

❖ Schrodinger Wave Equation for a Linear Harmonic Oscillator & Its Solution by Polynomial Method

A diatomic molecule is the quantum-mechanical analog of the classical version of the harmonic oscillator. It represents the vibrational motion and is one of the few quantum-mechanical systems for which an exact solution is available. In this section, we will discuss the classical and quantum mechanical oscillator and their comparative study.

➤ The Classical Treatment of Simple Harmonic Oscillator

In order to understand the vibrational states of a simple diatomic molecule, we must understand the classical oscillator first. In order to do so, consider a spring of length r in which a displacement ' x ' is incorporated by expending or compressing it.

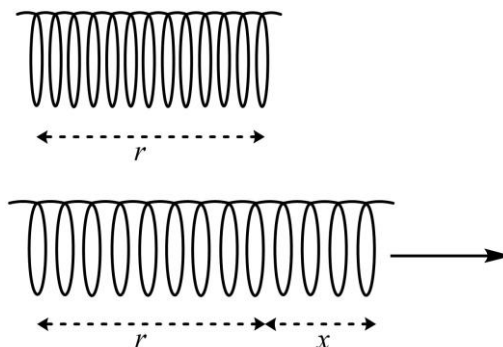


Figure 2. The pictorial representation of the displacement-inducing in a typical spiral.

For a moment, imagine that the spiral is extended by a displacement of ' x '; then the restoring force (F) developed in the spiral can be obtained using Hook's law as

$$F = -kx \quad (35)$$

Where k is the constant of proportionality. The minus sign is because the restoring force and the displacement both are vector quantity but in the opposite direction. In other words, if we expend the spiral, the spiral will try to compress itself and vice-versa. From equation (35), it seems that the restoring force depends only upon displacement induced only, however, it is found that stronger spirals have larger restoring force than the weaker ones for the same magnitude of displacement, indicating a larger force constant. Therefore, the physical significance of the force constant lies in the fact that it can be used to comment on the strength of oscillator.

Since the potential energy in this expended state is simply the amount of work done in the process of incorporating the displacement ' x ', we need calculate the same for further analysis. The restoring force is proportional to the displacement, and therefore, is a variable quantity; suggesting that we need to carry out the integration force curve vs displacement. Suppose that the total displacement " x " is fragmented in very small

“ dx ” segments. The amount of work done in inducing ‘ dx ’ displacement will be ‘ dw ’ and can be given by the following relation

$$dw = F \cdot dx \quad (36)$$

The total work from zero displacement to ‘ x ’ displacement will be

$$W = \int_0^x F \cdot dx \quad (37)$$

$$= \int_0^x -kx \cdot dx \quad (38)$$

$$= -k \left[\frac{x^2}{2} \right]_0^x \quad (39)$$

$$W = -\frac{1}{2} kx^2 \quad (40)$$

Since there is no electrostatic attraction, the potential energy (V) of the system at displacement will simply be

$$V = \frac{1}{2} kx^2 \quad (41)$$

The above equation represents a parabolic behavior and shows that the potential energy varies continuously with the displacement. Larger the displacement, higher will be the potential energy.

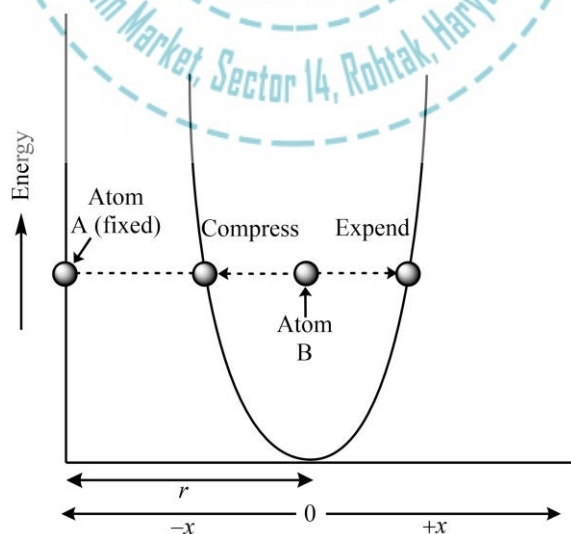


Figure 3. The variation of potential energy as a function of displacement in a classical oscillator.

If ' m ' is the reduced mass of the diatomic molecule, the equilibrium vibrational frequency ' ν ' of the oscillator can be given as

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (42)$$

Where m is the reduced mass defined by the ratio of the product to the sum of individual masses i.e. $m = m_1 m_2 / (m_1 + m_2)$. It is obvious that the energy levels of a simple harmonic oscillator in classical mechanics are continuous (including zero), and have a limit over the expansion and compression for each value. Furthermore, the classical oscillator is bound to spend most of its time in the extreme state (fully compressed and fully expanded) and the least time in the equilibrium position.

➤ **The Quantum Mechanical Treatment of Simple Harmonic Oscillator**

In order to find out the quantum mechanical behavior of a simple harmonic oscillator, assume that all the vibrational states can be described by a mathematical expression ψ . Since we don't know the exact nature of ψ , we need to follow the postulates of quantum mechanics. Therefore, after applying the Hamiltonian operator over this symbolic wave function, we have

$$H\psi = E\psi \quad (43)$$

$$\left(\frac{-h^2}{8\pi^2m} \frac{\partial^2}{\partial x^2} + V \right) \psi = E\psi \quad (44)$$

or

$$\frac{-h^2}{8\pi^2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi - E\psi = 0 \quad (45)$$

Rearranging, we have

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2m}{h^2} (E - V)\psi = 0 \quad (46)$$

After putting the value of potential energy from equation (41) in equation (46), we get

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2m}{h^2} \left(E - \frac{1}{2} kx^2 \right) \psi = 0 \quad (47)$$

Now put the value of k from equation (42) in equation (47) i.e.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2m}{h^2} (E - 2\pi^2\nu^2 m x^2) \psi = 0 \quad (48)$$

or

$$\frac{\partial^2 \psi}{\partial x^2} + \left(\frac{8\pi^2 m E}{h^2} - \frac{16\pi^4 m^2 v^2 x^2}{h^2} \right) \psi = 0 \quad (49)$$

After defining constants

$$\alpha = \frac{8\pi^2 m E}{h^2} \quad \text{and} \quad \beta = \frac{4\pi^2 m v}{h} \quad (50)$$

The equation (49) takes the form

$$\frac{\partial^2 \psi}{\partial x^2} + (\alpha - \beta^2 x^2) \psi = 0 \quad (51)$$

or

$$\frac{\partial^2 \psi}{\partial x^2} + (\alpha - \beta^2 x^2) \psi = 0 \quad (52)$$

Now define a new variable $y = \sqrt{\beta} x$, then we have the derivative as

$$\frac{dy}{dx} = \sqrt{\beta} \quad (53)$$

Squaring both side of the equation (53), and then rearranging

$$\frac{d^2 y}{dx^2} = \beta \quad \text{or} \quad dx^2 = d^2 y / \beta \quad (54)$$

Now put the value of dx^2 and βx^2 in equation (52), we get

$$\beta \frac{\partial^2 \psi}{\partial y^2} + (\alpha - \beta y^2) \psi = 0 \quad (55)$$

Dividing the above equation by β , we get

$$\frac{\partial^2 \psi}{\partial y^2} + \left(\frac{\alpha}{\beta} - y^2 \right) \psi = 0 \quad (56)$$

The equation (56) can be solved asymptotically i.e. at very large values of y . Thus, when $y \gg \alpha/\beta$, the equation (56) becomes

$$\frac{\partial^2 \psi}{\partial y^2} - y^2 \psi = 0 \quad (57)$$

The two possible solutions of the above equation are

$$\psi = e^{\pm y^2/2} \quad (58)$$

Nevertheless, only one of them is acceptable because for $\psi = e^{+y^2/2}$, the wavefunction becomes infinite as y tends to approach ∞ . Therefore, the only single-valued, continuous and finite solution we left with is

$$\psi = e^{-y^2/2} \quad (59)$$

Since the acceptable solution given above is valid only at very large values of y , it is quite reasonable to think that the exact solution may also contain some pre-exponential part to attain validity at all values of y . Therefore, after incorporating some y -dependent unknown function ' $F(y)$ ' in equation (59), we get

$$\psi = F(y) e^{-y^2/2} \quad (60)$$

In order to find the value of $F(y)$, differentiate the equation (60) first i.e.

$$\frac{d\psi}{dy} = -ye^{-y^2/2} \cdot F + \frac{dF}{dy} e^{-y^2/2} \quad (61)$$

Differentiating again, we get

$$\frac{d^2\psi}{dy^2} = \left[-y \cdot (-y) e^{-y^2/2} \cdot F(y) + (-1 \cdot e^{-y^2/2} \cdot F(y)) + \left(-y \cdot e^{-y^2/2} \frac{dF}{dy} \right) \right] \quad (62)$$

or

$$\frac{d^2\psi}{dy^2} = y^2 e^{-y^2/2} \cdot F(y) - e^{-y^2/2} \cdot F(y) - 2y \cdot e^{-y^2/2} \frac{dF}{dy} + e^{-y^2/2} \frac{d^2F}{dy^2} \quad (63)$$

or

$$\frac{d^2\psi}{dy^2} = \left[\frac{d^2F}{dy^2} - 2y \cdot \frac{dF}{dy} + (y^2 - 1) F \right] e^{-y^2/2} \quad (64)$$

Now, after using equation (60) and equation (64) in equation (56), we get

$$\left[\frac{d^2F}{dy^2} - 2y \cdot \frac{dF}{dy} + (y^2 - 1) F \right] e^{-y^2/2} + \left(\frac{\alpha}{\beta} - y^2 \right) F(y) e^{-y^2/2} = 0 \quad (65)$$

or

$$\left[\frac{d^2F}{dy^2} - 2y \cdot \frac{dF}{dy} + \left(\frac{\alpha}{\beta} - 1 \right) F(y) \right] e^{-y^2/2} = 0 \quad (66)$$

Now because of the quantity $e^{-y^2/2}$ will be zero only at $y = \pm\infty$, the sum of the terms present in the bracket must be zero at normal y -values i.e.

$$\frac{d^2 F}{dy^2} - 2y \cdot \frac{dF}{dy} + \left(\frac{\alpha}{\beta} - 1\right) F(y) = 0 \quad (67)$$

The above differential equation is a “Hermit differential equation” and can be solved to find the expression for the “unknown” function $F(y)$. The solution of equation (67) can be obtained by the polynomial method by expressing the function $F(y)$ as a power series in terms of variable ‘ y ’.

$$F = a_0 + a_1 y + a_2 y^2 + a_3 y^3 + a_4 y^4 \dots \dots \dots \quad (68)$$

Differentiating the above equation, we get

$$\frac{dF}{dy} = a_1 + 2a_2 y + 3a_3 y^2 + 4a_4 y^3 \dots \dots \dots \quad (69)$$

Differentiating again, we get

$$\frac{d^2 F}{dy^2} = 2a_2 + 6a_3 y + 12a_4 y^2 \dots \dots \dots \quad (70)$$

Using equation (68-70) in equation (67), we get

$$[2a_2 + 6a_3 y + 12a_4 y^2 \dots] - 2y[a_1 + 2a_2 y + 3a_3 y^2 + 4a_4 y^3 \dots] + \left(\frac{\alpha}{\beta} - 1\right)[a_0 + a_1 y + a_2 y^2 + a_3 y^3 + a_4 y^4 \dots] = 0 \quad (71)$$

or

$$[2a_2 + 6a_3 y + 12a_4 y^2 \dots] - [2a_1 y + 4a_2 y^2 + 6a_3 y^3 + 8a_4 y^4 \dots] + \left[\left(\frac{\alpha}{\beta} - 1\right)a_0 + \left(\frac{\alpha}{\beta} - 1\right)a_1 y + \left(\frac{\alpha}{\beta} - 1\right)a_2 y^2 + \dots\right] = 0 \quad (72)$$

After further rearranging

$$\left[2a_2 + \left(\frac{\alpha}{\beta} - 1\right)a_0\right] + \left[6a_3 y - 2a_1 y + \left(\frac{\alpha}{\beta} - 1\right)a_1 y\right] + \left[12a_4 y^2 - 4a_2 y^2 + \left(\frac{\alpha}{\beta} - 1\right)a_2 y^2\right] + \dots = 0 \quad (73)$$

or

$$\left[2a_2 + \left(\frac{\alpha}{\beta} - 1\right)a_0\right] + \left[6a_3 - 2a_1 + \left(\frac{\alpha}{\beta} - 1\right)a_1\right]y + \left[12a_4 - 4a_2 + \left(\frac{\alpha}{\beta} - 1\right)a_2\right]y^2 + \dots = 0 \quad (74)$$

The above equation is valid only when coefficients of the individual power of y are zero i.e.

For y^0

$$2a_2 + \left(\frac{\alpha}{\beta} - 1\right)a_0 = 0 \quad (75)$$

For y^1

$$6a_3 + \left(\frac{\alpha}{\beta} - 1 - 2\right)a_1 = 0 \quad (76)$$

For y^2

$$12a_4 + \left(\frac{\alpha}{\beta} - 1 - 4\right)a_2 = 0 \quad (77)$$

Similarly, for y^k

$$(k+1)(k+2)a_{k+2} + \left(\frac{\alpha}{\beta} - 1 - 2k\right)a_k = 0 \quad (78)$$

The above equation can be rearranged for the coefficient a_{k+2} i.e.

$$a_{k+2} = -\frac{\left(\frac{\alpha}{\beta} - 1 - 2k\right)a_k}{(k+1)(k+2)} \quad (79)$$

Where k is an integer. The expression given above is popularly known as the recursion formula, and allows one to determine the coefficient a_{k+2} of the term y^{k+2} in terms of a_k -coefficient of the y^k term. In simple words, we can calculate a_2, a_4, a_6 etc. in terms of a_0 if we set $a_1 = 0$; likewise, the coefficients a_3, a_5, a_7 etc. can be obtained in terms of a_1 if we set $a_0 = 0$.

However, the power series will still be made up of the infinite number of terms, making function $F(y)$ infinite at $y = \infty$. Therefore, we must restrict the number of terms so that the function remains acceptable. This can be made possible if, at a certain value of $k = n$, the numerator in equation (79) becomes zero i.e.

$$\frac{\alpha}{\beta} - 1 - 2k = \frac{\alpha}{\beta} - 1 - 2n = 0 \quad (80)$$

or

$$\frac{\alpha}{\beta} = 2n + 1 \quad (81)$$

Where $n = 0, 1, 2, 3 \dots$ etc. The series that is obtained so contains a finite number of terms and is called as “Hermit polynomial” i.e. $H_n(y)$. All these Hermit polynomials are generating-function defined and are given below.

$$H_n(y) = (-1)^n \cdot e^{y^2} \cdot \frac{d^n}{dy^n} \cdot e^{-y^2} \quad (82)$$

For instance, some of the Hermit polynomials for $n = 0, 1$ and 2 are calculated as given below.

For $n = 0$, the equation (82) becomes

$$H_0(y) = (-1)^0 \cdot e^{y^2} \cdot \frac{d^0}{dy^0} \cdot e^{-y^2} \quad (83)$$

$$H_0(y) = 1 \cdot e^{y^2} \cdot 1 \cdot e^{-y^2} = e^{y^2-y^2} = e^0 \quad (84)$$

$$H_0(y) = 1 \quad (85)$$

For $n = 1$, the equation (82) becomes

$$H_1(y) = (-1)^1 \cdot e^{y^2} \cdot \frac{d}{dy} \cdot e^{-y^2} \quad (86)$$

$$H_1(y) = (-1) \cdot e^{y^2} \cdot (-2y) \cdot e^{-y^2} \quad (87)$$

$$H_1(y) = (-1) \cdot (-2y) \cdot e^{y^2-y^2} = 2y \cdot e^0 \quad (88)$$

$$H_1(y) = 2y \quad (89)$$

For $n = 2$, the equation (82) becomes

$$H_2(y) = (-1)^2 \cdot e^{y^2} \cdot \frac{d^2}{dy^2} \cdot e^{-y^2} \quad (90)$$

$$H_2(y) = (+1) \cdot e^{y^2} \cdot \frac{d}{dy} \cdot (-2y) \cdot e^{-y^2} \quad (91)$$

$$H_2(y) = e^{y^2} [(-2y)e^{-y^2}(-2y) + (-2)e^{-y^2}] \quad (92)$$

$$H_2(y) = e^{y^2} [(4y^2 - 2)e^{-y^2}] \quad (93)$$

$$H_2(y) = (4y^2 - 2)e^{y^2-y^2} = (4y^2 - 2)e^0 \quad (94)$$

$$H_2(y) = 4y^2 - 2 \quad (95)$$

The total wavefunction: After knowing the unknown part $F(y)$, the complete eigenfunction for a simple harmonic oscillator in the quantum mechanical world can be written as

$$\psi_n(y) = N_n H_n(y) e^{-y^2/2} \quad (96)$$

Where N_n is the normalization constant for n th state while the symbol $H_n(y)$ represents the Hermit polynomial of n th order in terms of y -variable. Once the wavefunctions are obtained in terms of y , they can easily be converted into x -dependent function by simply putting $y = \sqrt{\beta}x$.

Table 1. Eigenfunctions representing various quantum mechanical states of a simple harmonic oscillator.

α/β	n	$H_n(y)$	$\psi_n(y)$	$\psi_n(x)$
1	0	1	$N_0 \cdot e^{-y^2/2}$	$N_0 \cdot e^{-\beta x^2/2}$
3	1	$2y$	$N_1 \cdot 2y \cdot e^{-y^2/2}$	$N_1 (2\sqrt{\beta}x) e^{-\beta x^2/2}$
5	2	$4y^2 - 2$	$N_2 (4y^2 - 2) e^{-y^2/2}$	$N_2 (4\beta x^2 - 2) e^{-\beta x^2/2}$
7	3	$8y^3 - 12y$	$N_3 (8y^3 - 12y) e^{-y^2/2}$	$N_3 (8\beta^{3/2}x^3 - 12\sqrt{\beta}x) e^{-\beta x^2/2}$

The normalization constant can be obtained by recalling the fact that every wave function must describe the corresponding state completely. This means that square of wave function under consideration over the whole configurational space must be equal to unity i.e.

$$\int_{-\infty}^{+\infty} \psi_n^2 dx = \int_{-\infty}^{+\infty} \left[N_n H_n(x) e^{-\frac{\beta x^2}{2}} \right]^2 = 1 \quad (97)$$

$$\frac{N_n^2}{\sqrt{\beta}} \frac{2^n n!}{\sqrt{\pi}} = 1 \quad (98)$$

$$N_n^2 = \frac{\sqrt{\beta}}{2^n n! \sqrt{\pi}} \quad (99)$$

$$N_n = \left(\frac{\sqrt{\beta}}{2^n n! \sqrt{\pi}} \right)^{1/2} \quad (100)$$

It can be clearly seen from the above equation that the normalization constants are different for different states. For instance, some of the normalization constants are given below.

$$N_0 = \left(\frac{\sqrt{\beta}}{2^0 0! \sqrt{\pi}} \right)^{1/2} = \left(\frac{\beta}{\pi} \right)^{1/4} \quad (101)$$

$$N_1 = \left(\frac{\sqrt{\beta}}{2^1 1! \sqrt{\pi}} \right)^{1/2} = \frac{1}{\sqrt{2}} \left(\frac{\beta}{\pi} \right)^{1/4} \quad (102)$$

$$N_2 = \left(\frac{\sqrt{\beta}}{2^2 2! \sqrt{\pi}} \right)^{1/2} = \frac{1}{2\sqrt{2}} \left(\frac{\beta}{\pi} \right)^{1/4} \quad (103)$$

The eigenvalues of energy: Since we have already proved that the total wavefunction for a simple harmonic oscillator is acceptable only when the following condition of equation (81) is satisfied i.e.

$$\frac{\alpha}{\beta} = 2n + 1 \quad (104)$$

Furthermore, we also know that

$$\alpha = \frac{8\pi^2 m E}{h^2} \quad \text{and} \quad \beta = \frac{4\pi^2 m \nu}{h} \quad (105)$$

After using the value of α and β , the equation (104) take the form

$$\frac{8\pi^2 m E}{h^2} \times \frac{h}{4\pi^2 m \nu} = 2n + 1 \quad (106)$$

or

$$E = (2n + 1) \frac{4\pi^2 m \nu}{h} \times \frac{h^2}{8\pi^2 m} \quad (107)$$

or

$$E_n = (2n + 1) \frac{h\nu}{2} \quad (108)$$

or

$$E_n = \left(n + \frac{1}{2}\right) h\nu \quad (109)$$

Where n is a discrete variable (vibrational quantum number) with values 0, 1, 2, 3... ∞ . The symbol E_n represents the vibrational energies of different vibrational states.

➤ The Classical and Quantum-Mechanical Interpretation of Vibrational States

In order to have a relative interpretation of vibrational states in the classical and quantum-mechanical framework, recall the classical expression for potential energy curve of simple harmonic oscillator i.e.

$$V = \frac{1}{2} kx^2 \quad (110)$$

Where k is the force constant and x is the displacement induced. Also, the general expressions for all the vibrational states and corresponding energies are

$$\psi_n(x) = N_n H_n(x) e^{-\beta x^2} \quad \text{and} \quad E_n = \left(n + \frac{1}{2}\right) h\nu \quad (111)$$

Where N_n and $H_n(x)$ are the normalization constant and Hermit polynomial for n th state.

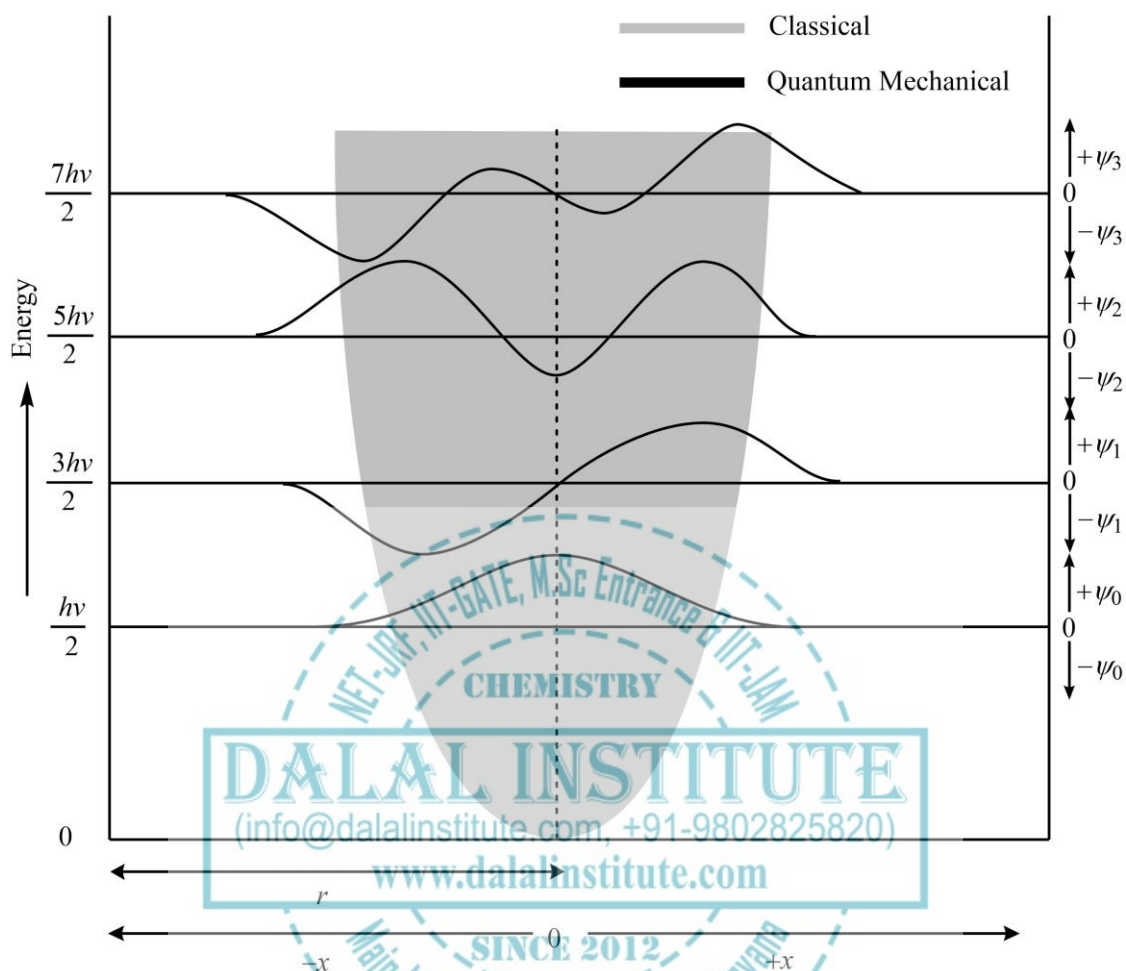


Figure 4. The depiction of various vibrational states of a simple harmonic oscillator in the classical and quantum mechanical framework.

After looking at the figure given above, the following points can be made about the differences and similarities in the classical and quantum mechanical oscillators.

- It can be clearly seen that the energy levels of a classical oscillator are continuous including zero while the energy levels the quantum-mechanical analog is discontinuous with zero-point energy of $h\nu/2$. In other words, the classical oscillator can have zero vibrational energy but the vibrational motion cannot be ceased completely in case of the quantum mechanical version of the simple harmonic oscillator.
- 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. On the other hand, since the function becomes zero only at infinite displacement, there is no limit over the compression and expansion in the quantum oscillator theoretically.

iii) The classical oscillator spends more time in the extreme states i.e. fully compressed and fully expanded, and spends the least time with equilibrium bond length. As far as the ground vibrational state of the quantum mechanical oscillator is concerned, it spends most time with equilibrium (because the function is maximum for r_{equ} or $x = 0$), and probability to spend time in compressed and expanded mode decreases as the magnitude of compression and expansion increases.

iv) If we plot the square of wavefunction vs displacement incorporated, it can be clearly seen that the most probable bond lengths shift towards the compressed and expanded states as the quantum number increases which is in accordance with the Bohr's correspondence principle.

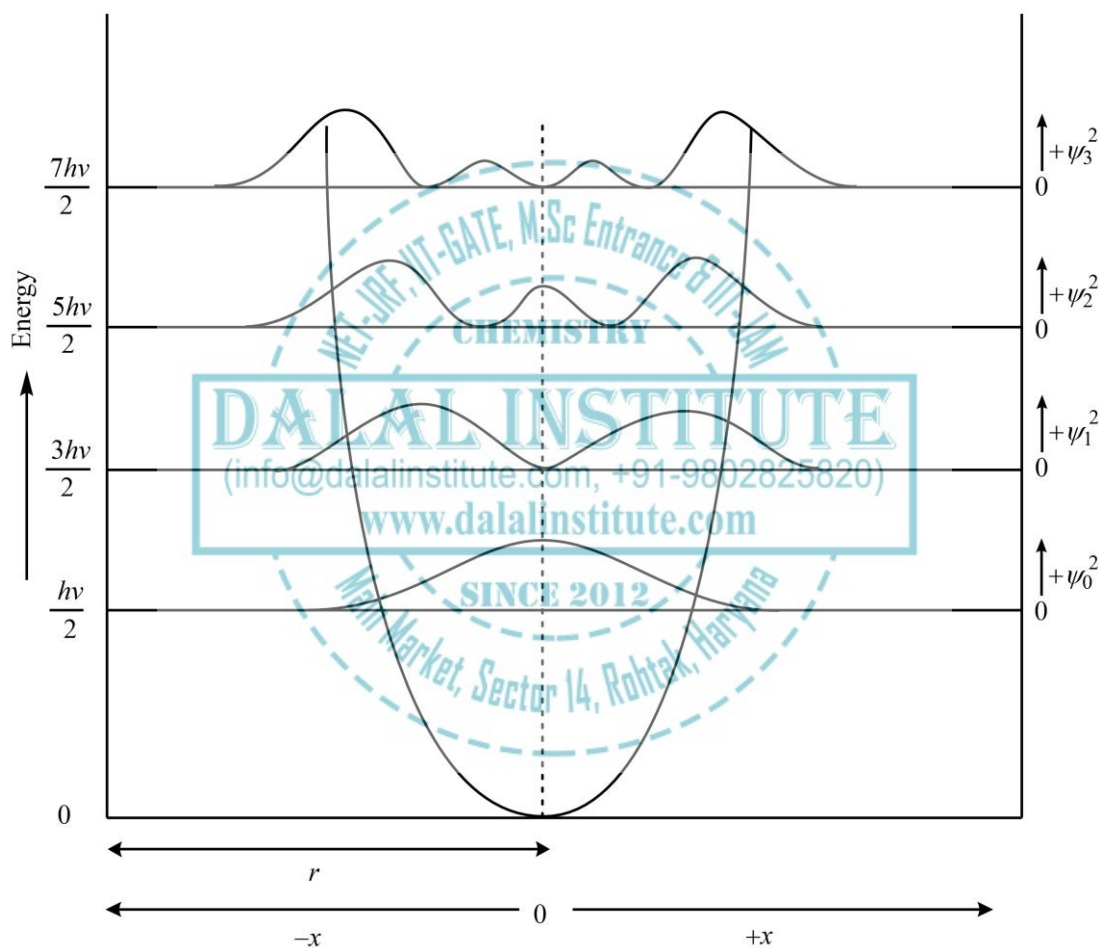


Figure 5. The variation of probability as a function of bond length or displacement in different vibrational states of a simple harmonic oscillator.

Furthermore, it is also worthy to note that all ψ_{even} states are symmetric while all ψ_{odd} wavefunctions are asymmetric in nature with n nodes.

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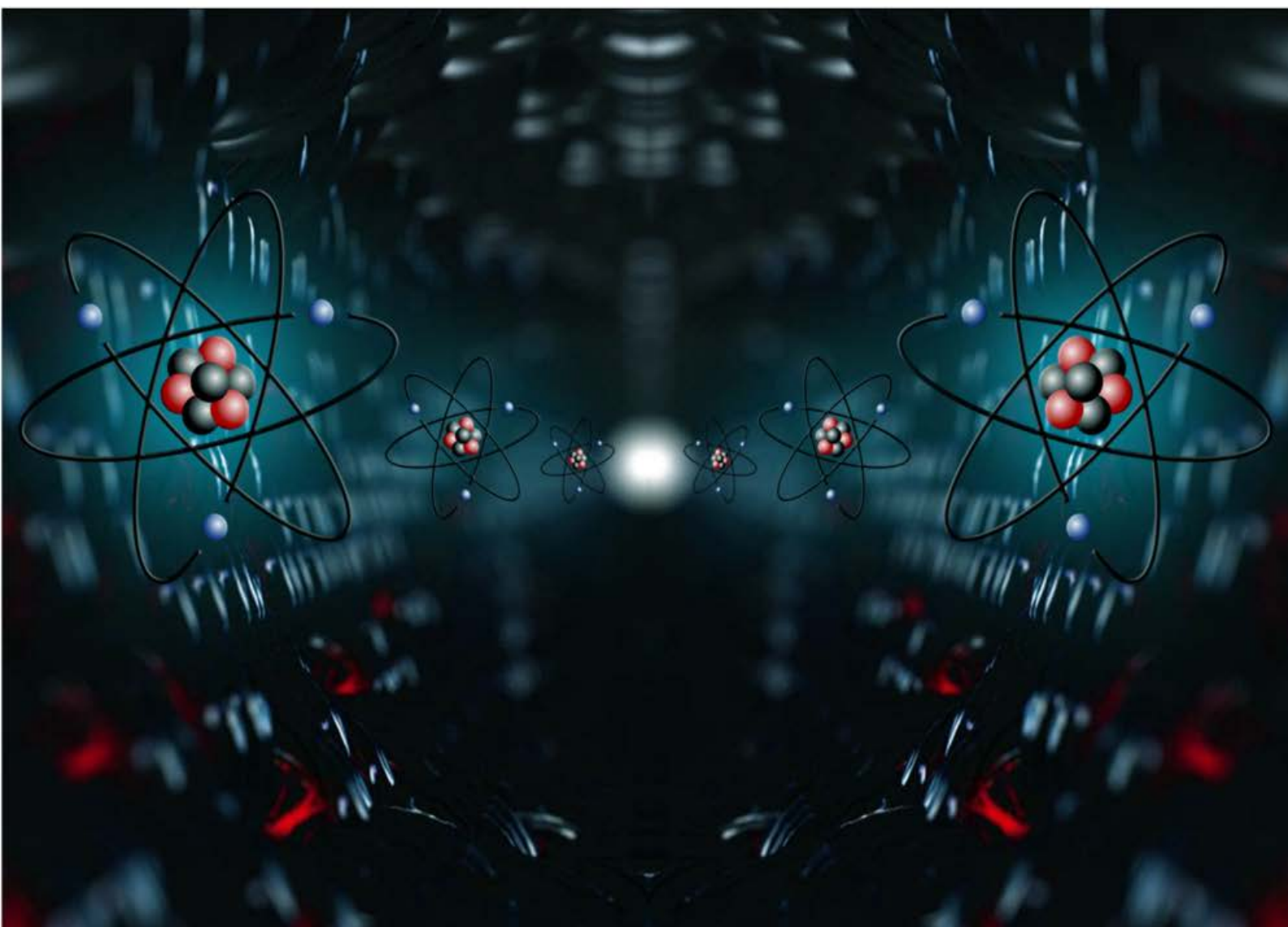
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Volume I

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