Radial equation for spherically symmetric potential

The SE in 3D in spherical coordinates is

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

(22-1)

using the ansatz \( \psi(r) = R(r) Y(\theta, \phi) \), and inserting for the angular function an eigenfunction

\[ Y(\theta, \phi) = Y_{lm}(\theta, \phi) = \langle \theta, \phi | l, m \rangle, \]  

(22-2)

we have, using \( L^2 Y_{lm}(\theta, \phi) = \hbar^2 (l + 1) Y_{lm}(\theta, \phi) \) after dividing by \( Y_{lm} \) for the radial equation,

\[ \left[ -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) + \frac{\hbar^2 l(l + 1)}{2mr^2} + V(r) \right] R_{nl}(r) = E_{nl} R_{nl}(r). \]  

(22-3)

Here, we have added two subscripts \( n, l \) to the radial wavefunction \( R(r) \) and the eigenenergy \( E \) because the SE for the radial part of the wavefunction depends on the total angular momentum \( l \) of the 3D wavefunction \( \psi(r) \).

Note. The \( z \)-component of angular momentum \( L_z \), and the corresponding magnetic quantum number \( m \), do not appear in the radial equation.

We can define an \( l \)-dependent effective potential,

\[ V_{eff,l} = V(r) + \frac{\hbar^2 l(l + 1)}{2mr^2}, \]  

(22-4)

where the additional term is the centrifugal barrier for a particle with angular momentum

\[ \langle L^2 \rangle = \hbar^2 l(l + 1). \]  

(22-5)

The radial equation can be brought into a more familiar-looking form by introducing a new function:

\[ u(r) = r R(r) \]
\[ R(r) = \frac{u(r)}{r} \]  

(22-6)

Then,

\[ R' = \frac{u' r - u}{r^2} = \frac{u'}{r} - \frac{u}{r^2} \]  

(22-7)
\[ \frac{2}{r} R' = \frac{2u'}{r^2} - \frac{2u}{r^3} \]  

(22-8)
\[ R'' = \frac{u'' r - u'}{r^2} - \frac{u'^2 - u2r}{r^4} = \frac{u''}{r} - \frac{2u'}{r^2} + \frac{2u}{r^3} \]  

(22-9)
\[ \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} \right) R(r) = R'' + \frac{2}{r} R' = \frac{u''}{r} \]  

(22-10)
and the radial equation is
\[
-\frac{\hbar^2}{2mr} \frac{\partial^2 u}{\partial r^2} + \left[ \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right] \frac{u(r)}{r} = E \frac{u(r)}{r} \tag{22-11}
\]
or
\[
\left[ -\frac{\hbar^2}{2mr} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2 l(l+1)}{2mr^2} + V(r) \right] \frac{u_{nl}(r)}{r} = E_{nl} u_{nl}(r) \tag{22-12}
\]
This equation for \(u(r) = rR(r)\) has the same form as the 1D SE in the effective potential
\[
V_{\text{eff},l}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}, \tag{22-13}
\]
but with slightly different boundary conditions. Therefore, \(u(r)\) looks like an anti-

Figure I: \(u(r) = rR(r)\) has the same form as the 1D SE in the effective potential \(V_{\text{eff},l}(r)\), but with slightly different boundary conditions.

symmetric solution in all space. Consequences are, e.g., that since an antisymmetric

bound state does not always exist in 1D, that a bound state does not always exist in 3D (in contrast to 1D, where a symmetric bound state always exist in a potential well). 3D wavefunctions \(u(r)\) are like antisymmetric 1D wavefunctions in the effective potential
\[
V_l(r) = V(r) + \frac{\hbar^2 l(l+1)}{2mr^2}. \tag{22-14}
\]
Hydrogen atom

\[ V(r) = -\frac{Ze^2}{4\pi\epsilon r} \quad \text{→ (and the radial equation is)} \quad (22-15) \]

\[ \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{Ze^2}{4\pi\epsilon r} + \frac{\hbar^2 l(l+1)}{2mr^2} - E \right) u(r) = 0 \quad (22-16) \]

We introduce a dimensionless position coordinate \( \rho \) by \( \rho^2 = \frac{8m\hbar^2}{E} r^2 \), and define for \( E < 0 \)

\[ \frac{Ze^2}{r16\pi\epsilon|E|} \sqrt{\frac{8m}{\hbar^2}} \sqrt{\frac{\hbar^2}{8m}} = \frac{Ze^2}{16\pi\epsilon\hbar} \sqrt{\frac{8m}{|E|}} \sqrt{\frac{\hbar^2}{8m|E|}} \quad (22-17) \]

\[ = \frac{Ze^2}{4\pi\epsilon\hbar} \sqrt{\frac{m}{2|E|}} \frac{1}{\rho} \quad (22-18) \]

\[ =: \frac{\lambda}{\rho} \quad (22-19) \]

The equation can be written as

\[ \frac{\partial^2}{\partial \rho^2} u + \left( \frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right) u = 0 \quad (22-20) \]

with \( \rho = \sqrt{\frac{8m|E|}{\hbar^2}} r \), \( \lambda = \frac{Ze^2}{4\pi\epsilon\hbar} \sqrt{\frac{m}{2|E|}} = Z\alpha \sqrt{\frac{m^2}{2|E|}} \), where \( \alpha = \frac{e^2}{4\pi\epsilon\hbar c} \approx 1.74 \ldots \) is the dimensionless fine structure constant. To solve this equation, we proceed as for the HO: We write a Taylor-expansion solution after having factored out the correct asymptotic behavior.

For very large \( \rho \) we have

\[ \frac{d^2}{d\rho^2} u = \frac{1}{4} u \quad (22-21) \]

\[ u(\rho) \propto e^{-\frac{1}{2}\rho} \quad (22-22) \]

For very small \( \rho \),

\[ \frac{d^2}{d\rho^2} u = \frac{l(l+1)}{\rho^2} u \quad (22-23) \]

\[ u(\rho) \propto \rho^{l+1} \quad (22-24) \]

Consequently, we try a solution of the form

\[ u(\rho) = s(\rho)\rho^{l+1} e^{-\frac{1}{2}\rho} \quad (22-25) \]
\[ u'(\rho) = \left( s'(\rho)\rho^{l+1} + s(\rho)(l+1)\rho^l - \frac{1}{2}s\rho^{l+1}\right) e^{-\frac{1}{2}\rho} \] (22-26)

\[ u''(\rho) = \left[ s''\rho^{l+1} + 2(l+1)s'\rho^l + s(l+1)l\rho^{l-1} - \frac{1}{2}(s'\rho^{l+1} + (l+1)s\rho^l) \right. \]

\[ \left. - \frac{1}{2}(s'\rho^{l+1} + (l+1)s\rho^l - \frac{1}{2}s\rho^{l+1}) \right] e^{-\frac{1}{2}\rho} \] (22-28)

\[ = \rho^{l+1} e^{-\frac{1}{2}\rho} \left[ s'' + 2(l+1)\frac{s'}{\rho} + \frac{(l+1)}{\rho^2} - s' - \frac{l+1}{\rho} s + \frac{1}{4}s \right] \] (22-29)

\[ \left( \frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right) u = \rho^{l+1} e^{-\frac{1}{2}\rho} \left( \frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right) s \] (22-30)

Inserting this into (??) leads to

\[ s'' + \left( \frac{2(l+1)}{\rho} - 1 \right) s' + \left( \frac{(l+1)}{\rho^2} - \frac{l+1}{\rho} + \frac{1}{4} + \frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2} \right) s = 0 \] (22-32)

\[ s'' + \left[ \frac{2l+2}{\rho} - 1 \right] s' + \frac{-l-1}{\rho} s = 0 \] (22-33)

To solve this differential equation, we write a Taylor expansion about \( \rho = 0 \):

\[ s(\rho) = \sum_{k=0}^{\infty} a_k \rho^k \] (22-34)

\[ s'' = \sum_{k=0}^{\infty} a_k k(k-1)\rho^{k-2} \] (22-35)

\[ = \sum_{k=0}^{\infty} a_{k+2} (k+2)(k+1)\rho^k \] (22-36)

\[ \left( \frac{2l+2}{\rho} - 1 \right) s' = \left( \frac{2l+2}{\rho} - 1 \right) \sum a_k \rho^{k-1} \] (22-37)

\[ = (2l+2) \sum_{k=0}^{\infty} a_{k+2} (k+2)\rho^k - \sum a_{k+1} (k+1)\rho^k \] (22-38)

\[ \frac{\lambda - l - 1}{\rho} s = (\lambda - l - 1) \sum_{k=0}^{\infty} a_{k+1} \rho^k \] (22-39)

which substituted into (??) results in

\[ \sum k \rho_k \{ (k+2)(k+1)a_{k+2} + 2(l+1)(k+2)a_{k+2} + (\lambda - l - 1 - k - 1)a_{k+1} \} = 0 \] (22-40)
This must vanish term by term, so we obtain a recursion relation

\[(k + 2)(k + 2l + 3)a_{k+2} = (k + l + 2 - \lambda)a_{k+1}\]  \hspace{1cm} (22-41)

or

\[
\frac{a_{k+1}}{a_k} = \frac{k + l + 1 - \lambda}{(k + 1)(k + 2(l + 1))} \rightarrow \text{recursion relation for expansion coefficients} \hspace{1cm} (22-42)
\]

If the series does not break off somewhere, we will have for large \(k\), \(a_k \propto \frac{1}{k} a_{k-1}\) or \(a_k \propto \frac{1}{k!}\), which gives a growth \(s(\rho) \propto e^{+\rho}\), which is not acceptable for \(u(\rho) = s(\rho)e^{-\frac{\rho}{2}}\). Consequently, we require the series to terminate, which implies \(\lambda = k + l + 1\) for some \(L\). Let us call \(n_r = k\) the integer with that property. It is customary to define the principal quantum number as

\[n = n_r + l + 1\]  \hspace{1cm} (22-43)

where \(n_r \geq 0\), so \(n \geq 0\), so \(n \geq l + 1\), \(n\) integer, and

\[\lambda_n = \frac{Ze^2}{4\pi\varepsilon_0 \hbar} \sqrt{\frac{m}{2|E_n|}}\]  \hspace{1cm} (22-44)

\[= Z\alpha \sqrt{\frac{mc^2}{2|E_n|}}\]  \hspace{1cm} (22-45)

\[= n\]  \hspace{1cm} (22-46)

Consequently, the eigenenergies of the hydrogen atom are

\[
E_n = -\frac{1}{2} mc^2 \left(\frac{Z\alpha}{n^2}\right)^2 \rightarrow \left(\begin{array}{c}
\text{eigenenergies of}
\text{hydrogenlike atoms}
\end{array}\right)\]  \hspace{1cm} (22-47)

This is the same energy eigenspectrum as obtained from the Bohr formula.

**Note.** There are important differences:

- The principal quantum number \(n = n_r + l + 1\) is really the sum of the radial quantum number \(n_r\) and the total angular momentum quantum number \(l\).

- We have obtained the full radial and angular distribution of the electron, which generalizes the classical concept of an orbit.
First few radial functions

\[ \rho^2_n = \frac{8m|E_n|}{\hbar^2} \left( \frac{Z\alpha}{a_0} \right)^2 \]

\[ = \frac{8m}{\hbar^2} \frac{1}{2} mc^2 \frac{(Z\alpha)^2}{n^2 - r^2} \]

\[ = \frac{(2mcZ\alpha)^2}{\hbar n^2} r^2 \]

\[ = \left( \frac{2Z\alpha}{a_0} \right)^2 r^2 \frac{1}{n^2} \]

\[ = \frac{2Zr}{na_0} \]

with the Bohr radius

\[ a_0 = \frac{\hbar^2}{mc\alpha} \]

Consequently, \( e^{-\frac{1}{2}\rho} = e^{-\frac{Zr}{na_0}} \)

1. \( n_r = l = 0, n = m = \lambda, a_1 = 0 \)

\[ u(r) = C\rho e^{-\frac{1}{2}\rho} = C_1 \left( \frac{Zr}{a_0} \right) e^{-\frac{Z\alpha}{a_0}} \]

\[ R(r) = \frac{u(r)}{r} = C_2 e^{-\frac{Zr}{a_0}} \]

Note. The probability to find the electron between \( r \) and \( r + dr \) is given by \( r^2|R(r)|^2 dr = |u(r)|^2 dr \).

2. \( (a) \) \( n_r = 1, l = 0, n = 2 = \lambda \)

\[ \frac{a_1}{a_0} = \frac{-1}{1 \cdot 2} = \frac{-1}{2} \]

\[ u_{20}(r) = C\rho e^{-\frac{1}{2}\rho} \left( 1 - \frac{1}{2}\rho \right) = C' \frac{Zr}{a_0} \left( 1 - \frac{Zr}{2a_0} \right) e^{-\frac{Zr}{2a_0}} \]

\[ R_{20}(r) = C' \left( 1 - \frac{Zr}{2a_0} \right) e^{-\frac{Zr}{2a_0}} \]
(b) \( n_r = 0, l = 1, n = 2 = \lambda \)

\[
\frac{a_1}{a_0} = 0 \quad \rightarrow \quad a_1 = 0 \tag{22-59}
\]

\[
u_{21}(r) = C \rho^2 e^{-\frac{1}{2} \rho} = C' \left( \frac{Zr}{a_0} \right)^2 e^{-\frac{Zr}{2a_0}} \tag{22-60}
\]

\[
R_{21}(r) = C'' \left( \frac{Zr}{a_0} \right) e^{-\frac{Zr}{2a_0}} \tag{22-61}
\]

\( R_{20} = R_{n=2,l=0} \) and \( R_{21} = R_{n=2,l=1} \) are different states that have the same eigenenergy. The occurrence of different eigenstates with the same energy, (or in general quantum number) is called **degeneracy**.