The hydrogen-like atom

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

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

are spherical harmonics $Y_\ell^m(\theta,\varphi)$ – complex functions that have two indices (quantum numbers): ℓ and m.

Now we turn to the radial part of the Schrödinger equation

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

It is convenient to make a substitution

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

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

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

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

$$V_{eff}(r) = V(r) + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}$$

This effective potential contains an extra repulsive term $\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}$. It effectively "pushes" the particle away from the center $(r=0)$. In a way it is analoguous 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

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

In fact m in this equation should actually be replaced by $\mu = \frac{m_e m_p}{m_e + m_p}$ – 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 μ.

Let us now introduce the notation $\varkappa = \frac{\sqrt{-2mE}}{\hbar}$ where E is negative (we consider the bound states only). Then

$$\frac{1}{\varkappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{mZe^2}{2\pi\epsilon_0\hbar^2\varkappa}\frac{1}{\varkappa r} + \frac{l(l+1)}{(\varkappa r)^2}\right]u$$

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

$$\rho = \varkappa r \qquad \rho_0 = \frac{me^2Z}{2\pi\epsilon_0\hbar^2\varkappa}$$

reduces the above equation to

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u$$

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

When $\rho \to \infty$ our equation becomes

$$\frac{d^2u}{d\rho^2} = u$$

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

At small ρ the centrifugal term dominates

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

The general solution is $C\rho^{l+1} + D\rho^{-l}$. Again, we require square integrability and hence $D = 0$

$$u(\rho) \underset{\rho\to 0}{\sim} C\rho^{l+1}$$

Now we make a substitution

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho)$$

$$\frac{du}{d\rho} = \rho^{\ell} e^{-\rho} \left[(\ell+1-\rho) v + \rho \frac{dv}{d\rho} \right]$$

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

and obtain the following equation for $v(\rho)$

$$\rho \frac{d^2v}{d\rho^2} + 2(\ell+1-\rho) \frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)] v = 0$$

Assuming the solution as a power series

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{i=0}^{\infty} (i+1) c_{i+1} \rho^i$$

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$$

Plugging it into the equation yields

$$\sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^j + 2(\ell+1) \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j - 2 \sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(\ell+1)] \sum_{j=0}^{\infty} c_j \rho^j = 0$$

or

$$j(j+1) c_{j+1} + 2(\ell+1)(j+1) c_{j+1} - 2j c_j + [\rho_0 - 2(\ell+1)] c_j = 0$$

or

$$c_{j+1} = \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)} c_j$$

Consider the case when $j \to \infty$:

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j \Rightarrow c_j = \frac{2^j}{j!} c_0$$

$$v(\rho) = C_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = C_0 e^{2\rho}$$

This gives $u(\rho) = C_0 \rho^{l+1} e^{\rho}$ ← blows up at large ρ.

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

$$C_{j_{max}+1} = 0$$

$$2(j_{max} + l + 1) - \rho_0 = 0$$

Let us now define $n \equiv j_{max} + l + 1$. Then

$$\rho_0 = 2n$$

$$E = -\frac{\hbar^2 \varkappa^2}{2m} = -\frac{me^4 Z^2}{8\pi^2 \epsilon_0^2 \hbar^2 \rho_0^2}$$

The allowed energies are

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

In the literature they often introduce the natural length scale – Bohr radius : $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$ (in Gaussian units $a_0 = \frac{\hbar^2}{me^2}$). Then $\varkappa = \frac{mZe^2}{4\pi\epsilon_0 \hbar^2}\frac{1}{n} = \frac{Z}{a_0 n}$

$$\rho = \varkappa r = \frac{Zr}{a_0 n}$$

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

n, l, and m

n is called the principal quantum number

l is called the azimuthal quantum number

m is called the magnetic quantum number.

Sometimes, in order to empasize the number of radial nodes the radial quantum number is used:

$$n = n_r + l + 1$$

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

$$\Psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi)$$

where $R_{nl}(r) = \frac{A_{nl}}{r} \rho^{l+1} e^{-\rho} v(\rho)$ $\quad$ A_{nl} is the normalization factor

The coefficients of the polynomial v are determined by the formula

$$c_{j+1} = \frac{2(j+l+1-n)}{(j+1)(j+2l+2)} c_j$$

In mathematics such polynomials are known as the associated Laguerre polynomials

$$v(\rho) = L_{n-l-1}^{2l+1}(2\rho)$$

$$L_{q-p}^{p}(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \quad ; \quad L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$$

Few first few associated Laguerre polynomials

$L_0^0 = 1$ $\qquad$ $L_1^0 = 1 - x$ $\qquad$ $L_2^0 = 2 - 4x + x^2$

$L_0^2 = 2$ $\qquad$ $L_1^2 = 18 - 6x$ $\qquad$ $L_2^2 = 144 - 96x + 12x^2$

$L_0^1 = 1$ $\qquad$ $L_1^1 = 4 - 2x$ $\qquad$ $L_2^1 = 18 - 18x + 3x^2$

The ground state energy and wave function are :

$$E_1 = -\left[\frac{m}{2\hbar^2}\left(\frac{Ze^2}{4\pi\epsilon_0}\right)^2\right] = -\frac{1}{2}\text{ Hartree} = -13.6\text{ eV}$$

$$\psi_{100}(r,\theta,\phi) = R_{10}(r)\,Y_0^0(\theta,\phi) = \sqrt{\frac{Z}{\pi a_0^3}}\;e^{-\frac{Zr}{a_0}}$$

For $n=2$

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

$$R_{21}(r) = \frac{1}{2a_0^{5/2}}\,Z^{5/2}r\,e^{-\frac{Zr}{2a_0}}$$