Lecture Notes in Quantum Mechanics

Chapter-II : Hydrogen Atom

II M.Sc Physics

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Contents

Chapter 2

Exactly Soluble Eigenvalue Problems

2.1   Introduction

In this chapter we will be studying as illustrative examples of the application of the Schrö dinger Equation, the Hydrogen Atom problem and the one dimensional Linear Harmonic Oscillator. The Hydrogen atom is an example of a two body problem consisting of a central heavy nucleus and a lighter electron orbiting around it. Hence for studying the Hydrogen atom, we should have to set up the Hamiltonian function for this two body problem and then move on to setting up the Schrö dinger Equation and solving it.
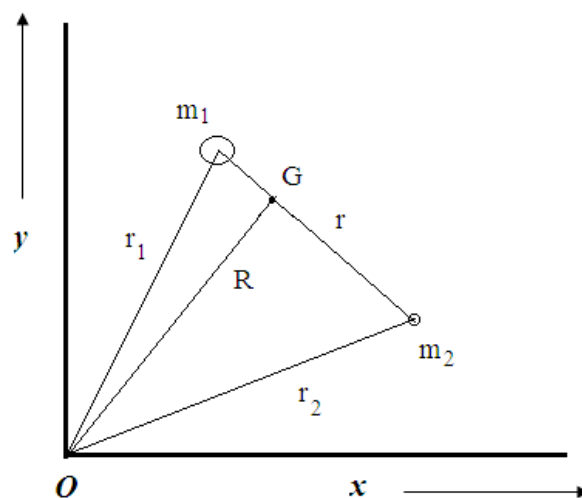

<small>FIGURE 2.1: Center of Mass coordinates and relative coordinates for a two body system,</small>

2.2 Reduction of Two Body Hamiltonian

Let as consider a two body system, consisting of particles m_1 and m_2 having position co-ordinates r_1 and r_2 as shown in Fig. 2.1.

Then the Hamiltonian of this system is given as the sum of the kinetic energies of the two particles and the potential energy due to their interactions, namely $V(r_1 - r_2)$.

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(r_1 - r_2) \tag{2.1}$$

where

$$\nabla_1 \equiv f\left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial y_1}, \frac{\partial}{\partial z_1}\right)$$

and

$$\nabla_2 \equiv f\left(\frac{\partial}{\partial x_2}, \frac{\partial}{\partial y_2}, \frac{\partial}{\partial z_2}\right)$$

are the gradient operators for the two particles in terms of their position coordiantes.

2.2.1 Center of Mass Coordinates and Relative Coordinates

If the center of mass of the system, say G, is at a distance R from the origin and the relative distance between the two particles is r, then

$$r = r_1 - r_2 \tag{2.2}$$

and

$$(m_1 + m_2)R = m_1 r_1 + m_2 r_2$$

or

$$R = \frac{m_1 r_1 + m_2 r_2}{(m_1 + m_2)} \tag{2.3}$$

The coordinate R is called as the *center of mass coordinate* while the coordinate r is called as the *relative coordinate*

2.2.2 Hamiltonian in terms of Center of Mass Coordinates and Relative Coordinates

The gradients in terms of the center of mass co-ordinates R and relative co-ordinates r are given as

$$\nabla_R \equiv f\left(\frac{\partial}{\partial X}, \frac{\partial}{\partial Y}, \frac{\partial}{\partial Z}\right)$$

and

$$\nabla_r \equiv f\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

Let the ith component of ∇_1 be given as

$$\frac{\partial X}{\partial x_1} = \left(\frac{m_1}{m_1 + m_2}\right)$$
$$\frac{\partial x}{\partial x_1} = 1.$$

$$\frac{\partial}{\partial x_1} = \frac{\partial X}{\partial x_1}\frac{\partial}{\partial X} + \frac{\partial x}{\partial x_1}\frac{\partial}{\partial x} \quad \text{or}$$
$$\frac{\partial}{\partial x_1} = \left(\frac{m_1}{m_1 + m_2}\right)\frac{\partial}{\partial X} + \frac{\partial}{\partial x} \tag{2.4}$$

From Eqn. (2.4) we have

$$\frac{\partial^2}{\partial x_1^2} = \left\{\left(\frac{m_1}{m_1 + m_2}\right)\frac{\partial}{\partial X} + \frac{\partial}{\partial x}\right\}\left\{\left(\frac{m_1}{m_1 + m_2}\right)\frac{\partial}{\partial X} + \frac{\partial}{\partial x}\right\}$$

or

$$\frac{\partial^2}{\partial x_1^2} = \left(\frac{m_1}{m_1 + m_2}\right)^2\frac{\partial^2}{\partial X^2} + \left(\frac{2m_1}{m_1 + m_2}\right)\frac{\partial}{\partial X}\frac{\partial}{\partial x} + \frac{\partial^2}{\partial x^2}$$

Hence

$$\nabla_1^2 = \left(\frac{m_1}{m_1 + m_2}\right)^2\nabla_R^2 + \left(\frac{2m_1}{m_1 + m_2}\right)\nabla_R\nabla_r + \nabla_r^2 \tag{2.5}$$

In a similar manner,

$$\nabla_2^2 = \left(\frac{m_2}{m_1 + m_2}\right)^2\nabla_R^2 - \left(\frac{2m_2}{m_1 + m_2}\right)\nabla_R\nabla_r + \nabla_r^2 \tag{2.6}$$

The Eqns. (2.5 & 2.6) give the expressions for the Laplacian operators in terms of the position vectors $(r_1 \& r_2)$ for the first and second particle respectively.

Substituting Eqns. (2.2), (2.5 & 2.6) in Eqn. (2.1) gives

$$H = -\frac{\hbar^2}{2(m_1 + m_2)}\nabla_R^2 - \frac{\hbar^2}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\nabla_r^2 + V(r)$$

or

$$H = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(r). \tag{2.7}$$

Eqn. (2.7) shows that the Hamiltonian H for a two body system is the sum of two commuting parts depending on independent sets of variables, (i.e) $H = H_{CM} + H_{relative}$.

The first part

$$H_{CM} = -\frac{\hbar^2}{2M}\nabla_R^2, \tag{2.8}$$

gives the kinetic energy of the system as a whole. It describes the free motion of the center of mass of the system G and depends on the center of mass coordinate R alone. The second part

$$H_{relative} = -\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r), \tag{2.9}$$

depends on the relative variables r only. It is identical with the Hamiltonian of a single particle of mass μ (reduced mass) moving in a central potential $V(r)$.

Total Mass M:

Here in the Eqn. (2.7), the expression $m_1 + m_2$ represents the total mass of the two particle system as a whole and is given as

$$M = m_1 + m_2. \tag{2.10}$$

Reduced Mass μ: Similarly in the Eqn. (2.7), μ represents the reduced mass of the two particle system and is given as

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad \text{or}$$

$$\frac{1}{\mu} = \frac{m_2 + m_1}{m_1 \times m_2} \quad \text{or}$$

$$\mu = \frac{m_1 \times m_2}{m_2 + m_1}. \tag{2.11}$$

2.2.3 Separation of Schrӧedinger's Into Energy Eigen Value Equations

Let the Schrӧedinger equation for the system be given as

$$H\vartheta(R, r) = E'\vartheta(R, r)$$

(i.e)

$$\left[-\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]\vartheta(R, r) = E'\vartheta(R, r) \tag{2.12}$$

Factorizing the wave function $\vartheta(R, r)$ as

$$\vartheta(R, r) = W(R)\, u(r) \tag{2.13}$$

and separating Eqn. (2.12) in terms of the center of mass variables R and relative co-ordinate variables r, we have

$$\frac{1}{W(R)}\left[-\frac{\hbar^2}{2M}\nabla_R^2\right]W(R) - E' = -\frac{1}{u(r)}\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]u(r) = -E$$

where $E =$ separation constant. Then equating both the parts of the above equation to the separation constant gives

$$-\frac{\hbar^2}{2M}\nabla_R^2 - [E' - E]\,W(R) = 0. \tag{2.14}$$

and

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]u(r) = Eu(r). \tag{2.15}$$

Method of Separation of Variables:

Substituting Eqn. (2.13) in Eqn. (2.12) we have

$$\left[-\frac{\hbar^2}{2M}u(r)\nabla_R^2 W(R) - \frac{\hbar^2}{2\mu}W(R)\nabla_r^2 u(r) + V(r)W(R)u(r)\right] = E'W(R)u(r).$$

Dividing both the sides of the above equation by $W(R)u(r)$ gives

$$\frac{1}{W(R)}\left[-\frac{\hbar^2}{2M}\nabla_R^2\right]W(R) + \frac{1}{u(r)}\left[-\frac{\hbar^2}{2\mu}\nabla_r^2\right]u(r) + V(r) = E'.$$

Rearranging the equation and equating it to a separation constant E, gives

$$\frac{1}{W(R)}\left[-\frac{\hbar^2}{2M}\nabla_R^2\right]W(R) - E' = -\frac{1}{u(r)}\left[-\frac{\hbar^2}{2\mu}\nabla_r^2\right]u(r) - V(r) \quad = -E, \quad \text{or}$$

$$\left[-\frac{\hbar^2}{2M}\nabla_R^2\right]W(R) - \left[E' - E\right]W(R) = 0, \quad \text{and}$$

$$\left[\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right]u(r) = Eu(r).$$

Equation (2.14) is in fact the energy eigen value equation of motion of a free particle of mass M. The energy spectrum for such a particle is a continuous one.

On the other hand Eqn. (2.15) gives the energy eigen value equation, for the relative motion between the two particles. This equation has the appearance of the Schröedinger'sr equation for the motion of a single particle of mass μ in a central potential $V(r)$.

Let us consider one electron atoms such as Hydrogen (H), singly ionized Helium He^+ ion, doubly ionized Lithium Li^{++} ion etc. These are two body systems consisting of atomic nucleus of charge Ze and electron of charge $-e$ with the Coulombic Electrostatic Potential $V(r) = -\left(\dfrac{Ze^2}{r}\right)$. If the nucleus is remaining stationary, then the Hamiltonian in the Center of Mass frame H_{CM} becomes zero (i.e) $H_{CM} = 0$. This is because the kinetic energy of the nucleus in zero.

Hence the two body central force problem gets reduced to just the relative motion of a single particle, namely the electron, with respect to the nucleus due to the electrostatic potential $V(r)$. The Schröedinger'sr equation for this one electron atom can therefore be given as

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right] u(r) = E u(r). \tag{2.16}$$

This Eqn. (2.16) will be the starting point for the discussion of the Hydrogen atom problem in the next section.

2.3   Hydrogen Atom

The Hydrogen atom is an example of a two particle system consisting of an atomic nucleus of charge Ze and an electron of charge $-e$. As the nucleus is stationary, the Schröedinger's equation for the Hydrogen atom is just that for a single particle, namely, the electron moving in a central Coulomb potential $V(r) = \left(\dfrac{-Ze^2}{r}\right)$. It is given as

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right] u(r) = E u(r) \tag{2.17}$$

where $\dfrac{1}{\mu} = \left(\dfrac{1}{m_n} + \dfrac{1}{m_e}\right) \simeq \dfrac{1}{m_e}$, or $\mu \simeq m_e$. This means that the reduced mass for the Hydrogen atom is just approximately equal to the mass of the electron itself.

As the Hydrogen atom is a spherically symmetric problem, we will convert the Schröedinger's equation from Cartesian coordinates to spherical polar coordinates. Once this has been done, we will then split it into two parts, namely the *radial part* and *angular part* and will try to solve these parts individually.

To solve the radial equation, we convert the equation into the associated Lagurré Differential equation- a standard mathematical equation and obtain the radial wave function in terms of the associatied Lagurré polynomial functions which are well known in mathematical theory of Special Functions.

To solve the angular part of the equation, we convert it into the Legendre differential equation, another standard mathematical equation whose solutions are well known and obtain the angular wave function in terms of the spherical harmonics.

When the solutions of the radial wave equation and angular part of the Schröedinger's equation are obtained, the complete wave function for the electron can be constructed.

Expressing the Laplacian operator ∇_r^2 in spherical polar coordinates and the wave function in terms of those coordinates, that is $u(r) \equiv u(r, \theta, \phi)$, Eqn. (2.17) can be expanded as

$$-\frac{\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 sin\theta} \frac{\partial}{\partial \theta} \left(sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] u(r, \theta, \phi) +$$

$$V(r)u(r, \theta, \phi) = Eu(r, \theta, \phi) \qquad (2.18)$$

2.3.1 Separation of Radial and Angular Parts

Let us factorize the wave function into radial $R_{nl}(r)$ and angular parts $Y_l^m(\theta, \phi)$ such that

$$u(r, \theta, \phi) = R_{nl}(r)Y_l^m(\theta, \phi) \qquad (2.19)$$

Substituting this in Eqn. (2.18) and separating it into radial and angular parts and multiplying it through out by $-\left(\frac{2\mu r^2}{\hbar^2} \right)$ we have

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu r^2}{\hbar^2} [E - V(r)] = -\frac{1}{Y} \left[\frac{1}{sin\theta} \frac{\partial}{\partial \theta} \left(sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] Y \quad (2.20)$$

When the R.H.S of Eqn(2.20) is multiplied by $\hbar^2$, it just gives the angular momentum operator L^2 in spherical polar coordinates, that is

$$L^2 = -\hbar^2 \left[\frac{1}{sin\theta} \frac{\partial}{\partial\theta} \left(sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \tag{2.21}$$

Therefore Eqn. (2.20) can be rewritten as

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu r^2}{\hbar^2}\left[E - V(r) \right] \quad = \quad \frac{L^2 Y}{\hbar^2 Y} \tag{2.22}$$

However the angular momentum operator L^2 satisfies the eigen value equation

$$L^2 Y = l(l+1)\hbar^2 Y \tag{2.23}$$

where l is the angular momentum quantum number.

Hence Eqn (2.22) becomes

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu r^2}{\hbar^2}\left[E - V(r) \right] \quad = \quad l(l+1). \tag{2.24}$$

Rearranging the above equation, dividing by r^2, multiplying by R and substituting $V(r) = -\left(\frac{Ze^2}{r} \right)$ gives

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{r} - \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R = 0 \tag{2.25}$$

This Eqn. (2.25) gives the radial wave equation for the electron in a Hydrogen atom.

2.3.2   Bound States $E < 0$: Change of Variables

Let us consider the bound state for the electron, for which $E < 0$ and define two positive real parameters α and λ given by

$$\alpha^2 \quad = \quad -\frac{8\mu E}{\hbar^2} \tag{2.26a}$$

$$\lambda \quad = \quad \frac{2\mu Ze^2}{\alpha\hbar^2} \tag{2.26b}$$

Dividing Eqn. (2.25) throughout by α^2 gives

$$\frac{1}{\alpha^2 r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2\mu}{\alpha^2\hbar^2}\left[E + \frac{Ze^2}{r} - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R = 0. \tag{2.27}$$

Let us change the independent variable from r to ρ such that $\rho = \alpha r$,
$$\frac{d}{dr} = \left(\frac{d\rho}{dr}\right)\frac{d}{d\rho} \text{ and hence } \frac{d}{dr} = \alpha\frac{d}{d\rho}$$

Substituting these quantities in Eqn. (2.27) gives

$$\frac{\partial^2 R}{\partial\rho^2} + \frac{2}{\rho}\left(\frac{\partial R}{\partial\rho}\right) + \left[\frac{\lambda}{\rho} - \frac{1}{4} - \frac{l(l+1)}{\rho^2}\right]R(\rho) = 0. \tag{2.28}$$

$$\text{Here we have} \quad \frac{1}{\alpha^2 r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) = \frac{1}{\alpha^2 r^2}\frac{\partial}{\partial\rho}\left(\alpha^2 r^2\frac{\partial R}{\partial\rho}\right)$$
$$= \frac{1}{\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial R}{\partial\rho}\right)$$
$$= \frac{\partial^2 R}{\partial^2} + \frac{2}{\rho}\left(\frac{\partial R}{\partial\rho}\right)$$

$$\text{while} \quad \frac{2\mu E}{\alpha^2\hbar^2} = \frac{2\mu E}{\hbar^2}\left\{\frac{1}{\alpha^2}\right\}$$
$$= \frac{2\mu E}{\hbar^2}\times\left\{\frac{\hbar^2}{-8\mu E}\right\}$$
$$= -\frac{1}{4}$$

$$\frac{2\mu}{\alpha^2\hbar^2}\times\left(\frac{Ze^2}{r}\right) = \frac{2\mu Ze^2}{\alpha\hbar^2}\times\frac{1}{\alpha r}$$
$$= \frac{\lambda}{\rho}$$

$$\text{and} \quad \frac{2\mu}{\alpha^2\hbar^2}\times-\left\{\frac{l(l+1)\hbar^2}{2\mu r^2}\right\} = -\frac{l(l+1)}{\alpha^2 r^2})$$
$$= -\frac{l(l+1)}{\rho^2}$$

Case1: Solution in the Asymptotic Region $\rho \to \infty$

As $\rho \to \infty$, all the terms in Eqn. (2.28) having ρ in the denominator will vanish. The only dominant term will be $-\left(\dfrac{1}{4}\right)$. Therefore Eqn. (2.28) reduces to

$$\frac{\partial^2 R}{\partial \rho^2} - \frac{1}{4}R(\rho) = 0. \tag{2.29}$$

Solving this equation, we obtain the physically admissible solution as

$$R(\rho) = Const \; e^{-\rho/2}. \tag{2.30}$$

Case 2: Solution at the Origin $\rho \to 0$

As $\rho \to 0$, the dominant term in Eqn. (2.28) is $\dfrac{l(l+1)}{\rho^2}$. Hence Eqn.(2.28) reduces to

$$\frac{\partial^2 R}{\partial \rho^2} - \frac{l(l+1)}{\rho^2}R(\rho) = 0. \tag{2.31}$$

The physically admissible solution in this case is

$$R(\rho) = Const \; \rho^{+l}. \tag{2.32}$$

We find that $R(\rho)$ is discontinuous at the origin. To over come this singularity, we associate a factor $\mathcal{L}(\rho)$, such that

$$R(\rho) = \rho^{+l}e^{-\rho/2}\mathcal{L}(\rho) \tag{2.33}$$

Differentiating this twice, and substituting, Eqn. (2.28) becomes

$$\rho\frac{\partial^2 \mathcal{L}}{\partial \rho^2} + [2(l+1) - \rho]\frac{\partial \mathcal{L}}{\partial \rho} + [\lambda - (l+1)]\mathcal{L}(\rho) = 0 \tag{2.34}$$

To solve this equation, we assume $L(\rho)$ to be a power series of the form

$$\mathcal{L}(\rho) = c_0 + c_1\rho^l + c_2\rho^2 + c_3\rho^3 + c_4\rho^4 + ...c_s\rho^s$$

or

$$\mathcal{L}(\rho) = \sum_{s=0}^{\infty} c_s\rho^s \tag{2.35}$$

The recursion relation between the coefficients of the successive terms of the series solution of Eqn. (2.34) is given by

$$\frac{c_{s+1}}{c_s} = \frac{s+l+1-\lambda}{(s+1)[s+2(l+1)]} \tag{2.36}$$

In the asymptotic limit $s \to \infty$ Eqn. (2.36) becomes

$$\frac{c_{s+1}}{c_s} = \frac{1}{s} \tag{2.37}$$

Proof:

Differentiating Eq. 2.35 with respect to ρ gives

$$\frac{\partial \mathcal{L}(\rho)}{\partial \rho} = \sum_{s=0}^{\infty} c_s s \rho^{s-1}$$

$$\frac{\partial^2 \mathcal{L}(\rho)}{\partial \rho^2} = \sum_{s=0}^{\infty} c_s s(s-1)\rho^{s-2}$$

Substituting these in Eq. (2.34) gives

$$\rho \left\{ \sum_{s=0}^{\infty} c_s s(s-1)\rho^{s-2} \right\} + [2(l+1) - \rho] \left\{ \sum_{s=0}^{\infty} c_s s \rho^{s-1} \right\}$$

$$+ [\lambda - (l+1)] \sum_{s=0}^{\infty} c_s \rho^s = 0$$

$$\sum_{s=0}^{\infty} c_s \left[\lambda - (l+1) - s \right] \rho^s + \sum_{s=0}^{\infty} c_s s \left[2(l+1) + (s-1) \right] \rho^{s-1} = 0$$

For the above equation to hold good, we require that each individual term in the series should be equal to zero. Hence taking the coefficient of ρ^s and equating it to zero, we find that

$$c_s \left[\lambda - (l+1) - s \right] \rho^s + c_{s+1}(s+1) \left[2(l+1) + s \right] \rho^s = 0$$

Rearranging the above equation gives

$$\frac{c_{s+1}}{c_s} = \frac{-\left[\lambda - (l+1) - s \right]}{(s+1)[s+2(l+1)]} \qquad \text{or}$$

$$=$$

$$\frac{c_{s+1}}{c_s} = \frac{\left[s + (l+1) - \lambda \right]}{(s+1)[s+2(l+1)]}$$

If $s \to \infty$, we have

$$\frac{c_{s+1}}{c_s} \simeq \frac{s}{s^2} \qquad \text{or}$$

$$\frac{c_{s+1}}{c_s} = \frac{1}{s}$$

Hence the proof.

The equation (2.37) tells that the series for $\mathcal{L}(\rho)$ behaves as an exponential series, that is

$$\mathcal{L}(\rho) \simeq e^{\rho} \tag{2.38}$$

Proof:

Let us consider the exponential series

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots \frac{x^{n-1}}{(n-1)!} + \frac{x^n}{n!} \qquad \text{or}$$

$$e^x = \sum_{n=10}^{\infty} \frac{x^n}{n!}$$

Hence the ratio of successive coefficients becomes

$$\frac{R_{n+1}}{R_n} = \frac{1/n!}{1/(n-1)!} \qquad \text{or}$$

$$\frac{R_{n+1}}{R_n} = \frac{(n-1)!}{n!} \qquad \text{or}$$

$$\frac{R_{n+1}}{R_n} = \frac{1}{n}$$

Comparing the above equation with Eq. (2.37), we find that the function $\mathcal{L}(\rho)$ also behaves as an exponential series in the asymptotic limit, that is

$$\mathcal{L}(\rho) \simeq e^{\rho}$$

if $s \to \infty$. Hence the proof.

Then the equation (2.33) becomes

$$R(\rho) = \rho^{+l} e^{-\rho/2} e^{\rho} \qquad \text{or}$$

$$R(\rho) = \rho^{+l} e^{+\rho/2} \tag{2.39}$$

From this we find that $R(\rho)$ behaves as $e^{+\rho}$, and diverges to infinity as $\rho \to \infty$. This violates the condition for admissibility, namely $R(\rho) \to 0$ as $\rho \to \infty$. Hence the mathematical solution of the radial wave equation, namely Eqn. (2.28) is inadmissible on physical grounds.

To over come this difficulty, we truncate the series at some finite term, say n' by taking a positive integer value for λ such that

$$s = n' \tag{2.40a}$$

$$\lambda = n = n' + l + 1 \tag{2.40b}$$

Equation (2.36) then becomes

$$\frac{c_{s+1}}{c_s} = \frac{c_{n'+1}}{c'_n} = 0. \tag{2.41}$$

The infinite series $L(\rho)$ will now get terminated at c_s and will behave as a finite degree polynomial, namely the Associated Lauguerre polynomial of order n'. As n' is $+ve$, the above equation 2.40(b) tells that

$$n' = n - (l + 1) > 0 \tag{2.42}$$

or

$$l < (n - 1) \tag{2.43}$$

This means l cannot exceed $(n - 1)$, (i.e) l should vary in the range $0 < l \leq (n - 1)$. Here n' is called the radial quantum number and n is to be taken as the total quantum number, while l is to be taken as the angular momentum quantum number. Here n varies as $n = 1, 2, 3, ...$ and l varies as $l = 0, 1, 2, ...(n - 1)$. The $z - component$ of angular momentum is given by the quantum number m. It can take $(2l + 1)$ values starting from $-l$ to $+l$.

2.3.3 Energy Eigen Values

From Eqns. 2.26b (a) & (b), we have

$$\lambda = \frac{2\mu Z e^2}{\alpha \hbar^2}$$

or

$$\lambda = \frac{2\mu Z e^2}{\hbar^2} \left\{ \frac{\hbar^2}{-8\mu E} \right\}^{1/2} \tag{2.44}$$

But from Eqn. 2.40(b) we know that

$$\lambda = n. \tag{2.45}$$

Combining these two equations, the energy eigen values for the nth level can be obtained as

$$E_n = -|E_n| = -\frac{\mu Z^2 e^4}{2\hbar^2 n^2}$$

or

$$E_n = -\frac{1}{2}\frac{Ze^2}{(a/Z)}\frac{1}{n^2} \tag{2.46}$$

where $a = \left(\dfrac{\hbar^2}{\mu e^2}\right)$ is the radius of the Hydrogen atom. The energy eigen values given by Eqn. 2.46 are in agreement with old quantum theory and experimental results.

The energy levels given by Eqn. (2.46) for various quantum states described by the quantum numbers n, l, m are shown in Fig. (2.2).

The energy eigen values are independent of l and m and are dependent only on the value of n. This condition of the energy state is known as *degeneracy* (i.e) the energy levels of a Hydrogen atom are degenerate w.r.t energy states l and m. The degeneracy in l arises due to the *Central Coulombian Potential* and the degeneracy in m arises due to *spherical asymmetry of the Coulombian Potential*. The degree of degeneracy is given by

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

2.3.4   Energy Eigen functions

The associated Lauguerre polynomial equation is written as

$$\rho\,\mathcal{L}_q^{p\,\prime\prime}(\rho) + (p+1-\rho)\,\mathcal{L}_q^{p\,\prime}(\rho) + (q-p)\,\mathcal{L}_q^p(\rho) = 0 \tag{2.48}$$
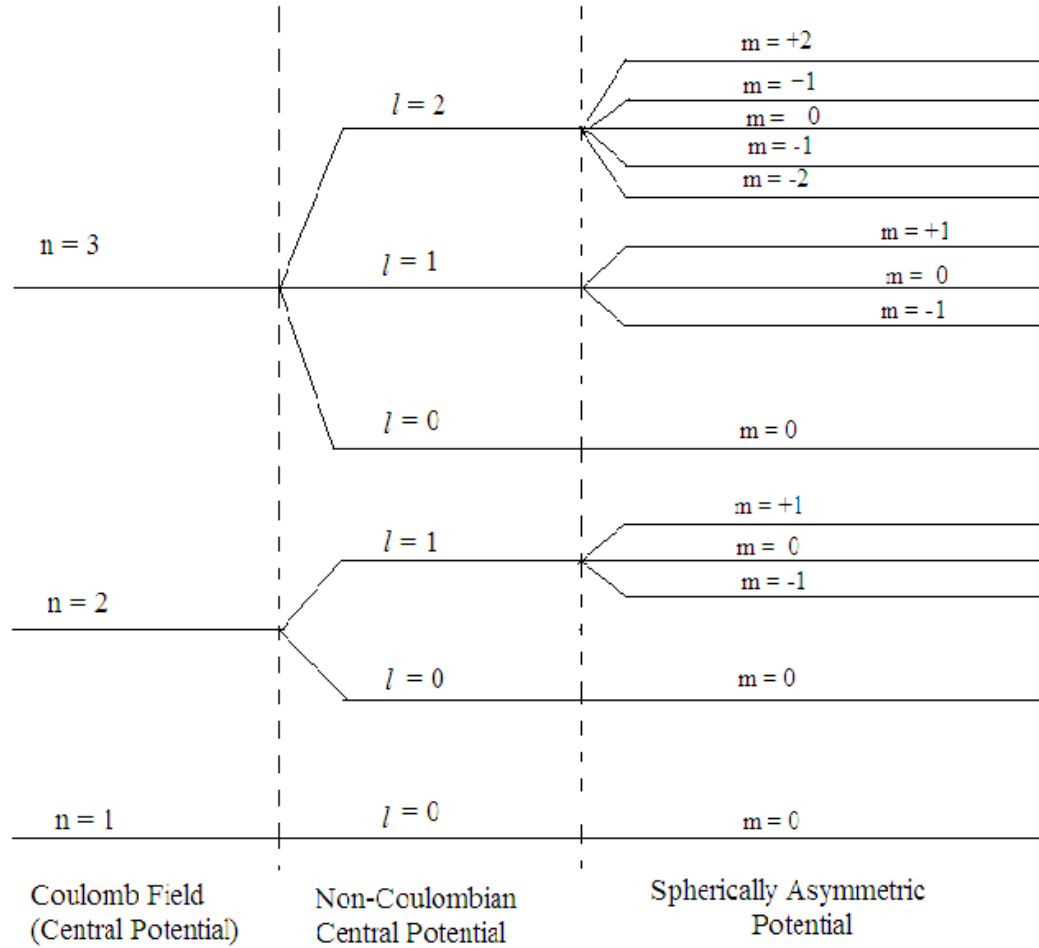
FIGURE 2.2: Energy Levels corresponding to various quantum states defined by n, l and m values

Taking the values for λ, p and q as

$$\lambda = n \tag{2.49}$$

$$p = 2l + 1 \tag{2.50}$$

$$q = n + l. \tag{2.51}$$

the Associated Laguerre equation, Eqn. (2.48) becomes

$$\rho \frac{\partial^2 \mathcal{L}_q^p}{\partial \rho^2} + [2(l+1) - \rho] \frac{\partial \mathcal{L}_q^p}{\partial \rho} + [n - (l+1)] \mathcal{L}_q^p(\rho) = 0. \tag{2.52}$$

This equation, Eqn(2.52) reduces to just the radial wave equation, Eqn. (2.34) for the Hydrogen atom, whose solution is the *associated Lauguerre polynomial* and is given by

$$\mathcal{L}_q^p(\rho) \equiv \frac{d^p}{d\rho^p} \mathcal{L}_q(\rho) = \mathcal{L}_{n+l}^{2l+1}(\rho) \tag{2.53}$$

multiplied by an arbitrary constant, N_{nl}. Correspondingly, the wave functions $R(\rho)$ for a given set of n and l values are

$$R_{nl}(\rho) = N_{nl}\,\rho^l\,e^{-\rho/2}\,\mathcal{L}_{n+l}^{2l+1}(\rho) \tag{2.54}$$

where $\rho = \alpha\,r = \dfrac{2Zr}{n\,a}$ and $a = \left(\dfrac{\hbar^2}{\mu e^2}\right)$.

To Determine Normalization Constant

The condition for normalization of wave function is

$$\int |R_{nl}(r)|^2\,r^2\,dr = 1. \tag{2.55}$$

Substituting Eqn. (**??**), the above equation gives

$$N_{nl}^2\,\int_0^\infty e^{-\rho}\,\rho^{2l}\,[\mathcal{L}_q^p(\rho)]^2\,\frac{\rho^2}{\alpha^2}\,\frac{d\rho}{\alpha} = 1. \tag{2.56}$$

From the orthogonal property of the Associated Lauguerre Plynomials, namely

$$\int_0^\infty e^{-\rho}\,\rho^{(2l+1)}\,[\mathcal{L}_q^p(\rho)]^2\,d\rho = \frac{(2q-p+1)(q!)^3}{(q-p)!} \tag{2.57}$$

Taking $p = 2l+1$ and $q = n+l$ and substituting Eqn. (2.57) in Eqn. (2.56) gives

$$\frac{N_{nl}^2}{\alpha^3}\,\frac{2n\,[(n+l)!]^3}{(n-l-1)!} = 1.$$

or

$$N_{nl} = \sqrt{\frac{\alpha^3\,(n-l-1)!}{2n\,[(n+l)!]^3}}. \tag{2.58}$$

Substituting these in Eqn. (2.54), the radial wave functions can be written as

$$R_{nl}(r) = \left\{\left(\frac{2Z}{na}\right)^3\,\frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2}\,e^{-\frac{Zr}{na}}\left(\frac{2Z}{na}.r\right)^l\,\mathcal{L}_{n+l}^{2l+1}\left(\frac{2Z}{na}.r\right) \tag{2.59}$$

The first few radial wave functions are given in the Table 1. The behaviour of the radial wave functions for various values of n are shown below in Figs. 2.3, 2.4 and 2.5. From the graphs it is seen that the wave function crosses the ρ axis $(a/2r)$ axis $(n-l-1)$ times in the region $\rho = 0$ to $\rho = \infty$.
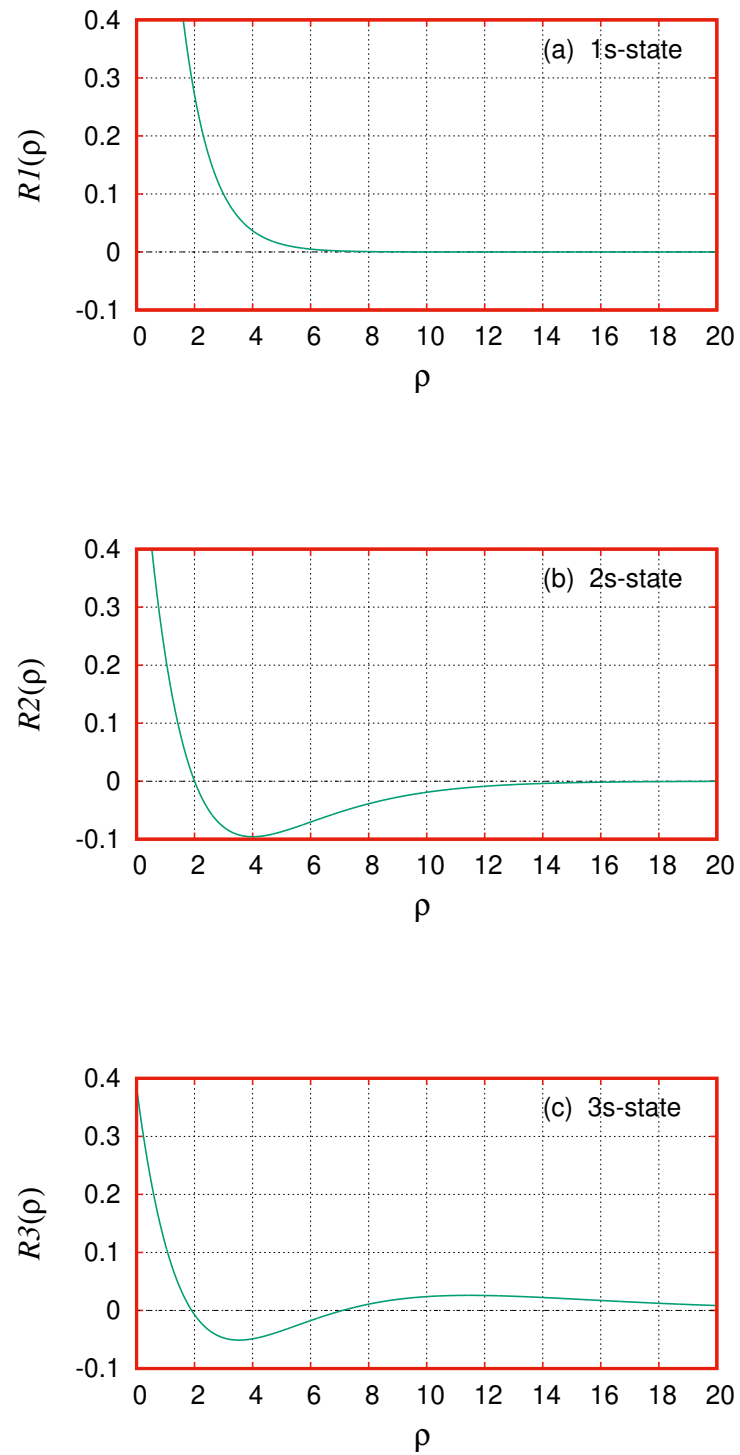
FIGURE 2.3: s-state(l=0) Radial Wavefunctions for various n values
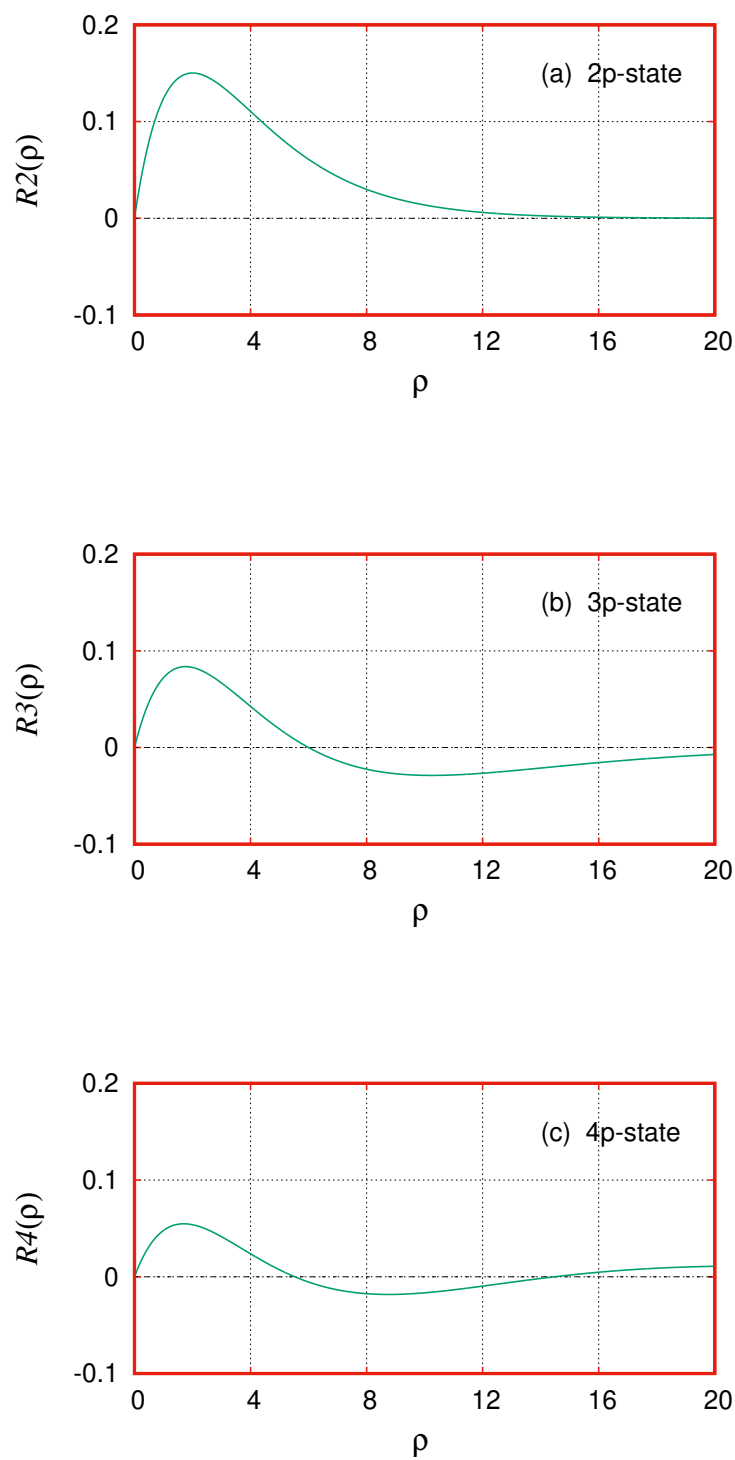
FIGURE 2.4: p-state (l=1) Radial Wavefunctions for various n values

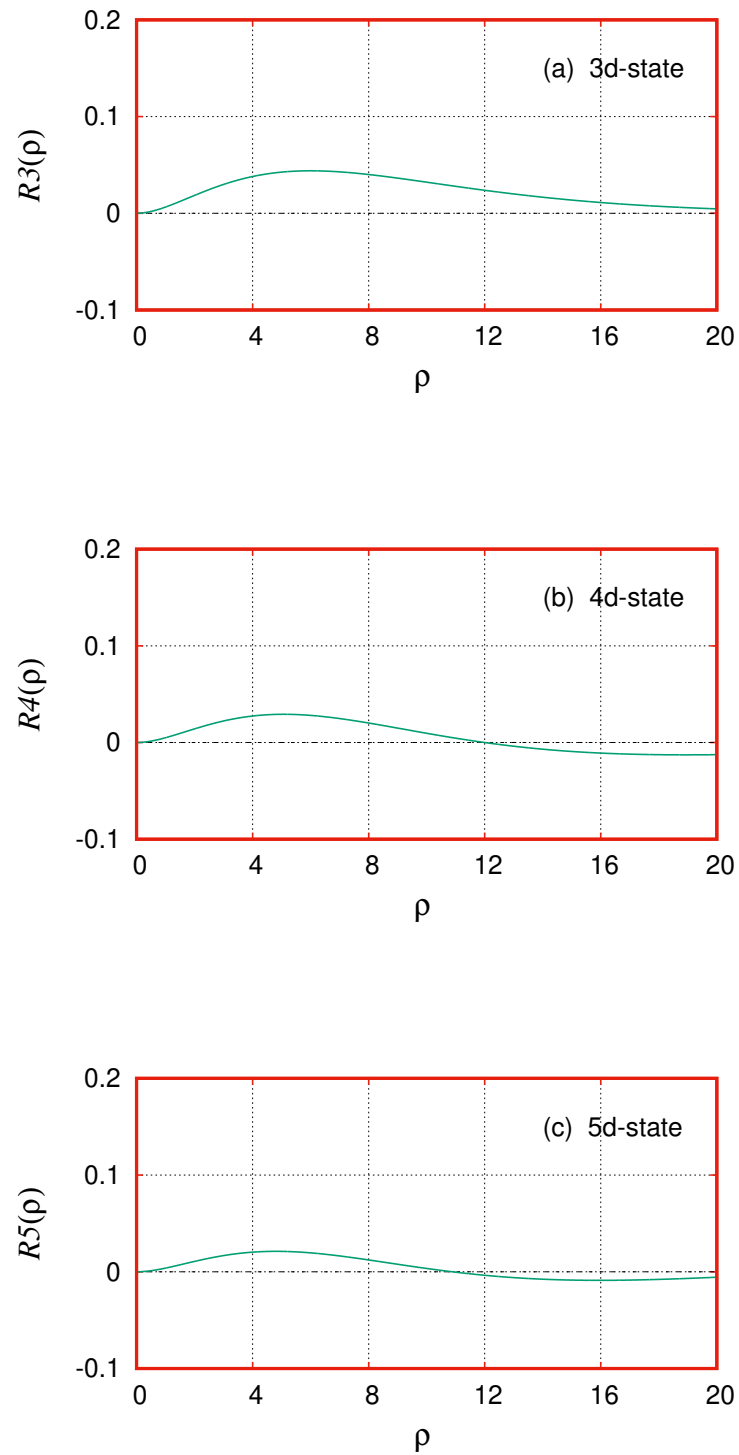FIGURE 2.5: d-state (l=2) Radial Wavefunctions for various n values

TABLE 2.1: Radial Wave functions and their spectroscopic notations

n	l	Spectroscopic Notation	Radial Wavefunctions $R_{nl}(r)$
1	0	1 - s state	$2\left(\frac{z}{a}\right)^{3/2} e^{-Zr/a}$
2	0	2 - s state	$\frac{1}{\sqrt{2}}\left(\frac{z}{a}\right)^{3/2}\left(1 - \frac{Zr}{2a}\right) e^{-Zr/2a}$
2	1	2 - p state	$\frac{1}{\sqrt{24}}\left(\frac{z}{a}\right)^{5/2} r\, e^{-Zr/a}$
3	0	3 - s state	$\frac{2}{\sqrt[3]{3}}\left(\frac{z}{a}\right)^{3/2}\left[1 - \frac{2Zr}{3a} + \frac{2Z^2 r^2}{27a^2}\right] e^{-Zr/3a}$

2.3.5 Complete Hydrogen Atom Wavefunctions

The complete Hydrogen atom wave function is then given

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

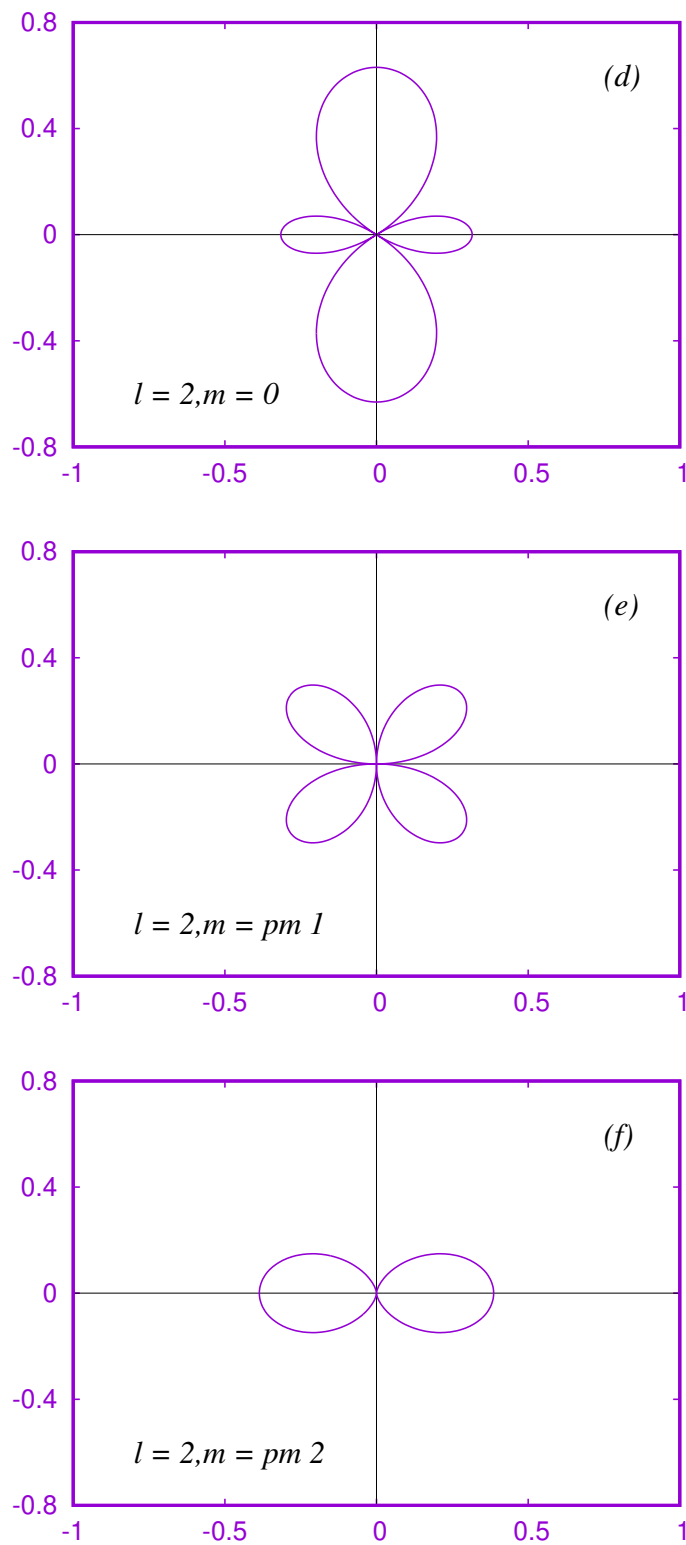where the *spherical harmonic* $Y_l^m(\theta,\phi)$ is given as

$$Y_l^m(\theta,\phi) = (-1)^m \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\, P_l^m(\cos\theta)\, e^{\pm im\phi} \tag{2.60}$$

The first few spherical harmonics are listed in Table 2. Plotting $|Y_{l,m}(\theta\phi)|^2$ for various angles ($\theta\&\phi$), the polar diagrams obtained in the $(x-y)$ plane are shown in Figs. (2.6) and (2.7).

TABLE 2.2: Spherical Harmonics and their Mathematical Expressions

Spherical Harmonic	Mathematical Expression
$Y_{0,0}$	$\left(\frac{1}{4\pi}\right)^{1/2}$
$Y_{1,0}$	$\left(\frac{3}{8\pi}\right)^{1/2}\cos\theta$
$Y_{1,\pm1}$	$\mp\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\, e^{\pm i\phi}$
$Y_{2,0}$	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta - 1)$
$Y_{2,\pm1}$	$\mp\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\,\cos\theta\, e^{\pm i\phi}$
$Y_{2,\pm2}$	$\mp\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta,\, e^{\pm 2i\phi}$
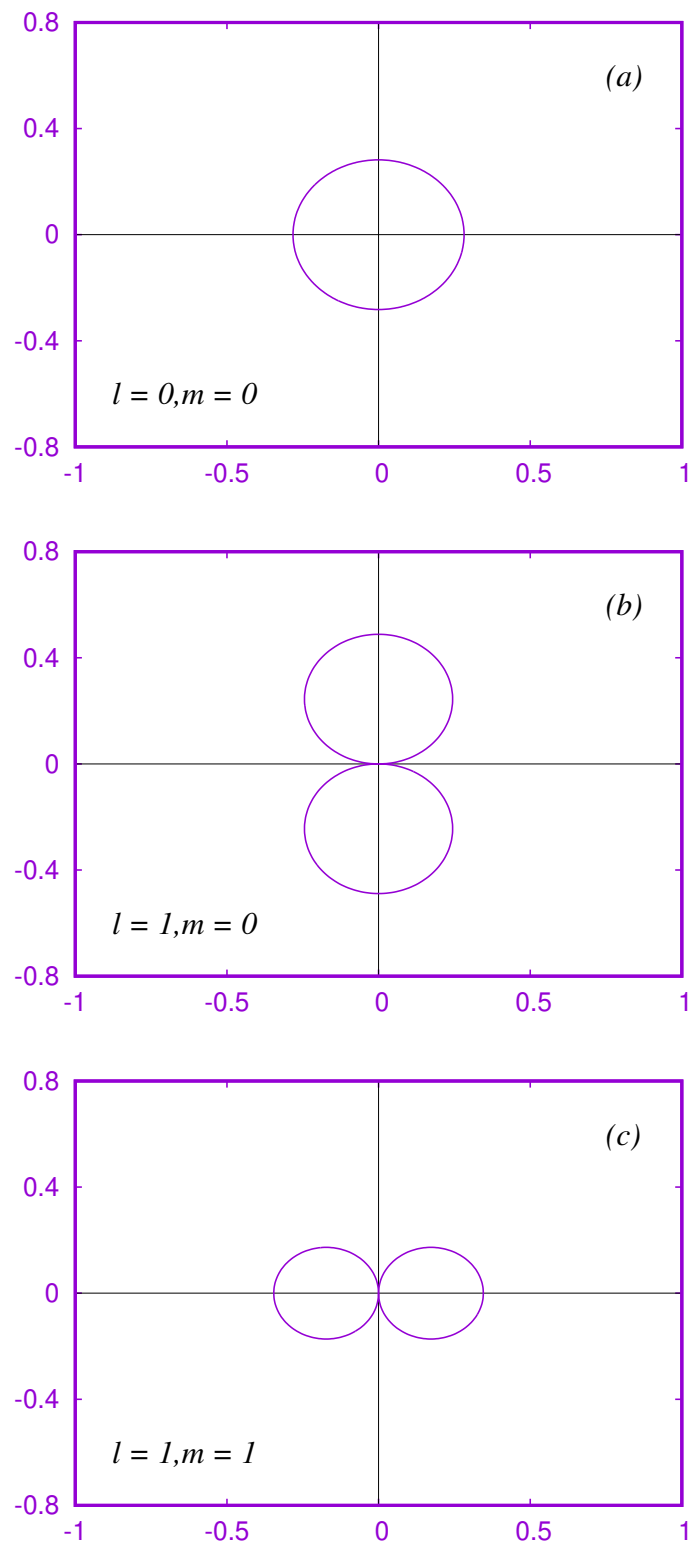
FIGURE 2.6: Spherical Harmonics for various l and m values

$l = 2, m = 0$

$l = 2, m = pm\ 1$

$l = 2, m = pm\ 2$

FIGURE 2.7: Spherical Harmonics for various l and m values

Probability Densities

The probability that the electron is within the spherical shell between radii r and $r + dr$ from the nucleus in given by

$$P_{n,l}(r)dr = |R_{n,l}(r)|^2 \, r^2 dr$$

The total probability may therefore be given as

$$P_{n,l}(r) = |R_{n,l}(r)|^2 \, r^2 \tag{2.61}$$

The probability densities for various quantum states defined by n and l values are given in Fig. (2.8)
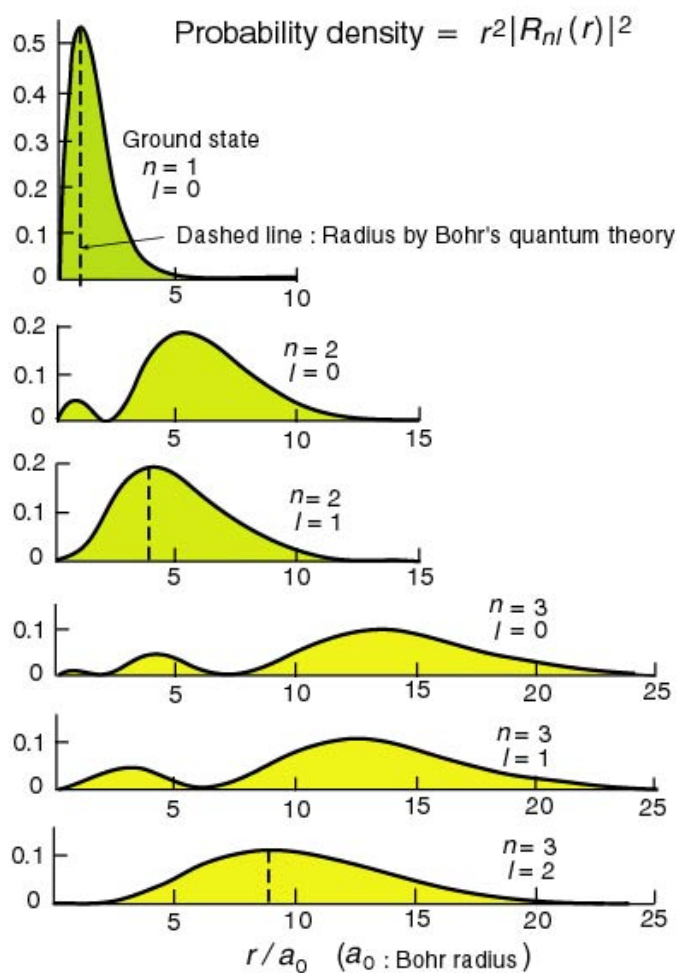

FIGURE 2.8: Probability Densities for various quantum states defined by n and l values

Ground State Probability

For the ground state of the Hydrogen atom, $(n = 1, l = 0)$. Hence the radial wave function is given as

$$R_{1,0}(r) = 2\left(\frac{1}{a}\right)^{3/2} e^{-(r/a)} \tag{2.62}$$

Therefore the ground state probability density is given as

$$
\begin{aligned}
P_{1,0}(r) &= |R_{1,0}(r)|^2 \, r^2 \\
P_{1,0}(r) &= \frac{4}{a^3} \, e^{-2r/a} . r^2
\end{aligned} \tag{2.63}
$$

The total probability is maximum if $\dfrac{dP}{dr} = 0$. Hence

$$\frac{dP}{dr} = \frac{4}{a^3} \, e^{-2r/a} \left[2r - \frac{2r^2}{a} \right] = 0$$

or

$$\left[2r - \frac{2r^2}{a} \right] = 0$$

or

$$r = a \tag{2.64}$$

Thus we find that the probability distribution of the radial position of the electron rises to a maximum at $r = a$ in the ground state. Here a is equivalent to the first Bohr radius of Hydrogen atom as per the old quantum theory of Neil Bohr.

Similarly the maximum probability of the $2s - state$ electron lies at $4a$ and $3s - state$ electron lies at $13a$ etc. These are shown in the $P_{n,l}(\rho)$ vs ρ graph drawn in Fig. (2.8).