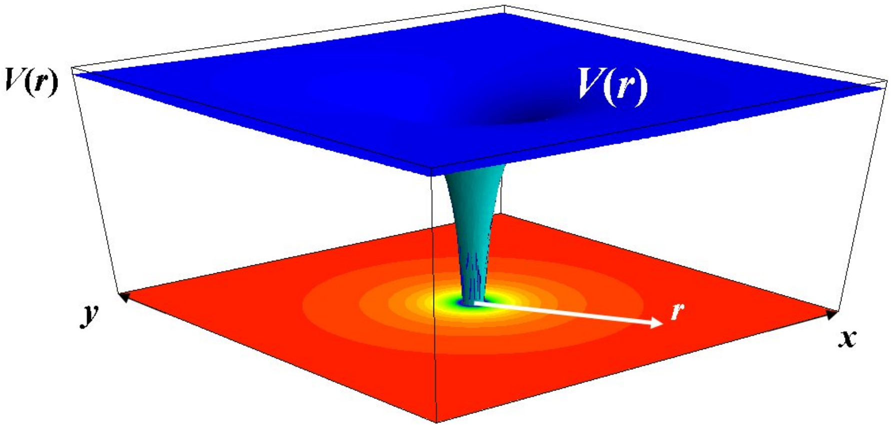
Direct solution of differential equations

The hydrogen atom → Schrödinger equation with spherical symmetry

coordinates: relative to position of proton



"reduced mass": $m = \dfrac{m_e m_p}{m_e + m_p} \approx m_e \left(1 - \dfrac{1}{1836}\right) \approx 0.9995 \cdot m_e$

$$H = T + V = \left(-\frac{\hbar^2 \Delta}{2m} + V(r) \right) =$$

$$\frac{1}{\sin\vartheta}\partial_\vartheta\left(\sin\vartheta\,\partial_\vartheta\right) + \frac{1}{\sin^2\vartheta}\partial_\varphi^2$$

$$= \left(-\frac{\hbar^2}{2m} \left\{ \frac{1}{r^2}\partial_r r^2 \partial_r + \frac{1}{r^2}\Delta_{\vartheta,\varphi} \right\} + V(r) \right)$$

→ Schrödinger equation (SE) in spherical coordinates:

$$\boxed{\left(-\frac{\hbar^2}{2m} \left\{ \frac{1}{r^2}\partial_r r^2 \partial_r + \frac{1}{r^2}\Delta_{\vartheta,\varphi} \right\} + V(r) \right) \cdot \psi(r,\vartheta,\varphi) = E \cdot \psi(r,\vartheta,\varphi)}$$

ansatz for wavefunction → separation of variables

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

with $\dfrac{1}{r^2}\partial_r r^2 \partial_r \dfrac{R(r)}{r} = \dfrac{1}{r}\partial_r^2 R(r)$

$$\rightarrow \underbrace{\frac{r^2}{R(r)}\partial_r^2 R(r) + r^2 \frac{2m}{\hbar^2}\left(E - V(r)\right) = \ell(\ell+1)}_{\text{radial SE}} = \frac{-1}{Y(\vartheta,\varphi)}\Delta_{\vartheta,\varphi} Y(\vartheta,\varphi)$$

$$\underbrace{\ell(\ell+1) = \frac{-1}{Y(\vartheta,\varphi)}\Delta_{\vartheta,\varphi} Y(\vartheta,\varphi)}_{\text{angular SE}}$$

with $V(r) = -\dfrac{e^2}{r}$

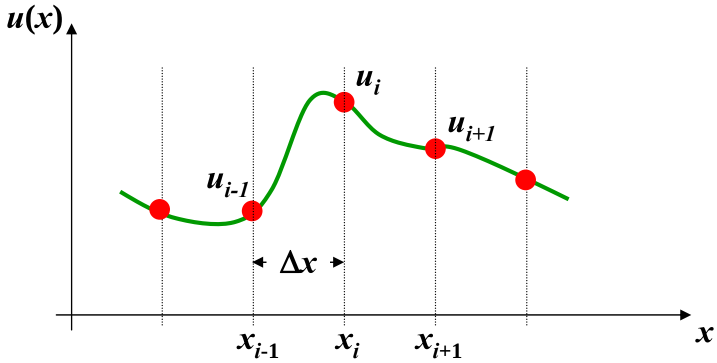
$$\boxed{\rightarrow \quad -\frac{\hbar^2}{2m}\partial_r^2 R_\ell(r) + \left\{ \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2} - \frac{e^2}{r} \right\} R_\ell(r) = E \cdot R_\ell(r)}$$

numerical solution of SE:

Numerov (Fox-Goodwin) algorithm

for differential equation $u''(x) + w(x)u(x) = 0$

equidistant grid points:



$$u(x_n) = u_n \quad \to \quad u_{n\pm1} = u_n \pm \Delta u_n' + \frac{1}{2}\Delta^2 u_n'' \pm \frac{1}{3!}\Delta^3 u_n''' + \frac{1}{4!}\Delta^4 u_n^{(IV)} \pm \ldots$$

$$\to \quad u_n'' = \frac{u_{n+1} - 2u_n + u_{n-1}}{\Delta^2} - \frac{\Delta^2}{12} u_n^{(IV)} + O(\Delta^4)$$

$$\to \quad u_n^{(IV)} = -(wu)'' = -\frac{w_{n+1}u_{n+1} - 2w_n u_n + w_{n-1}u_{n-1}}{\Delta^2} + O(\Delta^2)$$

collection of terms:

$$\left(1 + \frac{\Delta^2}{12} w_{n+1}\right) u_{n+1} - \left(2 - 10\frac{\Delta^2}{12} w_n\right) u_n + \left(1 + \frac{\Delta^2}{12} w_{n-1}\right) u_{n-1} = 0$$

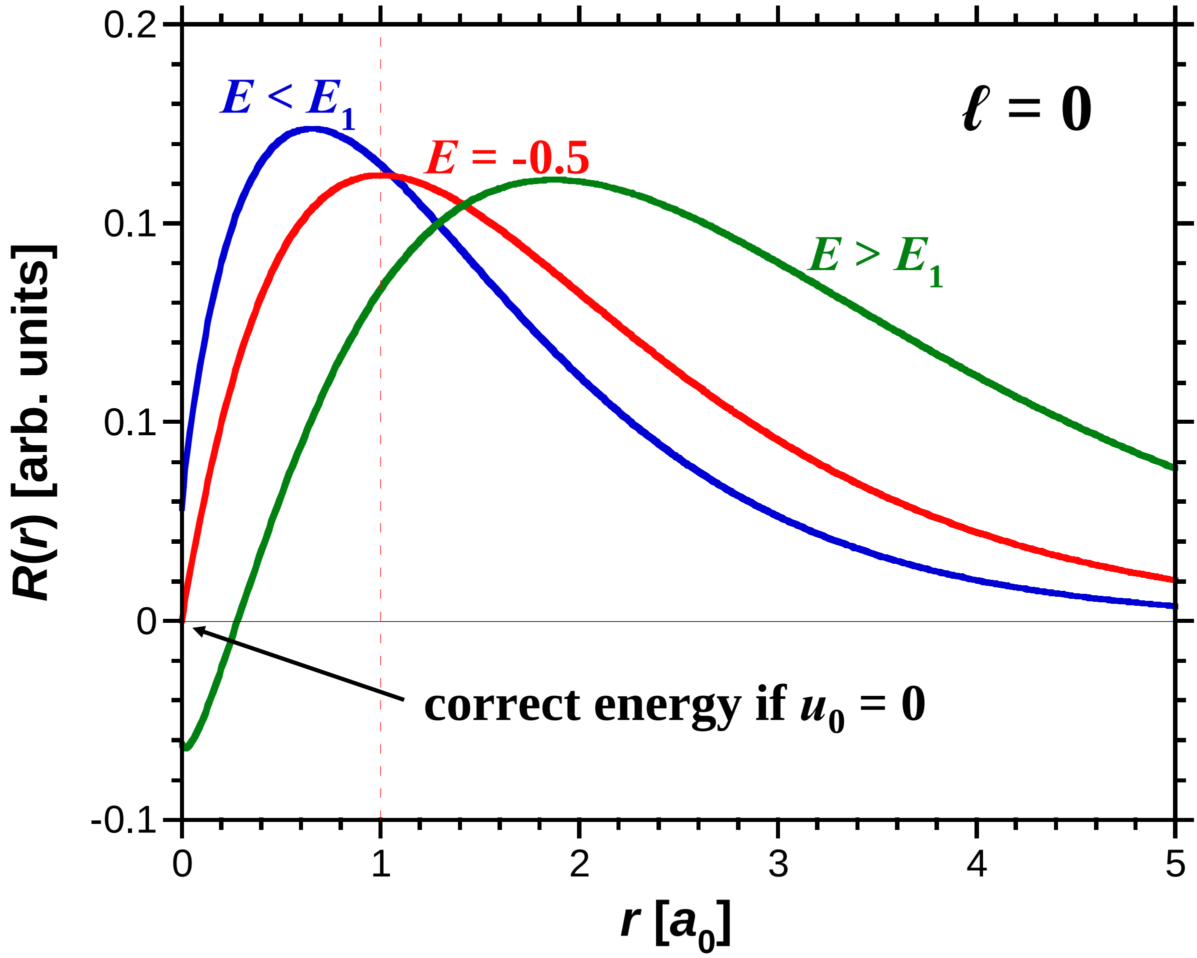
$$\boxed{Q_{n+1} = 12u_n - 10Q_n - Q_{n-1}\,; \quad Q_n = \left(1 + \frac{\Delta^2}{12} w_n\right) u_n}$$

knowledge of u_n, u_{n-1} (e.g. from boundary conditions) → $u(x)$

$$\partial_r^2 u(r) + \underbrace{\left\{\frac{2m}{\hbar^2}\left(E + \frac{e^2}{r}\right) - \frac{\ell(\ell+1)}{r^2}\right\}}_{w(r)} u(r) = 0$$

start the iteration at large r:

boundary condition for large r: $u(r) = C\exp(-\kappa r) \quad \to \quad u_{n-1} > u_n > 0$
boundary condition for $r = 0$: $u(r) = 0$
search numerically for correct E to fulfill simultaneously both boundary conditions



Aufgaben

- Schreiben Sie ein Programm, das die radiale Schrödingergleichung für das Wasserstoffatom mithilfe des Numerov-Verfahrens löst.
- Verwenden Sie das Schießverfahren (Nullstellensuche) zur Ermittlung der Bindungsenergien der Zustände mit Quantenzahlen (n=1,l=0), (2,0), (2,1), (3,0), (3,1), (3,2).
- Zeigen Sie numerisch, daß die Wellenfunktionen aufeinander orthogonal stehen.