Chapter 4

QUANTUM MECHANICS

- **OBJECTIVES:**
  - **To learn the application of Schrödinger equation to a bound particle and to learn the quantized nature of the bound particle, its expectation values and physical significance.**
  - **To understand the tunneling behavior of a particle incident on a potential barrier.**
  - **To understand the behavior of quantum oscillator.**

Quantum Mechanics deals with the study of wave function (Ψ) of the matter waves associated with a particle, through the Schrödinger equation.

AN INTERPRETATION OF QUANTUM MECHANICS

Experimental evidences proved that both matter and electromagnetic radiation exhibit wave and particle nature depending on the phenomenon being observed.

Making a conceptual connection between particles and waves, for an electromagnetic radiation, we have the probability per unit volume of finding a photon in a given region of space at an instant of time as

$$\frac{\text{Probability}}{V} \propto E^2$$

AN INTERPRETATION OF QUANTUM MECHANICS

$$\frac{\text{Probability}}{V} \propto E^2$$

Taking the analogy between electromagnetic radiation and matter- the probability per unit volume of finding the particle is proportional to the square of the amplitude of a wave representing the particle, even if the amplitude of the de Broglie wave associated with a particle is generally not a measurable quantity.

AN INTERPRETATION OF QUANTUM MECHANICS

The amplitude of the de Broglie wave associated with the particle is called probability amplitude, or the wave function, and is denoted by ψ.

In general, the complete wave function ψ for a system depends on the positions of all the particles in the system and on time and can be written as $\psi(r_j)\, e^{-i\omega t}$, where r_j is the position vector of the j^{th} particle in the system.

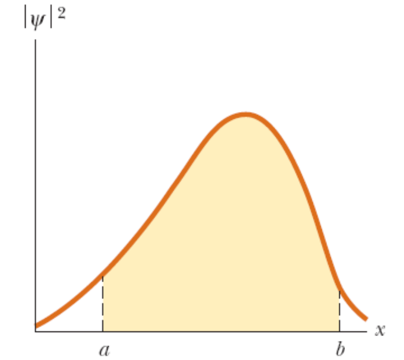
The wave function ψ contains within it all the information that can be known about the particle.

AN INTERPRETATION OF QUANTUM MECHANICS

$|\Psi|^2$ is always real and positive, and is proportional to the probability per unit volume, of finding the particle at a given point at some instant. If Ψ represents a single particle, then $|\Psi|^2$ is called probability density – is the relative probability per unit volume that the particle can be found at any given point in the volume.

One- Dimensional Wave Functions and Expectation Values

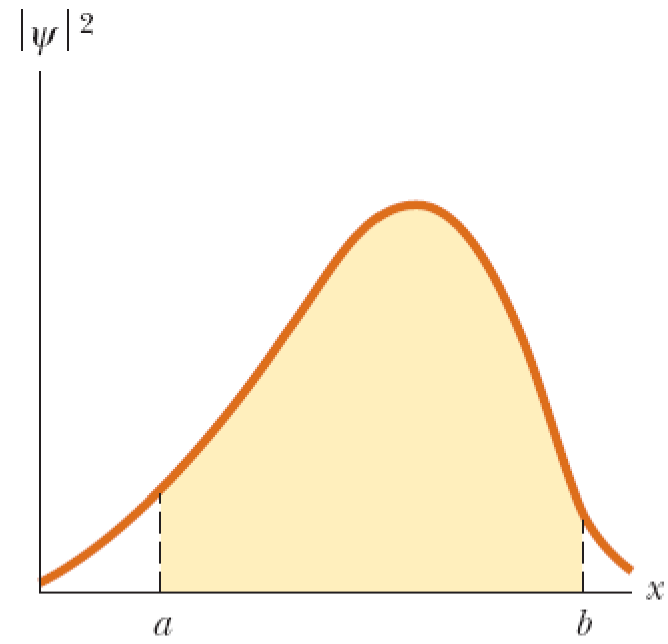
$P(x)\,dx = |\Psi|^2\,dx$ is the probability to find the particle in the infinitesimal interval dx around the point x. The probability of finding the particle in the arbitrary interval $a \le x \le b$ is



AN INTERPRETATION OF QUANTUM MECHANICS

$$P_{ab} = \int_a^b |\Psi|^2 \, dx$$

The probability of finding a particle being in the interval a ≤ x ≤ b is the area under the probability density curve from *a* to *b*.



The total probability of finding the particle is 1. Forcing this condition on the wave function is called normalization.

$$\int_{-\infty}^{\infty} |\psi|^2 \, dx = 1$$

AN INTERPRETATION OF QUANTUM MECHANICS

Average position at which one expects to find the particle after many measurements is called the expectation value of x and is defined by the equation

$$\langle x \rangle \equiv \int_{-\infty}^{\infty} \psi^* x \, \psi \, dx$$

AN INTERPRETATION OF QUANTUM MECHANICS

The important mathematical features of a physically reasonable wave function $\Psi(x)$ for a system are

(i) $\Psi(x)$ may be a complex function or a real function, depending on the system;

(ii) $\Psi(x)$, must be finite, continuous and single valued every where;

(iii) The space derivatives of the wave function, must be finite, continuous and single valued every where;

(iv) Ψ must be normalizable.

SJ: Section 41.1 P -1 **A free electron has a wave function $\psi(x) = Ae^{i(5.0\times10^{10}x)}$ where x is in meters. Find (a) its de Broglie wavelength, (b) its momentum, and (c) its kinetic energy in electron volts.**

$$\lambda = 1.26X10^{-10}m$$

$$p = 5.27X10^{-24}Kg.ms^{-1}$$

$$K = 95.5eV$$

SJ: P-SE 41.1 A wave Function for a particle

A particle wave function is given by the equation $\psi(x) = A\, e^{-ax^2}$

(A) What is the value of A if this wave function is normalized?

(B) What is the expectation value of x for this particle?

Given $\int_0^\infty e^{-2ax^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{2a}}$ **(From Gaussian Probability Integral)**

$$A = \left(\frac{2a}{\pi}\right)^{1/4}$$

THE SCHRÖDINGER EQUATION

The appropriate wave equation for matter waves was developed by Schrödinger. Schrödinger equation as it applies to a particle of mass *m* confined to moving along *x* axis and interacting with its environment through a potential energy function *U(x)* is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U\psi = E\psi$$

Where *E* is a constant equal to the total energy of the system (the particle and its environment).

THE SCHRÖDINGER EQUATION

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + U\psi = E\psi$$

The above equation is referred as the one-dimensional, time - independent Schrödinger equation.

Application of Schrödinger equation

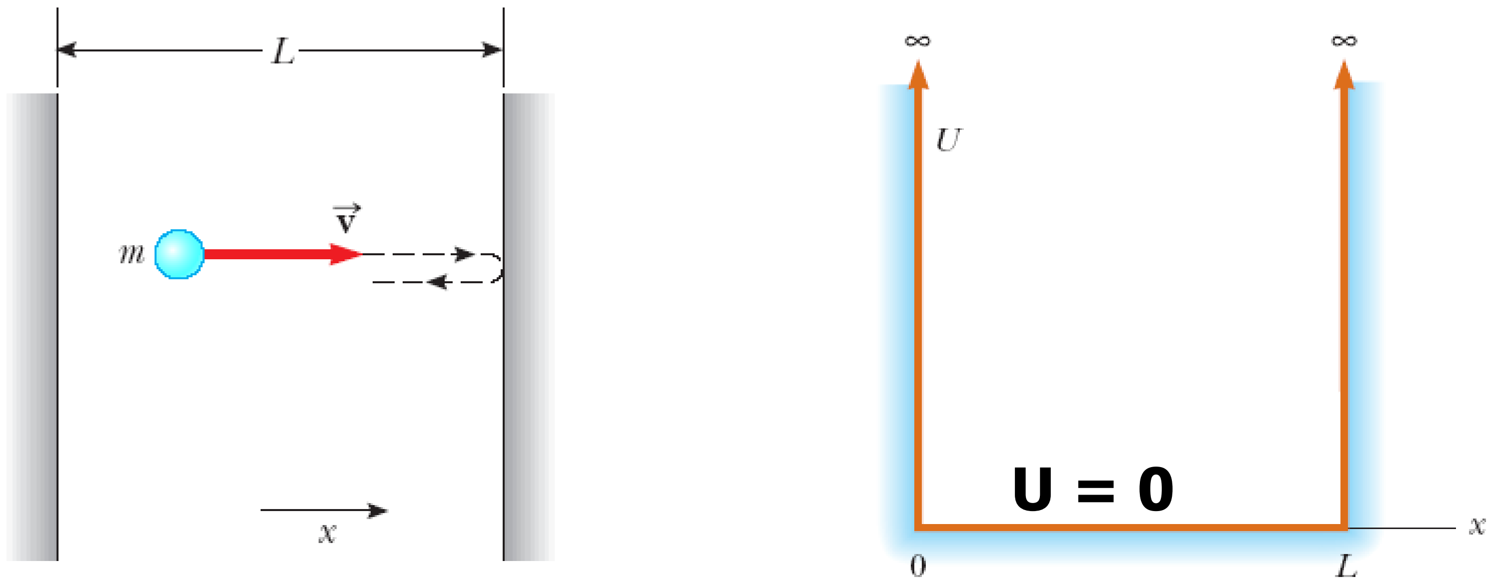
1. **Particle in an infinite potential well (Particle in a box)**
2. **Particle in a finite potential well**
3. **Tunneling**
4. **Quantum oscillator**

By solving the schrödinger equation, obtain the wave-functions for a particle of mass m in a one-dimensional “box” of length L. [5]

OR

Apply the schrodinger equation to a particle in a one-dimensional “box” of length L and obtain the energy values of the particle. [5]

PARTICLE IN A BOX (5 mark question)

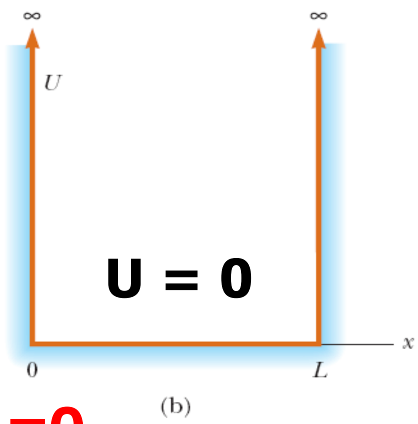


(a) (b)

In figure 1(a), a particle of mass *m* and velocity *v*, confined between two impenetrable walls separated by a distance *L* is shown. Figure 1(b) shows the potential energy function for the system.

Now we can apply boundary conditions

PARTICLE IN A BOX



$U(x) = 0$, for $0 < x < L$,

And $U(x) = \infty$, for $x \leq 0, x \geq L$

Since $U(x) = \infty$, for $x < 0, x > L$, $\psi(x) = 0$ in these regions. Also $\psi(x = 0) = 0$ and $\psi(x = L) = 0$.

Only those wave functions that satisfy these boundary conditions are allowed.

In the region $0 < x < L$, where $U = 0$, the Schrödinger equation takes the form

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E\psi = 0,$$

PARTICLE IN A BOX

$$\boxed{\frac{d^2\psi}{dx^2} = -k^2\psi}, \text{ where } \quad k^2 = \frac{2mE}{\hbar^2} \quad \text{or} \quad k = \frac{\sqrt{2mE}}{\hbar}$$

The most general form of the solution to the above equation is $\psi(x) = A\sin(kx) + B\cos(kx)$ where A and B are constants determined by the boundary and normalization conditions.

Applying the first boundary condition, i.e., at $x = 0$, $\psi = 0$ leads to

$\therefore \quad 0 = A\sin 0 + B\cos 0 \quad$ or $\quad B = 0$,

and at $x = L$, $\psi = 0$,

$\therefore \quad 0 = A\sin(kL) + B\cos(kL) = A\sin(kL) + 0$,

since $A \neq 0$, $\sin(kL) = 0$.

$\therefore \quad kL = \pi, 2\pi, 3\pi, \ldots\ldots$

ie., $\boxed{kL = n\pi}$; $(n = 1, 2, 3, \ldots\ldots\ldots)$

$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{L} \quad \text{or} \quad \boxed{L = n\left(\frac{\lambda}{2}\right)}$$

$$\text{Since } k = \frac{\sqrt{2mE}}{\hbar}, \text{we have, } kL = \frac{\sqrt{2mE}}{\hbar} L = n\pi$$

Each value of the integer *n* corresponds to a quantized energy value, E_n, *where*

PARTICLE IN A BOX

$$E_n = \left(\frac{h^2}{8\,m\,L^2}\right) n^2$$

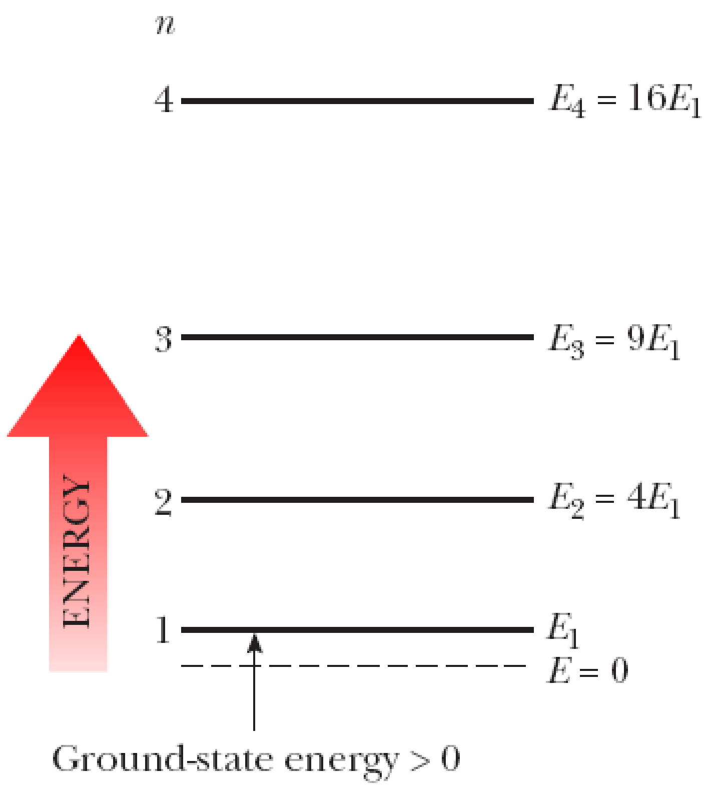
Where n = 1, 2 , 3 .....

$$\text{The lowest allowed energy } (n = 1),\ E_1 = \frac{h^2}{8\,m\,L^2}$$

This is the ground state energy for the particle in a box.

Excited states correspond to n = 2, 3, 4 ---- have energies given by $4E_1$, $9E_1$, $16E_1$ ---.

PARTICLE IN A BOX



Energy level diagram for a particle confined to a one-dimensional box of length *L*. The lowest allowed energy is

$$E_1 = h^2/8mL^2$$

According to quantum mechanics, the particle can never be at rest.

PARTICLE IN A BOX

The corresponding wave functions are given by

$$\psi_n(x) = A\sin\left(\frac{n\pi x}{L}\right)$$

(Because k = nπ/L)

To find the constant A, apply normalization condition,

$$\int_{-\infty}^{\infty} |\psi|^2 dx = 1.$$

In this case it is $$\int_0^L A^2\left[\sin\left(\frac{n\pi x}{L}\right)\right]^2 dx = 1$$

$$A^2 \int_0^L \tfrac{1}{2}\left[1 - \cos\left(\frac{2n\pi x}{L}\right)\right]dx \;=\; 1$$

$$solving, we\ get, \quad \boxed{\psi_n(x) \;=\; \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right)}$$

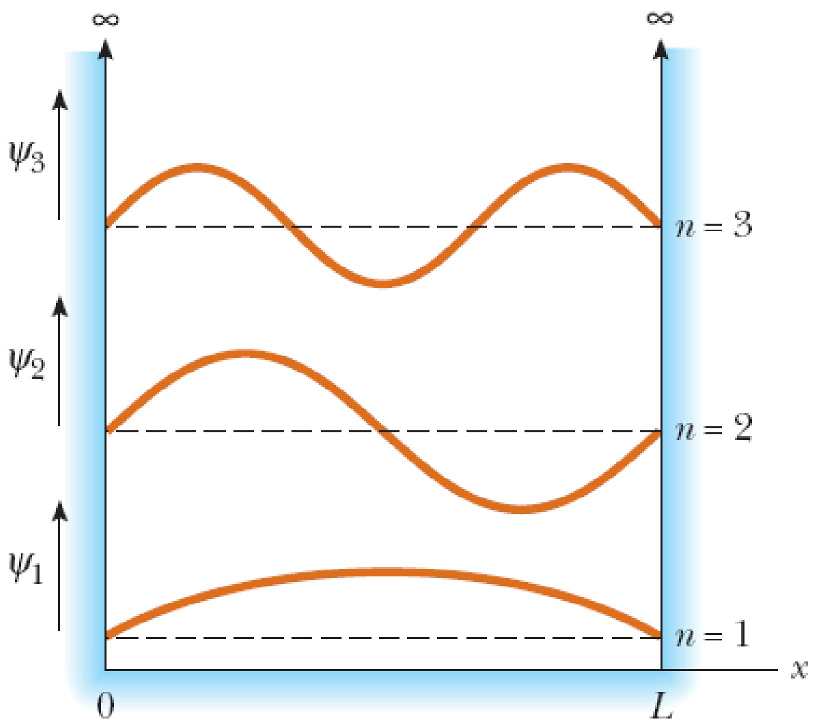
The first three allowed states for a particle confined to a one-dimensional box are shown next. The states are shown superimposed on the potential energy function of Figure 1b

PARTICLE IN A BOX

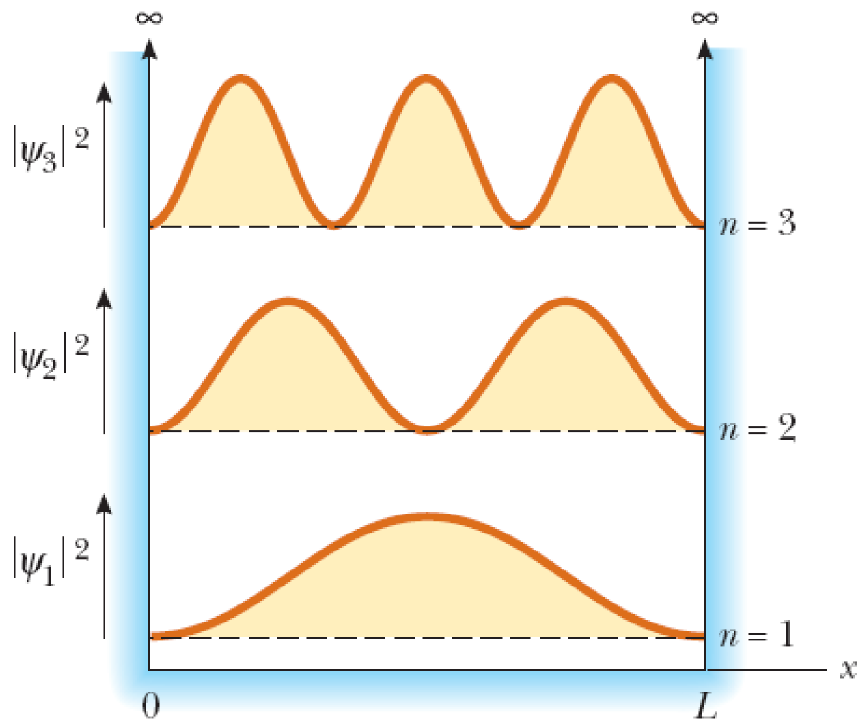
Fig. (a) The wave functions for *n* = 1, 2, and 3.

Fig. (b) The probability densities for *n* = 1, 2, and 3.

$$\psi_n(x) = \sqrt{\frac{2}{L}}\,\sin\left(\frac{n\pi x}{L}\right) \qquad P_n(x) = \frac{2}{L}\sin^2\left(\frac{n\pi x}{L}\right)$$



(a)



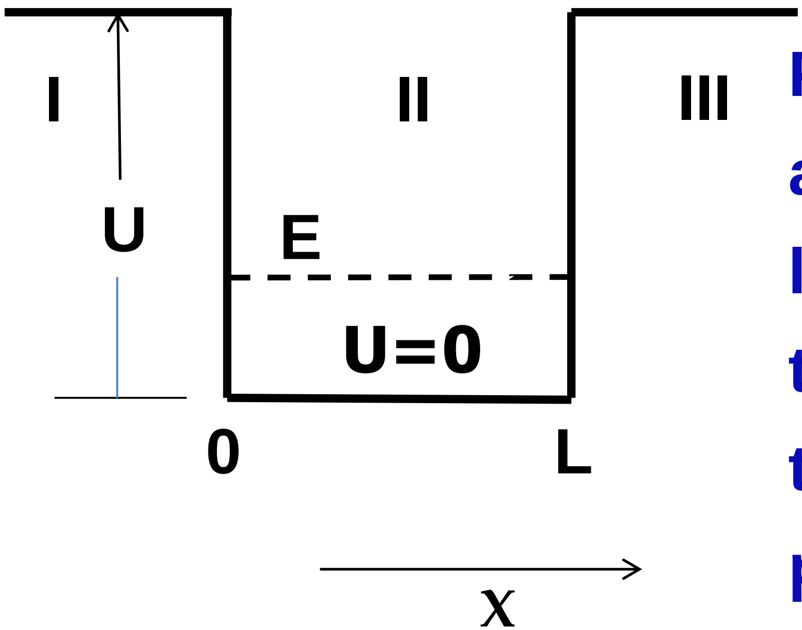
(b)

Sketch the potential-well diagram of finite height U and length L, obtain the general solution of the Schrödinger equation for a particle of mass m in it.

[5 marks]

A PARTICLE IN A WELL OF FINITE HEIGHT

(PARTICLE IN A SQUARE WELL POTENTIAL)



Potential energy diagram of a well of finite height U and length L. A particle is trapped in the well. The total energy E of the particle- well system is less than U

Explain the conditions, $U(x) = 0, \quad 0 < x < L,$

$U(x) = U, \quad x \leq 0, \quad x \geq L$

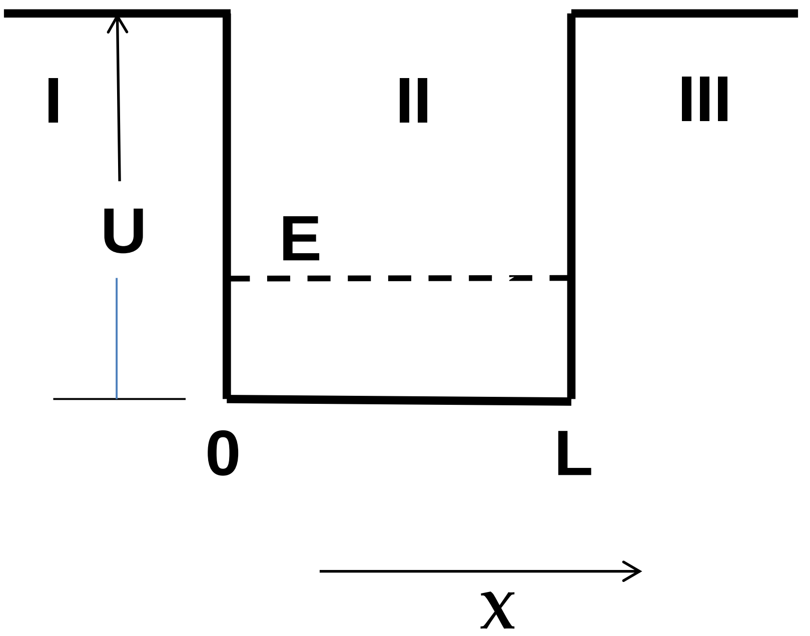
A PARTICLE IN A WELL OF FINITE HEIGHT

Particle energy = $E < U$; classically the particle is permanently bound in the potential well. However, according to quantum mechanics, a finite probability exists that the particle can be found outside the well even if $E < U$. That is, the wave function is generally nonzero in regions I and III.

In regions II, where $U = 0$, the allowed wave functions are again sinusoidal. But the boundary conditions no longer require that the wave function must be zero at the ends of the well.

A PARTICLE IN A WELL OF FINITE HEIGHT

The Schrödinger equation outside the finite well in regions I and III is:



$$\frac{d^2\Psi}{dx^2} = \frac{2m}{\hbar^2}(U - E)\Psi = C^2\,\Psi$$

where $$C^2 = \frac{2m}{\hbar^2}(U - E)$$

General solution of the above equation is

$$\Psi(x) = A\,e^{Cx} + B\,e^{-Cx}$$

A PARTICLE IN A WELL OF FINITE HEIGHT

A must be 0 in Region III and B must be zero in Region I, otherwise, the probabilities would be infinite in those regions. Solution should be finite.

ie., the wave functions outside the finite potential well are

$$\psi_I = A\, e^{Cx} \text{ for } x < 0 \quad (\text{region I})$$

$$\psi_{III} = B\, e^{-Cx} \text{ for } x > L \ (\text{region III})$$

$$\text{where } C = \frac{\sqrt{2m(U-E)}}{\hbar}$$

Results show that the wave function outside the potential well decay exponentially with distance.

Schrodinger equation inside the square well potential in region II, where U = 0 is

$$\frac{d^2\psi_{II}}{dx^2} + \underbrace{\left(\frac{2m}{\hbar^2}E\right)}_{k^2}\psi_{II} = 0$$

General solution of the above equation is

$$\psi_{II} = F \sin\left[\underbrace{\frac{\sqrt{2mE}}{\hbar}}_{k}\right]x + G \cos\left(\left[\underbrace{\frac{\sqrt{2mE}}{\hbar}}_{k}\right]x\right)$$

A PARTICLE IN A WELL OF FINITE HEIGHT

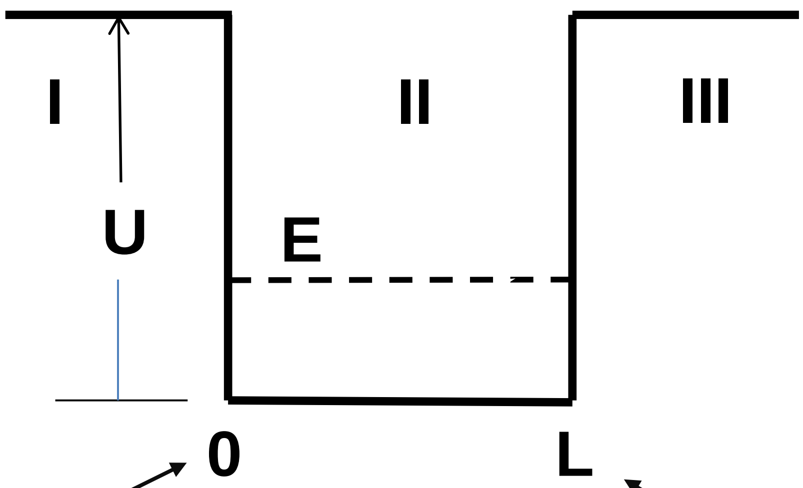
The boundary conditions require that,

$$\psi_{\mathrm{I}} = \psi_{\mathrm{II}} \text{ at } x = 0 \text{ and } \psi_{\mathrm{II}} = \psi_{\mathrm{III}} \text{ at } x = L$$

so the wave function is smooth where the regions meet.

To determine the constants A, B, F, G, & the allowed values of energy E, apply the four boundary conditions and the normalization condition.

A PARTICLE IN A WELL OF FINITE HEIGHT



Boundary conditions

$$\psi_{\mathrm{I}}(0) = \psi_{\mathrm{II}}(0)$$

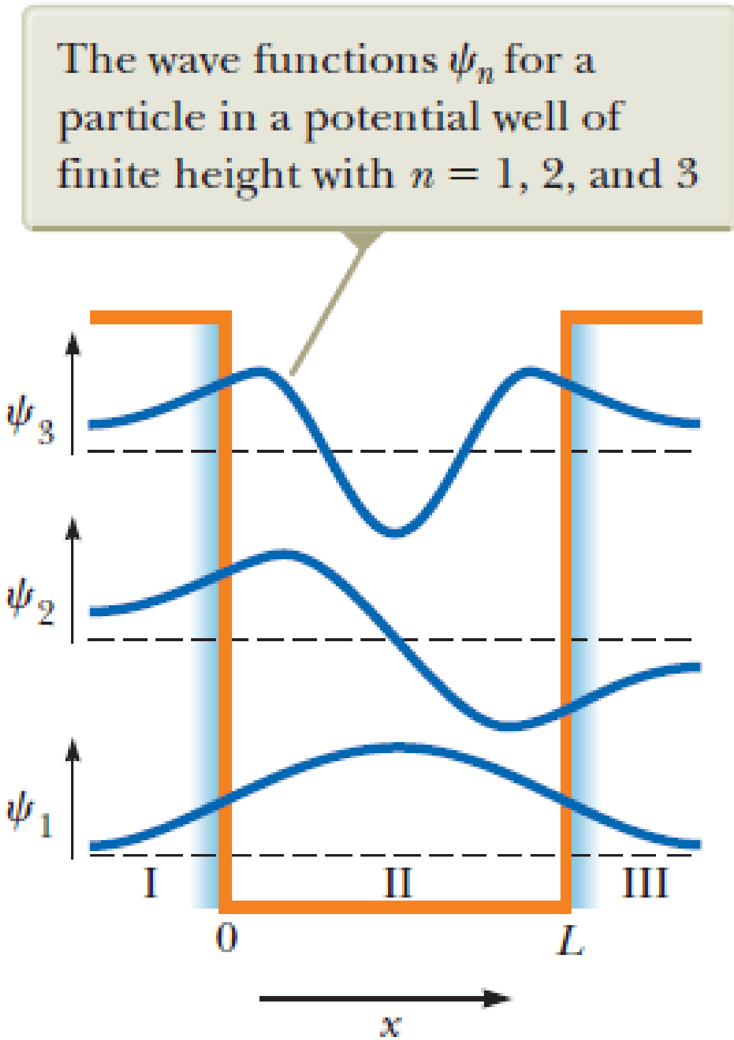
Boundary conditions

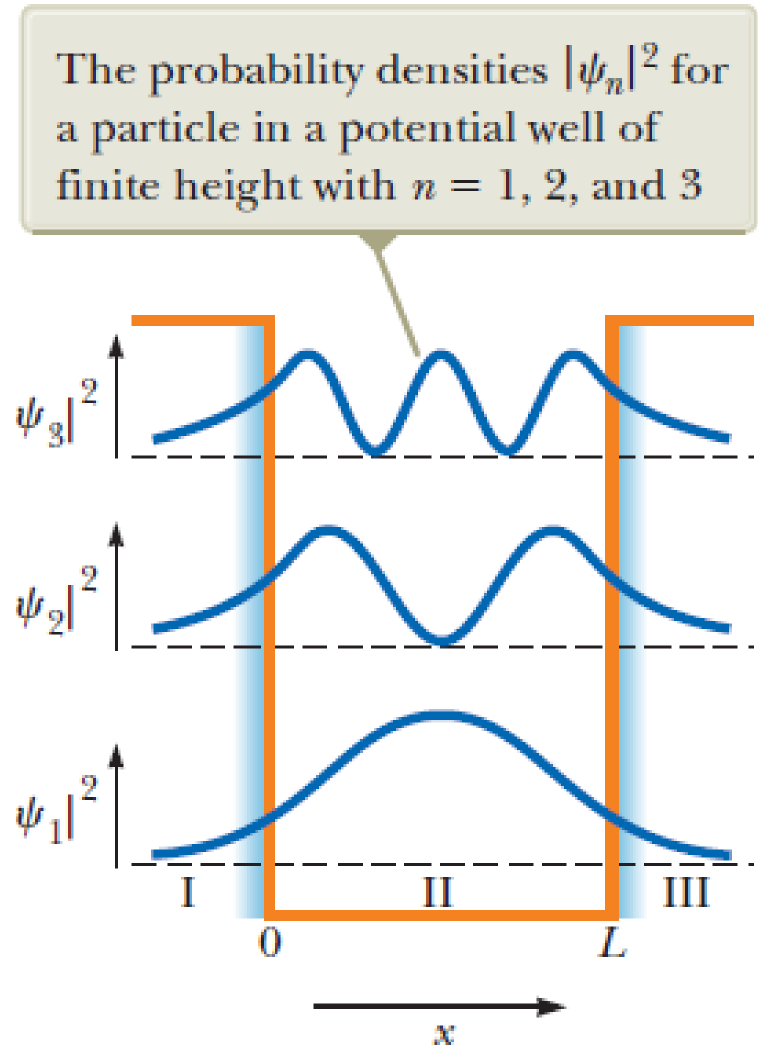
$$\psi_{\mathrm{II}}(L) = \psi_{\mathrm{III}}(L)$$

$$\left.\frac{d\psi_{\mathrm{I}}}{dx}\right|_{x=0} = \left.\frac{d\psi_{\mathrm{II}}}{dx}\right|_{x=0}$$

$$\left.\frac{d\psi_{\mathrm{II}}}{dx}\right|_{x=L} = \left.\frac{d\psi_{\mathrm{III}}}{dx}\right|_{x=L}$$

Sketch the lowest three energy states, wave-functions, probability densities for the particle in a potential well of finite height. **[3]**





SJ: P-SE 41.2 A Bound Electron

An electron is confined between two impenetrable walls 0.20 nm apart. Determine the energy levels for the states n =1 ,2 , and 3.

$$E_n = \left(\frac{h^2}{8\,m\,L^2}\right) n^2$$

$L=0.2\text{x}10^{-9}\text{m}$
$h=6.63\text{x}10^{-34}\text{Js}$
$m=9.1\text{x}10^{-31}\text{ Kg}$
$1\text{eV} = 1.6\text{x}10^{-19}\text{ J}$

$E_1 = 9.43$ eV ; $E_2 = 37.7$ eV ; $E_3 = 84.8$ eV

SJ: Section 41.2 P- 10

A proton is confined to move in a one-dimensional box of length 0.20 nm. (a) Find the lowest possible energy of the proton. (b) What is the lowest possible energy for an electron confined to the same box? (c) Account for the great difference in results for (a) and (b)

(a) 8.22×10^{-22} J = 5.13×10^{-3} eV

(b) 1.51×10^{-18} J = 9.41 eV

(c) Electron has higher energy because it is less massive.

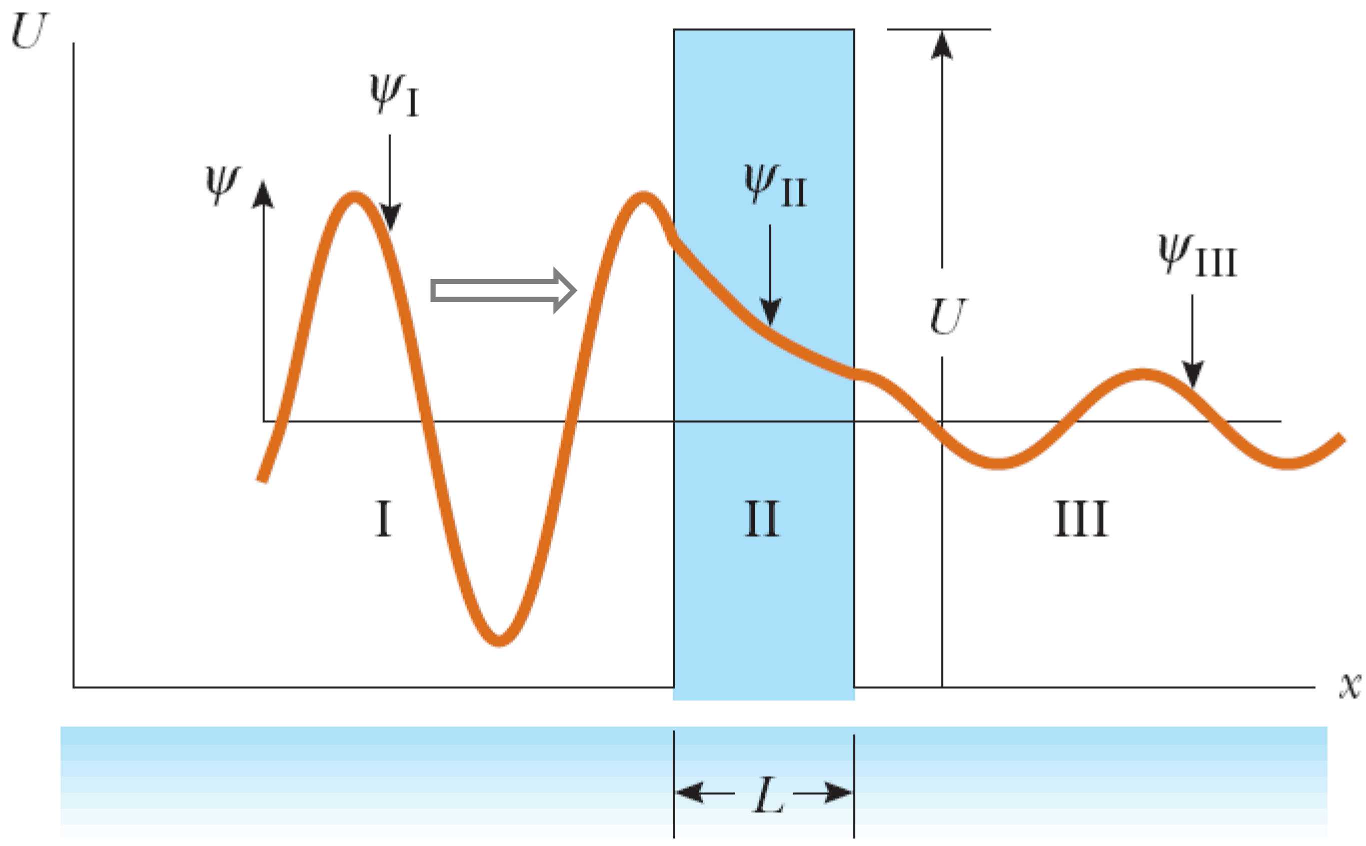
SJ: P-SE 41.4- Model of an Atom

(A) Using the simple model of a particle in a box to represent an atom, estimate the energy (in eV) required to raise an atom from the state n = 1 to the state n = 2. Assume the atom has a radius of 0.10 nm and that the moving electron carries the energy that has been added to the atom.

(B) Atoms may be excited to higher energy states by absorbing photon energy. Calculate the wavelength of the photon that would cause the transition from the state n =1 to the state n =2.

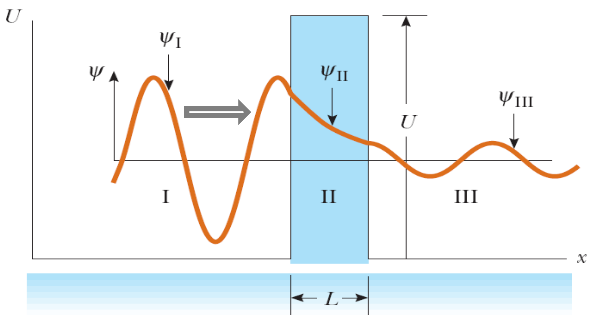
A) 28.3 eV B) 43.8 nm

TUNNELING THROUGH A POTENTIAL ENERGY BARRIER

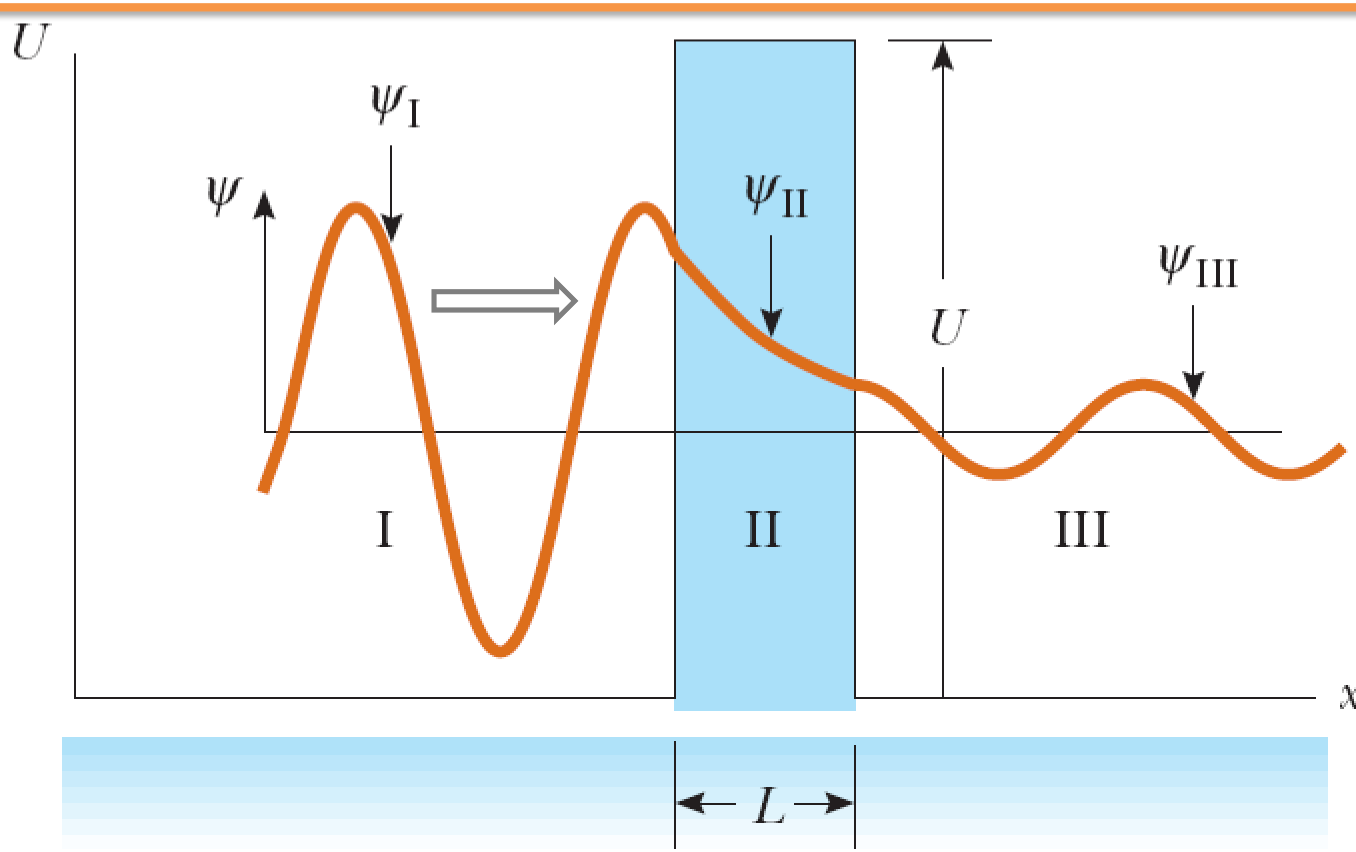


TUNNELING THROUGH A POTENTIAL ENERGY BARRIER

Consider a particle of energy *E* approaching a potential barrier of height *U*, (E < U). Potential energy has a constant value of *U* in the region of width *L* and is zero in all other regions. This is called a square barrier and *U* is called the barrier height. Since E < U, classically the regions II and III shown in the figure are forbidden to the particle incident from left. But according to quantum mechanics, all regions are accessible to the particle, regardless of its energy.



TUNNELING THROUGH A POTENTIAL ENERGY BARRIER



Potential energy function and wave function for a particle incident from the left on a barrier of height *U* and width *L*. The wave function is sinusoidal in regions I and III but exponentially decaying in region II.

TUNNELING THROUGH A POTENTIAL ENERGY BARRIER

By applying the boundary conditions, i.e. ψ and its first derivative must be continuous at boundaries (at x = 0 and x = L), full solution to the Schrödinger equation can be found which is shown in figure. The probability of locating the particle beyond the barrier in region III is non-zero. The movement of the particle to the far side of the barrier is called tunneling or barrier penetration.

The probability of tunneling can be described with a transmission coefficient *T* and a reflection coefficient *R*.

TUNNELING THROUGH A POTENTIAL ENERGY BARRIER

- **The transmission coefficient represents the probability that the particle penetrates to the other side of the barrier**
- **Reflection coefficient is the probability that the particle is reflected by the barrier.**
- **Because the particles must be either reflected or transmitted we have, $R + T = 1$.**

An approximate expression for the transmission coefficient, when $T << 1$ is

TUNNELING THROUGH A POTENTIAL ENERGY BARRIER

$$T \approx e^{-2CL} \quad \text{when } T << 1$$

$$\text{where} \quad C = \frac{\sqrt{2m(U - E)}}{\hbar}$$

TUNNELING THROUGH A POTENTIAL ENERGY BARRIER

SJ: P-SE 41.6 A 30- eV electron is incident on a square barrier of height 40 eV. What is the probability that the electron will tunnel through the barrier if its width is (A) 1.0 nm? (B) 0.10 nm?

Ans: E = 30 eV and U = 40 eV

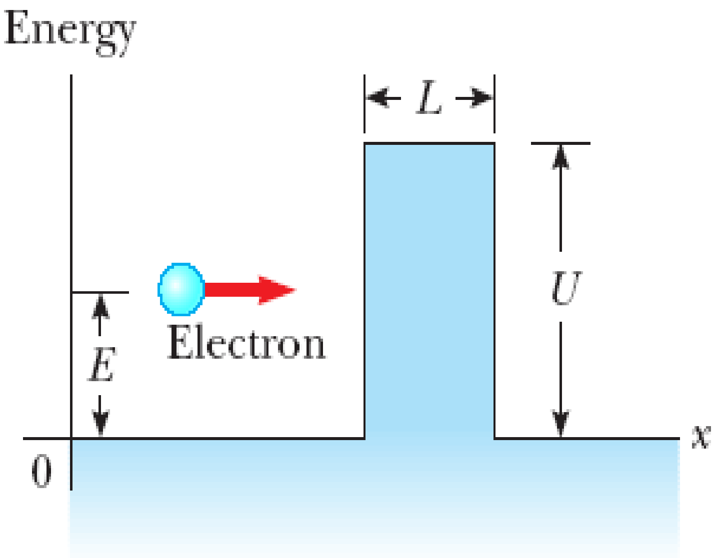
$C = 1.62 \times 10^{10}$

(A) $T \sim 8.5 \times 10^{-15}$ (B) $T \sim 0.039$

TUNNELING THROUGH A POTENTIAL ENERGY BARRIER

SJ: Section 41.6 P- 27

An electron with kinetic energy E = 5.0 eV is incident on a barrier with thickness L = 0.20 nm and height U = 10.0 eV as shown in the figure.



What is the probability that the electron (a) will tunnel through the barrier? (b) will be reflected?

$C = 1.14 \times 10^{10}$ $T = 0.01$ or 1% $R = 0.99$ or 99 %

The Simple Harmonic Oscillator

The Simple Harmonic Oscillator

- **Consider a particle that is subject to a linear restoring force $F = -kx$, where k is a constant and x is the position of the particle relative to equilibrium (at equilibrium position x=0).**

$$\boldsymbol{x = Asin\omega t}$$

- **Classically, the potential energy of the system is,**

$$\boldsymbol{KE = \frac{1}{2}m\dot{x}^2}$$

$$\boxed{U = \frac{1}{2}kx^2 = \frac{1}{2}m\omega^2 x^2}$$

where the angular frequency of vibration is $\omega = \sqrt{k/m}$.

- **The total energy E of the system is,**

$$E = \ Kinetic\ Energy + Potential\ Energy = K + U = \frac{1}{2}kA^2 = \frac{1}{2}m\omega^2 A^2$$

where A is the amplitude of motion.

- **A quantum mechanical model for simple harmonic oscillator can be obtained by substituting** $U = \frac{1}{2}m\omega^2x^2$ **in Schrödinger equation:**

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}m\omega^2x^2\psi = E\psi$$

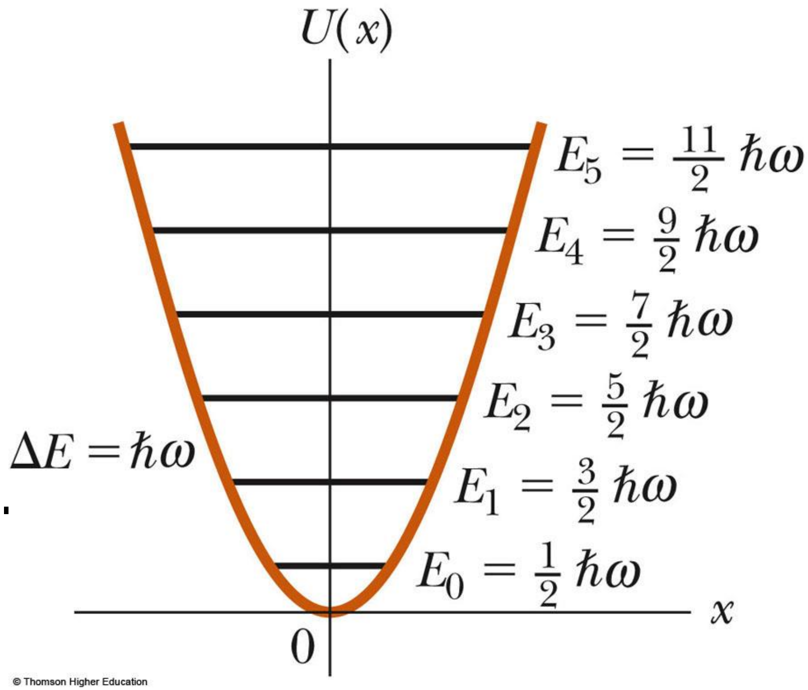
- **The solution for the above equation is**

$$\psi = Be^{-Cx^2}$$

where $C = m\omega/2\hbar$ **and** $E = \frac{1}{2}\hbar\omega$**.**

- **Energy of a state is given by**

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega;} \qquad n = 0, 1, 2 \ldots .$$



n is a quantum number identifying each state and energy level.

- **The state n=0 corresponds to the ground state, whose energy is** $E_0 = \frac{1}{2}\hbar\omega$

A quantum simple harmonic oscillator consists of an electron bound by a restoring force proportional to its position relative to a certain equilibrium point. The proportionality constant is 8.99 N/m. What is the longest wavelength of light that can excite the oscillator?

The longest wavelength corresponds to minimum photon energy, which must be equal to the spacing between energy levels of the oscillator:

$$\Delta E = \frac{hc}{\lambda} = \hbar\omega = \hbar\sqrt{\frac{k}{m}} \qquad \Longrightarrow \frac{hc}{\lambda} = \frac{h}{2\pi}\sqrt{\frac{k}{m}}$$

$$\Longrightarrow \lambda = 2\pi c\sqrt{\frac{m}{k}} \qquad = 2x3.14x3x10^{8}\sqrt{\frac{9.11x10^{-31}}{8.99}}$$

= 600 nm

1	What is a wave function ? What is its physical interpretation ?
2	What are the mathematical features of a wave function?
3	By solving the Schrödinger equation, obtain the wave-functions for a particle of mass m in a one-dimensional "box" of length L.
4	Apply the Schrödinger equation to a particle in a one-dimensional "box" of length L and obtain the energy values of the particle.
5	Sketch the lowest three energy states, wave-functions, probability densities for the particle in a one-dimensional "box".
6	The wave-function for a particle confined to moving in a one-dimensional box is $\psi(x) = A\sin\left(\frac{n\pi x}{L}\right)$. Use the normalization condition on ψ to show that $A = \sqrt{\frac{2}{L}}$.
7	The wave-function of an electron is $\psi(x) = A\sin\left(\frac{n\pi x}{L}\right)$. Obtain an expression for the probability of finding the electron between x = a and x = b.
8	Sketch the potential-well diagram of finite height U and length L, obtain the general solution of the Schrödinger equation for a particle of mass m in it.
9	Sketch the wave-functions and the probability densities for the lowest three energy states of a particle in a potential well of finite height.
10	Give a brief account of tunneling of a particle through a potential energy barrier.
11	Give a brief account of the quantum mechanical treatment of a simple harmonic oscillator.