

# 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

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

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

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

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  $\mu$  (we will leave this derivation for recitation)

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

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

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

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

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  $\rho$  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

$$p_0 = 2n$$

$$E = -\frac{\hbar^2 x^2}{2m} = -\frac{me^4 Z^2}{8\pi^2 \epsilon_0^2 \hbar^2 p_0^2}$$

The allowed energies are

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

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

$$p = xr = \frac{Zr}{a_0 n}$$

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

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

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 <sup>associated</sup>  $\sqrt{\phantom{x}}$  Laguerre polynomials

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

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

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:

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

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

For  $n=2$

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

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