

## Hydrogen Atom

The time independent Schrödinger's equation for the Hydrogen atom is:

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 |\underline{r}|} \right] \Psi(\underline{r}) = E \Psi(\underline{r})$$

where  $\mu$  is the reduced mass:  $\mu = \frac{m_e m_p}{m_e + m_p}$

If we use this equation, we are assuming protons are point-like particles and the equation is non-relativistic. This actually leads to small errors we will study later in this module.

We will assume that  $\Psi(\underline{r}) \rightarrow 0$  as  $r \rightarrow \infty$  and that the wavefunction is single valued.

Note that the potential in the equation is the electrostatic Coulomb potential, so it is spherically symmetric.

The Laplace operator  $\nabla^2$  is defined as:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

$$\Rightarrow \nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} \hat{L}^2$$

where we have used the total orbital angular momentum operator.

Notice then that the orbital and angular derivatives are in separate terms, implying we can introduce a separation of variables:

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

With this separation of variables, we can substitute the expanded Laplacian into the Schrödinger equation:

$$\frac{-\hbar^2}{2\mu} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{1}{\hbar^2 r^2} \hat{L}^2 \right\} R(r) Y(\theta, \varphi) - \frac{e^2}{4\pi\epsilon_0 |r|} R(r) Y(\theta, \varphi) = E R(r) Y(\theta, \varphi)$$

$$\Rightarrow -\frac{\hbar^2}{2\mu} Y(\theta, \varphi) \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{2\mu r^2} R(r) \hat{L}^2 Y(\theta, \varphi) - \frac{e^2}{4\pi\epsilon_0 |r|} R(r) Y(\theta, \varphi) = E R Y$$

$$-\frac{\hbar^2}{2\mu} \frac{1}{R(r)} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{2\mu r^2} \frac{1}{Y(\theta, \varphi)} \hat{L}^2 Y(\theta, \varphi) - \frac{e^2}{4\pi\epsilon_0 |r|} = E$$

$$-\frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{1}{\hbar^2} \frac{1}{Y} \hat{L}^2 Y - \frac{2\mu e^2 r}{4\pi\epsilon_0 \hbar^2} = \frac{2\mu E}{\hbar^2} r^2$$

$$\Rightarrow \frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu E}{\hbar^2} r^2 + \frac{2\mu e^2 r}{4\pi\epsilon_0 \hbar^2} = \frac{1}{\hbar^2} \frac{1}{Y} \hat{L}^2 Y$$

Notice now the left side only depends on  $r$  and right side only on  $\theta, \varphi$

In fact, we already know the solution for the right side from the angular momentum section:

$$\hat{L}^2 Y = \hbar^2 L(L+1) Y$$

The eigenfunctions  $Y$  are the spherical harmonics and are denoted with quantum numbers  $L$  (total orbital ang. mom.) and  $M$  (magnetic quantum number).  $-L \leq M \leq L$

These spherical harmonics were written out before but can also be written:

$$Y_{L,M}(\theta, \varphi) = a_{L,M} P_L^M(\cos\theta) e^{im\varphi}$$

$P_L^M$  are called associated Legendre polynomials.

so if  $\hat{L}^2 \psi = \hbar^2 L(L+1) \psi$

then  $\frac{1}{\hbar^2} \frac{1}{\psi} \hat{L}^2 \psi = L(L+1)$

$$\Rightarrow \frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu E}{\hbar^2} r^2 + \frac{2\mu e^2 r}{4\pi\epsilon_0 \hbar^2} = L(L+1)$$

$$\frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) R + \frac{1}{R} \frac{2\mu E}{\hbar^2} r^2 R + \frac{1}{R} \frac{2\mu e^2 r}{4\pi\epsilon_0 \hbar^2} R = L(L+1)$$

$$\Rightarrow \frac{1}{R} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu E}{\hbar^2} r^2 + \frac{2\mu e^2 r}{4\pi\epsilon_0 \hbar^2} \right] R = L(L+1)$$

$$\left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{2\mu e^2 r}{4\pi\epsilon_0 \hbar^2} - L(L+1) \right] R = -\frac{2\mu E}{\hbar^2} r^2 R$$

$$\left[ \underbrace{-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right)}_{\text{radial term}} - \underbrace{\frac{e^2}{4\pi\epsilon_0 |c|}}_{\text{electrostatic potential}} + \underbrace{\frac{\hbar^2 L(L+1)}{2\mu}}_{?} \right] R = E R$$

This is an eigenvalue problem that we are quite familiar with. It is the SE but we seem to have an extra term. What is it? It is a repulsive potential. This is in fact, the centrifugal term we saw last year in Classical Mechanics.

if we expand the derivatives and multiply through by  $-\frac{2\mu}{\hbar^2}$  :

$$\left[ \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} + \frac{2}{a_0} - \frac{L(L+1)}{r^2} \right] R = -\frac{2\mu E}{\hbar^2} R \quad (*)$$

for large  $r$ :  $\frac{d^2 R}{dr^2} \approx -\frac{2\mu E}{\hbar^2} R$

where  $a_0$  is bohr radius  $a_0 = \frac{4\pi \hbar^2 \epsilon_0}{\mu e^2}$

which we will explain later.

$$\text{so } \frac{d^2 R}{dr^2} = -\frac{2\mu E}{\hbar^2} R$$

if  $E > 0$ , this is simple harmonic motion and we will have oscillatory solutions (corresponding to unbound states). If it is negative, we will have bound state solutions.

$$\text{Let's define } a = \sqrt{\frac{\hbar^2}{-2\mu E}} \quad \text{so } \frac{d^2 R}{dr^2} = \frac{1}{a^2} R$$

we thus have solutions  $R \sim \exp(\pm \frac{r}{a})$

we choose  $R \sim e^{-r/a}$  since the +ve would give un-normalisable solutions.

$$\Rightarrow R = e^{-r/a} u(r) \quad \text{this is to correct for our large } r \text{ dependence.}$$

Substituting  $R$  back into (\*):

$$\frac{d^2 u}{dr^2} + \frac{2}{r} \frac{du}{dr} - \frac{L(L+1)}{r^2} u = 2 \left( \frac{1}{a} - \frac{1}{a_0} \right) \frac{u}{r} + \frac{2}{a} \frac{du}{dr} \quad (**)$$

This is quite tricky to solve, so let's make use of a power series:

$$u = \sum_{s=s_0}^{\infty} C_s r^s = r^{s_0} + C_{s_0+1} r^{s_0+1} + C_{s_0+2} r^{s_0+2} + \dots$$

where we choose  $s_0 = 1$  so  $u = r + C_2 r^2 + C_3 r^3 + \dots$

we could have similarly used  $u = \sum_{s=s_0}^{\infty} C_{s-1} r^{s-1}$

If we substitute  $\sum C_{s-1} r^{s-1}$  into the right hand side of (\*\*) and

$\sum C_s r^s$  into the left hand side of (\*\*), after some rearrangement:

$$[S(S+1) - L(L+1)] C_S = 2 \left( \frac{S}{a} - \frac{1}{a_0} \right) C_{S-1}$$

This is the recurrence relation.

if we consider  $s = s_0$ ,  $C_{s_0-1}$  cannot exist since  $s_0$  is the lowest. So:

$$[s_0^2 + s_0 - L(L+1)] C_{s_0} = 0 \Rightarrow s_0^2 + s_0 - L - L^2 = 0$$

$$\Rightarrow (s_0 - L)(s_0 - (-L-1)) = 0 \quad \therefore s_0 = L \quad \text{or} \quad s_0 = -L-1$$

but we can't use the 2nd solution since then the wavefunction diverges at  $r=0$ . So we know  $s_0 = L$



we can put  $S_0 = L$  back into the recurrence relation.

we can now compute higher order coefficients.

we find:

$$c_s \sim \frac{2}{s a} c_{s-1} \sim \frac{2^2}{s(s-1)a^2} c_{s-2} \sim \dots \sim \frac{1}{s!} \left(\frac{2}{a}\right)^s$$

$$\text{For large } r \quad u(r) \sim \sum_s r^s \frac{1}{s!} \left(\frac{2}{a}\right)^s = e^{2r/a}$$

but we previously said  $R(r) = e^{-r/a} u(r)$

if  $u(r) = e^{2r/a}$   $R(r) = e^{r/a}$  which we said gives us unnormalisable solutions. So this is a problem ...

But there is a fix!

$$[s(s+1) - L(L+1)] c_s = 2\left(\frac{s}{a} - \frac{1}{a_0}\right) c_{s-1}$$

The recurrence relation

If the RHS of this vanishes for some  $s = n \geq S_0 + 1 = L + 1$ , then all coefficients  $c_{s \geq n}$  will vanish, letting  $u(r)$  be a polynomial. This actually happens when  $a = n a_0$

making use of  $a = \sqrt{\frac{\hbar^2}{-2\mu E}}$ , this means

$$\sqrt{\frac{\hbar^2}{-2\mu E}} = n a_0 \Rightarrow$$

$$E = -\frac{\hbar^2}{2\mu a_0^2 n^2}$$

This is very important!

Together with the constraint  $L \leq n-1$ , we get

$$R_{n,L}(r) = e^{-r/na_0} \sum_{s=L}^{n-1} c_s r^s$$

so some examples are:

$$R_{1,0} = 2(a_0)^{-3/2} \exp(-r/a_0)$$

$$R_{2,0} = 2(2a_0)^{-3/2} (1 - r/2a_0) \exp(-r/2a_0)$$

where the subscript  $n$  is the principle quantum number and  $l$  is the total angular momentum number.

The bohr radius  $a_0 = \frac{4\pi\hbar^2\epsilon_0}{\mu e^2} \approx 5.3 \times 10^{-11} \text{ m}$

We can extract some properties from the quantum numbers:

- 1) orbitals with larger  $n$  extend further from nucleus
- 2) the probability density for finding the electron at the nucleus tends to 0 in all cases
- 3) The wavefunction tends to 0 for all cases except the  $L=0$  wavefunctions.
- 4) There are  $n-L-1$  "nodes" at  $r > 0$  in the radial wave fn. Nodes being points where probability density = 0 on a probability density against  $r$  plot.

The energy associated with these wavefunctions was found to be

$$E_n = \frac{-\hbar^2}{2\mu a_0^2 n^2} \quad \text{which we can also write as:}$$

$$E_n = -\frac{1}{4} \frac{2\mu}{\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{1}{n^2} \approx \frac{13.6}{n^2} \text{ eV}$$

we can also write it as:

$$E_n = \frac{-\alpha^2 \mu c^2}{2n^2}$$

$$\text{where } \alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}$$

$\alpha$  is called the fine structure constant which we will see later.

## Comparison with Experiments

Emission spectra from atomic hydrogen can be grouped into a number of series. The frequency of the lines could be predicted using Rydberg's formula:

$$\nu = \frac{E_1}{h} \left( \frac{1}{q^2} - \frac{1}{p^2} \right) = R \left( \frac{1}{q^2} - \frac{1}{p^2} \right)$$

where  $R$  is the Rydberg constant  $R = 3.288 \times 10^{15} \text{ Hz}$

and  $p$  and  $q$  are the energy levels the electron in the hydrogen atom moves between.

It actually turns out some of the lines predicted by the Rydberg formula are observed to be multiple lines, very close together. This is due to the fine structure of the hydrogen atom, something we will study later.