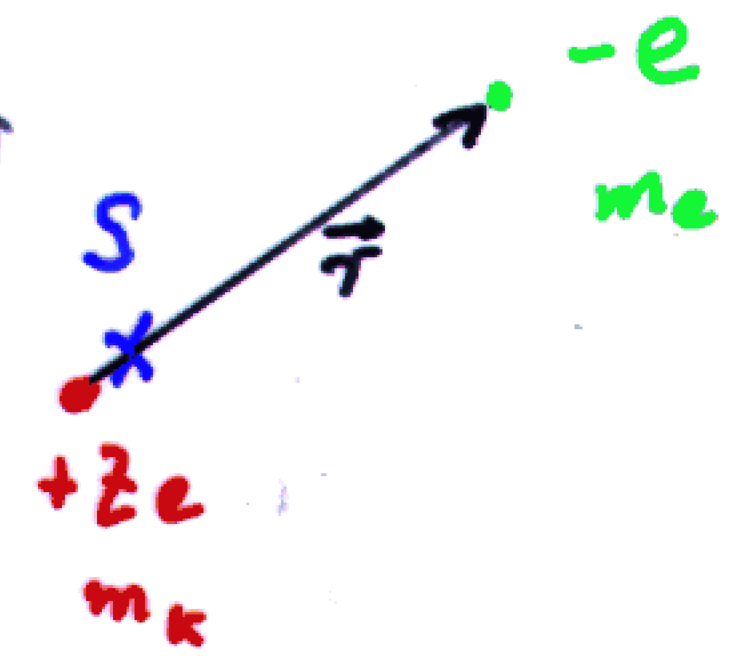
II.B Zeitfreie Schrödingergleichung des Einelektronenatoms

Schwerpunktbewegung + Relativbewegung



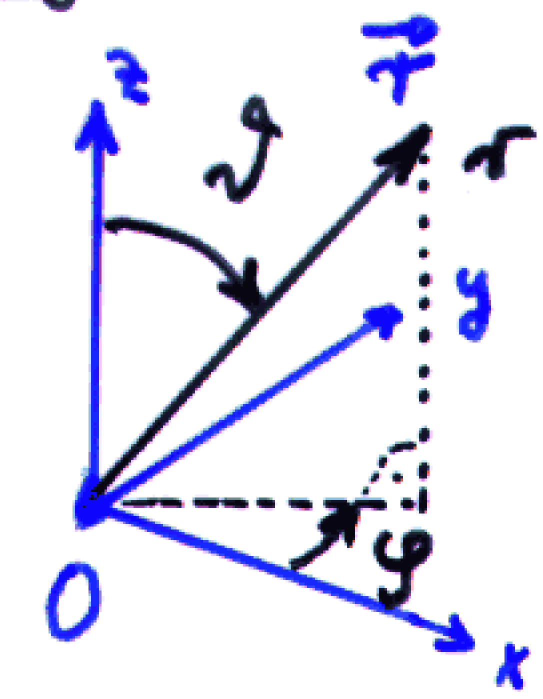
Schwerpunktsystem

$$m_e \rightarrow \frac{m_e}{1+\frac{m_e}{m_K}} = \mu$$

$$V(\vec{r}) = V(|\vec{r}|) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

Kugel-Symmetrie

$\rightarrow$ Polarkoordinaten r, ϑ, φ



$$-\frac{\hbar^2}{2\mu}\Delta\psi + (V(r) - E)\psi = 0$$

$$\boxed{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\left\{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial\psi}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2\psi}{\partial\varphi^2}\right\} + \frac{2\mu}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0 r} + E\right)\psi = 0}$$

keine gemischten Differentialquotienten

$\rightsquigarrow$ $\psi(r,\vartheta,\varphi) = f(r)\cdot g(\vartheta)\cdot h(\varphi)$

i) eindeutig

ii) normierbar

s. Kelvius, Luchner, Vonach Physik IV

$$\boxed{-\frac{\hbar^2}{2\mu}\Delta\psi + V(r)\,\psi = E\,\psi} \qquad \boxed{V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2}\left\{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,\frac{\partial\psi}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2\psi}{\partial\varphi^2}\right\} + \frac{2\mu}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0 r} + E\right)\psi = 0$$

$$\boxed{\psi(r,\vartheta,\varphi) = R(r)\cdot Y(\vartheta,\varphi)}$$

$$Y\cdot\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + R\left\{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,\frac{\partial Y}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2}\right\} + \frac{2\mu r^2}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0 r} + E\right)R\cdot Y = 0$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0 r} + E\right) = -\frac{1}{Y}\left\{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,\frac{\partial Y}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2}\right\}$$

$$\boxed{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\,\frac{\partial Y}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2} + C\cdot Y = 0}$$

→ unabhängig von E!

$$\boxed{\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0 r} + E\right)\cdot R - C\cdot R = 0}$$

$$\boxed{\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial\vartheta}\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2}+C\cdot Y=0}$$

$$\boxed{Y(\vartheta,\varphi)\equiv Y_1(\cos\vartheta,\varphi)\equiv Y_1(u,\varphi)}$$

$$\boxed{\cos\vartheta=u} \qquad \boxed{du=-\sin\vartheta\,d\vartheta}$$

$$\frac{\partial}{\partial u}\left((1-u^2)\frac{\partial Y_1}{\partial u}\right)+\frac{1}{1-u^2}\frac{\partial^2 Y_1}{\partial\varphi^2}+C\cdot Y_1=0$$

$$\boxed{Y_1=Y_1(u,\varphi)=f(u)\cdot g(\varphi)}$$

$$g(\varphi)\cdot\frac{\partial}{\partial u}\left\{(1-u^2)\frac{\partial f(u)}{\partial u}\right\}+\frac{1}{1-u^2}f(u)\frac{\partial^2 g(\varphi)}{\partial\varphi^2}+C\cdot f(u)\cdot g(\varphi)=0$$

$$(1-u^2)\cdot\frac{1}{f(u)}\frac{\partial}{\partial u}\left\{(1-u^2)\frac{\partial f(u)}{\partial u}\right\}+C\cdot(1-u^2)=-\frac{1}{g(\varphi)}\frac{\partial^2 g(\varphi)}{\partial\varphi^2}$$

$$=m^2$$

$$\boxed{\frac{\partial^2}{\partial\varphi^2}g(\varphi)=-m^2\,g(\varphi)}$$

$$\boxed{g(\varphi)=A\cdot e^{im\varphi}}$$

Physikalisch sinnvoll — eindeutig: $g(\varphi)=g(\varphi+2\pi)$

$$A\cdot e^{im\varphi}=A\,e^{im\varphi}\underbrace{e^{i2m\pi}}_{=1}$$

$$\rightarrow\quad\boxed{m=0,\pm1,\pm2,\ldots}$$

Quantenzahl aus Eindeutigkeitsforderung!

$$\boxed{\frac{d}{du}\left\{(1-u^2)\frac{df(u)}{du}\right\} + f(u)\left\{C - \frac{m^2}{1-u^2}\right\} = 0}$$

$f(u) = P_\ell^m(u)$ Legendre'sche Funktion

$u = \cos\vartheta = \pm 1$ (d.h. $\vartheta = 0°$ u. $\vartheta = 180°$)

Physikalische Bedingung: $f(u)$ stetig bei $u = \pm 1$

→ $C = \ell(\ell+1)$ mit $\ell = 0, 1, 2, \dots$ positiv, ganz

$|m| \le \ell \to m = 0, \pm 1, \pm 2, \dots \pm \ell$

→ Quantenzahl aus Stetigkeitsforderung!

zB $\ell = 0$ $m = 0$

$\ell = 1$ $m = 0, \pm 1$

$\ell = 2$ $m = 0, \pm 1, \pm 2$

⋮

ℓ $(2\ell+1)$ Werte von m

Legendre'sche Funktion: $P_\ell^{|m|}(u) = (1-u^2)^{\frac{|m|}{2}} \dfrac{d^{|m|}P_\ell(u)}{du^{|m|}}$

Legendre'sche Polynome: $P_\ell(u) = \dfrac{1}{2^\ell \cdot \ell!} \dfrac{d^\ell[(u^2-1)^\ell]}{du^\ell}$

$Y_1(u,\varphi) = Y_{\ell,m}(\vartheta,\varphi) = A_{\ell,m} \cdot P_\ell^{|m|}(\cos\vartheta)\, e^{im\varphi}$

$$\int_{-1}^{+1}\int_0^{2\pi} Y^*_{1_{\ell,m}}(u,\varphi)\, Y_{1_{\ell',m'}}(u,\varphi)\, d\varphi\, du = \delta_{\ell\ell'} \cdot \delta_{m,m'}$$

Normierte Kugelflächenfunktionen:

zB

$$\boxed{Y_{\ell,m}(\vartheta,\varphi) = \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\; P_\ell^{|m|}(\cos\vartheta)\, e^{im\varphi}}$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0 r} + E\right)\cdot R - l(l+1)\cdot R = 0$$

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{l(l+1)\hbar^2}{2\mu r^2} + E\right)\cdot R = 0$$

$$\boxed{\frac{d^2}{dr^2}R + \frac{2}{r}\frac{dR}{dr} + \frac{2\mu}{\hbar^2}\left(\frac{Ze^2}{4\pi\varepsilon_0 r} - \frac{l(l+1)\hbar^2}{2\mu r^2} + E\right)\cdot R = 0}$$

Radialanteil enthält Zentrifugalpotential

$$V_{eff} = V_{Coul} + V_l$$

$$W_{rot} = \frac{\vec{L}^2}{2\mu r^2} \Rightarrow V_l = \frac{l(l+1)\hbar^2}{2\mu r^2}$$

$$\boxed{\rho = \frac{Z\mu e^2}{4\pi\varepsilon_0\hbar^2}\, r = \frac{Z}{a_0}\cdot r}$$

$$\boxed{\varepsilon = \frac{-E}{hc\,R_y\cdot Z^2} = -E\,\frac{2\hbar^2}{\mu}\,\frac{(4\pi\varepsilon_0)^2}{Z^2e^4}}$$

$$\boxed{R(r) = R_1(\rho)}$$

$$\boxed{\frac{d^2R_1}{d\rho^2} + \frac{2}{\rho}\frac{dR_1}{d\rho} + \left(\frac{2}{\rho} - \frac{l(l+1)}{\rho^2} - \varepsilon\right)\cdot R_1 = 0}$$

Physikalische Forderung: $R_1(\rho)$ normierbar, eindeutig

$$\rightarrow \lim_{\rho\to\infty} R_1(\rho) = 0$$

$$\rightarrow \lim_{\rho\to 0} R_1(\rho) \text{ endlich}$$

Asymptotische Lösungen:

$\rho\to\infty$: $\quad \frac{d^2R_1^\infty}{d\rho^2} - \varepsilon R_1^\infty = 0 \quad ; \quad R_1^\infty = A\, e^{\cancel{+}-\sqrt{\varepsilon}\cdot\rho}$

$\rho\to 0$: $\quad \frac{d^2R_1^0}{d\rho^2} + \frac{2}{\rho}\frac{dR_1^0}{d\rho} - \frac{l(l+1)}{\rho^2}R_1^0 = 0$

$$R_1^0 = B_1\cdot\rho^l + \cancel{B_2}\,\rho^{-(l+1)}$$

$$R_1(\rho) = R_1^0\cdot R_1^\infty\cdot R_1^\rho(\rho)$$

$$\boxed{R_1^{\varrho}(\varrho) = \sum_{i=0}^{\infty} c_i \, \varrho^i} \qquad ; \qquad c_0 \neq 0$$

$$\rightsquigarrow \qquad c_{i+1} = \frac{2 c_i \cdot \sqrt{\varepsilon} \, (i + l + 1 - 1/\sqrt{\varepsilon})}{(i+1) \cdot (i + 2l + 2)}$$

Konvergenz? $\quad i \to \infty : \quad c_{i+1} \approx 2 c_i \sqrt{\varepsilon} \, \frac{1}{i}$

$$\rightsquigarrow \lim_{\varrho \to \infty} R_1^{\varrho}(\varrho) \neq 0$$

Forderung: $\quad c_{i_{max}} \neq 0 \quad ; \quad c_{i_{max}+1} = 0$

$$i_{max} + l + 1 - \frac{1}{\sqrt{\varepsilon}} = 0$$

$$\boxed{\varepsilon = \frac{1}{n^2}} \qquad \boxed{E_n = -hc R_y \frac{Z^2}{n^2}}$$

$$\boxed{n \geq l + 1}$$

aus Normierbarkeit folgt Quantisierung

$R_1^{\varrho}(\varrho)$: Laguerre sche Polynome

$$\boxed{R_{n,l}(r) = r^l \sum_{i=0}^{n-(l+1)} c_i \, r^i \, e^{-Z \cdot r / a_0 \cdot n}}$$

z.B.

mit
$$\int_0^{\infty} R_{n,l}^2(r) \, r^2 dr = \left(\frac{a_0}{Z}\right)^3 \int_0^{\infty} R_{n,l}^2(\varrho) \, \varrho^2 d\varrho = 1$$