The hydrogen-like atom

In the previous lecture we learned that for a particle moving in a spherically symmetric potential $V(r) = V(1r^1)$ variables can be separated. The solution for the angular part

$$
\frac{1}{\sin \theta} \frac{d}{d \theta} \sin \theta \frac{d Y}{d \theta} + \frac{\ell^2 Y}{\ell \ell^* + \ell^* \ell} = -\ell (\ell + 1) Y
$$

are spherical harmonics $Y_{\ell m}(\theta, \phi)$ — complex functions that have two indices (quantum numbers): $\ell$ and $m$.

Now we turn to the radial part of the Schrödinger equation

$$
\frac{d}{dr} \left( R \frac{d R}{dr} \right) - \frac{2m}{\hbar^2} \left[ V(r) - E \right] R = \frac{\ell (\ell + 1)}{r^2} R
$$

It is convenient to make a substitution

$$
R(r) = \frac{u(r)}{r} \quad \text{or} \quad u(r) = r R(r)
$$

This way the radial equation gets reduced to a more familiar form:

$$
- \frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[ V(r) + \frac{\ell^2}{2m} \frac{\ell (\ell + 1)}{r^2} \right] u = E u
$$

It is essentially the same 1D Schrödinger equation we had to deal before in this course. The only difference is that we now have an "effective" potential

$$
V_{\text{eff}}(r) = V(r) + \frac{\ell^2}{2m} \frac{\ell (\ell + 1)}{r^2}
$$
This effective potential contains an extra repulsive term \( \frac{\hbar^2}{2m} \ell (\ell+1) \). It effectively "pushes" the particle away from the center \((r=0)\). In a way it is analogous to the effect of the centrifugal force.

Remember that the normalization condition for \( R(r) \) was

\[
\int_0^\infty |R(r)|^2 r^2 dr = 1
\]

For \( u(r) \) it becomes

\[
\int_0^\infty |u(r)|^2 dr = 1
\]

Now let us use the explicit form of \( V(r) \) that corresponds to two interacting Coulomb particles with charges \(-e\) (electron) and \(+Ze\) (proton):

\[
V(r) = -\frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}
\]

With that we have

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

In fact in this equation should actually be replaced by \( m = \frac{m_e m_p}{m_e + m_p} \) — the reduced mass of an electron (rather than just the mass of the electron).

This can be seen if we consider a system of two particles with coordinates \( \vec{r}_e \) and \( \vec{r}_p \). This system of two particles is reduced to a system of just one particle of reduced mass \( \tilde{m} \).
Let us now introduce the notation \( x = \sqrt{\frac{-2mE}{\hbar}} \) where \( E \) is negative (we consider the bound states only). Then

\[
\frac{1}{x^2} \frac{d^2u}{dx^2} = \left[ 1 - \frac{mZe^2}{2\pi\varepsilon_0 \hbar^2 x} \frac{1}{x} + \frac{\ell(\ell+1)}{(x\pi)^2} \right] u
\]

As always we want to work in "natural" units. The substitution

\[
p = x\pi \quad p_0 = \frac{me^2Z}{2\pi\varepsilon_0 \hbar^2 x}
\]

reduces the above equation to

\[
\frac{d^2u}{dp^2} = \left[ 1 - \frac{p_0}{p} + \frac{\ell(\ell+1)}{p^2} \right] u
\]

Now we will apply the power series method, which we already used when solving the SE for quantum harmonic oscillator.

When \( p \to \infty \), our equation becomes

\[
\frac{d^2u}{dp^2} = u
\]

whose solution is \( Ae^{-p} + Be^{p} \). Since we are concerned with square integrable solutions, only the \( e^{p} \) term makes sense. Thus \( u(p) \sim Ae^{-p} \), \( p \to \infty \)

At small \( p \), the centrifugal term dominates

\[
\frac{d^2u}{dp^2} = \frac{\ell(\ell+1)}{p^2} u
\]

The general solution is \( Cp^{\ell+1} + Dp^{-\ell} \). Again, we require square integrability, and hence \( \ell = 0 \)

\[
u(p) \sim Cp^{\ell+1}
\]
Now we make a substitution

\[ u(p) = p^e e^{-p} v(p) \]

\[ \frac{du}{dp} = p^e e^{-p} \left[ (e+1-p) v + p \frac{dv}{dp} \right] \]

\[ \frac{d^2 u}{dp^2} = p^e e^{-p} \left\{ [-2e-2+p + \frac{e(e+1)}{p}] v + 2(e+1-p) \frac{dv}{dp} + p \frac{d^2 v}{dp^2} \right\} \]

and obtain the following equation for \( v(p) \)

\[ p \frac{d^2 v}{dp^2} + 2(e+1-p) \frac{dv}{dp} + \left[ p_0 - 2(e+1) \right] v = 0 \]

Assuming the solution as a power series

\[ v(p) = \sum_{j=0}^{\infty} c_j p^j \]

\[ \frac{dv}{dp} = \sum_{j=0}^{\infty} j c_j p^{j-1} = \sum_{i=0}^{\infty} (i+1) c_{i+1} p^i \]

\[ \frac{d^2 v}{dp^2} = \sum_{i=0}^{\infty} j(j+1) c_{j+1} p^{j-1} \]

Plugging it into the equation yields

\[ \sum_{j=0}^{\infty} j(j+1) c_{j+1} p^j + 2(e+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} p^j - 2 \sum_{j=0}^{\infty} j c_j p^j + \left[ p_0 - 2(e+1) \right] \sum_{j=0}^{\infty} c_j p^j = 0 \]

or

\[ j(j+1) c_{j+1} + 2(e+1)(j+1) c_{j+1} - 2 j c_j + [p_0 - 2(e+1)] c_j = 0 \]

or

\[ c_{j+1} = \frac{2(j+e+1) - p_0}{(j+1)(j+2e+2)} c_j \]

Consider the case when \( j \to \infty \)

\[ c_{j+1} \approx \frac{\frac{2j}{j(j+1)}}{c_j} = \frac{2}{j+1} c_j \implies c_j = \frac{2}{j!} c_0 \]
\[ u(p) = C_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} p^j = C_0 e^{2p} \]

This gives \( u(p) = C_0 e^{2p} \) blows up at large \( p \).

Such a solution is not physically meaningful. So we must require that the series is finite (a polynomial)

\[ C_{j_{max}} = 0 \]

\[ 2(j_{max} + l + 1) p_0 = 0 \]

Let us now define \( h = j_{max} + l + 1 \). Then

\[ p_0 = 2h \]

\[ E = -\frac{t^2 x^2}{2m} = -\frac{me^4 Z^2}{8\pi^2 \hbar^2 c^2 h^2 p_0^2} \]

The allowed energies are

\[ E_n = -\left[ \frac{\hbar}{2m} \left( \frac{Ze^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{h^2} \quad h = 1, 2, 3, \ldots \]

In the literature they often introduce the natural length scale - Bohr radius: \( a_0 = \frac{\hbar^2}{4\pi Ze^2} \)

(in Gaussian units \( a_0 = \frac{\hbar}{Ze} \)). Then

\[ \chi = \frac{mZe^2}{4\pi \hbar^2} \frac{1}{h} = \frac{Z}{a_0 h} \]

\[ p = \chi r = \frac{Ze}{a_0 h} \]

The hydrogen-like atom wave functions are defined by three quantum numbers

- \( h \), \( l \), and \( m \)

\( h \) is called the principal quantum number
\( l \) is called the azimuthal quantum number
\( m \) is called the magnetic quantum number

Sometimes, in order to emphasize the number of radial nodes, the radial quantum number is used: 
\[ n = \ell + l + 1 \]

When we combine the radial component of the wave function and the angular one we get

\[ \Psi_{\text{new}}(r, \theta, \phi) = R_{n\ell\mu}(r) Y_{\ell}^{m}(\theta, \phi) \]

where 
\[ R_{n\ell\mu}(r) = \frac{A_{n\ell\mu}}{r} e^{-\rho} \Phi_{\ell}(\rho) \]

\( A_{n\ell\mu} \) is the normalization factor.

The coefficients of the polynomial \( \Phi_{\ell}(\rho) \) are determined by the formula
\[ c_{j+1} = \frac{2((j+1)\ell + 1 - n)}{(j+1)(j+2\ell+2)} c_{j} \]

In mathematics, such polynomials are known as the associated Laguerre polynomials
\[ \Phi_{\ell}(\rho) = L_{n\ell-1}^{2\ell+1}(2\rho) \]

\[ L_{n\ell}^{\ell}(x) = (-1)^{\ell} \left( \frac{d}{dx} \right)^{\ell} L_{n}(x) \]

\[ L_{n}(x) = e^{x} \left( \frac{d}{dx} \right)^{n} (e^{-x} x^{n}) \]

Few first few associated Laguerre polynomials

\[ L_{0}^{0} = 1 \quad L_{1}^{0} = 1 - x \quad L_{2}^{0} = 2 - 4x + x^2 \]

\[ L_{0}^{2} = 2 \quad L_{1}^{2} = 18 - 6x \quad L_{2}^{2} = 144 - 96x + 12x^2 \]

\[ L_{0}^{1} = 1 \quad L_{1}^{1} = 4 - 2x \quad L_{2}^{1} = 18 - 18x + 3x^2 \]
The ground state energy and wave function are:

\[ E_1 = - \left[ \frac{\mu}{2\hbar^2} \left( \frac{Ze^2}{4\pi\varepsilon_0} \right)^2 \right] = -\frac{1}{2} \text{ Hartree} = -13.6 \text{ eV} \]

\[ \psi_{100}(r, \theta, \phi) = R_{10}(r) Y_{00}^0(\theta, \phi) = \frac{Z}{\sqrt{\pi a_0^3}} e^{-\frac{Zr}{a_0}} \]

For \( n = 2 \)

\[ R_{20}(r) = \frac{Z^{\frac{3}{2}}}{a_0} \left( 1 - \frac{2r}{a_0} \right) e^{-\frac{Zr}{2a_0}} \]

\[ R_{21}(r) = \frac{1}{2} \frac{Z^{\frac{1}{2}}}{a_0} \frac{Zr}{2a_0} e^{-\frac{Zr}{2a_0}} \]