

# THE HYDROGEN ATOM

VINOD G, SREE SANKARA COLLEGE, KALADY

May 6, 2020



# Chapter 1

## MOTION IN A CENTRAL POTENTIAL

### 1.1 Behaviour of the Radial Wave Function Near The Origin

The Hamiltonian of a two-body system with a potential energy of interaction that depends only on the magnitude of the distance separating the two bodies can be written as

$$H = \frac{\vec{p}^2}{2\mu} + V(|\vec{r}|) \quad (1.1)$$

where  $\mu$  is the reduced mass of the two-body system and  $\vec{r}$  is the relative coordinate of the system (difference between the position coordinates of the two particles). It can be shown that this Hamiltonian commutes with the angular momentum operators  $L_x, L_y$  and  $L_z$ . Since angular momentum is the generator of rotation, it follows that this system is invariant under rotations about any axis. Further, since the Hamiltonian commutes with the angular momentum operators, angular momentum is conserved. Thus rotational symmetry leads to conservation of angular momentum.

The angular momentum operators satisfy the commutation relation

$$[L_i, L_j] = i\hbar \varepsilon_{ijk} L_k \quad (1.2)$$

where  $i, j, k$  take on the values from 1 to 3 and  $\varepsilon_{ijk}$  is the Levi-Civita tensor (totally anti-symmetric tensor). Since the generators of rotations about

different axes do not commute with each other, we can not choose more than one of them to simultaneously label the eigenstates of the Hamiltonian. However, since each of the generators as well as the Hamiltonian commute with

$$\vec{L}^2 = L_x^2 + L_y^2 + L_z^2 \quad (1.3)$$

we can form simultaneous eigenstates of  $H, \vec{L}^2$ , and one of the components of the angular momentum, which is generally taken to be  $L_z$ . We then label these eigenstates by  $|E, l, m\rangle$ , where

$$H |E, l, m\rangle = E |E, l, m\rangle \quad (1.4)$$

$$\vec{L}^2 |E, l, m\rangle = l(l+1)\hbar^2 |E, l, m\rangle \quad (1.5)$$

$$L_z |E, l, m\rangle = m\hbar |E, l, m\rangle \quad (1.6)$$

If we use the position space representation of the operators  $\vec{p}^2$  and  $\vec{L}^2$  expressed in spherical polar coordinate system, the energy eigenvalue equation can be written as

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right] \langle \vec{r} | E, l, m \rangle = E \langle \vec{r} | E, l, m \rangle \quad (1.7)$$

If we express the wave function in the form

$$\langle \vec{r} | E, l, m \rangle = R(r)\Theta(\theta)\Phi(\phi) \quad (1.8)$$

The position space representation of the angular momentum operators depend only on the angles  $\theta$  and  $\phi$ , and not at all on the magnitude of the position vector. Rotating a position eigenstate changes its direction but not its length. Thus we can isolate the angular dependence and determine  $\langle \theta, \phi | l, m \rangle$ , which is the amplitude for a state of definite angular momentum to be at the angles  $\theta$  and  $\phi$ . These amplitudes, which are functions of the angles, are called spherical harmonics.

$$\langle \theta, \phi | l, m \rangle = Y_{l,m}(\theta, \phi) \quad (1.9)$$

Since the system possesses rotational symmetry, the angular part of the energy eigenfunction is written as

$$\Theta(\theta)\Phi(\phi) = Y_{l,m}(\theta, \phi) \quad (1.10)$$

### 1.1. BEHAVIOUR OF THE RADIAL WAVE FUNCTION NEAR THE ORIGIN 5

Thus, for a spherically symmetric potential, the energy eigen functions can be written as :

$$\langle \vec{r} | E, l, m \rangle = R_{E,l}(\vec{r}) Y_{l,m}(\theta, \phi) \quad (1.11)$$

Substituting this expression in equation (7), we get the Schrödinger equation for the radial wave function as

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right] R_{E,l}(r) = E R_{E,l}(r) \quad (1.12)$$

The subscripts have been inserted to indicate explicitly that the radial wave function depends on the values of  $E$  and  $l$ .

Put

$$R_{E,l}(r) = \frac{u_{E,l}(r)}{r} \quad (1.13)$$

The radial equation becomes

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right] u_{E,l}(r) = E u_{E,l}(r) \quad (1.14)$$

The normalisation of the eigen function reads:

$$\begin{aligned} \int |\langle r, \theta, \phi | E, l, m \rangle|^2 d\tau &= 1 \\ \text{i.e., } \int_0^\infty \int_0^\pi \int_0^{2\pi} |R_{E,l}(r)|^2 |Y_{lm}(\theta, \phi)|^2 r^2 \sin \theta dr d\theta d\phi &= 1 \end{aligned} \quad (1.15)$$

If we normalise the radial function separately,

$$\int_0^\infty |R_{E,l}(r)|^2 r^2 dr = \int_0^\infty |u_{E,l}(r)|^2 dr = 1 \quad (1.16)$$

Equation (14) has the same form as the one-dimensional Schrödinger equation except that the variable  $r$  runs from 0 to  $\infty$  instead of from  $-\infty$  to  $+\infty$ . Thus it is important to study the behaviour of the eigen function near the origin.

If the potential energy  $V(r)$  is not more singular than  $\frac{1}{r^2}$ , we get  $\lim_{r \rightarrow 0} r^2 V(r) = 0$ , then equation (7) has a regular singularity at  $r = 0$ . Then there can be

power series solutions for  $u_{E,l}(r)$ . Substituting  $u_{E,l}(r) = r^s$  in equation(14), we get

$$-\frac{\hbar^2}{2\mu}s(s-1)r^{s-2} + \frac{l(l+1)\hbar^2}{2\mu}r^{s-2} + V(r)r^s = Er^s \quad (1.17)$$

It is evident that if  $V(r)$  is less singular than  $\frac{1}{r^2}$ , that is, if

$$\lim_{r \rightarrow 0} r^2 V(r) = 0 \quad (1.18)$$

then the  $r^{s-2}$  term dominates for small  $r$ . In equation 9), the coefficient of each power of  $r$  should separately vanish. Equating the coefficients of  $r^{s-2}$  to zero, we get

$$-s(s-1) + l(l+1) = 0 \quad (1.19)$$

which means that either  $s = l + 1$  or  $s = -l$ .

We have to discard the solutions that behaves as  $r^{-l}$  for small  $l$ . For  $l \geq 1$ ,  $|u_{E,l}(r)|^2$  diverges at  $r = 0$  and hence the normalisation condition can not be satisfied. For  $l = 0$ , the leading behaviour of  $u$  for small  $r$  is a constant and the normalisation integral is finite. But if the leading term is constant, the wave function  $R_{E,l}(r)$  behaves as  $\frac{1}{r}$  near the origin, which is also unacceptable. The three-dimensional Schrödinger equation contains the operator  $\nabla^2$  and if  $R_{E,l}(r)$  behaves as  $\frac{1}{r}$  near the origin, the eigenvalue equation will involve a term proportional to  $\nabla^2 \left(\frac{1}{r}\right)$ . To get an idea of  $\nabla^2 \left(\frac{1}{r}\right)$ , consider the Poisson's equation in electrodynamics:  $\nabla^2 V(\vec{r}) = -\frac{\rho}{\epsilon_0}$ . For a point charge located at the origin,  $\rho(r) = q\delta^3(\vec{r})$  and the potential at a point with position vector  $\vec{r}$  is  $V(\vec{r}) = \frac{1}{4\pi\epsilon_0} \frac{q}{r}$ . Substituting these in the Poisson's equation,  $\nabla^2 \left(\frac{1}{r}\right) = -4\pi\delta^3(\vec{r})$ . Since we are presuming that the potential energy does not have a delta function singularity at the origin, we can not accept a  $\frac{1}{r}$  behaviour for  $R$ . Thus we see that  $r^{-l}$  is not acceptable for both  $l = 0$  and  $l \geq 1$ . Hence we discard the  $r^{-l}$  solutions for all  $l$ . Thus we are left with only the possibility  $s = l + 1$  for the power of  $r$ . That is,

$$\lim_{r \rightarrow 0} u_{E,l}(r) = r^{l+1} \quad (1.20)$$

Hence  $u_{E,l}(r)$  must satisfy

$$u_{E,l}(0) = 0 \quad (1.21)$$

### 1.1. BEHAVIOUR OF THE RADIAL WAVE FUNCTION NEAR THE ORIGIN

The radial probability density is  $|u_{E,l}(r)|^2 = r^{2(l+1)}$  for small  $r$ . Hence, as  $l$  increases, the system is less and less probable in the vicinity of the origin. The physical origin of this behaviour is the presence of the centrifugal barrier  $\frac{l(l+1)\hbar^2}{2\mu r^2}$  in equation(14), which tends to keep the particle away from the origin.

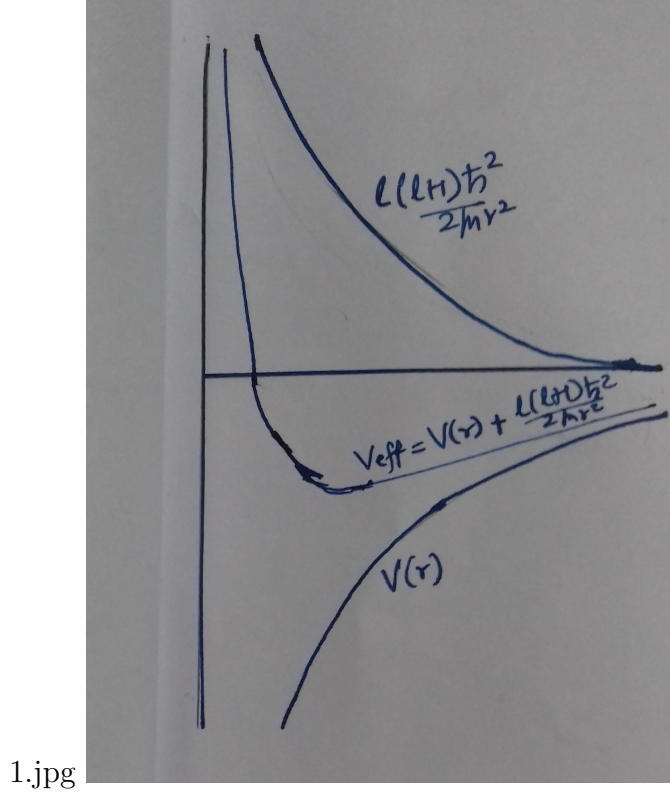


Figure 1.1: The Coulomb potential  $V(r) = -\frac{e^2}{r}$  and the centrifugal barrier  $\frac{l(l+1)\hbar^2}{2\mu r^2}$  add together to produce the effective potential

The behaviour of  $u_{E,l}(r)$  given by eqn(20 ) indicates that, the radial wave function behaves as

$$\lim_{r \rightarrow 0} R_{E,l}(r) = r^l \quad (1.22)$$

Thus, these wave functions vanish at the origin for all except  $l = 0$ . In other words, for a spherically symmetrical potential, only  $s$ -states exist at the ori-

gin. An example is given by the annihilation of positronium, which is a hydrogen like atom where the nucleus is a positron instead of proton. Positronium is formed by the capture of a positron by an electron in an excited state. This atom will then make a sequence of radiative transitions to finally reach the  $l = 0$  state where the annihilation of the electron-positron pair takes place.



# Chapter 2

## THE HYDROGEN ATOM

### 2.1 Energy Eigenvalues

Consider a hydrogenic atom which is composed of a nucleus of charge  $Ze$  and an orbiting electron. A hydrogenic atom may be an ionised atom with only a single electron left. In addition to the ordinary hydrogen atom,  $He^+, Li^{++}, etc.$  belong to this class. Usual hydrogen atom is a special case where  $Z = 1$ . The Hamiltonian for a hydrogen atom can be written in the Gaussian system of units as

$$H = \frac{\vec{p}^2}{2\mu} - \frac{Ze^2}{|\vec{r}|} \quad (2.1)$$

where  $\mu$  is the reduced mass of the nucleus-electron system and  $\vec{r}$  is the relative position coordinate of the system (difference between the position coordinates of the two bodies). The Coulomb interaction depends only on the distance between the two bodies involved and hence the system possesses spherical symmetry. The Hamiltonian is invariant under rotation and since the angular momentum is the generator of rotation, we can conclude that the angular momentum operators commute with the Hamiltonian. This means the angular momentum is conserved. Since the components of the angular momentum operator do not commute with each other, we can not choose more than one of them to simultaneously label the eigenstates of the Hamiltonian. However, since each of the generators as well as the Hamiltonian commute with

$$\vec{L}^2 = L_x^2 + L_y^2 + L_z^2 \quad (2.2)$$

we can form simultaneous eigenstates of  $H, \vec{L}^2$ , and one of the components of the angular momentum, which is generally taken to be  $L_z$ . We then label these eigenstates by  $|E, l, m\rangle$ , where

$$H |E, l, m\rangle = E |E, l, m\rangle \quad (2.3)$$

$$\vec{L}^2 |E, l, m\rangle = l(l+1)\hbar^2 |E, l, m\rangle \quad (2.4)$$

$$L_z |E, l, m\rangle = m\hbar |E, l, m\rangle \quad (2.5)$$

If we use the position space representation of the operators  $\vec{p}^2$  and  $\vec{L}^2$  expressed in spherical polar coordinate system, the energy eigenvalue equation can be written as

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial r^2} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r} \right] \langle \vec{r} | E, l, m \rangle = E \langle \vec{r} | E, l, m \rangle \quad (2.6)$$

We can express the wave function in the form

$$\langle \vec{r} | E, l, m \rangle = R(r)\Theta(\theta)\Phi(\phi) \quad (2.7)$$

Since the system possesses rotational symmetry, the angular part of the energy eigenfunction is the spherical harmonic  $Y_{l,m}(\theta, \phi)$ . and the energy eigenfunctions are written as :

$$\langle \vec{r} | E, l, m \rangle = R_{E,l}(\vec{r})Y_{l,m}(\theta, \phi) \quad (2.8)$$

Substituting this expression in equation ( 2.6), we get the Schrödinger equation for the radial wave function as

$$\left[ -\frac{\hbar^2}{2\mu} \left( \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r} \right] R_{E,l}(r) = ER_{E,l}(r) \quad (2.9)$$

The subscripts have been inserted to indicate explicitly that the radial wave function depends on the values of  $E$  and  $l$ .

Putting

$$R_{E,l}(r) = \frac{u_{E,l}(r)}{r} \quad (2.10)$$

the radial equation becomes

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{Ze^2}{r} \right] u_{E,l}(r) = Eu_{E,l}(r) \quad (2.11)$$

with the normalisation condition

$$\int_0^\infty |R_{E,l}(r)|^2 r^2 dr = \int_0^\infty |u_{E,l}(r)|^2 dr = 1 \quad (2.12)$$

We have chosen the zero of the potential energy as corresponding to when the two particles are very far apart, *ie*,  $r \rightarrow \infty$ . The potential energy  $V(r)$  is the work to be done for bringing the particles from infinity to a distance  $r$  apart with no kinetic energy. Since the Coulomb force is attractive in this case, we do negative work and hence the potential energy is negative. Classically, the energy of a bound state should be negative because in this case, there exists a radius beyond which the potential energy exceeds the total energy, which would require a negative kinetic energy.

Since the bound states correspond to a negative value for  $E$  in equation (2.11), it is convenient to write  $E = -|E|$ . Also, let us introduce the dimensionless variable

$$\rho = \sqrt{\frac{8\mu|E|}{\hbar^2}} r \quad (2.13)$$

In terms of this variable, eqn.(2.11) can be written as

$$\begin{aligned} -4|E| \frac{d^2 u}{d\rho^2} + 4|E| \frac{l(l+1)}{\rho^2} u - \sqrt{\frac{8\mu|E|}{\hbar^2}} \frac{Ze^2}{\rho} u &= -|E| u \\ -4|E| \left( \frac{d^2 u}{d\rho^2} - \frac{l(l+1)}{\rho^2} u + \sqrt{\frac{8\mu|E|}{\hbar^2}} \frac{Ze^2}{4|E|\rho} u \right) &= -|E| u \\ \frac{d^2 u}{d\rho^2} - \frac{l(l+1)u}{\rho^2} + \left( \frac{Ze^2}{\hbar} \sqrt{\frac{\mu}{2|E|}} \frac{1}{\rho} - \frac{1}{4} \right) u &= 0 \end{aligned}$$

Putting

$$\lambda = \frac{Ze^2}{\hbar} \sqrt{\frac{\mu}{2|E|}} \quad (2.14)$$

this is simplified to

$$\frac{d^2 u}{d\rho^2} - \frac{l(l+1)}{\rho^2} u + \left( \frac{\lambda}{\rho} - \frac{1}{4} \right) u = 0 \quad (2.15)$$

For large values of  $\rho$ , this equation reduces to

$$\frac{d^2 u}{d\rho^2} - \frac{u}{4} = 0 \quad (2.16)$$

General solution of this equation is

$$u(\rho) = Ae^{-\rho/2} + Be^{\rho/2} \quad (2.17)$$

exponentially increasing solutions cannot satisfy the normalisation condition (12) and hence we discard them. So for  $\rho \rightarrow \infty$ , we take the solution as  $u \sim e^{-\rho/2}$ . For small values of  $r$ , the radial part of the energy eigen function for a spherically symmetric potential behaves as  $R(r) \sim r^l$ . Thus for small  $\rho$ ,  $u(\rho) \sim \rho^{l+1}$ .

If we factor out small  $\rho$  behaviour as well as the large  $\rho$  behaviour, solution is of the form

$$u(\rho) = \rho^{l+1} e^{-\rho/2} F(\rho) \quad (2.18)$$

Then

$$\begin{aligned} \frac{du}{d\rho} &= \rho^{l+1} e^{-\rho/2} \left[ \frac{dF}{d\rho} + \left( \frac{l+1}{\rho} - \frac{1}{2} \right) F \right] \\ \frac{d^2u}{d\rho^2} &= \rho^{l+1} e^{-\rho/2} \left[ \frac{d^2F}{d\rho^2} + \left( \frac{2l+2}{\rho} - 1 \right) \frac{dF}{d\rho} + \left( \frac{l(l+1)}{\rho^2} + \frac{1}{4} - \frac{l+1}{\rho} \right) F \right] \end{aligned}$$

Substituting these in eqn.(15),

$$\frac{d^2F}{d\rho^2} + \left( \frac{2l+2}{\rho} - 1 \right) \frac{dF}{d\rho} + \left( \frac{\lambda}{\rho} - \frac{l+1}{\rho} \right) F = 0 \quad (2.19)$$

We have not used any approximation in obtaining this equation.

We assume a power series solution of the form

$$F(\rho) = \sum_{k=0}^{\infty} c_k \rho^k \quad (2.20)$$

with the condition that  $c_k \neq 0$ . (If  $c_k = 0$ , the condition that  $\lim_{r \rightarrow 0} u(r) = r^{l+1}$  cannot be satisfied.) Substituting the power series solution in eqn.(19), we get

$$\sum_{k=2}^{\infty} k(k-1) c_k \rho^{k-2} + \sum_{k=1}^{\infty} (2l+2) k c_k \rho^{k-2} + \sum_{k=0}^{\infty} [-k + \lambda - (l+1)] c_k \rho^k = 0 \quad (2.21)$$

Putting  $k-1 = k'$  and renaming  $k' = k$ , the first two terms become

$$\sum_{k'=0}^{\infty} k'(k'+1) c_{k'+1} \rho^{k'-1} = \sum_{k=0}^{\infty} k(k+1) c_{k+1} \rho^{k-1}$$

and

$$\sum_{k'=0}^{\infty} (2l+2)(k'+1)c_{k'+1}\rho^{k'-1} = \sum_{k=0}^{\infty} (2l+2)(k+1)c_{k+1}\rho^{k-1}$$

Substituting these two in eqn.(21),

$$\sum_{k=0}^{\infty} \{[k(k+1) + (2l+2)(k+1)]c_{k+1} + [-k + \lambda - (l+1)]c_k\}\rho^{k-1} = 0 \quad (2.22)$$

For the equation to hold for all values of  $\rho$ , the coefficient of each power of  $\rho$  should vanish. Hence  $[k(k+1) + (2l+2)(k+1)]c_{k+1} + [-k + \lambda - (l+1)]c_k = 0$ , or

$$\frac{c_{k+1}}{c_k} = \frac{k + l + 1 - \lambda}{(k+1)(k+2l+2)} \quad (2.23)$$

If we consider the ratio for large  $k$ , we see that

$$\lim_{k \rightarrow \infty} \frac{c_{k+1}}{c_k} = \frac{1}{k} \quad (2.24)$$

This shows that the the behaviour of the infinite series for large values is similar to the behaviour of  $e^\rho$ . (  $e^\rho = \sum_{k=0}^{\infty} \frac{\rho^k}{k!}$  so that  $\frac{c_{k+1}}{c_k} = \frac{k!}{(k+1)!} = \frac{1}{k+1}$ ;  $\lim_{k \rightarrow \infty} \frac{c_{k+1}}{c_k} = \frac{1}{k}$ . ) Thus,  $\lim_{k \rightarrow \infty} u(\rho) = \rho^l e^{-\rho/2} e^\rho \rightarrow e^{\rho/2}$ . So if we include all terms in the series expansion,  $u$  will behave as  $e^{\rho/2}$ , which blows up at large distances. The problem arises from the large  $k$  values. If we terminate the series at a particular value of  $k$ , the series will contain only a finite number of terms and it will become a polynomial. Let us assume that the series terminates at  $k = n_r$ , so that  $c_{k+1} = c_{n_r+1} = 0$  From eqn.(23),  $\frac{c_{k+1}}{c_k} = 0$  at  $k = n_r$  if

$$n_r + l + 1 - \lambda = 0 \quad (2.25)$$

Or

$$\lambda = 1 + l + n_r; \quad n_r = 0, 1, 2, \dots \quad (2.26)$$

The function  $F(\rho)$  will then be a polynomial of degree  $n_r$ , called the *associated Laguerre polynomial*.

Quantizing  $\lambda$  in eqn.(26) leads to a quantization of energy eigenvalue. From eqn.(14),  $|E| = \frac{\mu Z^2 e^4}{2\hbar^2 \lambda^2}$ , with  $E = -|E|$ . Substituting the value of  $\lambda$  from eqn.(26),

$$E = -\frac{\mu Z^2 e^4}{2\hbar^2 (1 + l + n_r)^2} \quad (2.27)$$

Since  $l$  and  $n_r$  are both integers and  $l, n_r \geq 0$ , we can define a new quantum number called the *principal quantum number*  $n$  as:

$$1 + l + n_r = n \quad (2.28)$$

Since  $l, n_r \geq 0$ , the minimum value of  $n$  is 1. Thus, in terms of the principal quantum number, the energy eigenvalues are given by:

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2}; \quad n = 1, 2, 3, \dots \quad (2.29)$$

where we have put appropriate subscripts on  $E$  to show the dependence of  $E$  on  $n$ . Thus for any  $Z$ , the Coulomb potential gives an infinite number of bound state energy eigen values starting with a finite negative value and ending all the way with zero. The existence of an infinite number of bound states is a consequence of the slowly falling nature of the Coulomb potential at large distances.

The energy eigen values of the hydrogen atom are obtained by putting  $Z = 1$ . Thus for hydrogen,

$$E_n = -\frac{\mu e^4}{2\hbar^2 n^2}; \quad n = 1, 2, 3, \dots \quad (2.30)$$

In atomic physics, the dimensional constant called the *fine structure constant* plays an important role. In Gaussian system, it is defined by

$$\alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137} \quad (2.31)$$

In SI system ( $\alpha = \frac{1}{4\pi\epsilon_0} \frac{e^2}{\hbar c}$ ) also,  $\alpha$  has the same numerical value. In terms of the fine structure constant,

$$E_n = -\frac{\mu c^2 Z^2 \alpha^2}{2n^2} \quad (2.32)$$

For hydrogen,  $\mu c^2 = 0.511 \text{ MeV}$ . Because of the smallness of  $\alpha$ , the atomic energy scale is  $eV$  rather than  $MeV$ .

In particular, for hydrogen,  $Z = 1$  and hence

$$E_n = -\frac{\mu c^2 \alpha^2}{2n^2} = -\frac{13.6}{n^2} eV \quad (2.33)$$

The energy eigen values of the hydrogen atom are shown in figure 2.

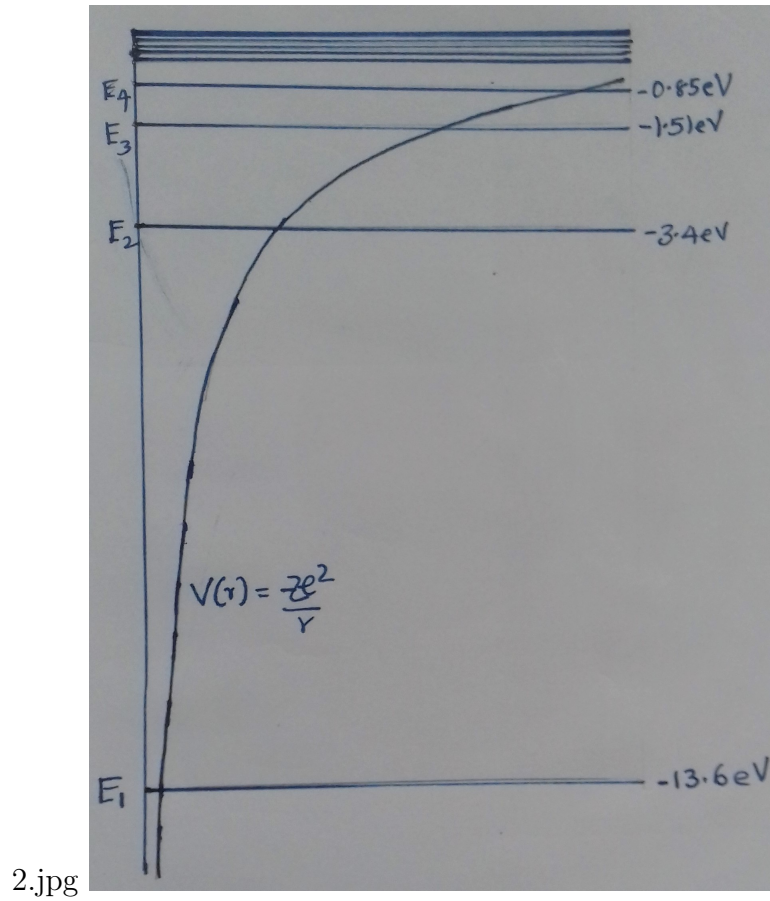


Figure 2.1: The energy levels of the hydrogen atom superposed on a graph of the Coulomb potential energy

When the hydrogen atom undergoes a transition from a state with principal quantum number  $n_i$  to a state with principal quantum number  $n_f$ , a photon is emitted with energy

$$h\nu = E_{n_i} - E_{n_f} = \frac{\mu c^2 \alpha^2}{2} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (2.34)$$

The reciprocal of wavelength of the emitted photon can be written as

$$\frac{1}{\lambda} = \frac{\mu c^2 \alpha^2}{2h} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (2.35)$$

The value of the Rydberg constant ( $R_H$ ) for hydrogen in the above equation is in agreement with experimental data. The set of transitions ending with a particular final state gives rise to a series. In hydrogen atom spectrum, the major spectroscopic series are:

Lyman series (ultra violet region) :  $n_i \rightarrow n_f = 1$

Balmer series (visible region) :  $n_i \rightarrow n_f = 2$

Paschen series (infra red region) :  $n_i \rightarrow n_f = 3$

From eqn.(33), we can see that  $|E_n| \ll m_e c^2$  where  $m_e c^2$  is the rest energy of electron. This justifies the use of the non-relativistic Schrödinger equation.

## 2.2 Hydrogenic Wave Functions

The energy eigen functions of a hydrogenic system is written as

$$\langle \vec{r} | E, l, m \rangle = R_{E,l}(\vec{r}) Y_{l,m}(\theta, \phi) = \frac{u_{E,l}(\vec{r})}{r} Y_{l,m}(\theta, \phi) \quad (2.36)$$

Also we have the variable

$$\rho = \sqrt{\frac{8\mu |E|}{\hbar^2}} r = \frac{2Z\mu c\alpha}{n\hbar} r = \frac{2Z}{na_0} r \quad (2.37)$$

where  $a_0 = \frac{\hbar}{\mu c\alpha}$  is called the Bohr radius. For hydrogen,  $a_0 = 0.529 \text{ \AA}$ . The ground state has  $n = 1$ ;  $l = 0$ ;  $n_r = 0$ . Hence the power series for  $F(\rho)$  terminates after the first term. Thus it contains only the constant term  $c_0$ . Then

$$u(\rho) = \rho^{l+1} e^{-\rho/2} F(\rho) = \rho e^{-\rho/2} c_0$$

At this stage, the constant  $c_0$  is arbitrary and it can be found out using the normalisation condition. The normalisation condition (12) can be written as

$$1 = \int_0^\infty |u(r)|^2 dr = \frac{2Z^{-1}}{a_0} \int_0^\infty |u(\rho)|^2 d\rho \quad (2.38)$$

Thus

$$|c_0|^2 \frac{2Z^{-1}}{a_0} \int_0^\infty \rho^2 e^{-\rho} d\rho = 1$$

Using

$$\int_0^\infty \rho^2 e^{-\rho} d\rho = \Gamma(3) = 2$$



We get

$$c_0 = \left( \frac{z}{a_0} \right)^{1/2}$$

Thus

$$u_{1,0}(\rho) = \left( \frac{z}{a_0} \right)^{1/2} \rho e^{-\rho/2}$$

Substituting for  $\rho$ , we get the normalised radial wave function for the ground state as

$$R_{1,0}(r) = 2 \left( \frac{z}{a_0} \right)^{3/2} e^{-\frac{z}{a_0} r} \quad (2.39)$$

For the ground state, orbital angular momentum is zero. This is in contrast with the Bohr model, in which the electron was allowed to follow a different orbit in each differing stationary state. Each state in the Bohr model had a non zero orbital angular momentum, in order to account for the stability of the atom. The only way to describe a bound state of zero angular momentum with classical trajectories would be to have the electron travelling through the proton in the atom in a straight line. Quantum mechanics accounts for the stability of the ground state through the uncertainty principle. For the first excited state,  $n = 2$ . Then

$$\rho = \frac{Z}{a_0} r$$

Since  $n = n_r + l + 1 = 2$  or  $n_r + l = 1$ . there are two choices : (i)  $n_r = 1$ ;  $l = 0$  and (ii)  $n_r = 0$ ;  $l = 1$

(i)  $n_r = 1$ ;  $l = 0$ :

In this case, the series for  $F(\rho)$  terminates after the first term ; hence  $F(\rho) = c_0 = \left( \frac{z}{a_0} \right)^{1/2}$ . Thus

$$u_{2,0}(\rho) = \rho^2 e^{-\rho/2} \left( \frac{z}{a_0} \right)^{1/2}$$

Let  $B_1$  be the normalisation constant. Then

$$|B_1|^2 \left( \frac{Z}{a_0} \right) \left( \frac{Z}{a_0} \right)^{-1} \int_0^\infty \rho^4 e^{-\rho} d\rho = 1$$

Using

$$\int_0^\infty \rho^4 e^{-\rho} d\rho = \Gamma(5) = 24$$

We get

$$B_1 = \frac{1}{2\sqrt{6}}$$

Thus

$$u_{2,0}(\rho) = \frac{1}{2\sqrt{6}} \rho^2 e^{-\rho/2} \left( \frac{z}{a_0} \right)^{1/2}$$

Substituting for  $\rho$ , we get

$$u_{2,0}(r) = \frac{1}{2\sqrt{6}} \left( \frac{Z}{a_0} \right)^2 r^2 e^{-\frac{Z}{2a_0}r} \left( \frac{z}{a_0} \right)^{1/2} = \frac{1}{\sqrt{3}} \left( \frac{Z}{2a_0} \right)^{3/2} \left( \frac{Z}{a_0} \right) r^2 e^{-\frac{Z}{2a_0}r} \quad (2.40)$$

(ii)  $n_r = 0$ ;  $l = 1$ :

In this case, the series for  $F(\rho)$  will have two terms;  $F(\rho) = c_0 + c_1\rho$ . Thus

$$u_{2,1}(\rho) = \rho e^{-\rho/2} (c_0 + c_1\rho)$$

Using the recursion relation(),

$$c_1 = \frac{0 + 0 + 1 - 2}{1 \cdot 2} c_0 = -\frac{1}{2} c_0 \quad (2.41)$$

Hence

$$u_{2,1}(\rho) = \rho e^{-\rho/2} c_0 (1 - \rho/2)$$

Let  $B_2$  be the normalisation constant. Then

$$|B_2|^2 \left( \frac{Z}{a_0} \right) \left( \frac{Z}{a_0} \right)^{-1} \int_0^\infty \rho^2 (1 - \rho/2)^2 e^{-\rho} d\rho = 1$$

$$ie, |B_2|^2 \left\{ \int_0^\infty \rho^2 e^{-\rho} d\rho + \frac{1}{4} \int_0^\infty \rho^4 e^{-\rho} d\rho - \int_0^\infty \rho^3 e^{-\rho} d\rho \right\} = 1$$

Using

$$\int_0^\infty \rho^2 e^{-\rho} d\rho = \Gamma(3) = 2$$

$$\int_0^\infty \rho^4 e^{-\rho} d\rho = \Gamma(5) = 24$$

$$\int_0^\infty \rho^3 e^{-\rho} d\rho = \Gamma(4) = 6$$

We get

$$B_2 = \frac{1}{\sqrt{2}}$$

Thus

$$u_{2,0}(\rho) = \frac{1}{\sqrt{2}} \rho (1 - \rho/2) e^{-\rho/2} \left( \frac{z}{a_0} \right)^{1/2}$$

Substituting for  $\rho$ , we get

$$u_{2,0}(r) = \frac{1}{\sqrt{2}} \left( \frac{Z}{a_0} \right)^2 r (1 - \rho/2) e^{-\frac{Z}{2a_0}r} \left( \frac{z}{a_0} \right)^{1/2} = 2 \left( \frac{Z}{2a_0} \right)^{3/2} r \left( 1 - \frac{Zr}{2a_0} \right) e^{-\frac{Z}{2a_0}r} \quad (2.42)$$

Using equations (40) and (42), the radial wave functions for the first excited states are obtained as

$$R_{2,0}(r) = 2 \left( \frac{Z}{2a_0} \right)^{3/2} \left( 1 - \frac{Zr}{2a_0} \right) e^{-\frac{Z}{2a_0}r} \quad (2.43)$$

$$R_{2,1}(r) = \frac{1}{\sqrt{3}} \left( \frac{Z}{2a_0} \right)^{3/2} \left( \frac{Zr}{a_0} \right) e^{-\frac{Z}{2a_0}r} \quad (2.44)$$

To obtain the complete wave functions  $\langle \vec{r} | E, l, m \rangle$  the radial wave functions  $R_{n,l}(r)$  should be multiplied by the spherical harmonics  $Y_{l,m}(\theta, \phi)$ . Spherical harmonics can give probability density as a function of  $\theta$  and  $\phi$ . Spherical harmonics are themselves normalised:

$$\int_0^\pi \sin \theta d\theta \int_0^{2\pi} d\phi |Y_{l,m}(\theta, \phi)|^2 = 1 \quad (2.45)$$

Hence

$$\int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta r^2 dr |\langle r | E, l, m \rangle|^2 = r^2 |\langle r | E, l, m \rangle|^2 dr$$

Thus the probability of finding the particle between  $r$  and  $r + dr$  is given by  $r^2 |\langle r | E, l, m \rangle|^2 dr$ .  $F(\rho)$  is a polynomial of degree  $n_r = n - l - 1$ . Thus  $F(\rho)$  has  $n_r$  radial nodes. This is the physical significance of the quantum number  $n_r$ .

The probability density  $r^2 |\langle r | E, l, m \rangle|^2$  will have  $n - l$  bumps. When, for a particular value of  $n$ ,  $l$  has its maximum value of  $n - 1$ , there will be only one

bump. Since  $n_r = 0$  in this case, the radial wave function  $R_{n,n-1} \propto r^{n-1} e^{-\frac{Zr}{a_0 n}}$  and hence the probability density is

$$r^2 |R_{n,n-1}|^2 \propto r^{2n} e^{-\frac{Zr}{a_0 n}}$$

The location of the peak of the probability density distribution can be found from

$$\frac{d}{dr} |R_{n,n-1}|^2 \propto \left(2n - \frac{2Z}{a_0 n} r\right) r^{2n-1} e^{-\frac{Zr}{a_0 n}} = 0$$

which yields

$$r_{maxprob} = \frac{n^2 a_0}{Z} \quad (2.46)$$

For example, for the ground state of hydrogen, the probability of finding the electron is maximum at a value  $r = a_0$ , the radius of the first Bohr radius.

## 2.3 Degeneracy

One of the most striking features of the hydrogen atom is the surprising degree of degeneracy, that is the number of linearly independent states with the same energy. For each  $n$ , the allowed values of  $l$  are:

$$l = 0, 1, 2, 3, \dots$$

For each  $l$ , there are  $(2l + 1)$  states specified by the  $m$  values. Thus the total degeneracy for a particular  $n$  is

$$\sum_{l=0}^{n-1} (2l + 1) = 2 \sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} 1 = 2 \frac{(n-1)n}{2} + n = n^2 \quad (2.47)$$

The independence of energy on  $m$  values is expected on the ground of rotational symmetry. All systems with spherically symmetric potentials exhibit such a degeneracy. But the lack of dependence of the energy on  $l$  is unexpected. The rotational symmetry would disappear if we apply an external magnetic field that picks out a particular direction, such as the  $z$ -direction. In that case the energy would depend on the projection of the angular momentum on the  $z$ -axis. Unlike the rotational symmetry which is responsible for the degeneracy of the different  $m$  states, there is no obvious symmetry that

indicates that the states with different  $l$  values to have exactly the same energy. This degeneracy is termed as accidental degeneracy and is a speciality of the Coulomb field.

***Reference:* A Modern Approach to Quantum Mechanics-J S Townsend**