❖ Zero Point Energy of a Particle Possessing Harmonic Motion and Its Consequence

In order to understand the minimum or the zero-point energy of a simple harmonic oscillator, recall the general wavefunction representing all the vibrational states of a simple harmonic oscillator i.e.

$$\psi_n(y) = N_n H_n(y)\, e^{-y^2/2} \tag{112}$$

Where y is a displacement-based variable with a value equal to $\sqrt{\beta}x$. The constant β depends upon the reduced mass of the oscillator (m) and equilibrium vibrational frequency (ν) as

$$\beta = \frac{4\pi^2 m\nu}{h} \tag{113}$$

The symbol N_n and $H_n(y)$ are the normalization constant and Hermit polynomial for nth state i.e.

$$N_n = \left(\frac{\sqrt{\beta}}{2^n\, n!\, \sqrt{\pi}}\right)^{1/2} \quad and \quad H_n(y) = (-1)^n . e^{y^2} . \frac{d^n}{dy^n} . e^{-y^2} \tag{114}$$

Also, the general expression for the energies is given below.

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{115}$$

Now, for the ground vibrational state ($n = 0$), N_0 and $H_0(y)$ can be obtained from equation (114) i.e.

$$N_0 = \left(\frac{\beta}{\pi}\right)^{1/4} \quad and \quad H_0(y) = 1 \tag{116}$$

After using the values of y, N_0 and $H_0(y)$ in equation (112), the ground state function becomes

$$\psi_0(x) = \left(\frac{\beta}{\pi}\right)^{1/4} . 1 . e^{-\beta x^2/2} \tag{117}$$

Hence, the ground state wave function does not collapse at $n = 0$, which means that corresponding energy can also be obtained by putting $n = 0$ in equation (115) i.e.

$$E_0 = \left(0 + \frac{1}{2}\right) h\nu \tag{118}$$

or

$$E_0 = \frac{1}{2} h\nu \tag{119}$$

The above equation gives the minimum energy which is always possessed by a simple harmonic oscillator.

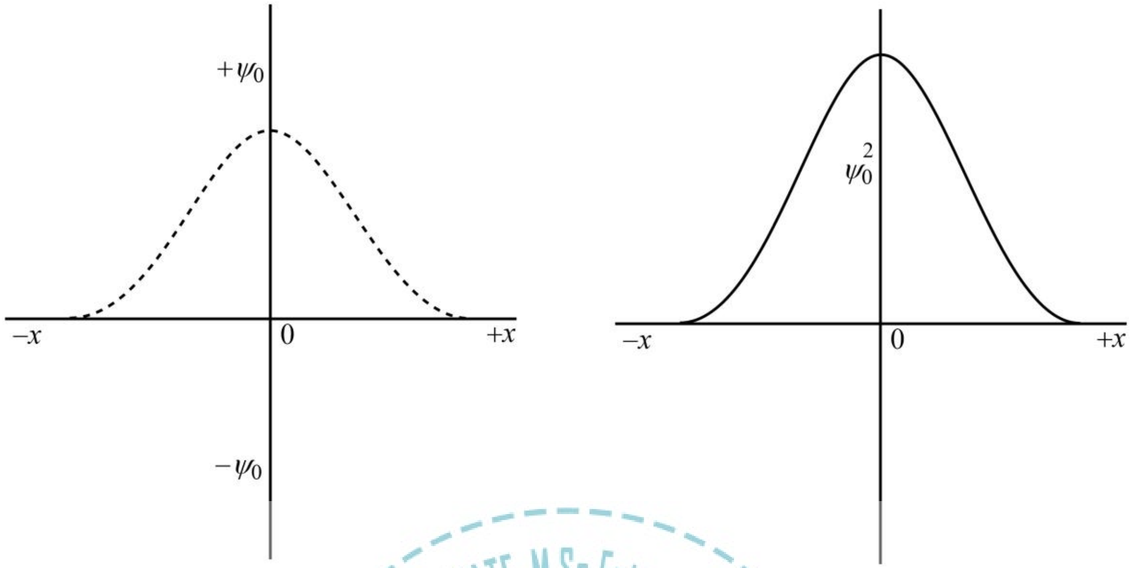

Figure 6. The variation of ground vibrational wavefunction and probability as a function of bond length or displacement in a simple harmonic oscillator.

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It is well-known that the classical oscillator spends more time in the extreme states i.e. fully compressed and fully expended, and spends the least time with equilibrium bond length. However, as far as the ground vibrational state of the quantum mechanical oscillator is concerned, it spends the most time with equilibrium (because the function is maximum for r_{equ} or $x = 0$), and probability to spend time in compressed and expended mode decreases as the magnitude of compression and expansion increases. Moreover, there is always a limit over the compression as well as over the expansion in the classical oscillator to have a certain amount of energy; however, since the function becomes zero only at infinite displacement, there is no limit over the compression and expansion in the quantum oscillator theoretically.

It is also worthy to note that the energy given by the equation (119) is in joules. However, in many textbooks or papers, it is also reported in terms of wavenumbers. To do so, we need first put the value of frequency as $\nu = c/\lambda$ and then $1/\lambda = \bar{\nu}$ in the equation (119) i.e.

$$E_0 = \frac{1}{2}h\frac{c}{\lambda} = \frac{1}{2}hc\bar{\nu} \tag{119}$$

Where c is the velocity of light. Now, to convert the zero-point energy in wavenumbers, divide equation (119) by hc i.e.

$$\bar{\nu}_0 = \frac{1}{2}\frac{hc\bar{\nu}}{hc} = \frac{\bar{\nu}}{2} \tag{120}$$

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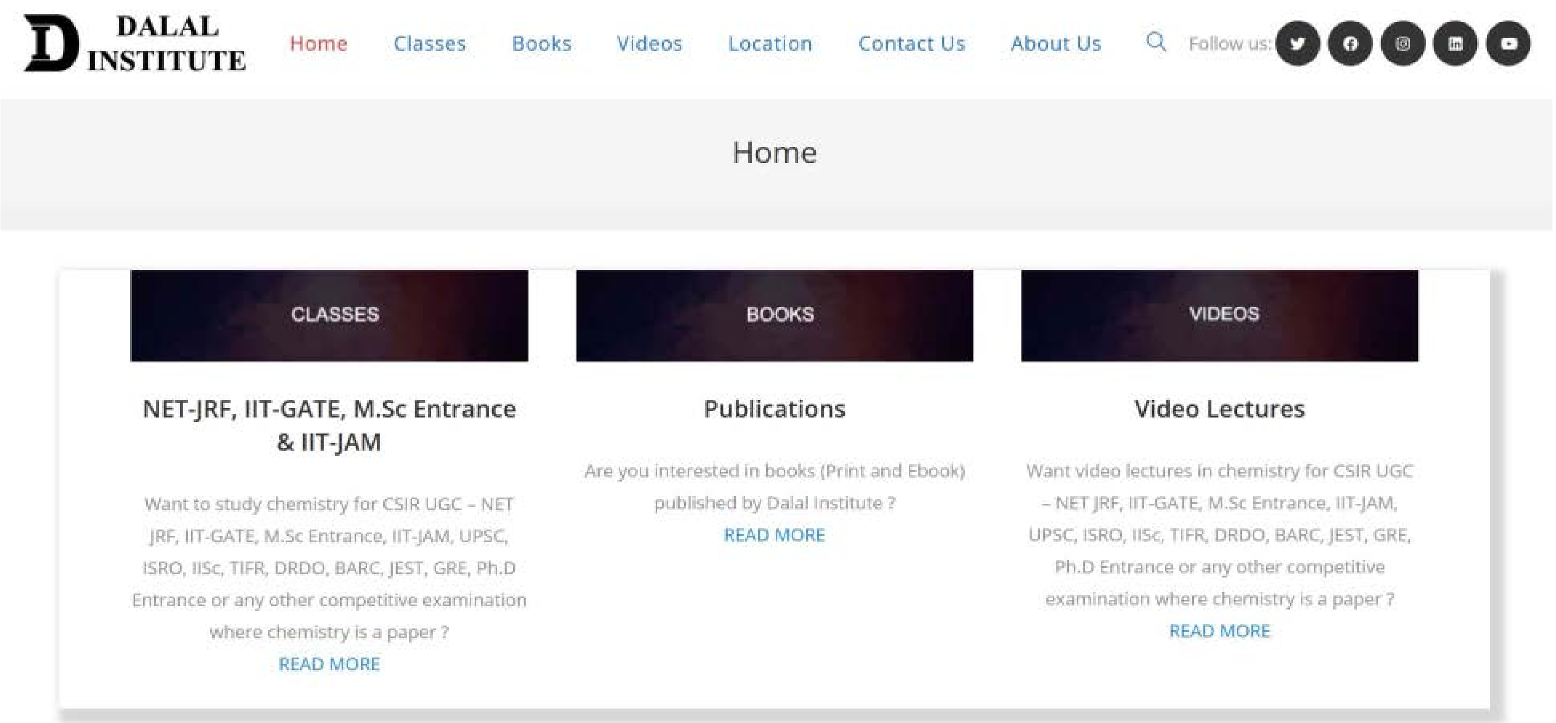

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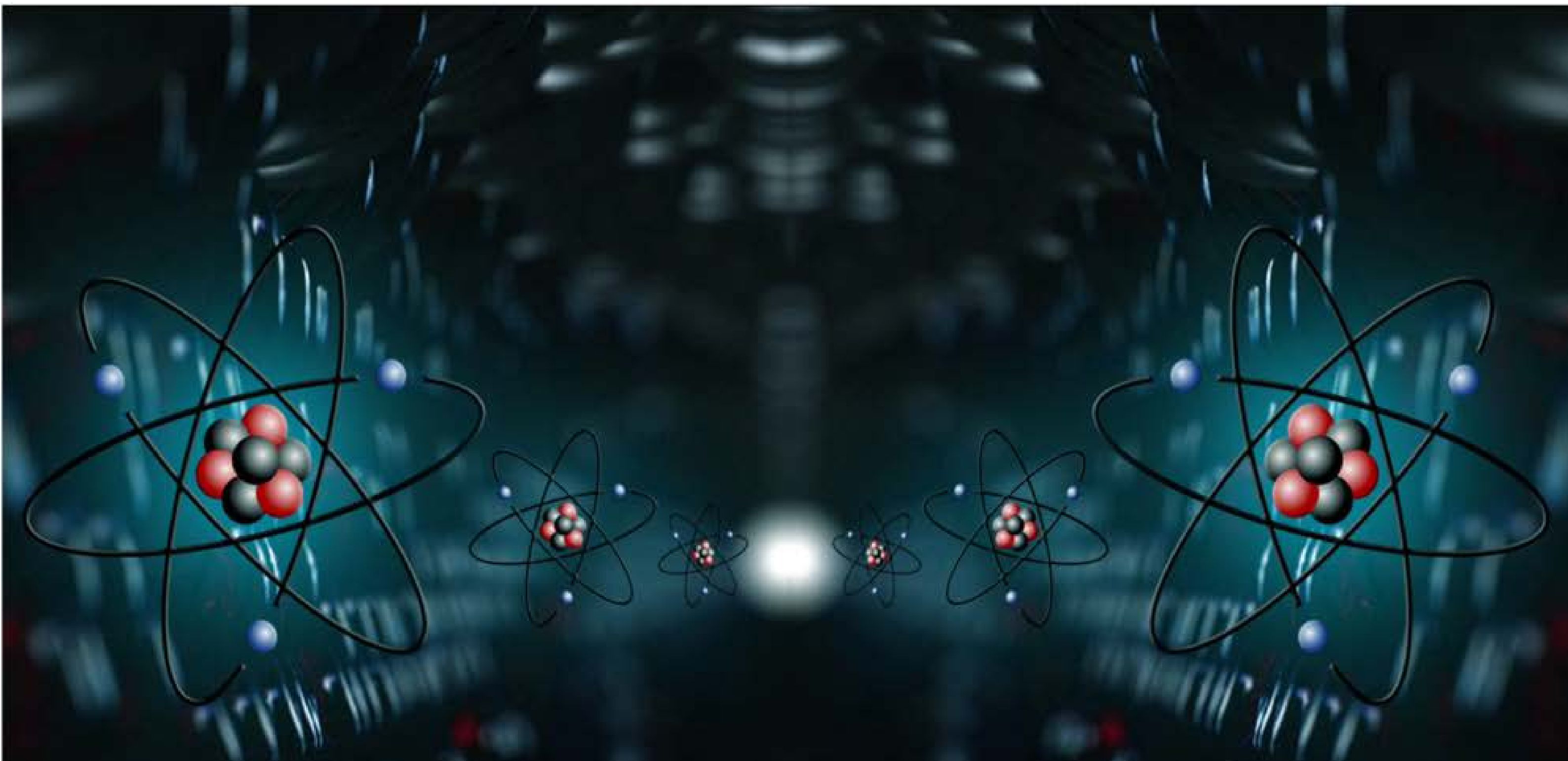

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