

The hydrogen-like atom

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

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

are spherical harmonics $Y_l^m(\theta, \phi)$ — complex functions that have two indices (quantum numbers): l and m .

Now we turn to the radial part of the Schrödinger equation

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

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:

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

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

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

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 analogous to 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

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

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 (we will leave this derivation for recitations)

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

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

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

$$\rho = \kappa r \quad \rho_0 = \frac{mZe^2}{2\pi\epsilon_0 \hbar^2 \kappa}$$

reduces the above equation to

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

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

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

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

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

At small ρ the centrifugal term dominates

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

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

$$u(\rho) \underset{\rho \rightarrow 0}{\sim} C\rho^{\ell+1}$$

Now we make a substitution

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

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

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

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

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

Assuming the solution as a power series

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

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

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

Plugging it into the equation yields

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

or

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

or

$$c_{j+1} = \frac{2(j+\ell+1) - p_0}{(j+1)(j+2\ell+2)} c_j$$

Consider the case when $j \rightarrow \infty$

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

$$v(p) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} p^j = c_0 e^{2p}$$

This gives $u(p) = c_0 p^{l+1} e^p \leftarrow$ blows up at large p .

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

$$c_{j_{\max}+1} = 0$$

$$2(j_{\max} + l + 1) - p_0 = 0$$

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

$$p_0 = 2n$$

$$E = -\frac{t^2 x^2}{2m} = -\frac{m e^4 z^2}{8\pi^2 \epsilon_0^2 t^2 p_0^2}$$

The allowed energies are

$$E_n = -\left[\frac{m}{2t^2} \left(\frac{ze}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} \quad n = 1, 2, 3, \dots$$

In the literature they often introduce the natural length scale - Bohr radius: $a_0 = \frac{4\pi\epsilon_0 t^2}{me^2}$
 (in Gaussian units $a_0 = \frac{t^2}{me^2}$) Then $x = \frac{mze^2}{4\pi\epsilon_0 t^2} \frac{1}{n} = \frac{Z}{a_0 n}$

$$p = \dots = x r = \frac{Zr}{a_0 n}$$

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 emphasize 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

$$\Psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell}^m(\theta, \phi)$$

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

The coefficients of the polynomial v are determined by the formula

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

In mathematics such polynomials are known as the ^{associated} Laguerre polynomials

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

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

Few first 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 :

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

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

For $n=2$

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

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