6 Radial equation and principle quantum number

Rewrite eq. (5.20)

\[ (5.46) \quad - \frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \left\{ V(r) + \frac{l(l+1)\hbar^2}{2mr^2} \right\} R(r) = ER(r) \]

Note:

- For a particle in a circular orbit, the orbital kinetic energy can be written as

\[ (5.47) \quad K_{\text{orb}} = \frac{1}{2} m \dot{r}^2 = \frac{m}{2} \left( \frac{\ddot{r}}{r} \right)^2 = \frac{l^2}{2mr^2} \]

\[ (5.41) \quad \frac{l(l+1)\hbar^2}{2mr^2} \text{ centrifugal term} \]

This additional term in the radial Schrödinger eq. implies a strong increase of the potential for small \( r \). As the orbital quantum number increases, the probability of finding the particle at small \( r \) decreases. (consistent with Bohr’s simple model).

- Substitution

\[ (5.48) \quad g(r) = r \cdot R(r) \]

is useful since

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) = r \frac{\partial^2 R}{\partial r^2} + 2 \frac{\partial R}{\partial r} \]

\[ (5.49) \quad \frac{\partial^2}{\partial r^2} g(r) = \frac{\partial^2}{\partial r^2} (r R) = \frac{\partial}{\partial r} \left( R + r \frac{\partial R}{\partial r} \right) = 2 \frac{\partial R}{\partial r} + r \frac{\partial^2 R}{\partial r^2} \]
With (5.48), we write the radial equation (5.46) as

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

This is a one-dimensional Schrödinger equation for a wave function \( q(r) \) in the effective potential \( V_{\text{eff}}(r) \).

To solve (5.50), consider first limiting cases:

1. Case: \( r \to 0 \) then \( V(r) \ll K_{\text{orb}}(r) \)

   eq. (5.50) is approximately:

   \[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} q(r) + \frac{l(l+1)\hbar^2}{2mr^2} q(r) = 0 \]  

   This has the solution

   \[ q(r) = a r^{l+1} + b r^{-l} \]

   BUT, this function must not be singular at \( r \to 0 \). This physical requirement implies \( b = 0 \)

   \[ q(r) \sim r^{l+1} \quad \text{for} \quad r \to 0 \]

   The larger the orbital quantum number \( l \), the more depleted is the wave function around \( r = 0 \).
2. case: \( r \to \infty \) now \( V(r) \) and \( K_{\text{orb}}(r) \) become unimportant, \( (5.50) \) is approx.

\[
\frac{\partial^2}{\partial r^2} q(r) = \frac{\sqrt{-2mE}}{\hbar^2} q(r) \quad \epsilon = \frac{2mE}{\hbar^2}
\]

Note: for a bound state, the energy \( E \) is negative, i.e. \(-2mE > 0\).

Solutions of \( (5.54) \) have the form

\[
q(r) = \alpha e^{-r\sqrt{\epsilon'}} + \beta e^{r\sqrt{\epsilon'}}
\]

Physically, the solution must vanish for \( r \to \infty \), so \( \beta = 0 \)

\[
(5.56) \quad q(r) \sim e^{-r\sqrt{\epsilon'}} \quad \text{for} \quad r \to \infty
\]

Combining the asymptotic behavior \( (5.53) \) and \( (5.56) \), we make the ansatz

\[
(5.57) \quad q(r) = r^{l+1} e^{-r\sqrt{\epsilon'}} \cdot W(r)
\]

Insert \( (5.57) \) into the diff. eq. \( (5.50) \) to find diff. eq. for \( W(r) \)

\[
(5.58) \quad W''(r) + \left\{ \frac{2(l+1) - 2r\sqrt{\epsilon'}}{r} \right\} W'(r) + \frac{\sqrt{\epsilon}}{r} W(r) = 0
\]

Substitute \( x = 2r\sqrt{\epsilon'} \)

\[
(5.59) \quad x W''(x) + \left\{ \frac{2l+2 - x^2}{x} \right\} W'(x) - \left( \frac{l+1 - \sqrt{\epsilon}}{x} \right) W(x) = 0
\]

Here \( \sqrt{\epsilon} = \frac{2m\hbar^2 k^2}{\hbar^2} \)
This diff. eq. has tabulated solutions known as confluent hypergeometric functions \( F \) with arguments \( a, y \)

\[
W(x) = F \left( a+1-\frac{1}{2\sqrt{y}};\ 2a+2;\ x=2\sqrt{y} \right)
\]

These functions are complicated (non-examinable).

For the wave function to have a physically acceptable behavior at \( r=0 \) and \( r=\infty \), one has to require

\[
\alpha = a+1-\frac{1}{2\sqrt{y}} = -n_r \quad \text{integer number} \geq 0
\]

Rewrite this

\[
\lambda + 1 + n_r = n = \frac{\sqrt{y}}{2\sqrt{y}}
\]

\[
E = -\frac{2mE}{\hbar^2} \quad \text{(from (5.54))}
\]

\[
E = \frac{\lambda^2}{2m} = \frac{1}{4n^2} \left( \frac{2mke^2}{\hbar^2} \right)^2
\]

\[\Rightarrow E_n = -\frac{\hbar^2}{2m} \cdot \frac{1}{4n^2} \cdot \frac{4m^2(k^2e^2)^2}{\hbar^2}\]

\[
E_n = -\frac{m^2k^2e^2}{2\hbar^2} \cdot \frac{1}{n^2} \quad n=1, 2, 3, \ldots
\]

\[
E_n = -R_n \left( \frac{1}{n^2} \right) \quad R_n = 13.6 \text{ eV}
\]

\[
\sqrt{-E} = \sqrt{-2mE_n} = \frac{mke^2}{\hbar^2} \frac{1}{n} = \frac{1}{\alpha_o \cdot n}
\]

\[
\alpha_o = \text{Bohr radius} \quad \alpha_o = 0.529 \text{ Å}
\]

see eq. (3.23)
The radial wave function \( R(r) \) depends on the principle quantum number \( n \) and the orbital quantum number \( l \):

\[
R(r) = c_{nm} \cdot r^l e^{-\frac{r}{n\alpha_0}} F(l+1-n; 2l+2; \frac{2r}{n\alpha_0})
\]

\[l < n\]

Explicit form of radial wave functions:

\[
R_{1,0}(r) = \left(\frac{1}{\alpha_0}\right)^{3/2} 2 e^{-\frac{r}{\alpha_0}}
\]

\[
R_{2,0}(r) = \left(\frac{1}{2\alpha_0}\right)^{3/2} (2 - \frac{r}{\alpha_0}) e^{-\frac{r}{2\alpha_0}}
\]

\[
R_{2,1}(r) = \left(\frac{1}{2\alpha_0}\right)^{3/2} \frac{r}{\sqrt{3} \alpha_0} e^{-\frac{r}{2\alpha_0}}
\]

Spectroscopic notation:

\[
\begin{array}{cc}
  n & \text{shell symbol} \\
  1 & K \\
  2 & L \\
  3 & M \\
  4 & N \\
\end{array}
\]

\[
\begin{array}{cc}
  l & \text{shell symbol} \\
  0 & s \\
  1 & p \\
  2 & d \\
  3 & f \\
\end{array}
\]

Entire wave function of electron in hydrogen:

\[
\Psi_{n\ell m}(r, \theta, \phi) = c_{nm} r^\ell e^{-\frac{r}{n\alpha_0}} F(...) \Gamma_{\ell m}(\theta, \phi)
\]

\[
|\Psi_{n\ell m}(r, \theta, \phi)|^2 \quad \text{defines probability for finding } e \text{ at } r, \theta, \phi
\]

is plotted for several quantum numbers in Serway, Figs 8.12, 8.13.