Electron in Coulomb Potential

Consider an electron in a Coulomb potential produced by a charge $+e$ fixed at the origin:

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}.$$  

Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V(r)\psi = E\psi$$

Wave function

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Angular wave function

$$Y_l^m(\theta, \phi)$$

Radial equation

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[ -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r} + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right] u = Eu \quad (1)$$

where $u(r) = rR(r)$. 
Radial Equation

The Coulomb potential admits continuation states (with \( E > 0 \)), describing electron-proton scattering, as well as discrete bound states, representing the hydrogen atom. Only the latter will be considered here.

The following is a summary of procedures for solving the radial equation (1). Please refer to the text book for details.

1. Tidy up the notation. Let

\[
\alpha = \frac{\sqrt{-2mE}}{\hbar} \quad \text{(dimension: length}^{-1}\text{)}
\]
\[
\rho = \alpha r \quad \text{(dimension less position)}
\]
\[
\beta = \frac{me^2}{2\pi \varepsilon_0 \hbar^2 \alpha} \quad \text{(dimension less constant)}
\]

The radial dinger equation becomes

\[
\frac{d^2 u}{d\rho^2} = \left[ 1 - \frac{\beta}{\rho} + \frac{l(l + 1)}{\rho^2} \right] u. \quad (2)
\]
2. Consider the asymptotic form at $\rho \to \infty$. When $\rho \to \infty$, Eq.(2) is approximately

$$\frac{d^2u}{d\rho^2} = u.$$  \hspace{1cm} (3)

The solution (physically valid) is

$$u(\rho) \approx Ae^{-\rho} \quad (\text{for } \rho \gg 1)$$

3. Consider the limit of $\rho \to 0$. When $\rho \to 0$, the Schrödinger equation is approximately

$$\frac{d^2u}{d\rho^2} = \frac{l(l + 1)}{\rho^2}u.$$  \hspace{1cm} (4)

The solution (physically valid) is

$$u(\rho) \approx C\rho^{l+1} \quad (\text{for } \rho \ll 1)$$

4. Assume the general solution (valid for all $\rho$) is

$$u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$$  \hspace{1cm} (5)

$v(\rho)$ must remain finite when $\rho \to 0$ or $\rho \to \infty$. 
5. Calculated $d^2u/d\rho^2$ and substitute into Eq.(2), we get the equation satisfied by $v(\rho)$

$$\rho \frac{d^2v}{d\rho^2} + 2(l + 1 - \rho) \frac{dv}{d\rho} + [\beta - 2(l + 1)]v = 0 \quad (6)$$

6. Assume the solution, $v(\rho)$, can be expressed as a power series in $\rho$

$$v(\rho) = a_0 + a_1\rho + a_2\rho^2 + \cdots = \sum_{j=0}^{\infty} a_j \rho^j$$

$$\frac{dv}{d\rho} = a_1 + 2a_2\rho + 3a_3\rho^2 + \cdots = \sum_{j=0}^{\infty} (j + 1) a_{j+1} \rho^j$$

$$\frac{d^2v}{d\rho^2} = 2a_2 + 6a_3\rho + 12a_4\rho^2 + \cdots = \sum_{j=0}^{\infty} j(j+1) a_{j+1} \rho^{j-1}$$

7. Substituting the above into Eq.(6) and equating the coefficients of like powers, we get the following recursion formula

$$a_{j+1} = \frac{2(j + l + 1) - \beta}{(j + 1)(j + 2l + 2)} a_j$$
8. The power series does not converge. For large \( j \) (large \( \rho \))

\[
a_{j+1} \approx \frac{2}{j+1} a_j, \quad a_j \approx \frac{2^j}{j!} A, \quad v(\rho) \approx A e^{2\rho}
\]

The power series must \textit{terminate}. Truncate the series beyond \( \rho^{j_m} \).

\[
a_{j_m+1} = 0
\]

This requires

\[
2(j_m + l + 1) - \beta = 0
\]

9. Define (the \textbf{principal quantum number})

\[
n = j_m + l + 1
\]

We get the allowed energies

\[
E_n = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} \frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots
\]

where the ground state energy \( E_1 \) is given by

\[
E_1 = -\frac{me^4}{2(4\pi\epsilon_0)^2\hbar^2} = -13.4 \text{ eV}
\]
10. The radial wave function

\[ R_{nl}(r) = \frac{u_{nl}(r)}{r} = \frac{1}{r} \rho^l e^{-\rho} v_{nl}(\rho) \]

\[ v(\rho) = a_0 + a_1 \rho + a_2 \rho^2 + \cdots = \sum_{j=0}^{\infty} a_j \rho^j \]

Since \( \beta = 2n \)

\[ a_{j+1} = \frac{2(j + l + 1 - n)}{(j + 1)(j + 2l + 2)} a_j \]

\[ a_1 = \frac{-2(n - l - 1)}{1 \cdot (2l + 2)} a_0 \]

\[ a_2 = \frac{-2(n - l - 2)}{2(2l + 3)} a_1 \]

\[ = \frac{2^2(n - l - 1)(n - l - 2)}{2!(2l + 3)(2l + 2)} a_0 \]

\[ a_3 = \frac{-2(n - l - 3)}{3(2l + 4)} a_2 \]

\[ = \frac{2^3(n - l - 1)(n - l - 2)(n - l - 3)}{3!(2l + 4)(2l + 3)(2l + 2)} a_0 \]
In general

\[ a_j = \frac{(-1)^j 2^j (n - l - 1)(n - l - 2) \cdots (n - l - j)}{j!(2l + j + 1)(2l + j) \cdots (2l + 3)(2l + 2)} a_0 \]

\[ = \frac{(-1)^j 2^j (n - l - 1)!(2l + 1)!}{j!(2l + j + 1)!(n - l - j - 1)!} a_0 \]

\[ v(\rho) = a_0 \sum_{j=0}^{n-l-1} \frac{(-1)^j (n - l - 1)!(2l + 1)!}{(2l + j + 1)!(n - l - 1 - j)!} \frac{(2\rho)^j}{j!} \]

Compare the above with the associated Laguerre polynomial

\[ L_n^\mu(x) = \sum_{k=0}^{n} (-1)^k \frac{(n + \mu)!}{(\mu + k)!(n - k)!} \frac{x^k}{k!} \]

we get

\[ v(\rho) = a_0 \frac{(n - l - 1)!(2l + 1)!}{(n + l)!} L_{n-l-1}^{2l+1}(2\rho) \]
(Associated) Laguerre Polynomial

The associated Laguerre polynomial can also be defined as

\[ L_{q-p}^p(x) = (-1)^p \left( \frac{d}{dx} \right)^p L_q(x) \]

where \( L_q(x) \) is the \( q \)th Laguerre polynomial and is given by

\[ L_q(x) = e^x \left( \frac{d}{dx} \right)^q (e^{-x}x^q) \]
Wave Function

Now
\[ \alpha = \frac{\sqrt{-2mE}}{\hbar} = \frac{1}{n a_0} \]

where
\[ a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.529 \times 10^{-10} \text{ m} = 0.529 \text{ Å} \]

is the Bohr Radius.

\[ \rho = \alpha r = \frac{r}{n a_0} \]

The normalized wave function is given by

\[ \psi_{nlm} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l \]

\[ \times L_{n-l-1}^{2l+1} \left(\frac{2r}{na_0}\right) Y_l^m(\theta, \phi). \]