_0} 1/\sqrt{4\pi}$$

$$\begin{aligned}
1 &= 4N_{20}^2\langle R_{20}|R_{20}\rangle = N_{20}^2\int r^2\mathrm{d}r\,(r/a_0-2)^2\,\mathrm{e}^{-r/a_0} \\
&= 4N_{20}^2\int \mathrm{d}r\left(\frac{r^4}{a_0^2}-4\frac{r^3}{a_0}+4r^2\right)\mathrm{e}^{-r/a_0} \\
&= 4N_{20}^2a_0^3\int \mathrm{d}\left(\frac{r}{a_0}\right)\left(\left(\frac{r}{a_0}\right)^4-4\left(\frac{r}{a_0}\right)^3+4\left(\frac{r}{a_0}\right)^2\right)\mathrm{e}^{-r/a_0} \\
&= 4N_{20}^2a_0^3\left(\int \mathrm{d}x x^4\mathrm{e}^{-x}-4\int \mathrm{d}x x^3\mathrm{e}^{-x}+4\int \mathrm{d}x^2\mathrm{e}^{-x}\right) \\
&= 4N_{20}^2a_0^3\,(24-24+8) = 32N_{20}^2a_0^3
\end{aligned}$$

$$N_{20} = \frac{a_0^{-3/2}}{\sqrt{32}} = \frac{a_0^{-3/2}}{4\sqrt{2}}$$

$$\Psi_{200} = \frac{a_0^{-3/2}}{4\sqrt{2}}2\,(r/a_0-2)\,\mathrm{e}^{-r/2a_0}\frac{1}{\sqrt{4\pi}} = \frac{a_0^{-3/2}}{\sqrt{8\pi}}\,(r/2a_0-1)\,\mathrm{e}^{-r/2a_0}$$

$2p_z$:

$$\Psi_{210} = N_{21}R_{21}(r)Y_{10}(\theta,\phi) = N_{21}6\frac{r}{a_0}\mathrm{e}^{-r/2a_0}\sqrt{3/4\pi}\cos\theta$$

$$\begin{aligned}
1 &= N_{21}^2\langle R_{21}|R_{21}\rangle = 36N_{21}^2\int r^2\mathrm{d}r\left(\frac{r}{a_0}\right)^2\mathrm{e}^{-r/a_0} \\
&= 36N_{21}^2a_0^3\int \mathrm{d}\left(\frac{r}{a_0}\right)\left(\frac{r}{a_0}\right)^4\mathrm{e}^{-r/a_0} = 36N_{21}^2a_0^3\int x^4\mathrm{e}^{-x}\mathrm{d}x \\
&= 36N_{21}^2a_0^3\cdot 24
\end{aligned}$$

$$N_{21} = a_0^{-3/2}/12\sqrt{6}$$

$$\Psi_{210} = \frac{a_0^{-3/2}}{12\sqrt{6}}6\frac{r}{a_0}\mathrm{e}^{-r/2a_0}\sqrt{3/4\pi}\cos\theta = \frac{a_0^{-3/2}}{4\sqrt{2\pi}}\frac{r}{a_0}\mathrm{e}^{-r/2a_0}\cos\theta$$

(b)

$$\rho_{nl}(r) = N_{nl}^2r^2\left|R_{nl}(r)\right|^2$$

$1s$:

$$\rho_{10}\left(r\right) = 4a_0^{-3}r^2\mathrm{e}^{-2r/a_0}$$

$$0 = \rho'\left(r\right) = 4a_0^{-3}\mathrm{e}^{-2r/a_0}\left(2r-2r^2/a_0\right),\quad \text{Maximum bei } r=a_0$$

$2s$:

$$\rho_{20}\left(r\right) = \frac{a_0^{-3}}{32}r^2(r/a_0-2)^2\mathrm{e}^{-r/a_0} = \left(\frac{a_0^{-5}}{32}r^4-\frac{a_0^{-4}}{8}r^3+\frac{a_0^{-3}}{8}r^2\right)\mathrm{e}^{-r/a_0}$$

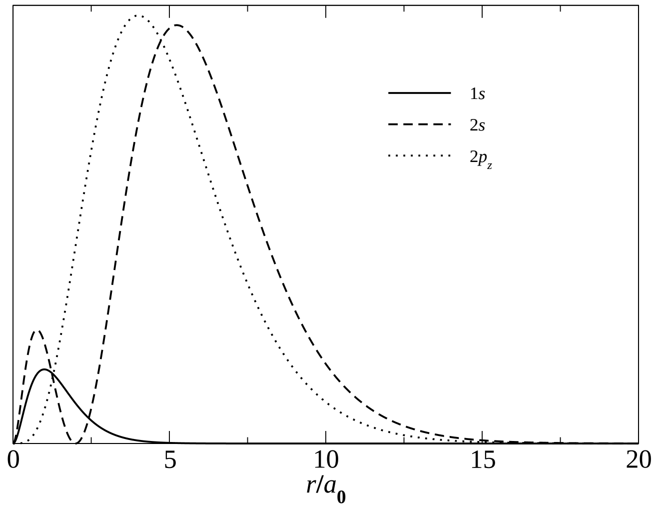
$$\begin{aligned}
0 &= \rho'\left(r\right) \\
&= \mathrm{e}^{-r/a_0}\frac{a_0^{-3}}{8}\left(\frac{a_0^{-2}}{4}(4r^3-r^4/a_0)-a_0^{-1}(3r^2-r^3/a_0)+(2r-r^2/a_0)\right)
\end{aligned}$$

$$\begin{aligned}
0 &= r\left(\left(2-\frac{r}{a_0}\right)\left(\frac{r^2}{4a_0^2}-\frac{r}{a_0}+1\right)-\frac{r}{2a_0}\left(2-\frac{r}{a_0}\right)\right);\quad r_1=0;\quad r_2=2a_0 \\
0 &= \frac{r^2}{4a_0^2}-\frac{3r}{2a_0}+1;\qquad r_{3/4}=3a_0\left(1\pm\sqrt{1-4/9}\right)=5.23606a_0, 0.7639a_0
\end{aligned}$$

$2p_z$:

$$\rho_{21}\left(r\right) = \frac{a_0^{-3}}{6\cdot 12^2}r^2 36\left(\frac{r}{a_0}\right)^2\mathrm{e}^{-r/a_0} = \frac{a_0^{-5}}{24}r^4\mathrm{e}^{-r/a_0}$$

$$0 = \rho'\left(r\right) = a_0^{-5}/24\left(4r^3-r^4/a_0\right),\quad \text{Maximum bei } r=4a_0$$



(c)

$$\langle r \rangle = \langle \Psi_{nlm} | r | \Psi_{nlm} \rangle = N_{nl}^2 \langle R_{nl} | r | R_{nl} \rangle$$

1s:

$$\langle r \rangle = N_{10}^2 \int r^2 \mathrm{d}r \mathrm{e}^{-2r/a_0} r = 4a_0^{-3}(a_0/2)^4 \int (2r/a_0)^3 \mathrm{d}(2r/a_0) \mathrm{e}^{-2r/a_0} = a_0/4 \cdot 3! = 3a_0/2$$

2s:

$$\begin{aligned} \langle r \rangle &= N_{20}^2 \int r^2 \mathrm{d}r 4(r/a_0 - 2)^2 \mathrm{e}^{-r/a_0} r = a_0^{-3}/8a_0^4 \int (r/a_0)^3 \mathrm{d}(r/a_0)(r/a_0 - 2)^2 \mathrm{e}^{-r/a_0} \\ &= a_0/8\,(5! - 4 \cdot 4! + 4 \cdot 3!) = 6a_0 \end{aligned}$$

2p_z:

$$\langle r \rangle = N_{21}^2 \int r^2 \mathrm{d}r 36(r/a_0)^2 \mathrm{e}^{-r/a_0} r = a_0^{-3}/24a_0^4 \int (r/a_0)^5 \mathrm{e}^{-r/a_0} \mathrm{d}(r/a_0) = a_0/24 \cdot 5! = 5a_0$$

(d)

$$\left\langle -\frac{\mathrm{e}^2}{4\pi\epsilon_0 r} \right\rangle = -\frac{\mathrm{e}^2}{4\pi\epsilon_0} \left\langle \frac{1}{r} \right\rangle$$

1s:

$$\langle 1/r \rangle = \left\langle R_{10} \left| \frac{1}{r} \right| R_{10} \right\rangle = N_{10}^2 \int \mathrm{d}r r^2 \frac{1}{r} \mathrm{e}^{-2r/a_0} = 4a_0^{-3}(a_0/2)^2 \int \mathrm{d}(2r/a_0) \mathrm{e}^{-2r/a_0}(2r/a_0) = 1/a_0 \cdot 1! = 1/a$$

$$\langle r \rangle = -\frac{\mathrm{e}^2}{4\pi\epsilon_0 a_0}$$

(e)

$$T = H - V$$

$$\langle T \rangle = \langle H \rangle - \langle V \rangle = E_1 + \frac{\mathrm{e}^2}{4\pi\epsilon_0 a_0} = \frac{\mathrm{e}^2}{8\pi\epsilon_0 a_0} = 13.67\mathrm{eV}$$

Aufgabe 8

$$\psi_{211} = f(r,\theta)\,\mathrm{e}^{\mathrm{i}\phi} = f(r,\theta)(\cos\phi + \mathrm{i}\sin\phi)$$
$$\psi_{21-1} = f(r,\theta)\,\mathrm{e}^{-\mathrm{i}\phi} = f(r,\theta)(\cos\phi - \mathrm{i}\sin\phi)$$

mit $f(r,\theta) = \frac{a_0^{-5/2}}{8\sqrt{\pi}} r\mathrm{e}^{-r/2a_0}\sin\theta$

$$\begin{aligned}\psi_{2p_y} &= -\frac{\mathrm{i}}{\sqrt{2}}(\psi_{211} - \psi_{21-1}) \\ &= \frac{1}{\sqrt{2}} f(r,\theta)(-\mathrm{i}\cos\phi + \sin\phi + \mathrm{i}\cos\phi + \sin\phi) \\ &= \frac{a_0^{-5/2}}{4\sqrt{2\pi}} r\mathrm{e}^{-r/2a_0}\sin\theta\sin\phi\end{aligned}$$

$\hat{H}\psi_{2lm} = -\frac{E_\mathrm{R}}{4}\psi_{2lm}$ ist unhabhängig von l, m.

ψ_{2p_y} ist normierte Linearkombination von Eigenfunktionen zum selben Eigenwert: ψ_{2p_y} ist ebenfalls Eigenfunktion zum selben Eigenwert, d.h.

$$\hat{H}\psi_{2p_y} = -\frac{E_\mathrm{R}}{4}\psi_{2p_y}$$

Dieselbe Argumentation gilt für $\hat{L}^2$:

$$\hat{L}^2\psi_{21m} = \hbar^2(1+1)\psi_{21m} = 2\hbar^2\psi_{21m}$$

$$\hat{L}^2\psi_{2p_y} = 2\hbar^2\psi_{2p_y}$$

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

Definition der Kugelkoordinaten:

$$\begin{aligned}x &= r\cos\phi\sin\theta \\ y &= r\sin\phi\sin\theta \\ z &= r\cos\theta\end{aligned}$$

$$\psi_{2p_y} = Ny\mathrm{e}^{-r/2a_0} = Ny\mathrm{e}^{-\sqrt{x^2+y^2+z^2}/2a_0}$$

$$\begin{aligned}\hat{L}_y\psi_{2p_y} &= -\mathrm{i}\hbar Ny\left(z\frac{\partial}{\partial x}\mathrm{e}^{-\sqrt{x^2+y^2+z^2}/2a_0} - x\frac{\partial}{\partial z}\mathrm{e}^{-\sqrt{x^2+y^2+z^2}/2a_0}\right) \\ &= -\mathrm{i}\hbar N\left(yz2x\frac{r^{-1}}{2a_0}\mathrm{e}^{-r/2a_0} - xy2z\frac{r^{-1}}{2a_0}\mathrm{e}^{-r/2a_0}\right) = 0\end{aligned}$$

(b)

Mögliche Messwerte: $\hbar m, m = -1, 0, +1$ wegen $l = 1$

Wahrscheinlichkeiten:

$$w_m = \left|\langle\psi_{21m} \mid \psi_{2p_y}\rangle\right|^2 = \left|-\frac{\mathrm{i}}{\sqrt{2}}\left(\langle\psi_{21m} \mid \psi_{211}\rangle - \langle\psi_{21m} \mid \psi_{21-1}\rangle\right)\right|^2$$

für $m = -1, +1$: $w_m = 1/2$; für $m = 0$: $w_m = 0$

Aufgabe 9

(a)

$$\hat{L}^2 Y_{l,m}(\theta,\phi) = \hbar^2 l(l+1) Y_{l,m}(\theta,\phi)$$

$$\Rightarrow \quad \left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) - E\right]\psi(r) Y_{l,m}(\theta,\phi) = 0$$

Da der Operator nicht mehr explizit von θ, ϕ abhängig ist und nur multiplikativ auf $Y_{l,m}$ wirkt, kann man durch $Y_{l,m}(\theta,\phi)$ teilen und erhält die "Radialgleichung":

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) - E\right]\psi(r) = 0$$

(b)

$$\left[\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right), \hat{L}^2\right] = 0$$

weil

$$\hat{L}^2 = -\frac{\hbar^2}{\sin^2\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2}\right]$$

nicht von r abhängt.