



# QUANTUM MECHANICS

## UNIT II Quantum Mechanics Lecture-7



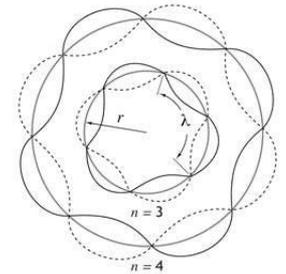
MODERN PHYSICS • XXIII.iii • Wave Mechanics and Atomic Theory

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### The De Broglie Wavelength

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

- $\lambda$  = wavelength
- $h$  = Planck's constant ( $6.63 \times 10^{-34} \text{ J} \cdot \text{s}$ )
- $p$  = momentum
- $m$  = mass
- $v$  = speed



De Broglie's extension of the concept of particle-wave duality from photons to include all forms of matter allowed the interpretation of electrons in the Bohr model as standing electron waves. De Broglie's work marked the start of the development of wave mechanics.



$$E\Psi = -\frac{\hbar^2}{2m} \frac{d^2\Psi}{dx^2} + V\Psi$$



## Linear Harmonic Oscillator (One Dimensional)

- ✓ The vibrations of Nuclei in the diatomic molecules along their internuclear axis can be considered as the vibrations of harmonic oscillator.
- ✓ The Simplest possible assumption about the form of vibrations is to treat the molecule as harmonic oscillator.
- ✓ In Simple Harmonic Motion the restoring force is proportional to displacement
- ✓ i.e.  $F = -kx$  -----(1)
- ✓ where  $k$  is a positive constant known as force constant



## Linear Harmonic Oscillator (One Dimensional) Contd..

- From the Newton's Second Law we may write

- $$F = m \frac{d^2x}{dt^2} \text{-----(2)}$$

- Where m is the mass of the particle
- Using the value of F in equation (1) we get

- $$m \frac{d^2x}{dt^2} + kx = 0$$

- Or 
$$\frac{d^2x}{dt^2} + \frac{k}{m} kx = 0 \text{-----(3)}$$

- Equation (3) represents a periodic motion of angular frequency

- $$\omega = \sqrt{\frac{k}{m}} \quad \text{or} \quad v = \frac{\omega}{2\pi} \sqrt{\frac{k}{m}}$$



# Linear Harmonic Oscillator (One Dimensional) Contd..

- The potential energy of the oscillator is

- $V = - \int_0^x kx \, dx$  assuming zero potential energy at  $x=0$

- Thus  $V = \frac{1}{2} kx^2$  -----(4)

- Now the Schrodinger wave equation for such motion can be given as

- $\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2} (E - \frac{1}{2} kx^2) \Psi = 0$  -----(5)

- Rearranging above equation we get

- $\frac{d^2\Psi}{dx^2} + 2 \sqrt{\frac{m}{\hbar^2}} \sqrt{\frac{mk}{\hbar^2}} \left[ \frac{E}{\sqrt{k}} - \frac{1}{2} \sqrt{k} x^2 \right] \Psi = 0$

- $\frac{1}{\sqrt{\frac{mk}{\hbar^2}}} \frac{d^2\Psi}{dx^2} + 2 \sqrt{\frac{m}{\hbar^2}} \left[ \frac{E}{\sqrt{k}} - \frac{1}{2} \sqrt{k} x^2 \right] \Psi = 0$



# Linear Harmonic Oscillator (One Dimensional) Contd..

- $$\frac{1}{\sqrt{\frac{mk}{\hbar^2}}} \frac{d^2\Psi}{dx^2} + \left[ 2\sqrt{\frac{m}{\hbar^2 k}} E - \sqrt{\frac{mk}{\hbar^2}} x^2 \right] \Psi = 0 \text{ -----(6)}$$

- For our convenience let us substitute

- $$\sqrt{\frac{mk}{\hbar^2}} = \alpha^2 \text{ -----7(i)} \quad \text{and} \quad 2E\sqrt{\frac{m}{\hbar^2 k}} = \lambda \text{ -----7(ii)}$$

- Using above substitution in equation (6) we get

- $$\frac{1}{\alpha^2} \frac{d^2\Psi}{dx^2} + (\lambda - \alpha^2 x^2) \Psi = 0 \text{ -----(8)}$$

- Let us introduce new variable q function of x

- $$q = \alpha x \text{ ----- (9)}$$

- Where  $\alpha$  is constant



# Linear Harmonic Oscillator (One Dimensional) Contd..

- Now, 
$$\frac{\partial \Psi}{\partial x} = \frac{\partial \Psi}{\partial q} \frac{\partial q}{\partial x} = \alpha \frac{\partial \Psi}{\partial q}$$

- $$\frac{d^2 \Psi}{dx^2} = \frac{\partial}{\partial x} \left( \frac{\partial \Psi}{\partial x} \right) = \frac{\partial}{\partial q} \left( \frac{\partial \Psi}{\partial x} \right) \frac{\partial q}{\partial x}$$

- $$\frac{d^2 \Psi}{dx^2} = \frac{\partial}{\partial q} \left( \alpha \frac{\partial \Psi}{\partial q} \right) \alpha = \alpha^2 \frac{d^2 \Psi}{dq^2} \text{ -----(10)}$$

- Now the equation (8) can be written as

- $$\frac{d^2 \Psi}{dq^2} + (\lambda - q^2) \Psi = 0 \text{ -----(11)}$$

- Let us try a solution of the following form to equation (11)

- $$\Psi(q) = C e^{\frac{-q^2}{2}} \phi(q) \text{ -----(12)}$$

- Where  $\phi(q)$  is the function of x



# Linear Harmonic Oscillator (One Dimensional) Contd..

- Differentiating Equation (12) we get

- $$\frac{d^2\Psi}{dq^2} = e^{-\frac{q^2}{2}} \left\{ \frac{d^2\Phi}{dq^2} - 2q \frac{\partial\Phi}{\partial q} + (q^2 - 1)\Phi \right\} = 0 \quad \text{--- (13)}$$

- Using the values of  $\Psi(q)$  and  $\frac{d^2\Psi}{dq^2}$  in equation (11) we get

- $$e^{-\frac{q^2}{2}} \left\{ \frac{d^2\Phi}{dq^2} - 2q \frac{\partial\Phi}{\partial q} + (q^2 - 1)\Phi \right\} + e^{-\frac{q^2}{2}} (\lambda - q^2) \Phi = 0$$

- or,

- $$e^{-\frac{q^2}{2}} \left\{ \frac{d^2\Phi}{dq^2} - 2q \frac{\partial\Phi}{\partial q} + (\lambda - 1)\Phi \right\} = 0$$

- $$\frac{d^2\Phi}{dq^2} - 2q \frac{\partial\Phi}{\partial q} + (\lambda - 1) \Phi = 0 \quad \text{-----(14)}$$

- If we replace  $(\lambda - 1)$  by  $2n$  then this equation becomes Hermite differential equation and we may write as



# Linear Harmonic Oscillator (One Dimensional) Contd..

- $\frac{d^2 H_n(q)}{dq^2} - 2q \frac{\partial H_n(q)}{\partial q} + 2n H_n(q) = 0$  ----- (15)
- This Shows that the solution of Eq(8) is obtained replacing  $\phi(q)$  by  $H_n(q)$  in equation (12)

$$\Psi(q) = C H_n(q) e^{-\frac{q^2}{2}} \text{-----}(16)$$

These solutions are responsible only  $n = 0, 1, 2, \dots$

- The restriction on  $n$  gives a corresponding restriction on  $E$ .
- We have

$$(\lambda - 1) = 2n$$

$$\lambda = 2n + 1$$

Substituting the value of  $\lambda$  in 7 (ii)

$$2E \sqrt{\frac{m}{\hbar^2 k}} = 2n + 1$$



# Linear Harmonic Oscillator (One Dimensional) Contd..

$$2E \left[ \sqrt{\frac{m}{\hbar^2(m\omega^2)}} \right] = 2n + 1$$

$$\frac{2E}{\hbar\omega} = 2n + 1$$

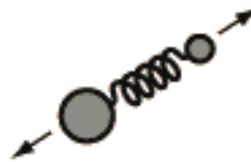
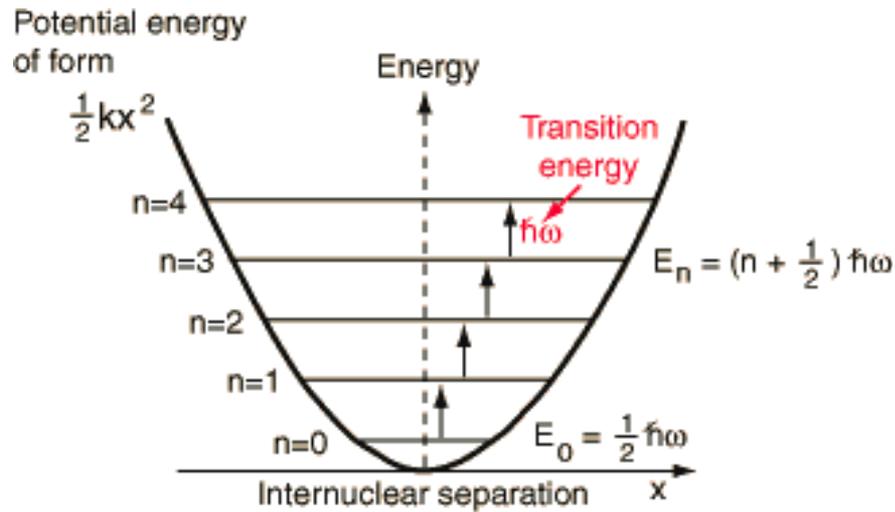
$$E = E_n = \left( n + \frac{1}{2} \right) \hbar\omega \dots \dots \dots (17)$$

Where,  $n = 0, 1, 2, \dots$

- The allowed integral values of  $n$  lead to certain discrete values of energy, represented by equation (17) is known as eigen values of the harmonic oscillator.
- Moreover this equation also indicates that the energy levels of harmonic oscillator are equally spaced.



# Energy Levels for a Quantum Mechanical Harmonic Oscillator



$x=0$  represents the equilibrium separation between the nuclei.



## Linear Harmonic Oscillator (One Dimensional) Contd..

- A comparison of  $E_n$  given in equation (17) with the result  $E = n \hbar \omega$  obtained old quantum theory suggest following.
- There is the only difference that all the equally spaced energy levels are shifted upward by an amount equal to half the separation of energy level i. e.  $\frac{1}{2} \hbar \omega$ .
- This energy is known as the zero point energy of the harmonic oscillator.
- Thus it is clear that in the lowest state, the harmonic oscillator has finite energy while according to classical mechanics the harmonic oscillator possesses zero energy at allowed state.
- The existence of zero point energy is in agreement with experiment and important feature of quantum mechanics.



# Molecular Spectra - Vibrational States

- For a simple harmonic oscillator, the classical frequency  $f$  of oscillation is given by

$$f = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$k$  is the stiffness constant  
 $\mu$  is the reduced mass

- Solution of the Schrodinger equation for the simple harmonic oscillator potential shows that the oscillator energy  $E_{\text{vib}}$  is quantised.

$$E_{\text{vib}} = \left(n + \frac{1}{2}\right) h\nu$$

Vibrational quantum number  $v = 0, 1, 2, 3, \dots$   $\nu$  is the frequency

- Note that the lowest vibrational energy ( for  $n = 0$ ) is not zero (as is the case for rotation) but  $h\nu/2$ . This is known as the zero point energy.
- Also note that the energy levels are equally spaced. Energy spacing is  $h\nu$ .



# Molecular Spectra – Vibrational States

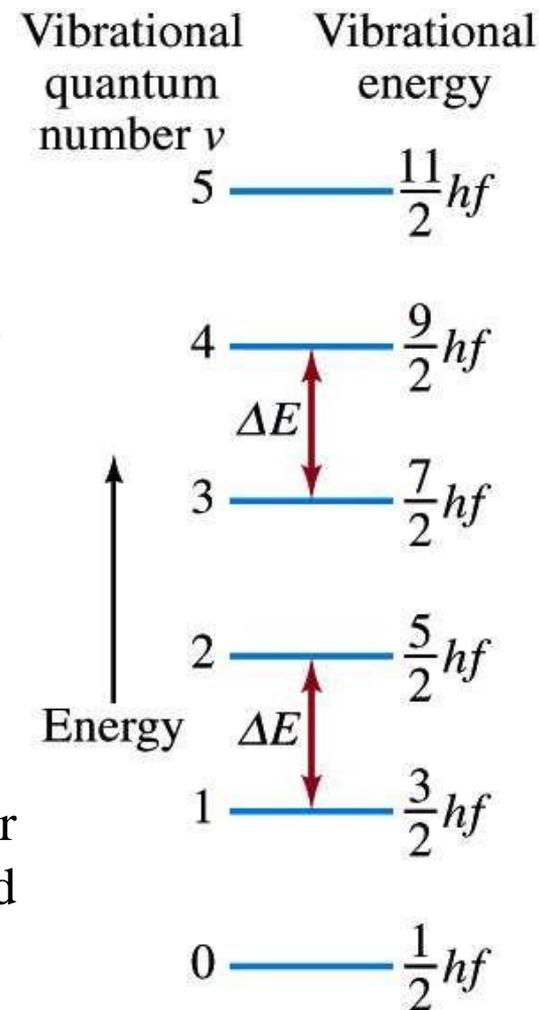
Vibrational transitions are subject to the following selection rules

$$\Delta v = \pm 1$$

- The selection rule shows that allowed vibrational transitions can only occur between adjacent vibrational energy levels.
- In the simple harmonic approximation, the energy  $\Delta E$  of emitted or absorbed photon is given by

$$\Delta E = hf$$

- Transition energies are 10 to 100 times those for rotational and wavelengths are in the infrared spectral region ( $\lambda \sim 1\mu\text{m to } 100\mu\text{m}$ )





## Example: 1

- The force constant of the bond in CO molecule is  $1870 \text{ N m}^{-1}$ . Find the energy of the lowest vibrational level. The reduced mass of CO molecule is  $1.14 \times 10^{-26} \text{ Kg}$ . Given  $h = 6.63 \times 10^{-34} \text{ Js}$  and  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ .

soln.: The frequency of vibration of CO molecule is

$$\nu_{\text{osc}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$
$$= \frac{1}{2 \times 3.14} \sqrt{\frac{1870 \text{ Nm}^{-1}}{1.14 \times 10^{-26} \text{ kg}}} = 6.45 \times 10^{13} \text{ s}^{-1}$$

The vibrational energy of a diatomic molecule is given by

$$E_n = h \nu_{\text{osc}} \left( n + \frac{1}{2} \right), \quad n = 0, 1, 2, \dots$$

For the lowest level corresponding to  $n=0$ . Its energy is

$$E_{n=0} = \frac{1}{2} h \nu_{\text{osc}}$$
$$= \frac{1}{2} (6.63 \times 10^{-34} \text{ Js}) (6.45 \times 10^{13} \text{ s}^{-1})$$
$$= 21.4 \times 10^{-21} \text{ J}$$
$$= \frac{21.4 \times 10^{-21} \text{ J}}{1.60 \times 10^{-19} \text{ J/eV}} = 0.134 \text{ eV.}$$



## Example: 2

- The force constant of the bond in CO molecule is  $1870 \text{ N m}^{-1}$ . Find the energy of the lowest vibrational level. Calculate the frequency of vibration of the molecule and the spacing between its vibrational energy levels in eV. Given that the reduced mass of CO molecule is  $1.14 \times 10^{-26} \text{ Kg}$ . Given  $h = 6.63 \times 10^{-34} \text{ Js}$  and  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ .

Sol<sup>n</sup>: As above the frequency of vibration of the CO molecule is

$$\nu_{\text{osc}} = 6.45 \times 10^{13} \text{ s}^{-1}$$

The separation between two successive vibrational energy levels is

$$\begin{aligned} \Delta E &= E_{n+1} - E_n \\ &= h\nu_{\text{osc}} \left( n + \frac{3}{2} \right) - h\nu_{\text{osc}} \left( n + \frac{1}{2} \right) \\ &= h\nu_{\text{osc}} \\ &= (6.63 \times 10^{-34} \text{ Js}) \times (6.45 \times 10^{13} \text{ s}^{-1}) \\ &= 42.8 \times 10^{-21} \text{ J} \\ &= \frac{42.8 \times 10^{-21} \text{ J}}{1.6 \times 10^{-19} \text{ J/eV}} = 0.2675 \text{ eV} \end{aligned}$$



## **Assignment Based on this Lecture**

- Solve the problem of one dimensional Harmonic Oscillator.
- Obtain the expression of energy levels in harmonic oscillator.
- Compare the expression of energy levels in classical and quantum harmonic oscillator.
- Discuss the importance of harmonic oscillator to deal the problems of vibrational spectroscopy.