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# UNIT 9 SPHERICALLY SYMMETRIC SYSTEMS: HYDROGEN ATOM

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## 9.1 INTRODUCTION

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In the previous unit you have obtained eigenfunctions and eigenvalues of a number of one-dimensional systems. In this unit, we shall extend our study to a three-dimensional system. Thus now there will be three independent variables,  $x$ ,  $y$  and  $z$ , in Cartesian coordinate system or  $r$ ,  $\theta$  and  $\phi$  in spherical polar coordinate system. Hence, the degree of freedom of the particle will increase from one to three and the time independent Schrodinger equation will be a three-dimensional differential equation.

In general, the potential in which a particle moves in a three-dimensional space is a function of all the three coordinates. However, in the present unit we shall confine ourselves to those potentials which depend only upon the radial coordinate  $r$  and are independent of the polar coordinates  $\theta$  and  $\phi$ . Such potentials are known as spherically symmetric potentials and the corresponding systems are called spherically symmetric systems.

When quantum mechanics was developed in the 1920s, one of its first (and also one of the most important) applications was to the understanding of hydrogen and hydrogen-like atoms (atoms with one valence electrons). In this unit, our main focus will be on the hydrogen atom. As you know, a hydrogen atom consists of a proton and an electron moving in the Coulomb potential of the proton. The motion of an electron in the Coulomb potential of the nucleus is also referred to as the Kepler problem of quantum mechanics — it is exactly solvable. You know that the Coulomb potential of the proton at a distance  $r$  is  $-\frac{e^2}{4\pi\epsilon_0 r}$ , Hence the potential is spherically symmetric.

In this unit we shall solve the three-dimensional Schrödinger equation for the hydrogen atom to obtain eigenfunctions and eigenenergies for the stationary states of hydrogen atom. In the course of solving this problem, when we find that the mathematics is becoming too difficult, we shall restrict ourselves to a qualitative discussion of the problem. We shall consider bound as well as continuum states of the hydrogen atom. To further simplify our study we shall begin by considering the motion of a particle in a spherically symmetric potential and then extend these ideas to the hydrogen atom. In the next unit we shall apply the results of this unit to hydrogen-like and other multielectron atoms and understand their optical spectra.

### Objectives

After studying this unit you should be able to

- separate the time independent Schrödinger equation for a spherically symmetric system into its radial and angular parts,

- show that the angular **momentum** is a constant of motion for such systems,
  - explain the concept of space quantization,
  - reduce the two-body hydrogen atom system to two one-body systems,
  - obtain the **eigenfunctions** and energy eigenvalues for the stationary state of a hydrogen atom,
- explain the spectra of the hydrogen atom,
- specify the constants of motion and the corresponding quantum numbers for the hydrogen atom problem.

## 9.2 THREE DIMENSIONAL SCHRÖDINGER EQUATION FOR A CENTRAL POTENTIAL

Let us consider the three-dimensional motion of a particle of **mass**  $\mu$  in a spherically symmetric potential. For its stationary states, the time independent **Schrödinger** equation is given by

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \psi(\mathbf{r}) = E \psi(\mathbf{r}) \quad (9.1)$$

where  $E$  is the total energy of the particle and  $V(r)$  is its potential energy. **Note** that  $V(r)$  is independent of the polar angles  $\theta$  and  $\phi$ . The force  $\mathbf{F}$  acting on such a particle will be directed along  $\mathbf{r}$ . So classically, the torque  $\boldsymbol{\tau}$  on the particle is equal to  $\mathbf{r} \times \mathbf{F}$ . **Since**  $\mathbf{F}$  and  $\mathbf{r}$  are in the same direction,  $|\boldsymbol{\tau}|$  is equal to zero. Furthermore, torque is equal to the rate of change of angular **momentum**  $\mathbf{L}$ . Hence, the angular momentum of a particle moving under a spherically symmetric potential (also known as central potential) will not change with time. Thus, it will be a constant of motion for that object. Recall that you have solved this problem in Unit 6 of the elective PHE-01 in the classical domain to obtain Keplerian orbits for planetary motion around the sun.

However, a constant  $\mathbf{L}$  means that all its three components  $L_x$ ,  $L_y$ , and  $L_z$  are **constant** simultaneously. This is not possible in quantum mechanics because the three components of  $\mathbf{L}$  do not commute among themselves (see Unit 7). Thus, there is a difference between the classical and quantum introductions to angular momentum. Instead of **relating** angular momentum to **torque** (as in classical mechanics), in quantum mechanics we find that the Hamiltonian can be written in such a way that it depends only on the angular momentum. This is how angular momentum makes its entry into the scheme of quantum mechanics.

Let us see how it is done. You know **from** Unit 3 of PHE-04, that in spherical polar coordinates,  $\nabla^2$  is given by

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

Putting this expression for  $\nabla^2$  in Eq. (9.1) we obtain

$$\left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{2\mu}{\hbar^2} (E - V(r)) r^2 \right] \psi = - \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \psi \quad (9.2)$$

Eq. (9.2) suggests that  $(r, \theta, \phi)$  can be separated in the variables  $r$ ,  $\theta$  and  $\phi$  as follows:

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi) \quad (9.3)$$

Putting Eq. (9.3) in Eq. (9.2) and using the method of separation of variables (refer to **Unit 6** of PHE-05 entitled Mathematical Methods in Physics-I), we get the **following** two equations

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R(r)}{\partial r} \right) + \left[ \frac{2\mu}{\hbar^2} (E - V(r)) - \frac{K}{r^2} \right] R(r) = 0 \quad (9.4)$$

and

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} = -K Y(\theta, \phi) \quad (9.5)$$

where K is a constant. We can further show that the operators  $L^2$  and  $L_z$  in spherical polar coordinates are given by

$$L^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (9.6a)$$

$$L_z = \frac{\hbar}{2\pi i} \frac{\partial}{\partial \phi} \quad (9.6b)$$

You should quickly establish Eqs. (9.4) and (9.5) before studying further.

In fact, you may like to do this exercise yourself. Try the following SAQ.

Spend 15 min

#### SAQ 1

- (a) Prove Eqs. (9.6a) and (9.6b).
- (b) Show that  $L^2$  and  $L_z$  commute with the Hamiltonian.

Note: We will make use of this result in Sec. 9.2.1.

Using Eq. (9.6a), we can write Eq. (9.5) as:

$$L^2 Y(\theta, \phi) = K\hbar^2 Y(\theta, \phi) \quad (9.7)$$

Thus  $Y(\theta, \phi)$  is an eigenfunction of the operator  $L^2$  with  $K\hbar^2$  as the eigenvalue. Let us study the functions  $Y(\theta, \phi)$  in somewhat greater detail.

#### 9.2.1 Eigenfunctions and Eigenvalues of the Angular Momentum Operator

Let us obtain the eigenvalues of Eq. (9.7) and determine the form of  $Y(\theta, \phi)$ . From Eq. (9.7) we can readily see that  $Y(\theta, \phi)$  is an eigenfunction of the operator  $L^2$  with the eigenvalue  $K\hbar^2$ . Further, you have established in SAQ 1 that  $L^2$  commutes with the Hamiltonian of the particle:

$$[L^2, H] = 0 \quad (9.8a)$$

Now recall Eq. (7.32b) of Unit 7. If  $[D, H] = 0$  in that equation,  $\frac{d\langle D \rangle}{dt} = 0$ , i. e.,  $\langle D \rangle$  is constant. Applying this result to the square of angular momentum ( $L^2$ ) we obtain

$$\langle L^2 \rangle = \text{constant} \quad (9.8b)$$

i. e., the square of the angular momentum is a constant of motion for a central potential.

We can solve for  $Y(\theta, \phi)$  by separating the variables  $\theta$  and  $\phi$  and writing

$$Y(\theta, \phi) = P(\theta) \Phi(\phi) \quad (9.9a)$$

Substituting Eq. (9.9a) and Eq. (9.6a) in Eq. (9.7), and using separation of variables, we obtain

$$\left[ \frac{\sin \theta}{P(\theta)} \frac{d}{d\theta} \left( \sin \theta \frac{dP(\theta)}{d\theta} \right) + K \sin^2 \theta \right] = -\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} \quad (9.9b)$$

Eq. (9.9b) shows that both sides are equal to the same constant, say  $m_l^2$ . Hence, we can write

$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m_l^2 \quad (9.10)$$

and its solution is

$$\Phi(\phi) = e^{im_l \phi} \quad (9.11)$$

Now  $\Phi(\phi)$  has to be single valued. Hence we must have

$$e^{im_l \phi} = e^{im_l(\phi + 2\pi)} \quad (9.12)$$

because angles  $\phi = 0$  and  $\phi = 2\pi$  are actually the same. Therefore  $m_l$  must be an integer. For the operator  $L_z$  (Eq. 9.6b) operating upon  $e^{im_l \phi}$ , we obtain

$$L_z e^{im_l \phi} = m_l \hbar e^{im_l \phi} \quad (9.13)$$

Thus,  $e^{im_l \phi}$  is an eigenfunction of the operator  $L_z$  with the eigenvalue  $m_l \hbar$ .

The differential equation for  $P(\theta)$  is given by

$$\sin \theta \frac{d}{d\theta} \left( \sin \theta \frac{dP(\theta)}{d\theta} \right) + K P(\theta) \sin^2 \theta = m_l^2 P(\theta) \quad (9.14)$$

Eq. (9.14) can be solved analytically. However, the procedure is lengthy and out of place here. Hence here we only quote the results and discuss them qualitatively. If we take the constant  $K$  equal to  $l(l+1)$  then it is found that quantum mechanically acceptable solutions of Eq. (9.14) are obtained only if the constant  $l$  is equal to one of the integers

$$l = |m_l|, |m_l| + 1, |m_l| + 2, \dots \quad (9.15)$$

Alternatively, we can also say that for a given integer  $l$  there will be following  $(2l+1)$  values of  $m_l$ :

$$-l, -l+1, -l+2, \dots, 0, \dots, l-1, l \quad (9.16)$$

Then the acceptable solutions are given by

$$P_l^{m_l}(\theta) = \sin^{l-m_l}(\theta) F_{l, m_l}(\cos \theta) \quad (9.17)$$

where  $F_{l, m_l}(\cos \theta)$  are polynomials in  $\cos \theta$  and  $P_l^{m_l}(\theta)$  are known as the *associated Legendre polynomials*. Thus, substituting Eqs. (9.11) and (9.17) in Eq. (9.9a) we obtain the eigenfunctions of  $L^2$ :

$$Y_{l, m_l}(\theta, \phi) = P_l^{m_l}(\theta) e^{im_l \phi} \quad (9.18)$$

The functions given by Eq. (9.18) are known as *spherical harmonics*. Putting  $K = l(l+1)$  in Eq. (9.7) you can readily see that they are the eigenfunctions of the operator  $L^2$  with eigenvalues  $l(l+1)\hbar^2$ .

$$L^2 Y_{l, m_l}(\theta, \phi) = l(l+1)\hbar^2 Y_{l, m_l}(\theta, \phi) \quad (9.19)$$

Thus  $(2l+1)$  eigenfunctions  $Y_{l, m_l}(\theta, \phi)$  corresponding to the same  $l$  but different  $m_l$  (ranging from  $-l$  to  $l$ ) have the same eigenvalues. Hence we can say that these eigenfunctions are  $(2l+1)$ -fold degenerate. These functions specify the angular part of the steady state eigenfunctions of all particles moving under spherically symmetric potentials. They form an orthonormal set (as explained in Sec. 7.3 of Unit 7) and any function of  $\theta$  and  $\phi$  can be expressed as a linear combination of  $Y_{l, m_l}(\theta, \phi)$ . We give here the explicit forms of some of the lower order  $Y_{l, m_l}(\theta, \phi)$  for ready reference.

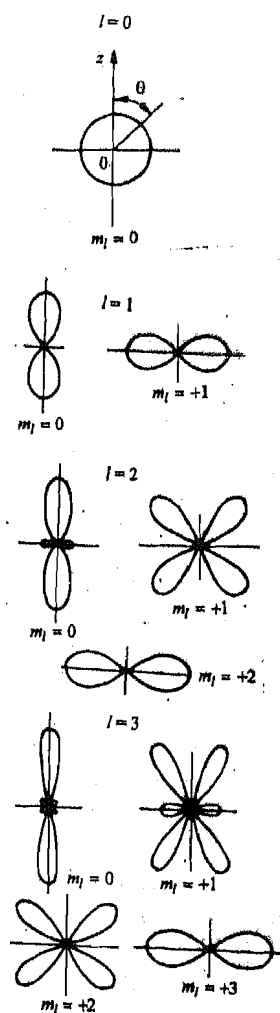


Fig. 9.1: Polar  $Y_{l, m_l}^2(\theta, \phi)$  for some values of  $l$  and  $m_l$ .

$$\begin{aligned}
 Y_{00} &= \left(\frac{1}{4\pi}\right)^{1/2}, \\
 Y_{10} &= \left(\frac{3}{4\pi}\right)^{1/2} \cos \theta \\
 Y_{1,\pm 1} &= \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin \theta e^{\pm i\phi} \\
 Y_{20} &= \left(\frac{5}{16\pi}\right)^{1/2} (3 \cos^2 \theta - 1) \\
 Y_{2,\pm 1} &= \mp \left(\frac{15}{8\pi}\right)^{1/2} \sin \theta \cos \theta e^{\pm i\phi} \\
 \text{and } Y_{2,2} &= \left(\frac{15}{32\pi}\right)^{1/2} \sin^2 \theta e^{\pm 2i\phi}
 \end{aligned} \tag{9.20}$$

The squares of some of these functions (which also represent the angular part of the wave function of the hydrogen atom) are shown in Fig. 9.1. You may now like to perform an exercise based on the ideas discussed so far.

Spend  
10 min

**SAQ 2**

- (a) Show that  $Y_{l,m_l}(\theta, \phi)$  is an eigenfunction of  $L_z$ . Determine its eigenvalues,  
 (b) Show that  $Y_{2,2}$  is normalised and is orthogonal to  $Y_{2,-2}$ .

Before studying further, it would do us well to examine the parity of the spherical harmonics. For this, we reflect  $Y_{l,m_l}(\theta, \phi)$  about the origin. In such a reflection  $\theta$  changes to  $\pi - \theta$  and  $\phi$  changes to  $\pi + \phi$ .

Now

$$e^{im_l(\pi + \phi)} = (-1)^{m_l} e^{im_l\phi} \tag{9.21a}$$

Further  $\sin(\pi - \theta) = \sin \theta$  and  $\cos(\pi - \theta) = -\cos \theta$ . Hence, it can be shown that

$$P_l^{m_l}(\pi - \theta) = (-1)^{l-m_l} P_l^{m_l}(\theta) \tag{9.21b}$$

Therefore, the parity of  $Y_{l,m_l}(\theta, \phi)$  is given by  $(-1)^{l-m_l+m_l}$  which is equal to  $(-1)^l$ . We shall make use of these concepts in the later sections of the Unit.

Spend  
2 min

**SAQ 3**

Use the expression given by Eq. (9.20) for  $Y_{2,1}(\theta, \phi)$  and verify that it is of even parity.

To sum up, so far we have obtained the solutions of the angular part of the stationary states of a particle moving in a spherically symmetric potential. These are **nothing** but the eigenfunctions of the angular momentum operator  $L^2$ . Their exact functional dependence on  $\theta$  and  $\phi$  is given by the spherical harmonics. The eigenvalues of the operator  $L^2$  are  $l(l+1)\hbar^2$  where  $l$  takes discrete integral values given by Eq. (9.15).

Let us now try to understand what these results mean physically, in terms of what is called space quantization.

**9.22 Space Quantization**

You have shown in SAQ 2(a) that the spherical harmonics  $Y_{l,m_l}(\theta, \phi)$  are eigenfunctions of  $L_z$  with eigenvalues  $m_l\hbar$ . Thus we can determine exact values of  $L^2$  and  $L_z$  simultaneously. However, since  $L_x, L_y, L_z$  cannot be determined simultaneously

according to the uncertainty principle,  $L_x$  and  $L_y$  will be uncertain. Thus, we are confronted with some surprises about the quantum mechanical angular momentum as compared with its classical counterpart.

Classically, for the same magnitude of the angular momentum, we can obtain an infinite number of states by changing the direction of the angular momentum vector. But quantum mechanically, for each value of angular momentum, there are only a finite number of states characterised by  $l$  and  $m_l$ . Moreover, in quantum mechanics, the components of  $L$  in two of the three directions being uncertain, we do not describe a state by specifying the directions of the angular momentum vector. Instead, we give the component of the angular momentum along a specific direction. We conveniently choose this direction to be along the z-axis. So how do we visualise this situation?

There is a useful pictorial way to communicate these quantum mechanical results — this is the so called vector model for the angular momentum. In this model we represent the angular momentum of the particle in motion by a vector  $L$  of length  $[l(l+1)]^{1/2}$ . The angular momentum vector precesses around the z-axis in such a way that the magnitude of  $L$  (hence  $L^2$ ) and  $L_z$  (projection of  $L$  on z-axis) are constants (see Fig. 9.2a).

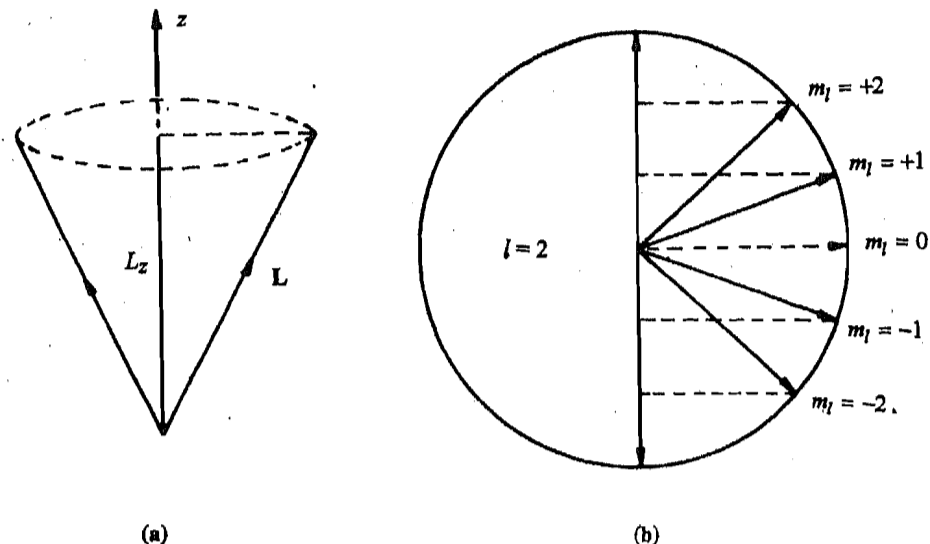


Fig. 9.3: (a) Precession of  $L$  about z-axis; (b) space quantization for  $l = 2$ . The radius of the circle is  $[2(2+1)]^{1/2}$ . The multiplicity of states is 5.

Since for a given value of  $l$ , the eigenvalues of  $L_z$  are  $m_l \hbar$  with integer values of  $m_l$  (ranging from  $-l$  to  $+l$ ), the component of  $L$  along the z-axis is quantized. A measurement of  $L_z$  will yield only the  $2l + 1$  quantized values, with a maximum value  $l$  less than the magnitude of the vector  $L$  for  $l \neq 0$ . Further, the vector  $L$  can make only certain quantized angles with the z-axis; the angle  $\theta$ , between  $L$  and  $L_z$  can take only discrete values given by

$$\cos \theta = \frac{m_l}{[l(l+1)]^{1/2}} \quad (9.22)$$

This phenomenon of the quantization of the direction of  $L$  with respect to one of the coordinate axes, is known as space quantization. Since  $|m_l|$  is always less than  $l(l+1)$  (except for  $l = 0$ ), the vector  $L$  can never be along z-axis. For  $l = 2$ , the values of  $m_l$  are 2, 1, 0, -1 and -2 as shown in Fig. 9.2b. Furthermore, although  $L_x$  and  $L_y$  are uncertain,  $L_x^2 + L_y^2$  being equal to  $L^2 - L_z^2$  have definite non-zero values unless  $l = 0$ ; however, the values of  $L_x$  and  $L_y$  are not quantized. Thus we can visualise the angular momentum vector sweeping out in all possible directions in the xy plane.

Having analysed the angular part of the wavefunction and some of its implications, let us now consider the radial part of the eigenfunctions for a spherically symmetric potential.

### 9.2.3 Radial Eigenfunctions

Putting  $K = l(l+1)$  in Eq. (9.4), we obtain the differential equation for the radial function  $R(r)$ . This is given by

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left\{ V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} \right\} R(r) = E R(r) \quad (9.23a)$$

This is a one-dimensional eigenvalue equation for the radial eigenfunction  $R(r)$ . The actual solution depends upon the form of potential energy function  $V(r)$ . However, the effective potential of the particle is

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 l(l+1)}{2\mu r^2} \quad (9.23b)$$

Thus, there is an extra term in the form of repulsive potential energy  $(l(l+1)\hbar^2/2\mu r^2)$  which increases with  $l$  (see Fig. 9.3). You can see that this term decreases the probability of finding the particle near the centre of force. This term is also known as the centrifugal potential energy, or the centrifugal barrier.

The origin of the centrifugal term can be understood in the following manner using classical correspondence. For a particle of mass  $\mu$  moving in a circular orbit of radius  $r$ , classically, there is a centrifugal force directed radially outward. The magnitude of the force is  $\mu v^2/r = L^2/\mu r^3$ , where  $L = \mu v r$  for a circular orbit. The potential corresponding to such a force is  $L^2/2\mu r^2$  (since  $F = \partial V/\partial r$ ). In quantum mechanics we must replace  $L^2$  by its eigenvalue  $l(l+1)\hbar^2$ , hence we obtain the quantum mechanical expression for the centrifugal potential.

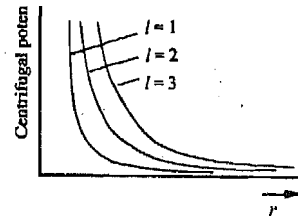


Fig. 9.3: The centrifugal barrier for some values of  $l$ .

For bound particles (such as a simple harmonic oscillator), the values of  $E$  (eigenvalues) are discrete. Otherwise  $E$  varies in a continuous manner. But whatever be the form of  $V(r)$ , as long as it is spherically symmetric, the angular part of the eigenfunction of the particle is given by the spherical harmonics  $Y_{l,m_l}(\theta, \phi)$ .

In the next section we shall take  $V(r)$  to be the Coulomb potential energy, appropriate to a hydrogen atom and shall obtain eigenfunctions and eigenvalues of a hydrogen atom.

## 9.3 THE HYDROGEN ATOM

Let us consider the hydrogen atom as an example of a three-dimensional quantum mechanical system. As you know, a hydrogen atom consists of a proton and an electron. Thus it is a two-particle system. The Hamiltonian for two-body motion in a central force field is given as

$$H = \frac{p_1^2}{2M} + \frac{p_2^2}{2m} + V(\mathbf{r}_1, \mathbf{r}_2) \quad (9.24a)$$

Thus the stationary states of the hydrogen atom are the solutions of the following time independent Schrodinger equation

$$\left[ -\frac{\hbar^2}{2M} \nabla_1^2 - \frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|} \right] \psi(\mathbf{r}_1, \mathbf{r}_2) = E_T \psi(\mathbf{r}_1, \mathbf{r}_2) \quad (9.24b)$$

where  $M$  and  $m$  are the masses of the proton and the electron, respectively;  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are the coordinates of the proton and the electron, respectively, with respect to an origin  $O$ .  $E_T$  is the total energy of the system and  $\epsilon_0$  is the permittivity constant. Thus we are required to solve a six-dimensional differential equation to obtain the eigenfunction  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  and eigenvalue  $E_T$ . However, we can reduce the above equation into two three-dimensional equations in the following manner.

Let  $\mathbf{R}$  be the coordinate of the centre of mass of the atom. Then

$$\mathbf{R} = \frac{M \mathbf{r}_1 + m \mathbf{r}_2}{M + m} \quad (9.25)$$

The separation between the proton and the electron is given by

$$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2 \quad (9.26)$$

Solving for  $\mathbf{r}_1$  and  $\mathbf{r}_2$  in terms of  $\mathbf{R}$  and  $\mathbf{r}$  we get

$$\mathbf{r}_1 = \mathbf{R} + \frac{m}{M+m} \mathbf{r} \quad (9.27)$$

and

$$\mathbf{r}_2 = \mathbf{R} - \frac{M}{M+m} \mathbf{r} \quad (9.28)$$

Now you know that

$$\frac{\partial \psi}{\partial x_1} = \frac{\partial \psi}{\partial \mathbf{X}} \frac{\partial \mathbf{X}}{\partial x_1} = \frac{\partial \psi}{\partial \mathbf{X}} \frac{\partial \mathbf{X}}{\partial x_1}$$

where  $x_1, \mathbf{X}$  and  $x$  are the  $x$  components of  $\mathbf{r}_1, \mathbf{R}$  and  $\mathbf{r}$ , respectively. Hence Eqs. (9.25) to (9.27) yield for the  $x$  component

$$\frac{\partial \psi}{\partial x_1} = \frac{M}{m+M} \frac{\partial \psi}{\partial \mathbf{X}} + \frac{\partial \psi}{\partial x} \quad (9.29)$$

Hence, in three-dimensions

$$\nabla_1 = \frac{M}{m+M} \nabla_{\mathbf{R}} + \nabla \quad (9.30)$$

where

$$\nabla = \hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \quad (9.31)$$

and  $(x_1, y_1, z_1), (x, y, z)$  and  $(X, Y, Z)$  are the components of  $\mathbf{r}_1, \mathbf{r}$  and  $\mathbf{R}$ , respectively. Similarly, from Eq. (9.28) we obtain

$$\nabla_2 = \frac{m}{m+M} \nabla_{\mathbf{R}} - \nabla \quad (9.32)$$

Eqs. (9.30) and (9.32) yield

$$\nabla_1^2 = \left(\frac{M}{m+M}\right)^2 \nabla_{\mathbf{R}}^2 + 2\left(\frac{M}{m+M}\right) \nabla_{\mathbf{R}} \cdot \nabla + \nabla^2 \quad (9.33a)$$

and

$$\nabla_2^2 = \left(\frac{m}{m+M}\right)^2 \nabla_{\mathbf{R}}^2 - 2\left(\frac{m}{m+M}\right) \nabla_{\mathbf{R}} \cdot \nabla + \nabla^2 \quad (9.33b)$$

Putting the expressions for  $\nabla_1^2$  and  $\nabla_2^2$  from Eqs. (9.33a and b) into Eq. (9.24b) we get

$$\left[ \frac{\hbar^2}{2(M+m)} \nabla_{\mathbf{R}}^2 - \frac{e^2}{4\pi\epsilon_0 R} \right] \psi(\mathbf{R}, \mathbf{r}) = E_T \psi(\mathbf{R}, \mathbf{r}) \quad (9.34)$$

where for our convenience we have replaced  $e^2/4\pi\epsilon_0$  by only  $e^2$  with

$$e^2 = 2.31 \times 10^{-28} \text{ Joule.metre.}$$

Eq. (9.34) is separable in the coordinates  $\mathbf{R}$  and  $\mathbf{r}$ . Taking

$$\psi(\mathbf{R}, \mathbf{r}) = \phi(\mathbf{R}) \psi(\mathbf{r}) \quad (9.35)$$

we find that  $\phi(\mathbf{R})$  and  $\psi(\mathbf{r})$  are the respective solutions of the following three-dimensional differential equations

$$\frac{\hbar^2}{2(M+m)} \nabla_{\mathbf{R}}^2 \phi(\mathbf{R}) = E_T \phi(\mathbf{R}) \quad (9.36)$$

and

$$\frac{\hbar^2}{2\mu} \nabla^2 \psi(\mathbf{r}) = (E - E_T) \psi(\mathbf{r}) \quad (9.37a)$$

where

$$\mu = \left(\frac{1}{m} + \frac{1}{M}\right)^{-1} \quad (9.37b)$$

and  $E_T = E + E_H$ . As you know,  $\mu$  is the reduced mass of the system.

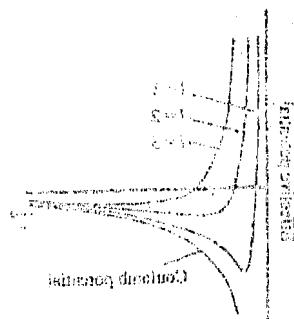


Fig. 9.2. The radial wavefunction  $R(r)$  and the effective potential  $V(r)$  for the hydrogen atom. The curves are labeled with their corresponding energy levels  $E_1, E_2, E_3, E_4, E_5$ . The curves for  $E_1, E_2, E_3$  are positive, while the curves for  $E_4, E_5$  are negative.



Eq. (9.36) shows that a particle of mass  $(m + M)$ , which is the total mass of the hydrogen atom, is moving freely in a **three-dimensional** space and its total energy is  $E_H$  (with zero potential energy). This is a problem that you have already solved in **Sec. 8.2**. Its eigenfunctions are given by plane waves

$$\phi(\mathbf{R}) = e^{i\mathbf{K}\cdot\mathbf{R}} \quad (9.38)$$

$$\text{with } \frac{\hbar^2 K^2}{2(m+M)} = E_H \quad (9.39)$$

The eigenvalue  $E_H$  and the corresponding quantum number  $K$  vary in a continuous manner.

On the other hand, **Eq. (9.37a)** describes the motion of a particle of mass  $\mu$  having potential energy  $-e^2/r$  with respect to a **fixed** centre. Thus by the above procedure we have **reduced a two-body** system into two one-body systems, one of mass  $(m+M)$  which moves freely in space and other of mass  $\mu$  and charge  $e$  which moves under an attractive potential  $-e^2/r$ . You should note that in the present model the relative motion of **electron** and proton with respect to each other has been replaced by the motion of a particle of mass  $\mu$  with respect to a fixed centre of force.

Now **Eq. (9.37a)** is exactly the same as **Eq. (9.1)** with  $V(r) = -e^2/r$ . Hence the eigenfunctions of the particle of mass  $\mu$ , which are also known as the eigenfunctions of the **hydrogen** atom, are given by

$$\psi(r, \theta, \phi) = R(r) Y_{l, m_l}(\theta, \phi) \quad (9.40)$$

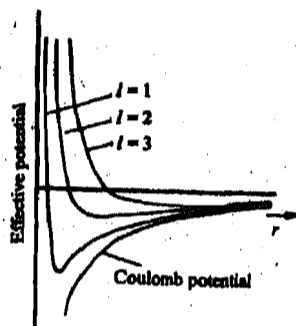
The radial function  $R(r)$  is the solution of the following one-dimensional differential equation

$$-\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) + \left\{ -\frac{e^2}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2} \right\} R(r) = E R(r). \quad (9.41)$$

The above **equation** has been obtained from **Eq. (9.23a)** by taking  $V(r) = -e^2/r$ . The **effective** potential energy in this case is

$$V_{\text{eff}}(r) = -\frac{e^2}{r} + \frac{\hbar^2 l(l+1)}{2\mu r^2}$$

It is shown in **Fig. 9.4**,



**Fig 9.4:** The Coulomb potential and the effective potential for some values of  $l$ . Compare this with **Fig. 9.3**.

You can see from **Fig. 9.4**, that near the origin  $\frac{\hbar^2 l(l+1)}{2\mu r^2}$  is much larger than  $-e^2/r$ . We will **now present** some results here without going into the detailed mathematical solution of **Eq. (9.41)**. We find that for finite values of  $E$ , the solution of **Eq. (9.41)** near the origin is given by  $R(r) = cr^l$ , where  $c$  is a constant. Further, at large values of  $r$ ,  $V(r)$  tends to zero and the differential **equation** reduces to

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR(r)}{dr} \right) = -\frac{2\mu E}{\hbar^2} R(r) \quad (9.42)$$

Let us take **zero** (or the reference level) of the energy  $E$  to be the energy of that state where the hydrogen atom is **ionised** but the free **electron of the** hydrogen atom has zero kinetic energy. Then the bound eigenstates of the hydrogen atom have negative total energy  $E$  (the **positive kinetic** energy of the **particle** of mass  $\mu$  being less than the magnitude of **negative** potential energy). On the other hand, the **free** eigenstates of the hydrogen atom have positive energy  $E$ . For the bound states  $E < 0$  and we put  $E = -|E|$  so that, the solution of **Eq. (9.42)** is given by

$$R(r) = c_2 \exp \left[ - \left( -\frac{2\mu E}{\hbar^2} \right)^{1/2} r \right] \quad (9.43)$$

$E$  being negative, the radial wave function decreases exponentially at large values of  $r$ . At the intermediate values of  $r$ , the solution for  $R(r)$  can be obtained by employing power series method. However, here we only state the final result. As you have noticed

for the bound states of other systems (say simple harmonic oscillator), the acceptable solutions of  $R(r)$  exist only for discrete values of  $E$  and these discrete values are given by

$$E_n = -\frac{\mu}{2\hbar^2} \frac{e^4}{n^2} \quad (9.44)$$

where  $n$  is a positive integer and for a given value of  $l$  ranges from

$$n = l + 1, l + 2, l + 3, \dots \quad (9.45)$$

Thus, we find that the radial eigenfunctions depend upon  $n$  as well as  $l$  and are given by

$$R_{nl}(r) = N_{nl} \exp\left(-\frac{r}{na_0}\right) \left(\frac{r}{a_0}\right)^l G_{nl}(r/a_0) \quad (9.46)$$

where  $G_{nl}(r/a_0)$  are the associated Laguerre polynomials and  $N_{nl}$  is the normalisation constant. The parameter  $a_0$  is given by

$$a_0 = \frac{\hbar^2}{\mu e^2} \quad (9.47)$$

It is interesting to note that  $a_0$  is equal to the radius of the first orbit of the electron in a hydrogen atom for the model proposed by Bohr, provided  $\mu$  is replaced by the rest mass of the electron  $m$ . Since the ratio of  $m/\mu$  is very close to unity (1.0005), we shall take  $a_0$  to be equal to the first Bohr radius with  $0.529 \times 10^{-10}$  metre as its value. Under the same approximation the eigenenergy  $E_n$  is given by

$E_n = -\frac{R}{n^2} \quad (9.48)$ <p style="text-align: center;">where</p> $R = \frac{me^4}{2A^2}$
--

As you know,  $R$  is the Rydberg constant.

You may now like to take a break, **Attempt** a simple exercise.

**SAQ 4**

Obtain the value of the Rydberg constant in the units of electron volts and  $\text{m}^{-1}$ .

*Spend  
'5 min*

A few of the lower radial eigenfunctions of the hydrogen atom are given by

$$R_{10}(r) = \frac{1}{a_0^{3/2}} e^{-r/a_0} \quad (9.49a)$$

$$R_{20}(r) = \frac{1}{(2a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} \quad (9.49b)$$

$$R_{21}(r) = \frac{1}{(2a_0)^{3/2}} \frac{r}{a_0\sqrt{3}} e^{-r/2a_0} \quad (9.49c)$$

$$R_{30}(r) = \left(\frac{1}{3a_0}\right)^{3/2} 2 \left[1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right] e^{-r/3a_0} \quad (9.49d)$$

$$R_{31}(r) = \left(\frac{1}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3} \frac{r}{a_0} \left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0} \quad (9.49e)$$

$$R_{32}(r) = \left(\frac{1}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{27\sqrt{5}} \frac{r^2}{a_0^2} e^{-r/3a_0} \quad (9.49f)$$

SAQ 5

Spend 10 min

Show that  $R_{20}(r)$  is normalised and is orthogonal to  $R_{10}(r)$ .

Finally, the eigenfunctions of a hydrogen atom are given by

$$\Psi_{nlm_l}(r, \theta, \phi) = R_{nl}(r)Y_{l, m_l}(\theta, \phi) \quad (9.50)$$

where  $R_{nl}(r)$  and  $Y_{l, m_l}(\theta, \phi)$  are given by Eq. (9.46) and Eq. (9.18), respectively. These eigenfunctions form an orthonormal set, i.e.,

$$\int \Psi_{n'l'm'_l}^*(r) \Psi_{nlm_l}(r) r^2 dr \sin \theta d\theta d\phi = \delta_{nn'} \delta_{ll'} \delta_{m_l m'_l} \quad (9.51)$$

where  $\delta_{jj'} = 1$  for  $j = j'$  and zero otherwise.

The radial part of some eigenfunctions are shown in Fig. 9.5.

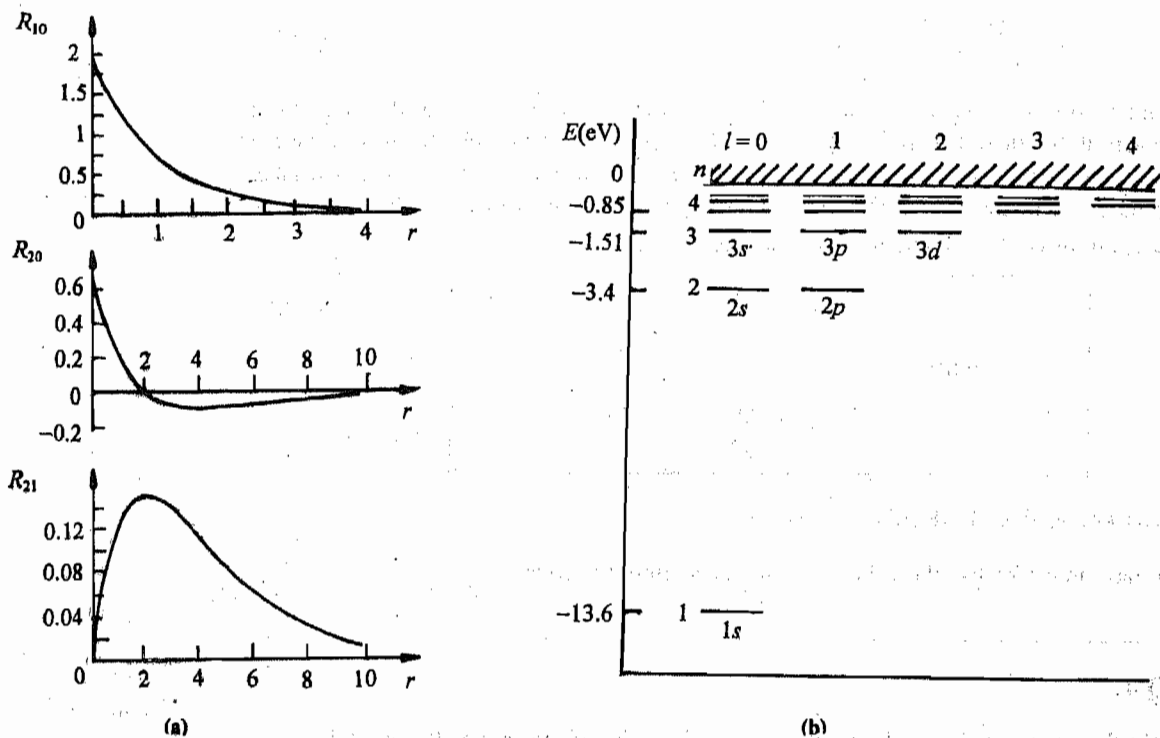


Fig. 9.5: (a) A few radial eigenfunctions; (b) eigenenergies of bound and continuum states of a hydrogen atom.

We can now make some observations about the Coulomb potential energy problem in relation to the hydrogen atom. Eq. (9.46) tells us that the bound state eigenfunctions ( $E < 0$ ) for the Coulomb potential go to zero as  $r$  goes to infinity. Notice that this potential gives an infinite number of bound states starting at energy  $-\mu e^4/2\hbar^2$  and ending at 0. The eigenenergy given by Eq. (9.44) varies in a discrete manner. The difference between the energies of the two consecutive energy states decreases as  $n$  increases (see Fig. 9.5b). For large  $n$ , the energy difference becomes quite small. The states with high  $n$  are called *Rydberg states*. Finally at  $n = \infty$ , the eigenenergy becomes zero and the hydrogen atom is ionised into a proton and an electron with zero total energy. The eigen states with  $E > 0$  are *continuum states*. They are shown by the shaded portion of Fig. 9.5b. The eigenfunctions of such states do not go to zero as  $r$  goes to infinity and  $E$  varies in a continuous manner. The eigenfunctions of continuum states of a hydrogen atom are Coulomb waves.

The atomic electrons having  $l = 0, 1, 2, 3 \dots$  are known as *s, p, d, f, ...* electrons, respectively. It is evident from Eqs. (9.46) and (9.50) that only for *s* electrons, for which  $l = 0$ , the eigenfunction  $\Psi_{nlm_l}$  is finite at  $r = 0$ , which is practically the position of the nucleus. Hence only *s* electrons have a finite probability of their existence at the nucleus whereas for the electrons having non-zero angular momentum ( $l > 0$ ) the probability is zero. Such a behaviour can be understood from Eq. (9.41). The centrifugal

potential energy  $(\hbar^2/2\mu) l(l+1)/r^2$  for  $l > 0$  does not allow  $p, d, f, \dots$  electrons to come very close to the nucleus.  $n = 1$  state is known as the ground state of the hydrogen atom while  $n = \infty$  corresponds to its lowest ionised state. Thus we require one Rydberg energy to ionise a hydrogen atom.

There is another interesting feature worth commenting upon: we have a degeneracy in the spectrum, the  $l$ -degeneracy. The energy does not depend on  $l$ , but only on  $n$ ; yet for a fixed  $n$ , possible  $l$  values are  $l = 0, 1, 2, \dots, n-1$ . In addition to the  $l$ -degeneracy, there is also the  $m_l$ -degeneracy, the result of spherical symmetry. For each  $l$ ,  $m_l$  goes from  $-l$  to  $+l$ , giving us  $2l+1$  degenerate levels. For any  $n$ , the total degeneracy, then, is

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

And if we take into account the two-valuedness called spin, which you will study in Unit 10, the total degeneracy is  $2n^2$ .

The discussion so far helps us to beautifully explain the spectra of the hydrogen atom.

### 9.3.1 Spectra of the Hydrogen Atom

When the electron in a hydrogen atom makes a transition from its excited states ( $n > 1$ ) to a lower excited state or to the ground state ( $n = 1$ ), it emits electromagnetic radiations of characteristic frequencies of the hydrogen atom. The energy difference between two eigenstates of the hydrogen atom is given by

$$\Delta E = R \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad (9.52)$$

If we take  $R$  in the units of  $\text{m}^{-1}$  the wave number of emitted radiation is given by

$$\bar{\nu} = 1.097 \times 10^7 \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \text{m}^{-1} \quad (9.53)$$

For  $n_2 = 1$  and  $n_1 = 2, 3, 4, \dots$  we get a series of electromagnetic radiation of different wavelengths. This series is known as **Lyman series** and lies in the ultraviolet region of the electromagnetic spectrum. The **Balmer series** correspond to the transitions from  $n_1 = 3, 4, 5, \dots$  to  $n_2 = 2$ . Similarly, **Paschen and Brackett series** are produced due to transitions from  $n_1 = 4, 5, 6, \dots$  to  $n_2 = 3$  and  $n_1 = 5, 6, 7, \dots$  to  $n_2 = 4$ , respectively. Thus, the theoretically obtained eigenenergy spectrum successfully explains the observed line spectra of the hydrogen atom.

However, when we compare the energy spectrum with very accurate experimental data, we find some discrepancies. This is because in the real hydrogen atom there are other interactions that we have neglected here. You will study about these interactions in higher level courses. We will now discuss an important concept regarding such systems — the concept of quantum numbers that are constants of motion and characterise the state of such a system.

### 9.3.2 Quantum Numbers and Constants of Motion

In the study of the hydrogen atom you have come across three integers namely  $n, l$  and  $m_l$ . These integers are known as **quantum numbers**. Since  $n$  is connected with the eigenenergy of the system (see Eq. 9.48) it is known as **energy quantum number** or **principal quantum number**. Its existence is due to the fact that the energy is a constant of motion, i.e., the states are stationary states. The energy quantum number exists for continuum states also with the difference that now it varies in a continuous manner. In the continuum, it is usually denoted by  $k$ .

Due to spherically symmetric potential the angular momentum  $\mathbf{L}$  of the object becomes a constant of motion. However, due to non-commutability of  $L_x, L_y$  and  $L_z$  the angular momentum vector  $\mathbf{L}$  is not a constant of motion in quantum mechanics but as you have seen,  $L^2$  is a constant of motion. This gives rise to another quantum number  $l$ , which varies in a discrete manner and is a positive integer. Since  $l$  is connected with the

orbital motion of the object it is called **orbital quantum number**. From Eq. (9.45) we can show that  $l$  is less than  $n$  and for a given value of  $n$  it takes the following values:

$$0, 1, 2, \dots, n-1 \quad (9.54)$$

Since a spherically symmetric potential is also axially symmetric, the  $z$  component of  $\mathbf{L}$  also becomes a constant of motion and gives rise to a third quantum number  $m_l$ . It can take negative as well as positive integer values. The energy of a free hydrogen atom depends only upon the quantum number  $n$ . However, it can be shown that if the atom is placed under a magnetic field, its energy depends upon  $m_l$ . Hence  $m_l$  is known as **magnetic quantum number**. For a given value of  $l$ , the permissible values of  $m_l$  are

$$-l, -l+1, \dots, 0, 1, 2, \dots, l-1, l \quad (9.55)$$

The existence of three quantum numbers is also a consequence of the fact that the time independent Schrödinger equation contains three independent variables  $r$ ,  $\theta$  and  $\phi$ . We have one quantum number for each space coordinate.

Spend  
5 min

#### SAQ 6

Show that for  $n = 3$  there are 9 degenerate eigenfunctions for a hydrogen atom.

Let us now summarise what you have studied in this unit.

### 9.4 SUMMARY

- In this unit we have discussed the quantum mechanical behaviour of a particle having *constant total energy* and moving under a **three-dimensional, spherically symmetric potential**.
- A **spherically symmetric potential** depends only upon the radial coordinate  $r$  and is independent of the polar coordinates  $\theta$  and  $\phi$ .
- In classical mechanics, the angular momentum  $\mathbf{L}$  of such a particle is a constant of motion. However, in quantum mechanics all the three components  $L_x$ ,  $L_y$  and  $L_z$  of the vector  $\mathbf{L}$  cannot be constants of motion simultaneously due to the fact that these three components do not commute among themselves. However, the magnitude of  $\mathbf{L}$  or  $L^2$  and any one of the components of  $\mathbf{L}$  (which we have taken as  $L_z$ ) can be a constant of motion.
- The **three-dimensional time independent Schrödinger** equation of a particle moving under central potential can be separated into three one-dimensional differential equations, each one of them being a function of only one coordinate,  $r$ ,  $\theta$  or  $\phi$ . The solution of the differential equation in  $\phi$  is  $e^{im_l\phi}$  whereas the solution of the differential equation in  $\theta$  is the associated legendre polynomial  $P_l^{m_l}(\theta)$ . For quantum mechanically acceptable solutions  $l$  and  $m_l$  are to be only integers. Thus,  $l$  takes only positive integer values and for a given  $l$  there are  $(2l+1)$  values of  $m_l$  given by

$$m_l = -l, -l+1, -l+2, \dots, 0, 1, \dots, l-1, l$$

The quantum numbers  $l$  and  $m_l$  are known as **orbital** and **magnetic quantum numbers**, respectively. The product of the two solutions in  $\theta$  and  $\phi$  is known as **spherical harmonics** and it is represented by  $Y_{l,m_l}(\theta, \phi)$ .

- The vector  $\mathbf{L}$  is never stationary in space but precesses around the  $z$ -axis. The angle between the  $z$ -axis and  $\mathbf{L}$  can take only discrete values given by  $\cos^{-1}(m_l/\sqrt{l(l+1)})$ . This quantization of the orientation of  $\mathbf{L}$  with respect to one coordinate axis is known as **space quantization**.

- The nature of the radial wave function  $R(r)$  depends upon whether the state is a bound state or a continuum state. For bound states the eigenfunction varies as  $\exp\left[-\left(\frac{2\mu}{\hbar^2} E\right)^{1/2} \frac{r}{a_0}\right]$  at large values of  $r$ . Hence the probability of finding the particle goes to zero as  $r$  increases to  $\infty$ . On the other hand, for continuum states the probability remains finite even as  $r$  goes to infinity. At small and intermediate values of  $r$ , different spherically symmetric potentials give rise to different radial functions. In this unit we have considered Coulomb potential, appropriate to a hydrogen atom.
- A hydrogen atom is a two-particle system consisting of a proton and an electron and its stationary state Schrödinger equation is a six-dimensional differential equation. However, it can be separated into two three-dimensional differential equations: One corresponding to the motion of a free particle having mass  $(m + M)$ . Its solutions are plane waves  $e^{i\mathbf{K}\cdot\mathbf{R}}$ , where the energy quantum number  $K$  varies in a continuous manner and is related to  $E_H$  by Eq. (9.39). The second three-dimensional differential equation describes the motion of a particle of mass  $\mu$  (reduced mass of the system) having a charge  $-e$  in a spherically symmetric potential (Coulomb potential) due to a fixed centre of force having charge  $+e$ . The latter differential equation again separates into three one-dimensional differential equations, one for each polar coordinate  $r$ ,  $\theta$  and  $\phi$ . These three degrees of freedom give rise to **three quantum numbers**  $n$ ,  $l$  and  $m_l$ .
- The **angular eigenfunctions of the hydrogen atom** are again **spherical harmonics** and the **radial eigenfunctions** for bound states are given in terms of the **associated Laguerre polynomials**. The quantum number  $n$  takes only positive integer values excluding zero. For a given value of  $n$ , the quantum number  $l$  takes  $n$  values given by

$$l = 0, 1, \dots, n-1$$

For each value of  $l$  the magnetic quantum number  $m_l$  takes the values

$$m_l = -l, -l+1, \dots, 0, l, \dots, l-1, l$$

- The energy  $E$  corresponding to different eigenfunctions  $\psi_{nlm_l}(r, \theta, \phi)$  depends only upon the quantum number  $n$ . Hence for a given  $n$  there are  $n^2$  degenerate eigenfunctions corresponding to different permissible values of  $l$  and  $m_l$ . For states with  $E > 0$ , the radial eigenfunctions are Coulomb waves and the energy quantum number  $k$  varies in a continuous manner. Now energy states are no longer discrete and we talk in terms of energy states per unit energy range.
- The quantum mechanical treatment of the hydrogen atom explains the production of various electromagnetic series experimentally observed in the spectrum of the atom.

## 9.5 TERMINAL QUESTIONS

Spend 30 min

1. Use the expressions given by Eq. (9.20) to show that

$$\sum_{m_l=-2}^2 |Y_{2, m_l}(\theta, \phi)|^2 = \frac{5}{4\pi}$$

You may note that in general

$$\sum_{m_l=-l}^2 |Y_{l, m_l}(\theta, \phi)|^2 = \frac{(2l+1)}{4\pi}$$

2. According to the virial theorem the average value of the potential energy of a particle subjected to a Coulomb potential in any stationary bound state is two times its total energy. Verify the above theorem for the ground state of the hydrogen atom. Further show that the average kinetic energy is equal to the magnitude of total energy.

- Use the uncertainty relation to show that the dimension of the most stable ground state hydrogen atom is of the order of the first Bohr radius  $a_0$ .
- Obtain the most probable value and expectation value of  $r$  for the ground state of a hydrogen atom.

## 9.6 SOLUTIONS AND ANSWERS

### Self-Assessment Questions

- We know that

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = r [\hat{\mathbf{e}}_r \times (-i\hbar\nabla)]$$

In spherical polar coordinates

$$\nabla = \hat{\mathbf{e}}_r \frac{\partial}{\partial r} + \hat{\mathbf{e}}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\mathbf{e}}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}$$

Therefore

$$\begin{aligned} \mathbf{L} &= -i\hbar r \hat{\mathbf{e}}_r \times \left[ \hat{\mathbf{e}}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{\mathbf{e}}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \right] \quad (\because \hat{\mathbf{e}}_r \times \hat{\mathbf{e}}_r = \mathbf{0}) \\ &= -i\hbar r \left[ \hat{\mathbf{e}}_\phi \frac{1}{r} \frac{\partial}{\partial \theta} - \hat{\mathbf{e}}_\theta \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \right] \\ &= -i\hbar \left[ \hat{\mathbf{e}}_\phi \frac{\partial}{\partial \theta} - \hat{\mathbf{e}}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right] \end{aligned}$$

Hence

$$L^2 = \mathbf{L} \cdot \mathbf{L} = -\hbar^2 \left( \hat{\mathbf{e}}_\phi \frac{\partial}{\partial \theta} - \hat{\mathbf{e}}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right) \cdot \left( \hat{\mathbf{e}}_\phi \frac{\partial}{\partial \theta} - \hat{\mathbf{e}}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right)$$

The derivatives of the unit vectors are given as

$$\frac{\partial}{\partial \theta} \hat{\mathbf{e}}_\theta = -\hat{\mathbf{e}}_r, \quad \frac{\partial}{\partial \phi} \hat{\mathbf{e}}_\theta = \hat{\mathbf{e}}_\phi \cos \theta$$

$$\frac{\partial}{\partial \theta} \hat{\mathbf{e}}_\phi = 0, \quad \frac{\partial}{\partial \phi} \hat{\mathbf{e}}_\phi = -(\hat{\mathbf{e}}_r \sin \theta + \hat{\mathbf{e}}_\theta \cos \theta)$$

Substituting in the equation for  $L^2$  above, we obtain after some algebra

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

$$\begin{aligned} L_z = \hat{\mathbf{e}}_z \cdot \mathbf{L} &= (\hat{\mathbf{e}}_r \cos \theta - \hat{\mathbf{e}}_\theta \sin \theta) \cdot \left( -i\hbar \hat{\mathbf{e}}_\phi \frac{\partial}{\partial \theta} + i\hbar \hat{\mathbf{e}}_\theta \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \right) \\ &= -i\hbar \frac{\partial}{\partial \phi} \end{aligned}$$

Now

$$\begin{aligned} [H, L^2] &= \left[ -\frac{\hbar^2 \nabla^2}{2\mu} + V(r), L^2 \right] \\ &= \left[ -\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{L^2}{2\mu r^2} + V(r), L^2 \right] \quad (\text{Using Eq. 9.6a}) \\ &= 0 \quad [\because r, \theta \text{ and } \phi \text{ are independent variables and } L^2 \text{ commutes with itself}] \end{aligned}$$

Similarly

$$[H, L_z] = \left[ -\frac{\hbar^2}{2\mu} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{L^2}{2\mu r^2} + V(r), L_z \right] = 0 \quad (\because [L^2, L_z] = 0)$$

2.a) Using Eq. (9.6b) we can write

$$L_z Y_{l, m_l}(\theta, \phi) = c Y_{l, m_l}(\theta, \phi)$$

or

$$-\frac{i\hbar}{2\pi} \frac{\partial}{\partial \phi} Y_{l, m_l}(\theta, \phi) = c Y_{l, m_l}(\theta, \phi)$$

where  $c$  is the eigenvalue of  $L_z$ , corresponding to  $Y_{l, m_l}(\theta, \phi)$ . Now  $L_z$  involves operation on  $\phi$  alone and the  $\phi$  component of  $Y_{l, m_l}(\theta, \phi)$  is just  $e^{im_l\phi}$ . Hence, using Eq. (9.18), we get

$$-\frac{i\hbar}{2\pi} im_l Y_{l, m_l}(\theta, \phi) = c Y_{l, m_l}(\theta, \phi)$$

$$\therefore c = m_l \hbar / 2\pi = m_l \hbar$$

(b) We have to show that

$$\int Y_{2,2}^*(\theta, \phi) Y_{2,2}(\theta, \phi) d\Omega = 1$$

or

$$\int_0^\pi \int_0^{2\pi} Y_{2,2}^* Y_{2,2} \sin\theta d\theta d\phi = 1$$

Let  $I_1 = \int_0^\pi \int_0^{2\pi} Y_{2,2}^* Y_{2,2} \sin\theta d\theta d\phi$

$$= \left(\frac{15}{32\pi}\right) 2\pi \int_0^\pi \sin^4\theta \sin\theta d\theta$$

$$= \frac{15}{16} \int_{-1}^1 (1 - 2\mu^2 + \mu^4) d\mu \text{ where } \mu = \cos\theta$$

or

$$I_1 = \frac{15}{16} \left(2 - \frac{4}{3} + \frac{2}{5}\right)$$

$$= \frac{15}{8} \frac{(15 - 10 + 3)}{15} = 1$$

Hence proved.

Next we have to show that  $\int Y_{2,2}^*(\theta, \phi) Y_{2,-2}(\theta, \phi) d\Omega = 0$

Let  $I_2 = \int_0^\pi \int_0^{2\pi} Y_{2,2}^* Y_{2,-2} \sin\theta d\theta d\phi$

$$= \frac{15}{32\pi} \int_0^\pi \int_0^{2\pi} \sin^4\theta e^{-4i\phi} d\theta d\phi$$

Now  $\int_0^{2\pi} e^{-4i\phi} d\phi = 0$ ,  $\therefore I_2 = 0$ . Hence proved.

3. Replacing  $\theta$  by  $\pi - \theta$  and  $\phi$  by  $\pi + \phi$  we obtain

$$Y_{2,1}(\pi - \theta, \pi + \phi) = - \left(\frac{15}{8\pi}\right)^{1/2} \sin(\pi - \theta) \cos(\pi - \theta) e^{i(\pi + \phi)}$$

$$= - \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta e^{i\phi} = Y_{2,1}(\theta, \phi)$$

Hence the parity of  $Y_{2,1}(\theta, \phi)$  is even.

4.  $R = \frac{me^4}{2\hbar^2} = 2.18 \times 10^{-18} \text{ Joules} = 13.6 \text{ eV}$

also in units of  $\text{m}^{-1}$ ,  $R = \frac{me^4}{2\hbar^2 ch} = 1.10 \times 10^7 \text{ m}^{-1}$

An accurate value of the Rydberg constant is

$$R = 1.09737373 \times 10^7 \text{ m}^{-1}$$



5. We have to show that  $\int_0^\infty R_{20}^*(r) R_{20}(r) r^2 dr = 1$

$$\text{Let } I = \int_0^\infty R_{20}^2(r) r^2 dr.$$

$$I = \frac{1}{(2a_0)^3} \int_0^\infty \left( 4 - 4\frac{r}{a_0} + \frac{r^2}{a_0^2} \right) r^2 e^{-r/a_0} dr.$$

Now we know that

$$\int_0^\infty r^p e^{-\beta r} dr = \frac{p!}{\beta^{p+1}}$$

$$\begin{aligned} \text{hence } I &= \frac{1}{8a_0^3} \left[ 4 \left( \frac{1}{a_0} \right)^3 - \frac{4}{a_0} \left( \frac{1}{a_0} \right)^4 + \frac{1}{a_0^2} \left( \frac{1}{a_0} \right)^5 \right] \\ &= \frac{1}{8} [8 - 24 + 24] \\ &= 1. \end{aligned}$$

Furthermore,

$$\begin{aligned} \int_0^\infty R_{20}^*(r) R_{10}(r) r^2 dr &= \frac{1}{(2a_0^6)^{1/2}} \int_0^\infty \left( 2 - \frac{r}{a_0} \right) r^2 e^{-(3r/2a_0)} dr \\ &= \frac{1}{\sqrt{2} a_0^3} \left[ 2 \left( \frac{3}{2a_0} \right)^3 - \frac{1}{a_0} \left( \frac{3}{2a_0} \right)^4 \right] = 0. \end{aligned}$$

6. Since  $n = 3$ , the permissible values of  $l$  are 0, 1 and 2. Hence, there are nine permissible values of  $m_l$  given by 0 (for  $l = 0$ ), -1, 0 and 1 (for  $l = 1$ ) and -2, -1, 0, 1 and +2 (for  $l = 2$ ). Each combination of  $n$ ,  $l$  and  $m_l$  gives rise to an eigenfunction. However the energy depends only upon  $n$ . Hence all these nine eigenfunctions are degenerate.

#### Terminal Questions

$$\begin{aligned} 1. \sum_{m_l=-2}^{+2} |Y_{2, m_l}(\theta, \phi)|^2 &= 2 \frac{15}{8\pi} \sin^2\theta \cos^2\theta + 2 \frac{15}{32\pi} \sin^4\theta + \frac{5}{16\pi} (3 \cos^2\theta - 1)^2 \\ &= \frac{5}{16\pi} [6 \cos^4\theta - 6 \cos^2\theta + 4 + 6 \sin^2\theta \cos^2\theta] \\ &= \frac{5}{4\pi}. \end{aligned}$$

You may note that the sum  $\sum_{m_l=-l}^{+l} |Y_{l, m_l}(\theta, \phi)|^2$  is always spherically symmetric.

$$2. V(r) = -\frac{e^2}{r}$$

$$\begin{aligned} \langle V(r) \rangle &= \int |\Psi_{100}(r)|^2 \left( -\frac{e^2}{r} \right) r^2 dr \sin\theta d\theta d\phi \\ &= \frac{1}{\pi a_0^3} 4\pi (-e^2) \int_0^\infty e^{-2r/a_0} r dr \\ &= -\frac{4e^2}{a_0^3} \frac{1}{\left( \frac{2}{a_0} \right)^2} = -\frac{e^2}{a_0} = 2E_0. \quad \left( \because a_0 = \frac{\hbar^2}{\mu e^2} \text{ and } E_0 = -\frac{\mu e^4}{2\hbar^2} \right) \end{aligned}$$

Since kinetic energy + potential energy = total energy

$$\langle \text{K.E.} \rangle = E_0 - \langle V(r) \rangle = -\frac{e^2}{2a_0} + \frac{e^2}{a_0} = \frac{e^2}{2a_0} = |E_0|$$

3. Let the size of the atom be  $R$ . Since the electron is inside the atom, the uncertainty in the momentum is  $p = \hbar/R$ . The linear momentum of magnitude  $p$  can be in any direction so its components can have values from  $-p$  to  $p$ . Hence the uncertainty in momentum is also approximately  $p$ . Hence we take  $\Delta p = p$ . Now we take

$$\langle \text{K.E.} \rangle = \frac{(\Delta p)^2}{2\mu} = \frac{\hbar^2}{2\mu R^2} = \text{K.E.}$$

$$E = \text{K.E.} + V = \frac{\hbar^2}{2\mu R^2} - \frac{e^2}{R} \text{ at } R.$$

$$\text{Now } \frac{dE}{dR} = -\frac{\hbar^2}{\mu R^3} + \frac{e^2}{R^2} = 0 \text{ for a stable atom,}$$

$$\text{hence } R = \frac{\hbar^2}{\mu e^2} = a_0.$$

Hence the size of the most stable atom is the first Bohr radius itself.

4. The probability of finding the electron between  $r$  and  $r + dr$  is given by

$$\begin{aligned} |\Psi_{100}(r)|^2 r^2 4\pi dr &= \frac{1}{\pi a_0^3} e^{-2r/a_0} r^2 4\pi dr \\ &= \frac{4}{a_0^3} r^2 e^{-2r/a_0} dr. \end{aligned}$$

Hence to determine the most probable value of  $r$  we differentiate  $r^2 e^{-2r/a_0}$  with respect to  $r$  and equate the result to zero. Thus we get

$$(r^2 (-\frac{2}{a_0}) + 2r) e^{-2r/a_0} = 0$$

or

$$r = a_0.$$

However the average value of  $r$  is given by

$$\begin{aligned} \langle r \rangle &= \int |\Psi_{100}(r)|^2 r r^2 dr \sin \theta d\theta d\phi \\ &= \frac{1}{\pi a_0^3} 4\pi \int_0^\infty e^{-2r/a_0} r^3 dr \\ &= \frac{4}{a_0^3} \left( \frac{6}{a_0} \right) \\ &= \frac{3}{2} a_0. \end{aligned}$$