

## UNIT 5

# HARMONIC OSCILLATOR AND RIGID ROTOR

## Structure

---

|     |  |     |                                       |
|-----|--|-----|---------------------------------------|
| 5.1 | Introduction   |     |                                       |
|     | Expected Learning Outcomes                               | 5.4 | Classical Rotational Motion           |
| 5.2 | Classical Harmonic Oscillator                            | 5.5 | Quantum Rigid Rotor                   |
| 5.3 | Quantum Harmonic Oscillator                              |     | Formulating Schrodinger Wave Equation |
|     | Formulating Schrödinger Wave Equation                    |     | Separation of Variables               |
|     | Solution of Schrödinger Equation: Series Solution Method | 5.6 | Summary                               |
|     | Wave Functions for Quantum Harmonic oscillator           | 5.7 | Terminal Questions                    |
|     | Determination of observables                             | 5.8 | Answers                               |

## 5.1 INTRODUCTION

---

In the previous two units you have learnt about three important model quantum mechanical systems viz., free particle, a particle confined to move in a one dimensional box and a particle confined to move in a three dimensional box. In this process you have learnt about the wave mechanical approach of dealing with quantum mechanical systems. In the context of a particle in three dimensional box system you have also learnt about an important technique viz., separation of variables. In this unit we will take up two more model systems viz., the harmonic oscillator and the rigid rotor. You will recall from your earlier study of molecular spectroscopy that the total energy of a polyatomic molecule consists of its quantised translational, rotational, vibrational and electronic energies. In the previous unit while discussing the particle in a three dimensional box we have in a way dealt quantum mechanically with the translatory motion. In this unit you will deal with the model systems for vibration and rotation motion and learn about the quantised vibrational and rotational energies. The quantisation of electronic energies will be discussed later in the course while studying the theories of chemical bonding.

We will begin the current unit by taking up the classical description of a harmonic oscillator. This will be followed by its quantum mechanical treatment wherein we will first formulate the Schrodinger wave equation for the system as per the general strategy discussed in Unit 2. Then the equation will be suitably modified so as to facilitate its solution. In this process you will learn about the series solution method and other strategies. The energy expression and the wave functions so obtained as the solution of the Schrödinger wave equation will be suitably analysed.

Having dealt with the harmonic oscillator as a model for vibration of a molecule and learning salient features of this system we will move on to the second model system i.e., rigid rotor. Here again, we will classically define the system and formulate the Schrödinger wave equation. This equation will then be converted to one for fixed distance between the two masses. The spherical harmonics equation so obtained will be separated into two expressions. We will state and discuss the results of their solution without going into detailed solutions.

In the next unit we will take up quantum mechanical treatment of hydrogen atom-a real system.

### Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ discuss the classical treatment of a harmonic oscillator and outline its significance in physical systems;
- ❖ formulate the Schrödinger wave equation for a quantum harmonic oscillator and apply appropriate boundary conditions;
- ❖ solve the Schrödinger equation for quantum harmonic oscillator using the series solution method;
- ❖ demonstrate the quantisation of vibrational energies of a harmonic oscillator;
- ❖ analyse the energy expression and describe the wave functions for a harmonic oscillator;
- ❖ calculate the average values of kinetic and potential energies for a harmonic oscillator and rationalise their relationship in terms of the Virial theorem;
- ❖ describe the rotational motion and treat it classically to understand its characteristics;
- ❖ formulate the Schrödinger wave equation for a rigid rotor and separate into two equations by using the technique of separation of variables; and
- ❖ outline the significance of the solutions of these equations.

## 5.2 HARMONIC OSCILLATOR: CLASSICAL TREATMENT

You would have learnt about linear harmonic oscillator in your earlier classes. Let us briefly recall it here. You will recall that a classical linear harmonic oscillator is a system in which a particle or object of mass  $m$  is attached to a spring of force constant  $k$  and is displaced from its equilibrium position. The object experiences a restoring force,  $\vec{F}_x$  proportional to its displacement from its equilibrium position. If the displacement is small, it follows simple harmonic motion (SHM), and the force is as per Hooke's Law, i.e.,

$$\vec{F}_x = -kx \quad \dots (5.1)$$

Here, 'x' is the displacement from the equilibrium position; the proportionality constant  $k$  is the **force** constant **that** is a measure of the stiffness of the spring. The negative sign here signifies that the force acts in the direction opposite to the displacement, and tends to restore the object to equilibrium. According to the Newton's second law, the force on an object is equal to its mass times its acceleration, i.e.,  $\vec{F} = m\vec{a}$  we can write

$$m\vec{a} = -kx(t) \quad \dots (5.2)$$

Now, since the acceleration 'a' is the second derivative of position,  $x(t)$  with respect to time, we can write:

$$m \frac{d^2 x(t)}{dt^2} = -kx(t) \quad \dots (5.3)$$

Rearranging, we get

$$\frac{d^2 x(t)}{dt^2} + \frac{k}{m} x(t) = 0 \quad \dots (5.4)$$

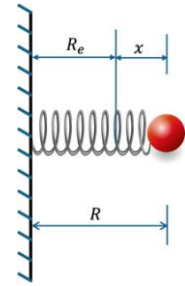
Thus, the simple harmonic motion is described by the differential equation given in Eq. (5.4). This is a second-order differential equation whose solution is a sinusoidal function, representing periodic motion. We can write the solution as

$$x(t) = A \sin(2\pi\nu t + \phi) \quad \dots (5.5)$$

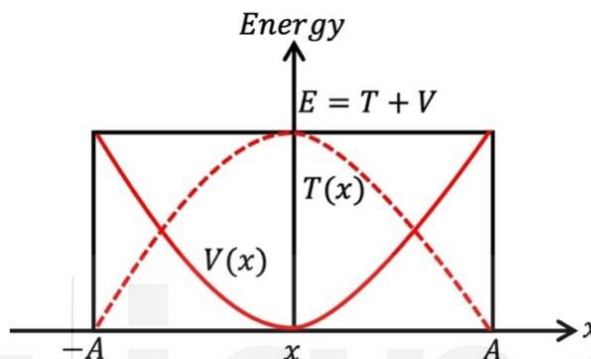
Here,  $A$  is the amplitude of the oscillation,  $\phi$  is the phase constant, determined by the initial conditions of the system, and  $\nu$  is the vibration frequency given by

$$\nu = \frac{1}{2\pi} \left( \frac{k}{m} \right)^{1/2} \quad \dots (5.6)$$

Since the value of the sine function in Eq. (5.5) varies from +1 to -1, the position  $x(t)$  oscillates between  $A$  and  $-A$ . Such a system oscillates with a constant total energy, with potential and kinetic energy components continuously exchanging with each other as the particle moves from the equilibrium position to the position of maximum displacement ( $A$ ) where the direction of motion of the particle reverses. At this stage (called turning point)



the potential energy of the particle is maximum. As the particle moves towards the equilibrium position from the turning point its kinetic energy increases at the expense of potential energy and becomes maximum at the equilibrium position where the potential energy becomes zero. In other words, the particle moves fastest at equilibrium and slowest at the extremities where the particle comes to rest for an instant and then reverses its direction of motion. The particle spends a slightly more time at the turning points. The overall motion is, confined to the region,  $-A \leq x \leq A$ . The relation between the potential and kinetic energies for a particle behaving as a harmonic oscillator is given in Fig.5.1.



**Fig. 5.1: The relation between the potential and kinetic energies for a particle behaving as a harmonic oscillator.**

Let us work out the expression for the energy of the system. Since the particle oscillates along one-dimension (say  $x$ ), the potential energy,  $V$  for the system will be related to the  $x$ -component of the force as follows.

$$F_x = -\frac{dV}{dx} = -kx \quad \dots (5.7)$$

Rearranging, and integrating the expression, we get

$$V = \int kx dx = \frac{1}{2} kx^2 + C, \quad \dots (5.8)$$

Where  $C$  is a constant i.e., the potential energy always has an arbitrary additive constant. The potential energy is chosen, by convention, to be zero at the equilibrium position i.e., at  $x=0$ . Thus  $C = 0$ , and we can write,

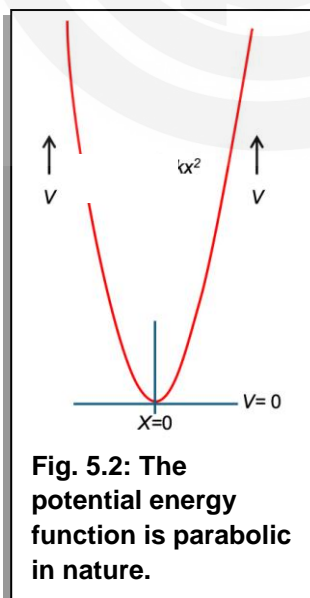
$$V = \frac{1}{2} kx^2 \quad \dots (5.9)$$

Substituting for  $k$ , from Eq. (5.6) we get

$$V = 2\pi^2 v^2 m x^2 = 2\pi^2 v^2 m A^2 \sin^2(2\pi vt + \phi) \quad \dots (5.10)$$

The graph of  $V(x)$  as a function of  $x$  will be a parabola as shown in Fig. 5.2. As regards the kinetic energy  $T$  we know that

$$T = \frac{1}{2} m \left( \frac{dx}{dt} \right)^2 \quad \dots (5.11)$$



**Fig. 5.2: The potential energy function is parabolic in nature.**

$$\frac{dx}{dt} = 2\pi\nu A \cos(2\pi\nu t + \phi) \quad \dots (5.12)$$

Substituting in Eq. (5.11) we get

$$T = \frac{1}{2} m (2\pi\nu A \cos(2\pi\nu t + \phi))^2 = 2m\pi^2\nu^2 A^2 \cos^2(2\pi\nu t + \phi) \quad \dots (5.13)$$

Adding T and V, we get total energy as

$$E = V + T = 2\pi^2\nu^2 m A^2 \sin^2(2\pi\nu t + \phi) + 2m\pi^2\nu^2 A^2 \cos^2(2\pi\nu t + \phi) \quad \dots (5.14)$$

$$E = 2\pi^2\nu^2 m A^2 [\sin^2(2\pi\nu t + \phi) + \cos^2(2\pi\nu t + \phi)] = 2\pi^2\nu^2 m A^2 \quad \dots (5.15)$$

As per Eq. (5.6),  $k = 4\pi^2\nu^2 m$ , we can write

$$E = T + V = \frac{1}{2} k A^2 \quad \dots (5.16)$$

Thus, according to Eq. (5.16) the total energy of the oscillator is proportional to the square of the amplitude, A.

Having recalled the classical aspects of Harmonic oscillator, we can now take up the quantum mechanical aspects of the system. You may ask that why do we study the motion of such a system by using quantum mechanics.

Apparently, there is no system in nature that behaves as a one-dimensional quantum oscillator. However, there are systems that behave approximately like this e.g., a vibrating diatomic molecule. This is an important application as it helps in understanding the quantum mechanical behaviour of vibrating chemical bonds. This in turn is useful in the domain of molecular spectroscopy whose basics you would have studied in your earlier classes. You will learn it in detail in course MCH-020.

Let us learn about the quantum harmonic oscillator. However, before that answer the following simple question to assess your understanding.

---

### SAQ 1

Give the value of the potential and kinetic energy of a classical harmonic oscillator at

- i) at equilibrium    ii) at  $x = \pm A$
- 

## 5.3 QUANTUM HARMONIC OSCILLATOR

---

You will recall from the previous three units that the first step in the quantum mechanical description of any system is to formulate the Schrödinger wave equation for the system. This in turn entails constructing the Hamiltonian operator (the operator for total energy) for the system. Let's do that.

### 5.3.1 Formulating the Schrödinger Wave Equation

---

You know from Unit 3 that the classical expression for the kinetic energy of the particle moving along x-axis is

$$K.E = \frac{1}{2} m v_x^2 = \frac{1}{2m} m^2 v_x^2 = \frac{1}{2m} p_x^2 \quad \dots (5.17)$$

Substituting the quantum mechanical operator for linear momentum along x-axis i.e.,  $-i\hbar\left(\frac{d}{dx}\right)$ , we get the operator for kinetic energy,  $\hat{T}$  as

$$\hat{T} = \frac{1}{2m} \left( -i\hbar \left( \frac{d}{dx} \right) \right)^2 \Rightarrow \hat{T} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} \quad \dots (5.18)$$

You have learnt above that the potential energy of a particle behaving as a harmonic oscillator is given by the following expression.

$$V = \frac{1}{2} kx^2 \quad \dots (5.9)$$

Thus, the Hamiltonian operator will be

$$\hat{H} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \quad \dots (5.19)$$

To get the Schrödinger wave equation, we substitute the expression for Hamiltonian in the general expression for SWE ( $H\psi = E\psi$ ) to get:

$$\frac{-\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{\kappa x^2}{2} \psi(x) = E\psi(x) \quad \dots (5.20)$$

Substituting the value of  $\kappa$  from Eq. (5.6) and rearranging we get

$$\frac{d^2\psi(x)}{dx^2} - \frac{4\pi^2 m^2 v^2 x^2}{\hbar^2} \psi(x) = -\frac{2mE}{\hbar^2} \psi(x) \quad \dots (5.21)$$

Let us define two parameters viz.  $\lambda = 2mE/\hbar^2$  and  $\alpha = 2\pi m v / \hbar$ . Substituting these in Eq. (5.21) and rearranging, we get

$$\frac{d^2\psi(x)}{dx^2} + (\lambda - \alpha^2 x^2) \psi(x) = 0 \quad \dots (5.22)$$

Introducing these parameters reduces the complexity of the constants.

*This is the desired Schrödinger wave equation for the harmonic oscillator.*

### Solving Schrödinger Equation: Making it solvable

Our next step is to solve this expression. However, it is difficult to solve this equation due to the  $x^2$  term in the potential energy expression. That is the potential energy depends on the coordinate x. You may recall that in the earlier systems the potential energy was a constant which was assumed to be zero for the sake of convenience. Now, there are two different approaches to solve this equation to get the wavefunctions and the energy expression for the quantum harmonic oscillator. One of these approaches called the “analytic” approach uses power series method to solve it whereas the other, “algebraic” approach involves using a type of operator called a “ladder” operator for the purpose. We will be following the first approach.

For this, we modify the equation by *non-dimensionalising the equation*. Here, we express x-a dimensional variable in terms of a new *dimensionless* variable,  $\xi$  defined as

$$\xi \equiv \alpha^{1/2} x \quad \dots(5.23)$$

Differentiating, we get

$$\frac{d\xi}{dx} = \alpha^{1/2} \quad \dots(5.24)$$

We can then replace  $\psi(x)$  by  $\psi(\xi)$ , as shown below.

$$\frac{d\psi(x)}{dx} = \frac{d\psi(\xi)}{d\xi} \cdot \frac{d\xi}{dx} = \alpha^{1/2} \frac{d\psi(\xi)}{d\xi} \quad \dots(5.25)$$

and

$$\frac{d^2\psi(x)}{dx^2} = \frac{d}{d\xi} \left[ \frac{d\psi(x)}{dx} \right] \frac{d\xi}{dx} = \frac{d}{d\xi} \left[ \alpha^{1/2} \frac{d\psi(\xi)}{d\xi} \right] \frac{d\xi}{dx} = \alpha \frac{d^2\psi(\xi)}{d\xi^2} \quad \dots(5.26)$$

The Eq. (5.22) can then be written as

$$\alpha \frac{d^2\psi(\xi)}{d\xi^2} + (\lambda - \alpha\xi^2)\psi(\xi) = 0 \quad \dots(5.27)$$

Dividing throughout by  $\alpha$  we get

$$\frac{d^2\psi(\xi)}{d\xi^2} + \left( \frac{\lambda}{\alpha} - \xi^2 \right) \psi(\xi) = 0 \quad \dots(5.28)$$

Thus, our SWE becomes a special type of differential equations called **Weber equations**. The solutions ( $\psi(\xi)$ ) of this differential equation are the products of Gaussian functions and Hermite polynomials. Thus, we need to find a well behaved wavefunctions (continuous, single-valued and finite at all values of  $\xi$ ,  $\psi(\xi)$ ) that satisfy Eq. (5.28). However, we find that no simple mathematical solution is available. As stated above, we will use power-series method, but we need to bring the expression to the form where we can do so. You must appreciate that we are dealing with a complicated potential energy function that varies with the variable  $x$  and goes to extremities.

### Possible solution in asymptotic region

At this stage, it is advisable to look for the asymptotic behavior (that is, the behavior at very large or very small values of  $\xi$ ) of the solutions to the equation. This will help in ensuring that  $\psi(\xi)$  remains finite as  $|\xi| \rightarrow \infty$  and gives a rough idea of form of  $\psi(\xi)$ . We can use this information to perform necessary modifications to make the solution suitable for *all* values of  $|\xi|$ . In other words, this will facilitate in separating the behavior of the solution in one regime from that in another, and the differential equation becomes simpler to solve. Let us look for the asymptotic solutions to the wave equation.

For any arbitrary constant value of  $E$ , the term  $\lambda/\alpha$  is negligible as compared to  $\xi^2$  for very large values of  $|\xi|$ . The Eq. (5.28) can then be written in the asymptotic form as

$$\frac{d^2\psi(\xi)}{d\xi^2} = \xi^2\psi(\xi) \quad (|\xi| \rightarrow \infty) \quad \dots(5.29)$$

The dimensionless variable can be seen as the dimensional variable divided by a reference quantity, having same dimensions.

This step simplifies the equation by removing dimensional units from the equation, making it easier to solve.

The solutions to this equation for large  $\xi$  are

$$\psi(\xi \rightarrow \pm\infty) = ae^{-\xi^2/2} + be^{\xi^2/2} \quad \dots(5.30)$$

We have seen above that for the harmonic oscillator, the potential energy goes to infinity as  $|\xi| \rightarrow \infty$ . This implies that the wavefunction  $\psi(\xi)$  must go to zero as  $\xi \rightarrow \pm\infty$ . An inspection of the expression reveals that only the negative exponential form is well-behaved, since the positive solution tends to infinity as  $(\xi)$  increases. That rules out the positive-exponential solutions, so the coefficient  $b$  in Eq. (5.30) must be zero and a satisfactory form of wave function for large values of  $|\xi|$  is

$$\psi(\xi) = ae^{-\xi^2/2}, \quad (|\xi| \rightarrow \infty) \quad \dots(5.31)$$

We can verify it to be the solution of Eq. (5.29) by substitution. We differentiate the expression for the wavefunction to get

$$\frac{d\psi(\xi)}{d\xi} = -\xi ae^{-\xi^2/2} \quad \dots(5.32)$$

Differentiating again, we get

$$\frac{d^2\psi(\xi)}{d\xi^2} = \xi^2 ae^{-\xi^2/2} - ae^{-\xi^2/2} \quad \dots(5.33)$$

Now, as  $\xi \rightarrow \infty$ , the second term becomes negligible compared to the first term and we can write

$$\frac{d^2\psi(\xi)}{d\xi^2} = \xi^2 ae^{-\xi^2/2} = \xi^2 \psi(\xi) \quad \xi \rightarrow \infty \quad \dots(5.34)$$

Thus, the solution given in Eq. (5.31) satisfies the asymptotic wave equation, Eq. (5.28). Therefore, a satisfactory form of wave function for large values of  $|\xi|$  is

$$\psi(\xi) = ae^{-\xi^2/2}, \quad (|\xi| \rightarrow \infty) \quad \dots(5.35)$$

The modified or trial wavefunction incorporates the exponential decay from the asymptotic analysis and a new function that is more manageable and will lead us to quantized solutions.

So, we have some idea for the possible wave function that will describe the behaviour of a quantum harmonic oscillator but it is valid only for  $(|\xi| \rightarrow \infty)$ . We need a solution that is valid for the whole range i.e.,  $(-\infty < \xi < \infty)$ . Let us try to find a general solution that is valid for the whole range.

### Search for the General Solution

To construct a generally acceptable wave function, we start with the asymptotic solution and modify it by substituting the constant 'a' in the asymptomatic solution by a new function  $H(\xi)$  which needs to be determined to make the function comply with the requirements of the system. That is, we try the following modified or trial wavefunction,

$$\psi(\xi) = e^{-\xi^2/2} H(\xi) \quad \dots(5.36)$$

The function  $H(\xi)$  should be such that it varies slowly as compared to the function  $e^{-\xi^2/2}$  such that the modified wavefunction,  $\psi(\xi) = e^{-\xi^2/2}H(\xi)$  vanishes as  $|\xi| \rightarrow \infty$ . To get an idea about the form of  $H(\xi)$ , we create a relatively easily solvable wave equation by substituting the modified wavefunction  $e^{-\xi^2/2}H(\xi)$ , into the Schrödinger wave equation, Eq. (5.28) designed above.

Differentiating the modified wavefunction,  $e^{-\xi^2/2}H(\xi)$  we get:

$$\frac{d\psi(\xi)}{d\xi} = \frac{d}{d\xi} \left( e^{-\xi^2/2}H(\xi) \right) = -\xi e^{-\xi^2/2}H(\xi) + e^{-\xi^2/2} \frac{dH(\xi)}{d\xi} \quad \dots(5.37)$$

Taking the second derivative,

$$\frac{d^2\psi(\xi)}{d\xi^2} = -e^{-\xi^2/2}H(\xi) + \xi^2 e^{-\xi^2/2}H(\xi) - \xi e^{-\xi^2/2} \frac{dH(\xi)}{d\xi} - \xi e^{-\xi^2/2} \frac{dH(\xi)}{d\xi} + e^{-\xi^2/2} \frac{d^2H(\xi)}{d\xi^2} \quad \dots(5.38)$$

Simplifying, we get

$$\frac{d^2\psi(\xi)}{d\xi^2} = e^{-\xi^2/2} \left[ -H(\xi) + \xi^2 H(\xi) - 2\xi \frac{dH(\xi)}{d\xi} + \frac{d^2H(\xi)}{d\xi^2} \right] \quad \dots(5.39)$$

Substituting the expressions for  $\psi(\xi)$  and  $d^2\psi(\xi)/d\xi^2$  into the Eq. (5.28), we get,

$$e^{-\xi^2/2} \left[ -H(\xi) + \xi^2 H(\xi) - 2\xi \frac{dH(\xi)}{d\xi} + \frac{d^2H(\xi)}{d\xi^2} \right] + \left( \frac{\lambda}{\alpha} - \xi^2 \right) e^{-\xi^2/2} H(\xi) = 0 \quad \dots(5.40)$$

Simplifying, we get,

$$e^{-\xi^2/2} \left[ -H(\xi) + \xi^2 H(\xi) - 2\xi \frac{dH(\xi)}{d\xi} + \frac{d^2H(\xi)}{d\xi^2} \right] + \frac{\lambda e^{-\xi^2/2}}{\alpha} H(\xi) - \xi^2 e^{-\xi^2/2} H(\xi) = 0 \quad \dots(5.41)$$

Dividing throughout by  $e^{-\xi^2/2}$  and simplifying further gives

$$\frac{d^2H(\xi)}{d\xi^2} - 2\xi \frac{dH(\xi)}{d\xi} + \left( \frac{\lambda}{\alpha} - 1 \right) H(\xi) = 0 \quad \dots(5.42)$$

This is a well-known differential equation called the **Hermite differential equation**.

You may be wondering that we have taken up such an exercise just to get another second-order differential equation. True, but it is worth the effort because the differential equation so obtained can be solved by the power-series method. Let us learn how we solve this equation. However, before that let us recall what all have we done so far in the context of quantum description of harmonic oscillator?

1. Setting up of the Schrödinger equation: We started by designing the Schrödinger wave equation by formulating the Hamiltonian operator for the system.

The differential equation for  $H(\xi)$  is a standard form, and its solutions are known Hermite polynomials. The quantization arises naturally from the structure of the Hermite polynomials.

2. Non-dimensionalise the equation: we simplified the SWE by introducing dimensionless variable  $\xi \equiv \alpha^{1/2} x$ . This made the equation, easier to solve.
3. Analysed the asymptotic behavior to guess part of the solution: this step provided a solution that could be suitably modified to be applicable for the whole range.
4. Introduce an unknown function: in this step we replaced the constant in the asymptotic solution by a new unknown function,  $H(\xi)$ . This helped in generating a well-known differential equation called the Hermite differential equation that could be solved by power series solution method. Let us continue further. We must now try to solve Eq. (5.42) to get the Eigen functions  $H(\xi)$  which can then be used to determine the wavefunction  $\psi(\xi) = e^{-\xi^2/2} H(\xi)$  that we created to represent the solution to SWE over the entire range. We also expect to generate the eigenvalues,  $[\frac{\lambda}{\alpha} - 1]$  which in turn will provide the quantised energy levels for the linear harmonic oscillator.

### 5.3.2 Solution of Schrödinger Equation: Power Series Method

The Eq. (5.42) is type of differential equation which cannot be solved in terms of elementary functions. Therefore, we resort to looking for its solution in terms of an infinite power series. Let us assume that it is possible to express the solution of Eq. (5.42) in the form of following series:

$$H(\xi) = \sum_{n=0}^{\infty} a_n \xi^n = a_0 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \dots \quad \dots(5.43)$$

We need to determine the coefficients  $a_0, a_1, a_2, \dots$ , in the proposed series. This can be achieved by substituting the proposed series solution into Eq. (5.42) and adjusting the coefficients in such a way that the resulting equation is satisfied for all values of  $\xi$ .

Differentiating  $H(\xi)$  we get

$$\frac{dH(\xi)}{d\xi} = \sum_{n=0}^{\infty} n a_n \xi^{n-1} = 1a_1 + 2a_2 \xi + 3a_3 \xi^2 + \dots \quad \dots(5.44)$$

$$\frac{d^2 H(\xi)}{d\xi^2} = \sum_{n=0}^{\infty} n(n-1) a_n \xi^{n-2} = 1 \cdot 2a_2 + 2 \cdot 3a_3 \xi + 3 \cdot 4a_4 \xi^2 + 4 \cdot 5a_5 \xi^3 + \dots \quad \dots(5.45)$$

Substituting the expressions (in series form) for  $H, dH/d\xi$ , and  $d^2 H/d\xi^2$  from Eq. (5.43) to Eq. (5.45) into Eq. (5.42) we get,

$$\left[ 1 \cdot 2a_2 + 2 \cdot 3a_3 \xi + 3 \cdot 4a_4 \xi^2 + 4 \cdot 5a_5 \xi^3 + \dots \right] - 2\xi \left[ 1a_1 + 2a_2 \xi + 3a_3 \xi^2 + \dots \right] + \left( \frac{\lambda}{\alpha} - 1 \right) \left[ a_0 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \dots \right] = 0 \quad \dots(5.46)$$

Simplifying, and inserting  $\xi^0$  we get

$$\begin{aligned} & \left[ 1 \cdot 2a_2 + \left( \frac{\lambda}{\alpha} - 1 \right) a_0 \right] \xi^0 + \left[ 2 \cdot 3a_3 + \left( \frac{\lambda}{\alpha} - 1 - 2 \cdot 1 \right) a_1 \right] \xi \\ & + \left[ 3 \cdot 4a_4 + \left( \frac{\lambda}{\alpha} - 1 - 2 \cdot 2 \right) a_2 \right] \xi^2 + \left[ 4 \cdot 5a_5 + \left( \frac{\lambda}{\alpha} - 1 - 2 \cdot 3 \right) a_3 \right] \xi^3 + \dots = 0 \end{aligned} \quad \dots(5.47)$$

Now for this expression to be valid for all values of  $\xi$ , it is necessary that the coefficients of individual powers of  $\xi$  are individually equal to zero. This can be shown by writing the above expression as

$$b_0 \xi^0 + b_1 \xi^1 + b_2 \xi^2 + b_3 \xi^3 + \dots = 0 \quad \dots(5.48)$$

where the  $b$  terms are the sums of the coefficients of individual powers of  $\xi$ . For  $\xi = 0$  all the terms other than  $b_0$  vanish implying that  $b_0$  must be zero for the series to be zero. Taking the derivative of Eq. (5.48), we get

$$b_1 + b_2 \xi + b_3 \xi^2 + \dots = 0 \quad \dots(5.49)$$

Setting  $\xi = 0$ , demands  $b_1$  to be zero. We can continue in the same manner and setting  $\xi = 0$  for  $n^{\text{th}}$  derivative and, we show that  $b_n$  must be zero. If we rewrite these coefficients in the tabular form as given below,

| Term      | Coefficient  |
|-----------|--|
| $\xi^0$ : | $1 \cdot 2a_2 + \left( \frac{\lambda}{\alpha} - 1 \right) a_0$             |
| $\xi^1$ : | $2 \cdot 3a_3 + \left( \frac{\lambda}{\alpha} - 1 - 2 \cdot 1 \right) a_1$ |
| $\xi^2$ : | $3 \cdot 4a_4 + \left( \frac{\lambda}{\alpha} - 1 - 2 \cdot 2 \right) a_2$ |
| $\xi^3$ : | $4 \cdot 5a_5 + \left( \frac{\lambda}{\alpha} - 1 - 2 \cdot 3 \right) a_3$ |
| $\vdots$  | $\vdots$   |
| $\xi^n$ : | $(n+1)(n+2)a_{n+2} + \left( \frac{\lambda}{\alpha} - 1 - 2n \right) a_n$   |

we find a pattern in the expression for the coefficients and can write the general expression for the coefficients of  $\xi^n$  term as given in the last row of the table and reproduced below.

$$(n+1)(n+2)a_{n+2} + \left( \frac{\lambda}{\alpha} - 1 - 2n \right) a_n = 0 \quad \dots(5.50)$$

We can rearrange and write

$$a_{n+2} = \frac{-\left( \frac{\lambda}{\alpha} - 1 - 2n \right)}{(n+1)(n+2)} a_n \quad \dots(5.51)$$

If we know any one of the even (or odd) coefficients, we can determine all the higher or lower even (or odd) coefficients by using the recursion formula.

This expression is called a **recursion formula** and can be used to generate the relative values of the coefficients in the  $H(\xi)$  series. The coefficients of the even terms will be in terms of an arbitrary constant  $a_0$  whereas those for odd terms will be in terms of arbitrary constant  $a_1$ . Thus, we may represent the  $H(\xi)$  series as the **sum** of two independent series, as given below.

$$H(\xi) = a_0 \left( 1 + \frac{a_2}{a_0} \xi^2 + \frac{a_2}{a_0} \cdot \frac{a_4}{a_0} \xi^4 + \frac{a_2}{a_0} \cdot \frac{a_4}{a_2} \cdot \frac{a_6}{a_4} \xi^6 + \dots \right) \dots(5.52)$$

$$+ a_1 \left( \xi + \frac{a_3}{a_1} \xi^3 + \frac{a_3}{a_1} \cdot \frac{a_5}{a_3} \xi^5 + \frac{a_3}{a_1} \cdot \frac{a_5}{a_3} \cdot \frac{a_7}{a_5} \xi^7 + \dots \right)$$

The appearance of two arbitrary constants is acceptable in the solution of any second-order differential equation.

where each of the coefficients is determined by the recursion formula given above, Eq. (5.51) using  $a_0$  or  $a_1$  for even and odd terms respectively. If we arbitrarily set  $a_0 = 0$ , the even series will vanish and only the odd series will remain and if we set  $a_1 = 0$  only the even series remains. For arbitrary values of  $\lambda/\alpha$  (arbitrary energies) each of the above series contains an infinite number of terms. When we apply the boundary conditions, one of these constants will be fixed at zero and the other constant will be determined in the process of normalisation. We will take it up later.

So, we have moved further and know the form of  $H(\xi)$  which in turn means that we have a fair idea of the trial or modified function defined in Eq. (5.36). We are so close, yet so far because as we show below,  $H(\xi)$  with an infinite number of terms is *not* a well-behaved function. It is so because it causes the total wave function  $\psi(\xi) = e^{-\xi^2/2} H(\xi)$  to diverge rather than vanish at  $|\xi| \rightarrow \infty$ . Let us see how?

### Why $H(\xi)$ is not a well behaved function?

Let us calculate the ratio of coefficients of successive powers of  $\xi$  in either the even or odd series of  $H(\xi)$  for large values of  $n$ , by using recursion formula.

$$\frac{a_{n+2}}{a_n} = \frac{-\frac{\lambda}{\alpha} + 1 + 2n}{(n+1)(n+2)} = \frac{2n + \left(1 - \frac{\lambda}{\alpha}\right)}{(n+1)(n+2)}$$

For large values of  $n$  and a given value of  $\lambda/\alpha$ , the terms containing  $n$  dominate the other terms in the numerator as well as the denominator. So, this ratio converges to

$$\frac{a_{n+2}}{a_n} \approx \frac{2n}{(n)(n)} \approx \frac{2}{n}$$

For comparison, we take up the Maclaurin series expansion of a related function,  $e^{\xi^2}$  as given below.

$$e^{\xi^2} = 1 + \xi^2 + \frac{\xi^4}{2!} + \frac{\xi^6}{3!} + \dots + \frac{\xi^n}{\left(\frac{n}{2}\right)!} + \frac{\xi^{n+2}}{\left(\frac{n}{2} + 1\right)!} + \dots$$

Here again, we evaluate the ratio of the coefficients of successive powers of  $\xi$  for large value of  $n$ . Considering the last two terms, in the expression for *large* values of  $n$ , we write,

$$\frac{a_{n+2}}{a_n} = \frac{\left(\frac{n}{2}\right)!}{\left(\frac{n}{2}+1\right)!} = \frac{\left(\frac{n}{2}\right)!}{\left(\frac{n}{2}+1\right)\left(\frac{n}{2}\right)!} = \frac{2}{(n+2)} \cong \frac{2}{n}$$

We find that this ratio is *identical* to the ratio for large values of  $n$  in the  $H(\xi)$  series. It implies that in the limit of large value of  $n$  the  $H(\xi)$  series behaves somewhat like  $e^{\xi^2}$  series. Using this information in Eq. (5.36), we can write

$$\psi(\xi) = e^{-\xi^2/2} H(\xi) \rightarrow \sim e^{-\xi^2/2} e^{\xi^2} \approx e^{\xi^2/2}$$

Since it is a positive exponent, it diverges in the limits of  $|\xi| \rightarrow \infty$ , which means that  $\psi(\xi)$  cannot be normalised and is not a physically realisable quantum wavefunction. In other words, it is not a well behaved function.

Now, the question arises that how do we get over this problem? Fortunately, there is a way out. That is, we somehow don't let the function  $H(\xi)$  have infinite terms and limit it to a *finite number of terms*. This way since the value of  $n$  is not large, the value of the wavefunction,  $\psi(\xi)$  will be dominated by the term  $e^{-\xi^2/2}$  and will approach zero as required. It will not get a chance to behave like  $e^{\xi^2}$  at large values of  $n$ . How do we achieve it? Let us learn.

### 5.3.3 Quantised Vibrational Energies

We can limit the function  $H(\xi)$  to a *finite number of terms* by defining either  $a_0$  or  $a_1$  to be zero and then limit the remaining series by equating the numerator in the recursion formula to zero. Let us understand it with an example, if we wish to terminate the series at the term corresponding to say,  $\xi^{\nu}$  ( $\nu = n$ ), it is necessary from Eq. (5.51) that

$$\frac{\lambda}{\alpha} - 1 - 2\nu = 0 \Rightarrow \frac{\lambda}{\alpha} = 1 + 2\nu \quad \dots(5.53)$$

Where,  $\nu = 0, 2, 4, \dots$ , if  $a_1 = 0$  and  $\nu = 1, 3, 5, \dots$ , if  $a_0 = 0$

The Eq. (5.53) implies that the energy parameter  $\lambda/\alpha$  (and therefore the energy  $E$ ) is quantised. It can have discrete values that depend on the value of ( $\nu = n$ ). You may note here that once again *the application of boundary conditions we naturally come across quantisation*. Let us formulate the energy expression for harmonic oscillator and analyse it.

Let us recall the original definition of the parameters, viz.  $\lambda = 2mE / \hbar^2$  &  $\alpha = 2\pi m\nu / \hbar$  and substitute them in Eq. (5.53). We get

$$\frac{\lambda}{\alpha} = 1 + 2\nu = \frac{2mE}{\hbar^2} \times \frac{\hbar}{2\pi m\nu} = \frac{E}{\pi\nu\hbar} = \frac{2E}{\nu h} = 1 + 2\nu \Rightarrow E_{\nu} = \left(\nu + \frac{1}{2}\right) h\nu \quad \dots(5.54)$$

Where,  $\nu = 0, 1, 2, 3, \dots$ , is called *vibrational quantum number*. It restricts the allowed energies of the simple harmonic oscillator to a set of discrete values.

Further, as you can notice, the harmonic-oscillator stationary-state energy levels are equally spaced.

$$E_{\nu+1} - E_{\nu} = \left( (\nu + 1) + \frac{1}{2} \right) h\nu - \left( \nu + \frac{1}{2} \right) h\nu = h\nu \quad \dots(5.55)$$

In addition to the energy expression, we also take note of the fact that the acceptable eigenfunctions are also limited to a discrete set of polynomials  $H_{\nu}(\xi)$  of degree  $\nu$ . The energy of the ground state ( $n=0$ ) i.e., the **zero-point energy** of harmonic oscillator is nonzero and is equal to  $\frac{1}{2}h\nu$ . It is an intrinsic property of the harmonic oscillator. This is the lowest energy, that cannot be decreased or removed. You may argue that if the frequency of oscillation decreases the energy will decrease. However, you must remember that decrease in the oscillator frequency amounts to a decrease in the force constant or increase in the mass. This in turn means that the oscillator has changed and has its own zero point energy. In other words, a harmonic oscillator vibrates with a characteristic frequency depending on the mass and the force constant.

The existence of zero-point energy has been experimentally proved by the crystal scattering of light. Classically we expect that with a decrease in the temperature the oscillation amplitude should decrease and vanish at 0 K. However, it has been observed that the scattering frequency reaches a threshold value on decreasing the temperature, which implies that the oscillations do not stop. In other words, the zero point energy can be seen as the vibrational energy of a harmonic oscillator absolute zero.

The  $H_{\nu}(\xi)$  polynomials that are the solutions of the Hermite differential equation, Eq. (5.42) are called **Hermite polynomials**. Since  $\nu$  is even or odd, these polynomials will have either even or odd powers of  $\xi$ . A yet another important observation here is that since for each energy level  $E_{\nu}$ , there is only one polynomial  $H_{\nu}(\xi)$ , the vibrational energy levels are **non-degenerate**.

### Formulating Hermite polynomials

Let us learn how do we formulate the Hermite polynomial for any selected value of  $\nu$ . For this we refer to the  $H(\xi)$  series as derived above, Eq. (5.52) and choose the even or odd series depending on whether the value of  $\nu$  is even or odd and evaluate its coefficients. We do not choose an arbitrary value of the coefficient  $a_0$  or  $a_1$ , rather we arbitrarily define the coefficient of the highest power term as  $a_{\nu} = 2^{\nu}$ , and then evaluate the coefficients of the lower-power terms from the recursion formula, Eq. (5.51). Let us take  $\nu = 4$ ; the chosen even series will be

$$H_4(\xi) = a_0 + a_2\xi^2 + a_4\xi^4 \quad \dots(5.56)$$

With the highest power term involving  $\xi^4$ . We arbitrarily take the coefficient of this term,  $a_4 = 2^4 = 16$  and use the recursion formula, to derive the coefficient of highest minus 2<sup>nd</sup> term as shown below. First we formulate the following general expression by substituting  $\left(\frac{\lambda}{\alpha} = 1 + 2\nu\right)$  in the recursion formula and

rearranging

$$a_n = a_{n+2} \frac{(n+1)(n+2)}{(2n-2\nu)} \quad \dots(5.57)$$

Now substituting the value of  $n$ , we can get the coefficient of the current minus 2<sup>nd</sup> term as.

$$a_2 = a_4 \frac{(3)(4)}{(-4)} = 16 \frac{12}{(-4)} = -48$$

Similarly, we can find  $a_0 = a_2 \frac{(1)(2)}{(-8)} = -48 \times \left(-\frac{1}{4}\right) = +12$ ,

Thus, we can write the Hermite polynomial for  $\nu = 4$  as,

$$H_4(\xi) = 12 - 48\xi^2 + 16\xi^4 \quad \dots(5.58)$$

The first six Hermite polynomials so calculated are

|                                     |  |
|-------------------------------------|--|
| $H_0(\xi) = 1$                      | $H_1(\xi) = 2\xi$                        |
| $H_2(\xi) = -2 + 4\xi^2$            | $H_3(\xi) = -12\xi + 8\xi^3$             |
| $H_4(\xi) = 12 - 48\xi^2 + 16\xi^4$ | $H_5(\xi) = 120\xi - 160\xi^3 + 32\xi^5$ |

The arbitrariness in the selection of the value of  $a_\nu$  in the  $H_\nu(\xi)$  polynomial disappears when the final  $\psi_\nu(\xi)$  eigenfunction is normalised. There are other ways available to generate the Hermite polynomials. Let us learn about these. However, before that answer the following simple question to assess your understanding.

### SAQ 2

Formulate the expression for  $H_3(\xi)$ . Assume the coefficient of the highest power term as  $a_\nu = 2^\nu$ .

### Rodrigues' formula and Hermite polynomials

The Hermite polynomials can be generated by using the following formula called **Rodrigues' formula**.

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2}) \quad \dots(5.59)$$

For the variable  $\xi$  we write

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} (e^{-\xi^2}) \quad \dots(5.60)$$

We can generate the polynomials just by repeated differentiation of  $e^{-\xi^2}$  and multiplying by  $(-1)^n e^{\xi^2}$ . Generally, the first few polynomials are generated in this way and for rest we use a recursion formula derived below. Let us evaluate the first three polynomials.

$$H_0(\xi) = (-1)^0 e^{\xi^2} \frac{d^0}{dx^0} (e^{-\xi^2}) = (1)e^{\xi^2} e^{-\xi^2} = 1 \quad \dots(5.61)$$

$$H_1(\xi) = (-1)e^{\xi^2} \frac{d}{dx} (e^{-\xi^2}) = (-1)e^{\xi^2} (-2\xi)e^{-\xi^2} = 2\xi \quad \dots(5.62)$$

$$\begin{aligned} H_2(\xi) &= (-1)^2 e^{\xi^2} \frac{d^2}{dx^2} (e^{-\xi^2}) = (-1)^2 e^{\xi^2} \left[ \frac{d}{dx} \left( \frac{d}{dx} e^{-\xi^2} \right) \right] \\ &= (-1)^2 e^{\xi^2} \left[ \frac{d}{dx} (-2\xi e^{-\xi^2}) \right] = (-1)^2 e^{\xi^2} \left[ (-2\xi)(-2\xi)e^{-\xi^2} + e^{-\xi^2}(-2) \right] \\ &= (-1)^2 e^{\xi^2} \left[ (4\xi^2 - 2)e^{-\xi^2} \right] = (4\xi^2 - 2) \quad \dots(5.63) \end{aligned}$$

We can continue doing so and get the polynomial for any given value of  $n$ . However, the process gets quite elaborate. To simplify this the Rodrigues' formula can be used to derive a **recursion relation** as follows.

### Deriving recursion relation

The Rodrigues' formula given above, Eq. (5.60) satisfies the Hermite differential equation, Eq. (5.42)

$$\frac{d^2 H(\xi)}{d\xi^2} - 2\xi \frac{dH(\xi)}{d\xi} + \left( \frac{\lambda}{\alpha} - 1 \right) H(\xi) = 0 \quad \dots(5.42)$$

Substituting,  $\frac{\lambda}{\alpha} = 1 + 2n$  we can write the expression as

$$H_n''(\xi) - 2\xi H_n'(\xi) + 2n H_n(\xi) = 0 \quad \dots(5.64)$$

Taking the derivative of Eq. (5.60) we get

$$\begin{aligned} H_n'(\xi) &= (-1)^n \left[ e^{\xi^2} \left( \frac{d^{n+1}}{dx^{n+1}} (e^{-\xi^2}) \right) + (2\xi) e^{\xi^2} \frac{d^n}{dx^n} (e^{-\xi^2}) \right] \\ H_n'(\xi) &= (2\xi) \left[ (-1)^n e^{\xi^2} \frac{d^n}{dx^n} (e^{-\xi^2}) \right] - (-1)^{n+1} e^{\xi^2} \left( \frac{d^{n+1}}{dx^{n+1}} (e^{-\xi^2}) \right) \\ H_n'(\xi) &= 2\xi H_n(\xi) - H_{n+1}(\xi) \quad \dots(5.65) \end{aligned}$$

Rearranging, we get

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - H_n'(\xi) \quad \dots(5.66)$$

Differentiating Eq. 5.66 gives

$$\begin{aligned} \frac{d}{d\xi} H_{n+1}(\xi) &= \frac{d}{d\xi} (2\xi H_n(\xi) - H_n'(\xi)) \\ H_{n+1}'(\xi) &= \left[ 2\xi (H_n'(\xi)) + 2H_n(\xi) - H_n''(\xi) \right] \quad \dots(5.67) \end{aligned}$$

Substituting for  $H_n''(\xi)$  from Eq. (5.61) we get

$$H_{n+1}'(\xi) = \left[ 2\xi(H_n'(\xi)) + 2H_n(\xi) + (2nH_n(\xi) - 2\xi H_n'(\xi)) \right] \quad \dots(5.68)$$

Simplifying, we get

$$H_{n+1}'(\xi) = 2H_n(\xi) + (2nH_n(\xi)) = 2(n+1)H_n(\xi) \quad \dots(5.69)$$

For  $(n+1) \rightarrow (n)$ ;  $H_n'(\xi) = 2nH_{n-1}(\xi) \quad \dots(5.70)$

Substituting Eq. (5.70) into Eq. (5.69) we get

$$2nH_{n-1}(\xi) = 2\xi H_n(\xi) - H_{n+1}(\xi)$$

Rearranging, we get the desired recursion formula as

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi) \quad \dots(5.71)$$

We can use the recursion relation,  $H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi)$  along with the values  $H_0(\xi) = 1$  and  $H_1(\xi) = 2\xi$ . to get the desired polynomial. Let us take an example to understand its usage.

**Example 5.** : Determine the expressions for  $H_4(\xi)$  and,  $H_5(\xi)$  by using recursion relation.

**Solution:** We begin with  $H_2(\xi)$

$$H_2(\xi) = 2\xi H_1(\xi) - 2(1)H_0(\xi) = 2\xi(2\xi) - 2 \Rightarrow H_2(\xi) = 4\xi^2 - 2$$

$$H_3(\xi) = 2\xi H_2(\xi) - 2(2)H_1(\xi) = 2\xi(4\xi^2 - 2) - 4(2\xi)$$

$$H_3(\xi) = 8\xi^3 - 4\xi - 8\xi = 8\xi^3 - 12\xi \Rightarrow H_3(\xi) = 8\xi^3 - 12\xi$$

$$H_4(\xi) = 2\xi H_3(\xi) - 2(3)H_2(\xi) = 2\xi(8\xi^3 - 12\xi) - 6(4\xi^2 - 2)$$

$$= 16\xi^4 - 24\xi^2 - 24\xi^2 + 12 \Rightarrow H_4(\xi) = 16\xi^4 - 48\xi^2 + 12$$

$$H_5(\xi) = 2\xi H_4(\xi) - 2(4)H_3(\xi) = 2\xi(16\xi^4 - 48\xi^2 + 12) - 8(8\xi^3 - 12\xi)$$

$$= 32\xi^5 - 96\xi^3 + 24\xi - 64\xi^3 + 96\xi \Rightarrow H_5(\xi) = 32\xi^5 - 160\xi^3 + 120\xi$$

These are the same expressions as given above. Thus, we find that this recurrence relation provides a convenient method to derive the expressions for Hermite polynomials. These polynomials can then be substituted in Eq. (5.36) to get the wave functions that are solutions to the SWE for harmonic oscillator for the entire range.

$$\psi_n(\xi) = A_n e^{-\xi^2/2} H_n(\xi) \quad \dots(5.72)$$

Where,  $A_n$  is the normalisation constant. Our next step is the normalisation of the wavefunctions i.e., to find the value of  $A_n$ .

### Normalisation of the wavefunctions

You know that for a wavefunction  $\psi(x)$  to be normalised it must satisfy the following condition

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = 1 \quad \dots(5.73)$$

Recall we had made the following assumption

$$\xi \equiv \alpha^{1/2}x \Rightarrow d\xi \equiv \alpha^{1/2}dx \Rightarrow dx = \alpha^{-1/2}d\xi$$

Therefore, we can write,

$$\int_{-\infty}^{\infty} \psi^*(x)\psi(x)dx = \alpha^{-1/2} \int_{-\infty}^{\infty} \psi^*(\xi)\psi(\xi)d\xi = 1 \quad \dots(5.74)$$

Substituting the wave function from Eq. (5.72), we can write

$$\begin{aligned} \alpha^{-1/2} \int_{-\infty}^{\infty} \psi_n^*(\xi)\psi_n(\xi)d\xi &= \alpha^{1/2} \int_{-\infty}^{\infty} \left[ A_n e^{-\xi^2/2} H_n(\xi) \right]^* \left[ A_n e^{-\xi^2/2} H_n(\xi) \right] d\xi = 1 \\ &= |A_n|^2 \alpha^{-1/2} \int_{-\infty}^{\infty} |H_n(\xi)|^2 e^{-\xi^2} d\xi = 1 \end{aligned} \quad \dots(5.75)$$

This is a tricky integral to solve and we will not venture into it. Instead we will use the known value, i.e.,

$$\int_{-\infty}^{\infty} |H_n(\xi)|^2 e^{-\xi^2} d\xi = 2^n n! (\pi^{1/2}) \quad \dots(5.76)$$

This gives

$$|A_n|^2 \alpha^{-1/2} \left[ 2^n n! (\pi^{1/2}) \right] = 1 \Rightarrow |A_n|^2 = \frac{1}{\alpha^{-1/2} \left[ 2^n n! (\pi^{1/2}) \right]} \quad \dots(5.77)$$

On simplification, we get,

$$A_n = \left( \frac{\alpha}{\pi} \right)^{1/4} \frac{1}{\sqrt{2^n n!}} \quad \dots(5.78)$$

Thus, the normalised wave function for linear harmonic oscillator is

$$\psi_n(\xi) = \left( \frac{\alpha}{\pi} \right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n(\xi) e^{-\xi^2/2} \quad \dots(5.79)$$

Replacing  $n$  by  $\nu$  and simplifying, we get

$$\psi_\nu(\xi) = \left( \frac{\alpha}{\pi} \right)^{1/4} \left( \frac{1}{2^\nu \nu!} \right)^{-1/2} e^{-\xi^2/2} H_\nu(\xi) \quad \dots(5.80)$$

Replacing  $\xi$  by  $\alpha^{1/2}x$  in the exponential term, we can write

$$\psi_v(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{1}{2^v v!}\right)^{-1/2} e^{-\alpha x^2/2} H_v(x) \quad \dots(5.81)$$

Let us analyse these wavefunction in terms of their appearance and significance.

### 5.3.3 Wave Functions for Harmonic Oscillator

A look at the expression for the wavefunctions reveals that there are three parts of the wave function. These are a constant term, an exponential term and a polynomial term. The nature of wave function will depend on the value of the quantum number  $v$ . If it happens to be an even number, then the polynomial factor will have only even powers of  $x$ , which makes it an even function. The exponential term  $e^{-\xi^2/2}$  is also an even function which makes the overall wavefunction even. On the other hand if the value of the quantum number  $v$  happens to be odd, then the polynomial factor will have only odd powers of  $x$ , and since the exponential term  $e^{-\xi^2/2}$  is an even function the overall wavefunction will be an odd function.

Let us look at the ground state wavefunction; i.e.,  $v=0$ . The wavefunction will be

$$\begin{aligned} \psi_0(x) &= \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{1}{2^0 0!}\right)^{-1/2} e^{-\alpha x^2/2} H_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \times 1 \times e^{-\alpha x^2/2} \times 1 \\ &= \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \end{aligned} \quad \dots(5.82)$$

Similarly we can work out the expressions of other wavefunctions. The wavefunctions for the lowest five energy levels are given in Fig. 5.3(a) The ground state wavefunction is even whereas the higher-energy wavefunctions alternate between odd and even parity. You may note that the harmonic-oscillator wavefunctions are oscillatory in the classically allowed region whereas in the classically forbidden regions these decay exponentially. The higher-energy wavefunctions have increasing number of cycles between the classical turning points.

The squares of the wavefunctions, i.e., the probability densities for the five lowest-energy wavefunctions of the harmonic oscillator are shown in Fig. 5.3(b). You may note that for small values of  $n$ , i.e., at low energies, behavior of the quantum harmonic oscillator is quite different from that of the classical case. For example, for the oscillator in its ground state, the position is most likely to be near  $x=0$ . You may also note that the excited states have position within the classically allowed region where the probability is zero. Further, a closer look reveals that as  $n$  increases, the probability of the oscillator being near the classical turning points increases. That is, at large values of  $n$  the behaviour of quantum harmonic oscillator begins to be like that of the classical oscillator. This is in accordance with the Correspondence Principle.

Having learnt the determination of the normalised wavefunctions and the nature of their plots let us take up the determination of the observables for

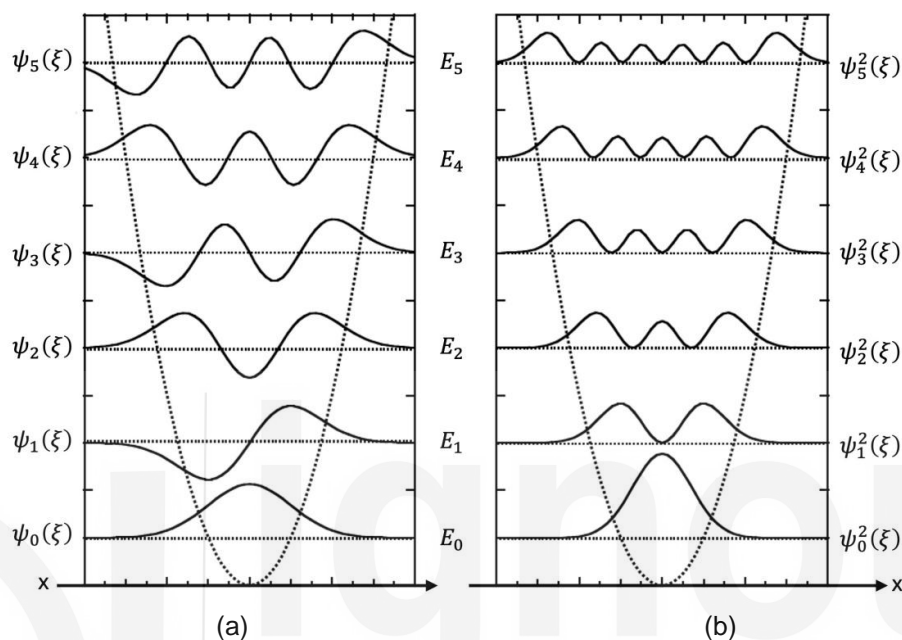
A function is said to be even function if  $f(-x) = f(x)$  and if the following is true,  $f(-x) = -f(x)$  the function is said to be an odd function.

The product of two even or two odd functions give an even function, whereas the product of an even and an odd function results in an odd function.

harmonic oscillator. However, it will be worthwhile to summarise the important results of the quantum harmonic oscillator considered as a model for vibration motion.

### Summary of important results of the quantum harmonic oscillator

1. The energies of the quantum harmonic oscillator are quantised. It is in contrast with the classical oscillator which could take up any energy.



**Fig. 5.3 : a) The wavefunctions for the lowest five energy levels of linear harmonic oscillator, b) the squares of the wavefunctions for the lowest five energy levels of linear harmonic oscillator. The dashed curves represent the potential energy, and the dotted lines indicate the first six eigenvalues of the total energy,  $E_n$ , in units of  $h\nu$ .**

2. The energies of the quantum harmonic oscillator are quantised. It is in contrast with the classical oscillator which could take up any energy.
3. The minimum energy of the quantum harmonic oscillator is non-zero, again in contrast with the classical oscillator which could have zero energy.
4. The energies of quantum harmonic oscillator are determined by a quantum number that has values  $n = 0, 1, 2, 3, \dots$ . This is in contrast with the one dimensional box (or infinite potential well) for which the quantum number could take the values as  $n = 1, 2, 3, \dots$
5. The energy levels are equidistant i.e., there is a constant difference in the energies of the successive energy levels. This is again in contrast with the one dimensional box (or infinite potential well) for which the energy difference is proportional to  $(2n+1)$ .
6. The probability of finding the quantum oscillator in the classically permissible region varies; different from classical oscillator.
7. The quantum harmonic oscillator penetrates the classically forbidden domain and has a finite probability to be found outside the classically allowed region.

Let us take up the determination of the observables for a quantum harmonic oscillator. However, before that answer the following simple questions to assess your understanding.

### SAQ 3

Check whether the following functions are even or odd?

(a)  $\sin x$ ; (b)  $x \sin x$ ; (c)  $e^x$ ; (d)  $\cos x$ ; (e)  $x \cos x$  (f)  $(a + x)(a - x)$ .

### SAQ 4

Sketch the wavefunction for the first excited state of a quantum harmonic oscillator and give its physical significance.

### SAQ 5

Compare the probability density distributions of the ground state and the first excited state of a quantum harmonic oscillator.

## 5.3.4 Determination of Observables

You will recall from Unit 2 that according to the third postulate of quantum mechanics, the values of different observables can be extracted from the wavefunctions by using appropriate operators. Let us do so for the wavefunction determined for the quantum harmonic oscillator.

### The maxima in the ground state wavefunction

We know that the ground-state wave function is

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \quad \dots(5.82)$$

To get the value of the maxima, we need to take the derivative of the function and set it equal to zero (i.e.,  $d\psi_0(x)/dx = 0$ ), we get

$$\frac{d\psi_0(x)}{dx} = \left(\frac{\alpha}{\pi}\right)^{1/4} \{-\alpha x \exp(-\alpha x^2/2)\} = 0 \quad \dots(5.83)$$

This will be true for  $x = 0$  and  $x = \pm\infty$ .

To find the point of maximum, we evaluate the second derivative

$\frac{d^2\psi_0(x)}{dx^2}$  which gives

$$\frac{d^2\psi_0(x)}{dx^2} = \left(\frac{\alpha}{\pi}\right)^{1/4} [-\alpha + (\alpha x)^2] \exp(-\alpha x^2/2) \quad \dots(5.84)$$

$d^2\psi_0/dx^2$  will be negative at  $x = 0$ . Therefore, the function  $\psi_0$  will exhibit a maximum at  $x = 0$  as shown in Fig. 5.3 (a).

### Kinetic energy

The ground-state normalized wave function for the harmonic oscillation is

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \quad \dots(5.82)$$

Since  $\psi_0(x)$  is normalized the expectation value of kinetic energy will be given by the following expression

$$\bar{T} = \int \psi_0(x) \hat{T} \psi_0(x) dx \quad \dots(5.85)$$

Substituting the wavefunction, we get

$$\bar{T} = \int_{-\infty}^{+\infty} \left\{ \left(\frac{\alpha}{\pi}\right)^{1/4} \exp(-\alpha x^2/2) \left[ -\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2} \left(\frac{\alpha}{\pi}\right)^{1/4} \exp(-\alpha x^2/2) \right] \right\} dx \quad \dots(5.86)$$

Simplifying,

$$\begin{aligned} &= \left(\frac{\alpha}{\pi}\right)^{1/2} \left(-\frac{\hbar^2}{8\pi^2 m}\right) \int_{-\infty}^{+\infty} \exp(-\alpha x^2/2) \left\{ \frac{d^2}{dx^2} \exp(-\alpha x^2/2) \right\} dx \\ &= \left(\frac{\alpha}{\pi}\right)^{1/2} \left(-\frac{\hbar^2}{8\pi^2 m}\right) \left[ -\alpha \int_{-\infty}^{+\infty} \exp(-\alpha x^2/2) dx + \alpha^2 \int_{-\infty}^{+\infty} x^2 \exp(-\alpha x^2/2) dx \right] \\ &= \left(\frac{\alpha}{\pi}\right)^{1/2} \left(-\frac{\hbar^2}{8\pi^2 m}\right) \left[ -(\pi\alpha)^{1/2} + \frac{1}{2}(\pi\alpha)^{1/2} \right] = \frac{\alpha \hbar^2}{16\pi^2 m} \quad \dots(5.87) \end{aligned}$$

Since  $\alpha = 2\pi m\nu / h$ , and  $\nu = \sqrt{k/m}$ , we get

$$\bar{T} = \left(\frac{2\pi m\nu}{h}\right) \left(\frac{\hbar^2}{16\pi^2 m}\right) = \frac{h\nu}{8\pi} = \frac{h}{8\pi} \sqrt{\frac{k}{m}} = \frac{h}{4} \nu_0 \quad \dots(5.88)$$

### Potential energy

$$\bar{V} = \int \psi_0(x) \hat{V} \psi_0(x) dx \quad \dots(5.89)$$

Substituting the wavefunction, we get

$$\bar{V} = \int_{-\infty}^{+\infty} \left(\frac{\alpha}{\pi}\right)^{1/4} \exp(-\alpha x^2/2) \left(\frac{1}{2} kx^2\right) \left(\frac{\alpha}{\pi}\right)^{1/4} \exp(-\alpha x^2/2) dx \quad \dots(5.90)$$

Simplifying,

$$\begin{aligned} &= \left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{k}{2}\right) \int_{-\infty}^{+\infty} x^2 \exp(-\alpha x^2/2) dx \\ &= \left(\frac{\alpha}{\pi}\right)^{1/2} \left(\frac{k}{2}\right) \left(\frac{\pi^{1/2}}{2\alpha^{3/2}}\right) \end{aligned}$$

$$\bar{V} = \frac{k}{4\alpha} = \left(\frac{k}{4}\right) \left(\frac{h}{2\pi m\nu}\right) = \frac{hk}{8\pi m} \sqrt{\frac{m}{k}} = \frac{h}{8\pi} \sqrt{\frac{k}{m}} = \frac{h}{4} \nu_0 \quad \dots(5.91)$$

It is interesting to note that the values of  $\bar{T}$  and  $\bar{V}$  are identical. This is in accordance with the **Virial theorem** that relates the average kinetic and potential energies of a stable, bound system. According to the theorem if the potential energy,  $V$ , due to interaction of any two particles is proportional to  $r^n$ , then  $\bar{T} = \frac{n}{2} \bar{V}$ . In the present case of harmonic oscillator,  $V = \frac{1}{2} kx^2$  i.e.,  $n=2$   $\Rightarrow \bar{T} = \bar{V}$  as shown above.

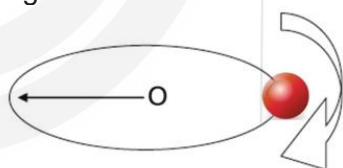
You will recall from above, that the total energy of a polyatomic molecule consists of its quantised translational, rotational, vibrational and electronic energies. We had set out a target to learn about the vibration and rotational motion in this unit. We have discussed the quantised vibrational motion by taking harmonic oscillator as the model system. Let us now take up the molecular rotational motion. We will do so by considering another model system viz. rigid rotor. However, before that answer the following simple question to assess your understanding.

### SAQ 6

State Virial theorem. How the potential energy and the kinetic energy of a quantum harmonic oscillator are related according to Virial theorem?

## 5.4 RIGID ROTOR

We begin with by understanding the classical rotational motion. Let us consider a particle of mass  $m$  moving in space in the absence of any force, but with the constraint that it is at a constant distance,  $r$ , from a fixed-point  $O$ . Such a particle is said to be executing rotation motion about the point  $O$  and since the distance  $r$  is fixed, we call it as rigid rotation. It is equivalent to the motion of a particle on a ring.



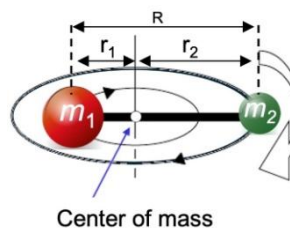
**Fig. 5.4: Depiction of rotational motion.**

Since the distance from the centre does not change, such a particle will have only two degrees of freedom. To describe the motion of such a particle, we use an axis system that is fixed in space with origin at the point  $O$ . It becomes convenient to use polar coordinate system, as shown later.

It is pertinent to point out here that our interest is not in the system described above but the rotational motion of a diatomic molecule, where two masses,  $m_1$  and  $m_2$  (representing two atoms) are connected through a rigid rod of length  $r$  equal to the distance between the two atoms of the molecule as shown in Fig. 5.5. We further consider that the molecule does not execute vibrational motion, thereby the distance between the atoms remains constant. That is, the molecule is rigid, and the system is said to be a **rigid rotor**.

Let this rigid rotator be rotated around an axis that is perpendicular to the plane of rotation and passes through the center of mass as shown in the Fig.

5.5. The distances of the individual masses from the center of mass and between the two masses are also indicated.



**Fig. 5.5: Schematic representation of a diatomic molecule as a rigid rotor.**

You may recall that in case of the Harmonic Oscillator, we reduced the two-body problem into an effective one-body problem by separating the problem into that of oscillatory motion and the translational motion of the center of mass of the molecule. Here also, since we are interested in the relative motion of the two masses, it is convenient to express the motion of the rigid rotor in the center-of-mass coordinates. We effectively separate the problem into that of the motion of the center of mass and rotation about the center of mass. For now, let us work out the expression for the energy of a classical rigid rotor.

### 5.4.1 Energy of Classical Rigid Rotor

Let  $v_1$  and  $v_2$  be the velocities of the mass  $m_1$  and  $m_2$  revolving about the axis of rotation. The total kinetic energy ( $T$ ) of the rotator can then be given as.

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 \quad \dots(5.92)$$

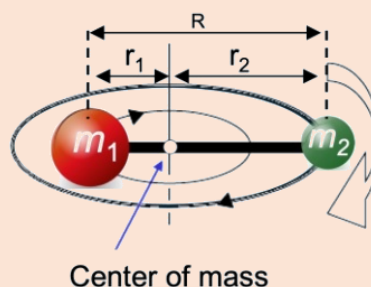
We know that linear velocity  $v$  is equal to the angular velocity multiplied by the radius of rotation  $r$  i.e.  $v = \omega r$ . Substituting in Eq. (5.92) we get

$$T = \frac{1}{2} m_1 (r_1 \omega)^2 + \frac{1}{2} m_2 (r_2 \omega)^2 \quad \dots(5.93)$$

$$T = \frac{1}{2} (m_1 r_1^2 + m_2 r_2^2) \omega^2 \quad \dots(5.94)$$

To simplify the description of the system, it is advisable to show as given below that the rotation of a rigid rotor of length  $r$  composed of two masses about the center of mass is equivalent to rotation of a single mass of  $\mu$ , with a radius equal to  $r$ .

#### Reducing two-body problem into an effective one-body problem



Let us define the rigid rotor as a system of two masses,  $m_1$  and  $m_2$ , connected by a rigid rod of length  $R$ . The center of mass (COM) is located at a distance  $r_1$  from the mass  $m_1$  and  $r_2$  from the mass  $m_2$ , where  $r_1 + r_2 = R$ .

The distances  $r_1$  and  $r_2$  are given by:

$$r_1 = \left( \frac{m_2}{m_1 + m_2} \right) R \quad \text{and} \quad r_2 = \left( \frac{m_1}{m_1 + m_2} \right) R$$

The moment of inertia  $I$  of the system about the center of mass is the sum of the moments of inertia of the individual masses. Therefore, we can write

$$I = m_1 r_1^2 + m_2 r_2^2$$

Substituting the values of  $r_1$  and  $r_2$  in the above expression gives

$$I = m_1 \left( \frac{m_2}{m_1 + m_2} \right)^2 R^2 + m_2 \left( \frac{m_1}{m_1 + m_2} \right)^2 R^2$$

Simplifying this expression leads to:

$$I = \left( \frac{m_1 m_2^2}{(m_1 + m_2)^2} \right) R^2 + \left( \frac{m_2 m_1^2}{(m_1 + m_2)^2} \right) R^2$$

Simplifying, we get

$$I = \left( \frac{m_1 m_2}{m_1 + m_2} \right) R^2$$

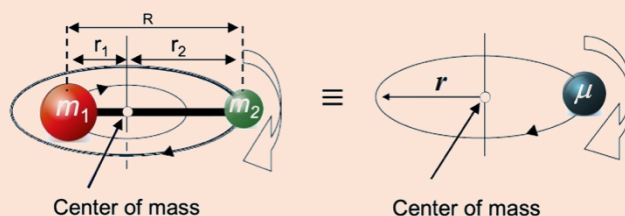
We know that the reduced mass  $\mu$  is defined as:

$$\mu = \left( \frac{m_1 m_2}{m_1 + m_2} \right)$$

Therefore, the moment of inertia can be written as:

$$I = \mu R^2$$

This shows that the moment of inertia of the two-mass system is equivalent to the moment of inertia of a single mass  $\mu$  rotating at a distance  $r$  from the center of mass. Pictorially we can represent it as



Since  $m_1 r_1^2 + m_2 r_2^2$  is equal to the moment of inertia for a two particle system, we can write Eq. (5.94) as

$$T = \frac{1}{2} I \omega^2 \quad \dots(5.95)$$

It implies that the kinetic energy takes on a form similar to that in linear motion with the moment of inertia playing the role of the mass and the angular velocity acting as linear velocity. Multiplying and dividing the Eq. (5.95), by  $I$ , and simplifying we get

$$T = \frac{I^2 \omega^2}{2I} = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \quad \dots(5.96)$$

Here,  $L$  is the angular momentum of the rotator. It is an important concept in both the classical as well as the quantum descriptions of the rotational motion of a particle. The angular momentum,  $L$ , of a classical particle about the point  $O$  is a vector quantity defined by

$$\vec{L} = \vec{r} \times \vec{p} \quad \dots(5.97)$$

The direction of the angular momentum is perpendicular to the plane formed by the position ( $\vec{r}$ ) vector and the linear momentum vector, ( $\vec{p}$ ). Its magnitude is,  $rps \sin(\theta)$ , where  $r$  and  $p$ , are the magnitudes of the position and linear momentum vectors, respectively, and ( $\theta$ ) is the angle between them. We will discuss about this in details in a later unit. Now, since no external force is working on the rotator, the potential can be taken as zero. Therefore, we can say that the total energy of a classical diatomic rigid rotator is given by Eq. (5.96).

Since, the classical mechanics does not restrict the direction or the magnitude of  $\vec{L}$ , its magnitude can change by any incrementally small amount. Since the energy is proportional to the square of the angular momentum, the energy can be increased by an infinitesimally small amount i.e., the classical rigid rotor has a continuous energy spectrum. Any amount of energy can be stored in the rigid rotor, and the increase in the energy appears as an increase in the angular frequency. In other words, we can say that the kinetic energy of a classical rotator is continuous.

### 5.4.2 Quantum Mechanical Description of Rigid Rotor

Let us consider the rigid rotor defined above again and allow it to rotate in the three dimensional space. This problem is mathematically quite cumbersome and can be simplified by reducing it to the motion of a particle on the surface of a sphere of radius  $R$ . As with all the quantum mechanical problems, let us begin by formulating the Schrödinger wave equation by deriving expression for the Hamiltonian operator.

#### **Formulating the Schrödinger wave equation**

As shown above, the classical kinetic energy of the rigid rotator can be written as

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} \quad \dots(5.98)$$

Here,  $p_1$  and  $p_2$  are the linear momentum of the two particles of rigid rotator. Since the potential energy is zero for a freely rotating rotator the total energy will be equal to the kinetic energy, i.e.,

$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + 0 \quad \dots(5.99)$$

This can be written in terms of the components ( $p_{x_1}$ ,  $p_{y_1}$ , and  $p_{z_1}$ ) of linear momenta along  $x$ -,  $y$ -, and  $z$ - axes.

$$E = \frac{(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2)}{2m_1} + \frac{(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2)}{2m_2} \quad \dots(5.100)$$

Replacing the terms for the components of the linear momentum with the corresponding quantum mechanical operators, and simplifying, we get the expression for the Hamiltonian operator for the rigid rotor as

$$\hat{H} = \frac{1}{2m_1} \left[ (-i\hbar \frac{\partial}{\partial x_1})^2 + (-i\hbar \frac{\partial}{\partial y_1})^2 + (-i\hbar \frac{\partial}{\partial z_1})^2 \right] + \frac{1}{2m_2} \left[ (-i\hbar \frac{\partial}{\partial x_2})^2 + (-i\hbar \frac{\partial}{\partial y_2})^2 + (-i\hbar \frac{\partial}{\partial z_2})^2 \right] \quad \dots(5.101)$$

Simplifying, we get

$$\hat{H} = \frac{-\hbar^2}{2m_1} \left[ \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right] - \frac{\hbar^2}{2m_2} \left[ \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right] \quad \dots(5.102)$$

It is convenient to express the rotation of a diatomic molecule in terms of the internal coordinates defined as

$$x = (x_2 - x_1); \quad y = (y_2 - y_1); \quad z = (z_2 - z_1) \quad \dots(5.103)$$

We can express the Hamiltonian in terms of the relative coordinates by finding the relationship between the relative and cartesian coordinates as follows

$$\frac{\partial^2}{\partial x_1^2} = \left( \frac{\partial}{\partial x_1} \right)^2 = \left[ \frac{\partial x}{\partial x_1} \frac{\partial}{\partial x} \right]^2 = \left[ -1 \frac{\partial}{\partial x} \right]^2 = \frac{\partial^2}{\partial x^2} \quad \dots(5.104)$$

We can find similar expressions for other differentials. Substituting these in Eq. (5.102) and simplifying, we get

$$\hat{H} = \frac{-\hbar^2}{2} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad \dots(5.105)$$

$$\hat{H} = \frac{-\hbar^2}{2\mu} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right] \quad \dots(5.106)$$

Using the expression for the Hamiltonian operator, we can write the Schrödinger wave equation for the motion of two particles, moving in a zero potential field in such a way that their centre of gravity remains at rest, as given below.

$$-\frac{\hbar^2}{2\mu} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = E\psi(x, y, z) \quad \dots(5.107)$$

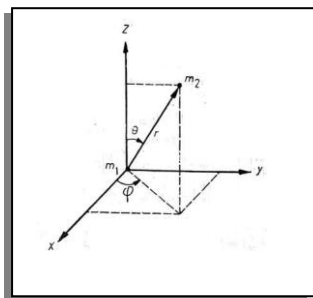
As defined above, the rigid rotor has a restriction that the distance between the two masses must be a constant. However, before invoking the restriction it is convenient to transform Eq. (5.97) into spherical polar coordinates  $(r, \theta, \phi)$ , which are defined as

$r$  = distance from the origin;  $0 \leq r < \infty$

$\theta$  = angle the distance vector  $r$  makes with positive  $z$ -axis;  $0 \leq \theta \leq \pi$

$\phi$  = angle made by the projection of the point with  $x$ -axis;  $0 \leq \phi \leq 2\pi$

Their relationship with the Cartesian coordinates is



$$x = r \sin\theta \cos\phi; y = r \sin\theta \sin\phi; z = r \cos\theta; r = \sqrt{x^2 + y^2 + z^2} \quad \dots(5.108)$$

The spherical polar coordinate system is defined and explained in the Appendix 5.1. The process of transformation is quite elaborate and is not given here. We just use the result of the transformation. The Eq. (5.107) in spherical polar coordinate system is

$$\frac{-\hbar^2}{2\mu r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] \psi(r, \theta, \phi) = E\psi(r, \theta, \phi) \dots \quad (5.109)$$

Now we impose the restriction that the distance between the two masses of the rotator remains constant, i.e.,  $r$  is constant. In such a case, the derivative with respect to  $r$  will not appear in Eq.(5.109). That is, the first term in the bracket is zero and we can write the equation as

$$\frac{-\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = EY(\theta, \phi) \quad \dots(5.110)$$

The functions  $Y(\theta, \phi)$  are known as the **spherical harmonic functions** This is the Schrödinger wave equation for the rigid rotor.

### Separation of variables

We would like to separate the equation into two simpler equations but the second term in the bracket has both the  $\theta$  as well as  $\phi$  terms. Therefore, we multiply both the sides of the equation by  $\sin^2\theta$  to get

$$-\sin^2\theta \frac{\hbar^2}{2\mu r^2} \left[ \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = \sin^2\theta EY(\theta, \phi) \dots(5.111)$$

Simplifying, we get

$$-\frac{\hbar^2}{2\mu r^2} \left[ \sin\theta \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{\partial^2}{\partial \phi^2} \right] Y(\theta, \phi) = (E \sin^2\theta) Y(\theta, \phi) \quad \dots(5.112)$$

To solve Eq. (5.112) we assume that the wavefunction is a product of two independent functions. One dependent on  $\theta$  and the other on  $\phi$ . That is, we write the function  $Y(\theta, \phi)$  in the form

$$Y(\theta, \phi) = \Theta(\theta) \Phi(\phi) \quad \dots(5.113)$$

Substituting into Eq. (5.112) we get,

$$-\frac{\hbar^2}{2\mu r^2} \left[ \sin\theta \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{\partial^2}{\partial \phi^2} \right] \Theta(\theta) \Phi(\phi) = (E \sin^2\theta) \Theta(\theta) \Phi(\phi) \dots(5.114)$$

$$-\frac{\hbar^2}{2\mu r^2} \left[ \sin\theta \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) \Theta(\theta) \Phi(\varphi) + \frac{\partial^2}{\partial\varphi^2} \Theta(\theta) \Phi(\varphi) \right] \quad \dots(5.115)$$

$$= (E \sin^2 \theta) \Theta(\theta) \Phi(\varphi)$$

You may note that in each terms in Eq. (5.115) the operand contains only that variable with respect to which the derivative is taken i.e., they are total derivative and accordingly we can rewrite the equation by changing the operator from  $\frac{\partial}{\partial x}$  to  $\frac{d}{dx}$ .

$$-\frac{\hbar^2}{2\mu r^2} \left[ \Phi(\varphi) \sin\theta \frac{d}{d\theta} \left( \sin\theta \frac{d}{d\theta} \right) \Theta(\theta) + \Theta(\theta) \frac{d^2}{d\varphi^2} \Phi(\varphi) \right] \quad \dots(5.116).$$

$$= (E \sin^2 \theta) \Theta(\theta) \Phi(\varphi)$$

Dividing throughout by  $\Theta(\theta) \Phi(\varphi)$  and rearranging we get

$$\left[ \frac{1}{\Theta(\theta)} \sin\theta \frac{d}{d\theta} \left( \sin\theta \frac{d}{d\theta} \right) \Theta(\theta) + \frac{1}{\Phi(\varphi)} \frac{d^2}{d\varphi^2} \Phi(\varphi) \right] \quad \dots(5.117)$$

$$= -\frac{2\mu r^2 E \sin^2 \theta}{\hbar^2}$$

Simplifying we get

$$\left[ \frac{1}{\Theta(\theta)} \sin\theta \frac{d}{d\theta} \left( \sin\theta \frac{d}{d\theta} \right) \Theta(\theta) + \frac{2\mu r^2 E \sin^2 \theta}{\hbar^2} + \frac{1}{\Phi(\varphi)} \frac{d^2}{d\varphi^2} \Phi(\varphi) \right] = 0 \quad \dots(5.118)$$

We find that there are three terms in the bracket on the left in the equation whose sum is equal to zero and one of these, i.e., the third term involves only the variable  $\phi$ . All the other terms involve  $\theta$ , therefore we can say that the third term is equal to a constant, A and we write

$$\left[ \frac{1}{\Phi(\varphi)} \frac{d^2}{d\varphi^2} \Phi(\varphi) \right] = A \quad \dots(5.119)$$

The remaining two terms should be equal to the same constant but with opposite sign. We write,

$$\frac{1}{\Theta(\theta)} \sin\theta \frac{d}{d\theta} \left( \sin\theta \frac{d}{d\theta} \right) \Theta(\theta) + \frac{2\mu r^2 E \sin^2 \theta}{\hbar^2} = -A \quad \dots(5.120)$$

Rearranging, we get

$$\frac{1}{\Theta(\theta)} \sin\theta \frac{d}{d\theta} \left( \sin\theta \frac{d}{d\theta} \right) \Theta(\theta) + \frac{2\mu r^2 E \sin^2 \theta}{\hbar^2} + A = 0 \quad \dots(5.121)$$

Thus, we have been able to separate the two equations. Our next step is to solve these equations. We will take up the detailed solution in the next unit when we discuss about hydrogen atom. For now, we will just state the results and outline their significance. The Eq. (5.109) is quite straight forward to solve. It gives

$$\Phi(\phi) = N e^{im\phi} \quad \text{where,} \quad m = 0, \pm 1, \pm 2, \pm 3, \dots, \pm\infty. \quad \dots(5.122)$$

The normalisation constant can be determined to be,  $N = \frac{1}{\sqrt{2\pi}}$ , and we can write the normalised wave function as

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}. \quad \dots(5.123)$$

We will take up the detailed solution of the Eq. (5.120) represents the part of spherical harmonics that depends on  $\theta$ . It can be solved to give a set of eigenfunctions and their corresponding eigenvalues. However, for now, we will go back to Eq. (5.110). We rearrange it and write,

$$\left[ -\hbar^2 \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right\} \right] Y = (2EI)Y \quad \dots(5.124)$$

Now according to Eq. (5.88), we have

$$T = \frac{L^2}{2I} = E \quad (\text{as } V = 0) \Rightarrow L^2 = 2EI \quad \dots(5.125)$$

Also you may note that, we have the operator for the square of angular momentum on the left side of Eq. (5.124), we can rewrite the Eq. (5.124) as

$$\hat{L}^2 Y = L^2 Y \quad \dots(5.126)$$

The solution of Eq. (5.124) provides the following expression for the quantised values of  $L^2$ .

$$L^2 = J(J+1)\hbar^2 \quad \dots(5.127)$$

Where,  $J$  is the rotational quantum number. We can write

$$L = \sqrt{J(J+1)} \hbar \quad \dots(5.128)$$

Thus is the quantum number  $J$  serves to quantise the total angular momentum of the system. As shown above, Eq. (5.125) the square of the angular momentum is related to the energy. We can write the corresponding expression for the energy as

$$E_J = \frac{\hbar^2}{2I} J(J+1), \quad \text{for } J = 0, 1, 2, 3, \dots \quad \dots(5.129)$$

Thus, the rotational quantum number  $J$  is associated with the total energy observable. Since the minimum allowed value of  $J$  is zero, which means that the corresponding value of angular momentum,  $L$  as well as the energy,  $E$  is zero. Thus, in the present case angular momentum  $L$  can have a precise value. Now, to understand the physical significance of the quantum number  $m$  in Eq. (5.113) we operate the function, Eq. (5.123) over by the operator for the  $z$ -component of angular momentum i.e.,  $\hat{L}_z = -i\hbar \frac{\partial}{\partial\phi}$ . We write

$$\hat{L}_z \left\{ \frac{1}{\sqrt{2\pi}} e^{im\phi} \right\} = -i\hbar \frac{\partial}{\partial\phi} \left\{ \frac{1}{\sqrt{2\pi}} e^{im\phi} \right\} = m\hbar \left\{ \frac{1}{\sqrt{2\pi}} e^{im\phi} \right\} \quad \dots(5.130)$$

According to Eq. (5.130) the z-component of angular momentum has a precise value as

$$L_z = m\hbar \quad \dots(5.131)$$

Thus, the quantum number  $m$  represents the quantisation of the z-component of the angular momentum. Since the permitted values of  $m$  are  $0, \pm 1, \pm 2, \dots$ , the z-component of angular momentum has precise values that correspond to specific orientation of the angular momentum with respect to the z-axis. Let us sum up what all have we discussed in this unit. However, before that answer the following simple question to assess your understanding.

---

### SAQ 7

Give the energy expression for a rigid rotor in three dimensions. What is the significance of  $J = 0$ ?

---

## 5.5 SUMMARY

---

In this unit we will take up two model quantum mechanical systems viz., the harmonic oscillator and the rigid rotor. These systems model for the vibration and rotation motion. We began the unit by taking up the classical description of a harmonic oscillator. It was followed by its quantum mechanical treatment wherein we formulated the Schrodinger wave equation and suitably modified so as to facilitate its solution. In this context we introduced the series solution method and other strategies of solving the SWE. After a detailed process we were able to get the energy expression and the wave functions. These were then suitably analysed. Having dealt with the harmonic oscillator as a model for vibration of a molecule and learning salient features of this system we moved on to the second model system i.e., rigid rotor. Here again, we initially dealt with the system classically and then formulated the Schrödinger wave equation. The equation was then converted to spherical harmonics equation for fixed distance between the two masses. This was then separated into two expressions. Towards the end we stated and discussed the results of their solution without going into detailed process of solving them.

## 5.6 TERMINAL QUESTIONS

---

1. Calculate the zero-point energy of a quantum harmonic oscillator with the force constant and the reduced mass as,  $k = 600\text{N/m}$ ,  $\mu = 1.5 \times 10^{-26}\text{kg}$
2. The vibrational energy levels are non-degenerate. Justify
3. The energy difference between two consecutive states vibrational energy states is  $\Delta E = 6.00 \times 10^{-20}\text{J}$ , calculate the frequency of oscillation.
4. Calculate  $H_3(\xi)$  by using Rodrigue formula
5. Determine the Hermite functions,  $H_6(\xi)$  by using recursion relation.
6. Evaluate the first three normalised wave functions for the harmonic oscillator for their nature being odd or even.
7. Formulate the Hamiltonian operator for a rigid rotor.

## 5.7 ANSWERS

### Self Assessment Questions

1. The potential and kinetic energy of a classical harmonic oscillator at the given positions are as under

i) At equilibrium position ( $x=0$ ), the potential energy is zero and the kinetic energy is maximum,  $= \frac{1}{2}mv_x^2$

ii) At  $x = \pm A$  where  $A$ , is the amplitude (maximum displacement) the potential energy is maximum,  $= \frac{1}{2}kA^2$  and the kinetic energy is zero.

2. Let us take  $\nu = 3$ ; the chosen series will be;  $H_3(\xi) = a_1 + a_3\xi^3$  with the highest power term involving,  $\xi^3$ . We arbitrarily take the coefficient of this term,  $a_3 = 2^3 = 8$  and use the recursion formula, to derive the coefficient,  $a_1$ . According to the recursion formula we have

$$a_n = a_{n-2} \frac{(n+1)(n+2)}{(2n-2\nu)}$$

Substituting the value of  $n$ , we can get

$$a_1 = a_3 \frac{(2)(3)}{(-4)} = 8 \frac{6}{(-4)} = -12$$

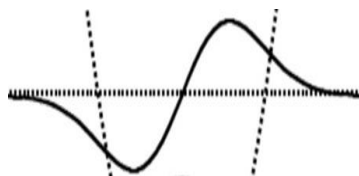
Thus, we can write the Hermite polynomial for  $\nu = 3$  as,

$$H_3(\xi) = -12 + 8\xi^3 = 8\xi^3 - 12$$

3. A function is said to be even function if it does not change (remains the same) when the the sign of the variable is reversed i.e.,  $f(-x) = f(x)$ . On the other hand, it is said to be odd if the function changes its sign on reversing the sign of the variable i.e.,  $f(-x) = -f(x)$ . Let us check the given functions

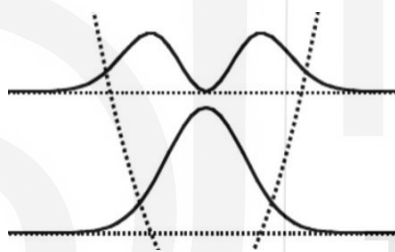
| S. no. | Given function | Function with reversed sign of variable     | Nature               |
|--------|----------------|---|----------------------|
| (a)    | $\sin x$       | $\sin(-x) = -\sin x$                        | odd                  |
| (b)    | $x \sin x$     | $(-x) \sin(-x) = (-x) - \sin x = x \sin x$  | even                 |
| (c)    | $e^x$          | $e^{-x}$ ; not related to $e^x$ as required | Neither odd nor even |
| (d)    | $\cos x$       | $\cos(-x) = \cos x$                         | even                 |
| (e)    | $x \cos x$     | $(-x) \cos(-x) = (-x) \cos x = -x \cos x$   | odd                  |
| (f)    | $(a+x)(a-x)$   | $(a+(-x))(a-(-x)) = (a-x)(a+x)$             | even                 |

4. A schematic plot for the wavefunction for the first excited state is given below. The dotted line refers to the potential energy curve for the harmonic oscillator.



There are two important characteristics.

- i) The wavefunction is characterized by a single node i.e., a point where the wave function crosses zero. It signifies the region in space where the probability is zero.
  - ii) The wavefunction penetrates the classically not allowed regions i.e., beyond A.
5. A schematic plot for the probability density distributions of the ground state and the first excited state of a quantum harmonic oscillator are given below. The dotted line refers to the potential energy curve for the harmonic oscillator.



We can note that in its ground state, the position of the oscillator is most likely to be near  $x = 0$  i.e., at the equilibrium. In the first excited state the position is spread out within the classically allowed region and the probability of the oscillator being near the classical turning points increases. However, in both the cases there is finite probability in the classically not allowed regions.

6. The Virial theorem states that if the potential energy,  $V$ , due to interaction of any two particles is proportional to  $r^n$ , then the average kinetic energy and average potential energy are related as,  $\bar{T} = \frac{n}{2} \bar{V}$ . Since for harmonic oscillator,  $V = \frac{1}{2} kx^2$  ( $n=2$ ) the average kinetic and average potential energies are expected to be equal i.e.,  $\bar{T} = \bar{V}$ . As these are found to be equal, we say that these are in accordance with the Virial theorem.
7. We can write the expression for the energy of a rigid rotor in three dimensions as

$$E_J = \frac{\hbar^2}{2I} J(J+1), \text{ for } J=0, 1, 2, 3, \dots$$

Since the minimum allowed value of  $J$  is zero, it means that the corresponding value of angular momentum,  $L$  as well as the energy,  $E$  is zero.

## Terminal Questions

1. The zero-point energy of a quantum harmonic oscillator is given by the formula:

$$E_0 = \frac{1}{2} \hbar \omega \quad \text{where } \omega = \sqrt{\frac{k}{\mu}}$$

We first calculate the angular frequency as

$$\omega = \sqrt{\frac{600}{1.5 \times 10^{-26}}} = \sqrt{4 \times 10^{28}} \approx 2 \times 10^{14} \text{ rad/s}$$

Substituting in the expression, we get the zero-point energy as:

$$E_0 = \frac{1}{2} \hbar \omega = \frac{1}{2} (1.0545718 \times 10^{-34}) (2 \times 10^{14}) = 1.05 \times 10^{-20} \text{ J}$$

2. Since for each energy level  $E_v$ , there is only one polynomial  $H_v(\xi)$ , which implies that there is only one wavefunction corresponding to a given vibrational energy level i.e., these energy levels are non-degenerate.
3. The angular frequency is related to the difference in the energy states as

$$\Delta E = E_1 - E_0 = \hbar \omega$$

Rearranging and substituting the values, we get

$$\omega = \frac{\Delta E}{\hbar} = \frac{6.00 \times 10^{-20}}{1.0545718 \times 10^{-34}} \approx 5.69 \times 10^{14} \text{ rad/s}$$

The frequency of oscillation is:

$$\nu = \frac{\omega}{2\pi} = \frac{5.69 \times 10^{14}}{2\pi} \approx 9.05 \times 10^{13} \text{ Hz}$$

4. We know that Hermite polynomials can be generated by using the following Rodrigue formula

$$H_n(\xi) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2})$$

Let us begin by substituting the values we write,

$$\begin{aligned} H_3(\xi) &= (-1)^3 e^{\xi^2} \frac{d^3}{d\xi^3} (e^{-\xi^2}) = \left(-e^{\xi^2}\right) \frac{d}{d\xi} \left[ \frac{d^2}{d\xi^2} (e^{-\xi^2}) \right] \\ &= \left(-e^{\xi^2}\right) \frac{d}{d\xi} \left[ \left[ \frac{d}{d\xi} \left( \frac{d}{d\xi} e^{-\xi^2} \right) \right] \right] = \left(-e^{\xi^2}\right) \frac{d}{d\xi} \left[ \left[ \frac{d}{d\xi} (-2\xi)(e^{-\xi^2}) \right] \right] \\ &= \left(-e^{\xi^2}\right) \frac{d}{d\xi} \left[ (-2\xi)(-2\xi)e^{-\xi^2} + e^{-\xi^2}(-2) \right] = \left(-e^{\xi^2}\right) \frac{d}{d\xi} \left[ (4\xi^2 - 2)e^{-\xi^2} \right] \\ &= \left(-e^{\xi^2}\right) \left[ (4\xi^2 - 2)(-2\xi)e^{-\xi^2} + e^{-\xi^2}(8\xi) \right] = \left(-e^{\xi^2}\right) \left[ (-8\xi^3 + 4\xi)e^{-\xi^2} + e^{-\xi^2}(8\xi) \right] \\ &= \left(-e^{\xi^2}\right) \left[ (-8\xi^3 + 12\xi)e^{-\xi^2} \right] = (8\xi^3 - 12\xi)e^0 = (8\xi^3 - 12\xi) \end{aligned}$$

5. We know that the Hermite polynomials can be determined by using the following recursion relation.

$$H_{n+1}(\xi) = 2\xi H_n(\xi) - 2nH_{n-1}(\xi) \text{ along with the following,}$$

$$H_0(\xi) = 1 \text{ and } H_1(\xi) = 2\xi.$$

To evaluate the expressions for  $H_6(\xi)$  we begin with  $H_2(\xi)$

$$H_2(\xi) = 2\xi H_1(\xi) - 2(1)H_0(\xi) = 2\xi(2\xi) - 2 = 4\xi^2 - 2$$

$$H_3(\xi) = 2\xi H_2(\xi) - 2(2)H_1(\xi) = 2\xi(4\xi^2 - 2) - 4(2\xi)$$

$$= 8\xi^3 - 4\xi - 8\xi = 8\xi^3 - 12\xi$$

$$H_4(\xi) = 2\xi H_3(\xi) - 2(3)H_2(\xi) = 2\xi(8\xi^3 - 12\xi) - 6(4\xi^2 - 2)$$

$$= 16\xi^4 - 24\xi^2 - 24\xi^2 + 12 = 16\xi^4 - 48\xi^2 + 12$$

$$H_5(\xi) = 2\xi H_4(\xi) - 2(4)H_3(\xi) = 2\xi(16\xi^4 - 48\xi^2 + 12) - 8(8\xi^3 - 12\xi)$$

$$= 32\xi^5 - 96\xi^3 + 24\xi - 64\xi^3 + 96\xi = 32\xi^5 - 160\xi^3 + 120\xi$$

$$H_6(\xi) = 2\xi H_5(\xi) - 2(5)H_4(\xi) = 2\xi(32\xi^5 - 160\xi^3 + 120\xi) - 2(5)(16\xi^4 - 48\xi^2 + 12)$$

$$= (64\xi^6 - 320\xi^4 + 240\xi^2) - (160\xi^4 - 480\xi^2 + 120) = (64\xi^6 - 480\xi^4 + 720\xi^2 - 120)$$

$$\text{Thus, } H_6(\xi) = (64\xi^6 - 480\xi^4 + 720\xi^2 - 120)$$

6. The normalised wave functions for linear harmonic oscillator are given by the following expression.

$$\psi_\nu(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{1}{2^\nu \nu!}\right)^{-1/2} e^{-\alpha x^2/2} H_\nu(x)$$

The first four wavefunctions correspond to the ones for  $\nu = 0, 1, \text{ and } 2$ . Let us derive these wavefunctions and assess them.

$$\begin{aligned} \nu = 0 : \quad \psi_0(x) &= \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{1}{2^0 0!}\right)^{-1/2} e^{-\alpha x^2/2} H_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \times 1 \times e^{-\alpha x^2/2} \times 1 \\ &= \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} \end{aligned}$$

Replacing  $(x \text{ by } (-x))$ , we get

$$\psi_0(-x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(-x)^2/2} = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha(x)^2/2} = \psi_0(x)$$

Therefore, it is an even wavefunction.

$$\begin{aligned} \nu = 1 : \quad \psi_1(x) &= \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{1}{2^1 1!}\right)^{-1/2} e^{-\alpha x^2/2} H_1(x) = \left(\frac{4\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} 2x \\ &= \left(\frac{64\alpha}{\pi}\right)^{1/4} x e^{-\alpha x^2/2} = \psi_1(x) = \left(\frac{64\alpha}{\pi}\right)^{1/4} x e^{-\alpha x^2/2} \end{aligned}$$

Replacing  $(x \text{ by } (-x))$ , we get

$$\psi_1(-x) = \left(\frac{64\alpha}{\pi}\right)^{1/4} (-x) e^{-\alpha(-x)^2/2} = -\left(\frac{64\alpha}{\pi}\right)^{1/4} (x) e^{-\alpha(x)^2/2} = -\psi_1(x)$$

Therefore, it is an odd wavefunction.

$$u=2 \quad \psi_2(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{1}{2^2 2!}\right)^{-1/2} e^{-\alpha x^2/2} H_2(x) = \left(\frac{64\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} (4x^2 - 2)$$

Replacing  $(x \text{ by } (-x))$ , we get

$$\psi_2(-x) = \left(\frac{64\alpha}{\pi}\right)^{1/4} e^{-\alpha(-x)^2/2} (4(-x)^2 - 2) = \left(\frac{64\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2} (4x^2 - 2) = \psi_2(x)$$

Therefore, this is also an even wavefunction. From these, we infer that the functions for odd values of the vibration quantum number  $v$  are odd and the ones for the even value of the quantum number the wavefunctions are even.

7. The classical expression for the kinetic energy of the rigid rotator can be written as

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2 = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2}$$

Here,  $p_1$  and  $p_2$  are the linear momentum of the two particles of rigid rotator. Since the potential energy is zero for a freely rotating rotator the total energy will be equal to the kinetic energy, i.e.,

$$E = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + 0$$

This can be written in terms of the components ( $p_{x_1}, p_{y_1}$ , and  $p_{z_1}$ ) of linear momenta along x-, y-, and z- axes.

$$E = \frac{(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2)}{2m_1} + \frac{(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2)}{2m_2}$$

Replacing the terms for the components of the linear momentum with the corresponding quantum mechanical operators, and simplifying, we get the expression for the Hamiltonian operator for the rigid rotator as

$$\hat{H} = \frac{-\hbar^2}{2m_1} \left[ \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2} \right] - \frac{\hbar^2}{2m_2} \left[ \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2} \right]$$

### Spherical Polar Coordinates

You know that we need three coordinates to locate a point in a three dimensional space. Suppose you wish to state the location of a ceiling fan in your room you may say 'start from the corner of the room, move seven feet along the length followed by five feet along the width of the room and then go nine feet upwards towards the roof. The coordinates will be (7,5,9). You need to specify all the three coordinates. Similarly, spherical polar coordinates are an alternate set of coordinates for locating a point in a three dimensional space. These are denoted as  $(r, \theta, \phi)$  and are defined as shown in the figure given below. The choice of a coordinate system is generally a matter of convenience. Spherical coordinates are convenient to use for a system like atom that has a natural center.

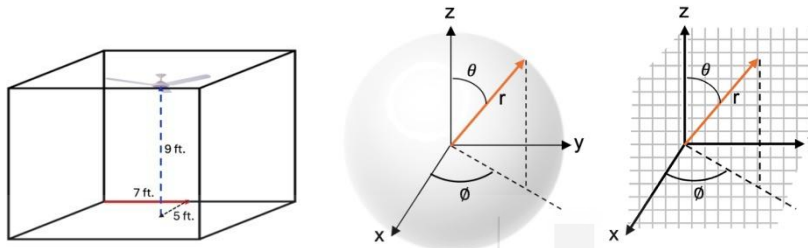


Fig.A.1: Locating a point in a three dimensional space.

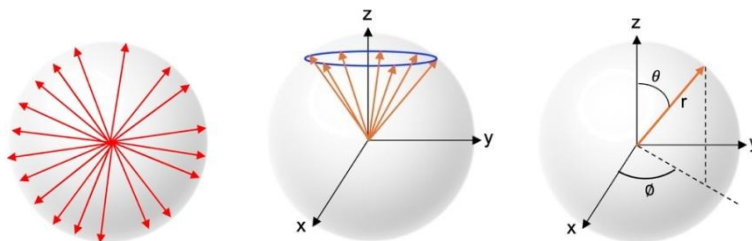
The coordinate  $r$  gives the distance of the point 'P' in a three-dimensional space (or on the surface of a sphere) from the origin, 'O'  $(0,0,0)$  (or the center of the sphere). The coordinate  $\theta$  is the angle made by the distance vector (OP) with the vertical direction (z-axis) and is called **polar angle**. To define the coordinate  $\phi$  we draw a projection from the point 'P' on the x-y plane and join it to the origin. The angle made by the line OQ with the x-axis as we move from x axis to y-axis is called  $\phi$  or **azimuthal angle**. In the absence of a natural zero value for angle  $\phi$  it is measured from x-axis. The two sets of coordinates are interrelated mathematically as

| Cartesian coordinates in terms of spherical polar coordinates | Spherical polar coordinates in terms of Cartesian coordinates |
|---|---|
| $x = r \sin\theta \cos\phi$                                   | $r = (x^2 + y^2 + z^2)^{1/2},$                                |
| $y = r \sin\theta \sin\phi$                                   | $\theta = \cos^{-1} \frac{z}{r}$                              |
| $z = r \cos\theta$  | $\phi = \tan^{-1} \frac{y}{x}$                                |

The distance coordinate can range from zero to infinity. Since the polar angle gives the declination from the vertical direction it can vary from  $0 \rightarrow \pi$ . On the other hand, the azimuthal angle represents the orientation around the z-axis it varies from  $0 \rightarrow 2\pi$ . In other words, the motion along phi corresponds to the circular motion around z-axis. Thus, the ranges of polar coordinates are:

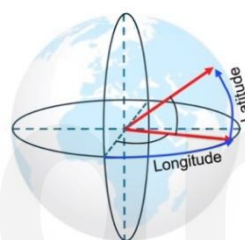
$$0 \leq r < \infty; \quad 0 \leq \theta \leq \pi; \quad 0 \leq \phi < 2\pi.$$

In spherical polar coordinates if we specify only the  $r$  coordinate then we can be anywhere on the sphere as all the points on the surface of the sphere are equidistant from its center. If we specify  $r$  and  $\theta$  then we can be anywhere on the cone as shown in the figure below. Therefore, we need to specify all the three coordinates to reach the unique point in a three dimensional space.



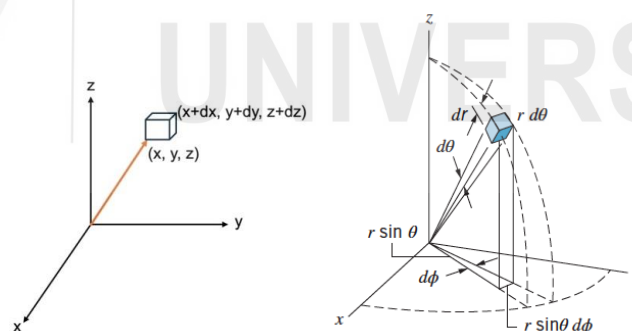
**Fig. A.2: Understanding location of a point in a three dimensional space in terms of spherical polar coordinates.**

We can understand the spherical polar coordinates by taking the example of the globe. The globe represents the surface of the earth and all the points on the globe are equidistant from the center of the earth (i.e.,  $r$  is fixed). The location of any point on the earth is given in terms of two coordinates viz., the longitude and latitude. The latitude in a way is like the polar angle  $\theta$  though it represents the inclination of the point in question from the  $y$ -axis (i.e., equator). The longitude on the other hand, is like the azimuthal angle  $\phi$ . It is the angle the point makes with the prime meridian as shown below.



**Fig. A.3: Outlining significance of latitude and longitude on a globe.**

You would have learnt about the volume element in cartesian coordinate system in your earlier classes. It is the volume of an infinitesimally small cube with sides  $dx$ ,  $dy$  and  $dz$  at point  $P(x, y, z)$ . We get it by moving infinitesimally small distances along the  $x$ -,  $y$ -, and  $z$ - axes in the vicinity of the point  $P$  as shown in the figure given below. The volume element is  $(dx \cdot dy \cdot dz)$ .



**Fig. A.4: Representation of volume element in a) Cartesian and b) spherical polar coordinates.**

In case of spherical polar coordinates, the volume element at  $(r, \theta, \phi)$  can be created by making infinitesimal changes in the three coordinates i.e.,  $r \rightarrow r + dr$ ,  $\theta \rightarrow \theta + d\theta$ ,  $\phi \rightarrow \phi + d\phi$ . The corresponding volume element so obtained is shown in figure given the differential volume element in spherical coordinates will be

$$d\tau = (r \sin \theta d\phi)(r d\theta) dr = r^2 \sin \theta dr d\theta d\phi$$

Accordingly, we can integrate a function  $f(r, \theta, \phi)$  over the full range of the spherical polar coordinates as given below.

$$F = \int_0^{\infty} r^2 dr \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi f(r, \theta, \phi).$$