Unit 3.1

Wave Mechanics

Contents

- Matter waves
- De Broglie wavelength
- properties of wavefunction
- Physical significance
- Schrodinger time dependent and time-independent wave equation
- Particle in a 1-D box

Matter waves

The properties of light can be divided into two distinct groups w.r.t properties

Reflection
Refraction
interference
Diffraction
polarization

→ These properties arising out of propagation of light can be explained only by assigning wave nature to light

Emission
Absorption
Black body radiation
Photoelectric effect
Compton effect
Pair production

→ These properties arise due to interaction of light with matter and can be explained only by assigning particle like properties to light

Conclusion: In order to explain all the properties of light both wave and particle properties should be assigned to it. Hence light is said to possess dual nature of wave and particles simultaneously. The wave and particle properties can be connected with help of the relation

$$E = h\nu = mC^2$$

Momentum of the particle $P = mC = h\nu/C \rightarrow \lambda = h/p$ as $C = \nu\lambda$

Matter waves-deBroglie wavelength

Louis deBroglie argued that since symmetry is always conserved in nature, just as light exhibits dual nature of waves and particles, the materials particles like electrons should also possess wave nature and should exhibit wave properties.

According to de Broglie's hypothesis, a moving particle is associated with a wave which is known as deBroglie's wave or matter wave. The wavelength of the matter wave is given by

$$\lambda = h/mv = h/p$$

Where m is the mass of the particle, v is its velocity, p its momentum

From Plancks theory of radiation,

$$E = h\nu = hc/\lambda$$

Where c is the velocity of light and λ the wavelength

According to Einstein mass-energy relation

$$E = mC^2 = hc/\lambda$$

Hence $\lambda = h/mc$, where mc represents the momentum of the photon

In case of a material particle like electron of mass m and moving with a velocity v, momentum becomes mv,

$$\lambda = h/mv = h/p$$

Matter waves - Properties

- Lighter is the particle, greater is the wavelength associated with it
- Smaller is the velocity of the particle, greater is the wavelength associated with it
- When v =o, then λ =infinity which means the wave becomes indeterminate and if v = infinite, then $\lambda = 0$. This shows the matter waves are generated by the motion of particles
- The velocity of matter waves depends on the velocity of material particle. It is not a constant while the velocity of electromagnetic wave is constant
- The velocity of matter waves is greater than the velocity of light.

$$E = h\upsilon \text{ and } E = mc^2$$

$$h\upsilon = mc^2$$

$$\upsilon = mc^2 /h$$

The wavevelocity is given by $\omega = \upsilon \times \lambda = mc^2 /h \times h/mv = c^2/v$

As particle v cannot exceed C, hence ω is greater than velocity of light C.

- The wave and particle aspects of moving bodies can never appear together in the same experiment.
- The wave nature of matter introduces an uncertainty in the location of the position of the particle because a wave cannot be located exactly at a point.

de BroglieWavelength in terms of Kinetic energy

If E is the kinetic energy of the particle then,

$$K.E. = E = 1/2mv^2 = p^2/2m$$

Hence

$$p = \sqrt{2mE}$$

$$\lambda = h/\sqrt{2mE}$$

de BroglieWavelength in terms of potential

In the case of an electron of mass m and charge e, which is accelerated by a potential V volts from rest to a velocity v, then

$$\frac{1}{2}mv^2 = eV$$

$$v = \sqrt{2eV/m}$$

$$\lambda = \frac{h}{mv} = h/m\sqrt{\frac{2eV}{m}}$$

$$= h/\sqrt{2eVm}$$

$$= 6.6 \times 10^{-34} / (2xVx1.6x10^{-19}x9.1x10^{-31})^{1/2}$$

$$= 12.26/\sqrt{V}\ \text{Å}$$

Wave function – Properties and Physical significance

- ‘ψ’ is the wave function and it measures the variation of the matter waves. Thus it connects the particles and its associated wave statistically.
- ‘ψ’ must be finite, continuous, and single valued every where.
- ‘ψ’ must be a well-behaved function. That is not only ψ, but also its first and second derivatives should exist and must be single-valued , finite and continous.
- The wave function ‘ψ’ is a complex function, it does not have a direct physical meaning, but when we multiply this with its complex conjugate ψ^* , the product $\psi^* \psi$ or $|\psi|^2$ has the physical meaning.
- The wave function Ψ(r, t) describes the position of a particle with respect to time.
- The probability of finding a particle in a particular volume is

  i.e., ‘ψ’ must be normalizable.

$$\int_{-\infty}^{+\infty} \psi^* \psi \, d\tau = 1$$

$$where\; d\tau = dx\, dy\, dz$$

Schrodinger’s wave equation

- According to classical mechanics, a particle is completely determined by its initial position and momentum simultaneously.
- From Heisenberg uncertainty principle, the initial position and momentum of a particle like electron can not be measured with desired accuracy.
- According to de-broglie theory of matter waves a material particle can be associated with a wave called matter wave.
- By considering the above mentioned theories, Schrodinger proposed the mathematical reformations called wave mechanics which interpret the dual nature of matter.
- Schrodinger gave two wave equations to describe matter waves. One is the Time-dependent and the other is the Time-independent wave equation

Schrodinger Time Dependent wave equation

Let us consider the motion of a particle in one dimension.

Let $\psi(x, t)$ is the wave function associated with the particle .

The displacement of a particle executing Simple Harmonic motion is given by

$$Y = A \sin (kx - \omega t)$$

By taking analogy between the particle and wave function ψ

we can write $\psi = A\, e^{i(kx - \omega t)}$ ----------- (1)

A is amplitude

K is propagation vector and $K = 2\pi / \lambda$

w is angular frequency and $\omega = 2\pi\upsilon$

υ Is the frequency and λ is the wave length of the matter waves

From Planck's law we have

$$E = h \upsilon$$

$$= (h \upsilon)\, 2\pi / 2\pi$$

$$= (2\pi \upsilon)\; h/ 2\pi$$

$$E = \omega h/ 2\pi$$

$$\omega = E / \hbar \text{ ---------- } (2)$$

Where $\omega = 2\pi \upsilon$ & $\hbar = h/ 2\pi$

From de Broglie's theory we have

$$P = h / \lambda$$

$$= (h/ \lambda)\, 2\pi / 2\pi$$

$$= (h/ 2\pi) \times (2\pi / \lambda) = \hbar K$$

Hence $K = p/ \hbar$ ----------------- (3)

Substituting equations 2 and 3 in equation 1

$$\psi = A\, e^{i[(p/\hbar)x - (E/\hbar)t]}$$

Differentiating w.r.t. 'x' we get

$$\partial\psi / \partial x = A\, e^{i[(p/\hbar)x - (E/\hbar)t]}\,(i/\hbar)\,P$$

$$=\psi (i/\hbar)\,P$$

$$P\psi = (\partial\psi / \partial x)\,\hbar / i$$

$$= (-i^2)\,(\partial\psi / \partial x)\,\hbar / i \text{ where } (-i^2 = 1)$$

$$P\psi = (-i\hbar\partial / \partial x)\psi \text{--------} (4)$$

This equation represents momentum operator

Differentiating ψ w.r.t. 't' we get

$$\partial\psi / \partial t = A\, e^{i[(p/\hbar)x - (E/\hbar)t]} (-i/\hbar)\, E$$

$$= -\psi (i/\hbar)\, E$$

$$E\psi = -(\partial\psi / \partial t)\, \hbar / i$$

$$= (i^2)(\partial\psi / \partial t)\, \hbar / i$$

$$E\Psi = (i\hbar \partial / \partial t)\psi \text{ -------- } (5)$$

The equation 5 represents energy operator

The partial derivatives with respect to x and t are connected by means of the relation between energy and momentum.

From the law of conservation of energy we have

$$\frac{P^2}{2m} + V = E$$

V is the potential energy, $P^2/2m$ is the kinetic energy and E is the total energy

By associating wave function ψ to the above expression

$$\left(\frac{P^2}{2m} + V\right)\psi = E\psi$$

$$\frac{(-i\hbar\,\partial/\partial x)(-i\hbar\,\partial/\partial x)}{2m}\psi + V\psi = (i\hbar\partial/\partial t)\psi$$

$$(-\hbar^2/2m)\,\partial^2\psi/\partial x^2 + V\psi = (i\hbar\partial/\partial t)\psi \text{----------- } (6)$$

This is Schrodinger Time Dependent Wave equation

This can be also written as $H\psi = E\psi$

Where $H = ((-\hbar^2/2m)\,\partial^2/\partial x + V)$ is called Hamiltonian operator

Schrodinger Time independent wave equation

According to de-Broglie's hypothesis, the particle in motion is always associated with a wave. To describe the motion of a particle in terms of its associated wave, Schrödinger derived a wave equation, which is termed as Schrödinger's wave equation.

Consider a particle of mass 'm' ,moving with velocity 'v' is associated with group of waves, let 'ψ' be the wave function of the particle.

A one dimensional wave equation for the steady wave associated with a particle is

$$\psi = A\, e^{\,i(kx - \omega t)} \text{ ----------- } (1)$$

A is amplitude

K is propagation vector and $K = 2\pi / \lambda$

ω is angular frequency and $\omega = 2\pi\upsilon$

υ Is the frequency and λ is the wave length of the matter waves

Differentiating equation partially w.r.t 'x' we get

$$\frac{\partial \psi}{\partial x} = Aike^{i(kx-\omega t)} = ik\psi$$

$$\frac{\partial^2 \psi}{\partial x^2} = -Ak^2 e^{i(kx-\omega t)} = k^2\psi$$

$$\therefore \frac{\partial^2 \psi}{\partial x^2} + k^2\psi = 0 \text{-------}(2)$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2}{\lambda^2}\psi = 0 \left(\because k = \frac{2\pi}{\lambda}\right)$$

According to de-Broglie's $\lambda = \frac{h}{mv}$

$$\therefore \frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 m^2 \mathrm{v}^2}{h^2}\psi = 0 ------(3)$$

The total energy E of the particle is the sum of its kinetic energy and potential energy(V)

i.e., $\mathrm{E} = \frac{1}{2}\ \mathrm{mv}^2 + V$

$$\therefore \quad \mathrm{m}^2\mathrm{v}^2 = 2m(E - V) ------(4)$$

Substituting the equation (4) into equation (3), we get

$$\therefore \frac{\partial^2 \psi}{\partial \mathrm{x}^2} + \frac{8\pi^2 \mathrm{m}}{\mathrm{h}^2}(\mathrm{E} - \mathrm{V})\psi = 0 ------(5)$$

Now, extending above equation for a three dimensional wave

$$\therefore \frac{\partial^2 \psi}{\partial \mathrm{x}^2} + \frac{\partial^2 \psi}{\partial \mathrm{y}^2} + \frac{\partial^2 \psi}{\partial \mathrm{z}^2} + \frac{8\pi^2 \mathrm{m}}{\mathrm{h}^2}(\mathrm{E} - \mathrm{V})\psi = 0 -----(6)$$

$$(or)$$

$$\therefore \nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

$$(or)$$

$$\therefore \nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0 \quad \left(\because \frac{h}{2\pi} = \hbar\right)$$

$$\text{Where } \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \text{ is Laplacian Operator}$$

This is the Schrödinger Time Independent wave equation

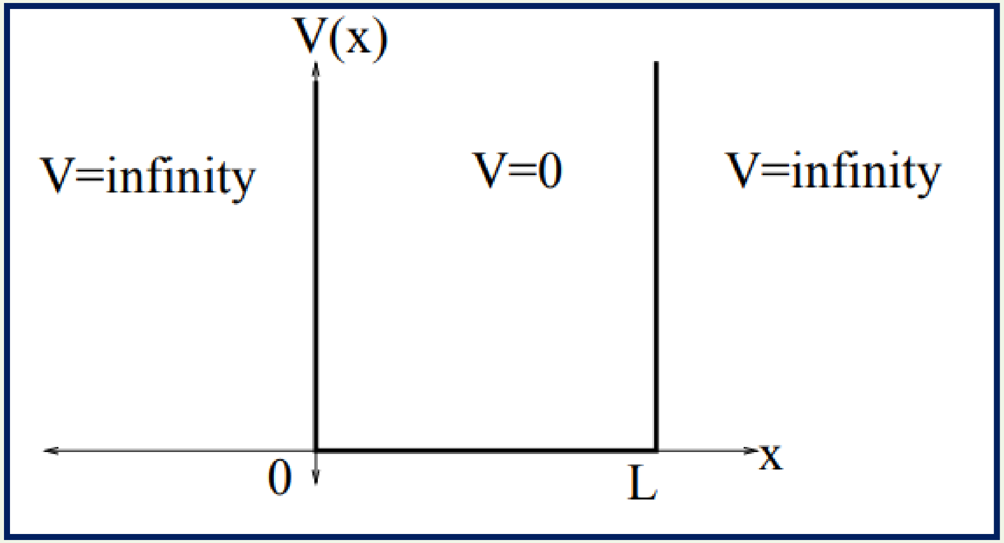
Application of Schrodinger wave equation - Particle in a one-dimensional potential box

Consider an electron of mass 'm' in an infinitely deep one-dimensional potential box with a width of ' L' units in which potential is constant and zero as shown.

The potential V (x) may be defined as follows

$V(x) = 0$ for $0 < x < L$

$= \infty$ otherwise



The motion of the electron in one dimensional box can be described by the Schrödinger's equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}[E - V]\psi = 0$$

Inside the box the potential V =0

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

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

The solution to above equation can be written as

$$\psi(x) = A\sin kx + B\cos kx - - - - (1)$$

Where A,B and K are unknown constants

To calculate the constants A & B, it is necessary to apply boundary conditions

- When $X = 0$ then $\Psi = 0$ i.e. $|\Psi|^2 = 0$ .... (a)
- $X = L$ then $\Psi = 0$ i.e. $|\Psi|^2 = 0$ ...... (b)
- Applying boundary condition (a) to equation (1)
- $A \sin K(0) + B \cos K(0) = 0 \rightarrow B = 0$
- Substitute B value in equation (1)

$$\boxed{\psi(x) = A\sin(Kx)}$$

Applying second boundary condition for equation (1)

$$0 = A\sin kL + (0)\cos kL$$

$$A\sin kL = 0$$

$$\sin kL = 0$$

$$kL = n\pi$$

$$k = \frac{n\pi}{L}$$

Substitute B & K value in equation (1)

$$\psi(x) = A\sin\frac{(n\pi x)}{L}$$

To calculate unknown constant A, consider normalization condition

Normalization condition

$$\int_0^L |\psi(x)|^2 dx = 1$$

$$\int_o^L A^2 \sin^2[\frac{n\pi x}{L}]dx = 1$$

$$A^2 \int_o^L \frac{1}{2}[1 - \cos[\frac{2n\pi x}{L}]dx = 1$$

$$\frac{A^2}{2}[x - \frac{L}{2\pi n}\sin\frac{2\pi n x}{L}]_0^L = 1$$

$$\frac{A^2}{2}L = 1$$

$$A = \sqrt{2/L}$$

The normalized wave function is

$$\psi_n = \sqrt{2/L}\sin\frac{n\pi}{L}x$$

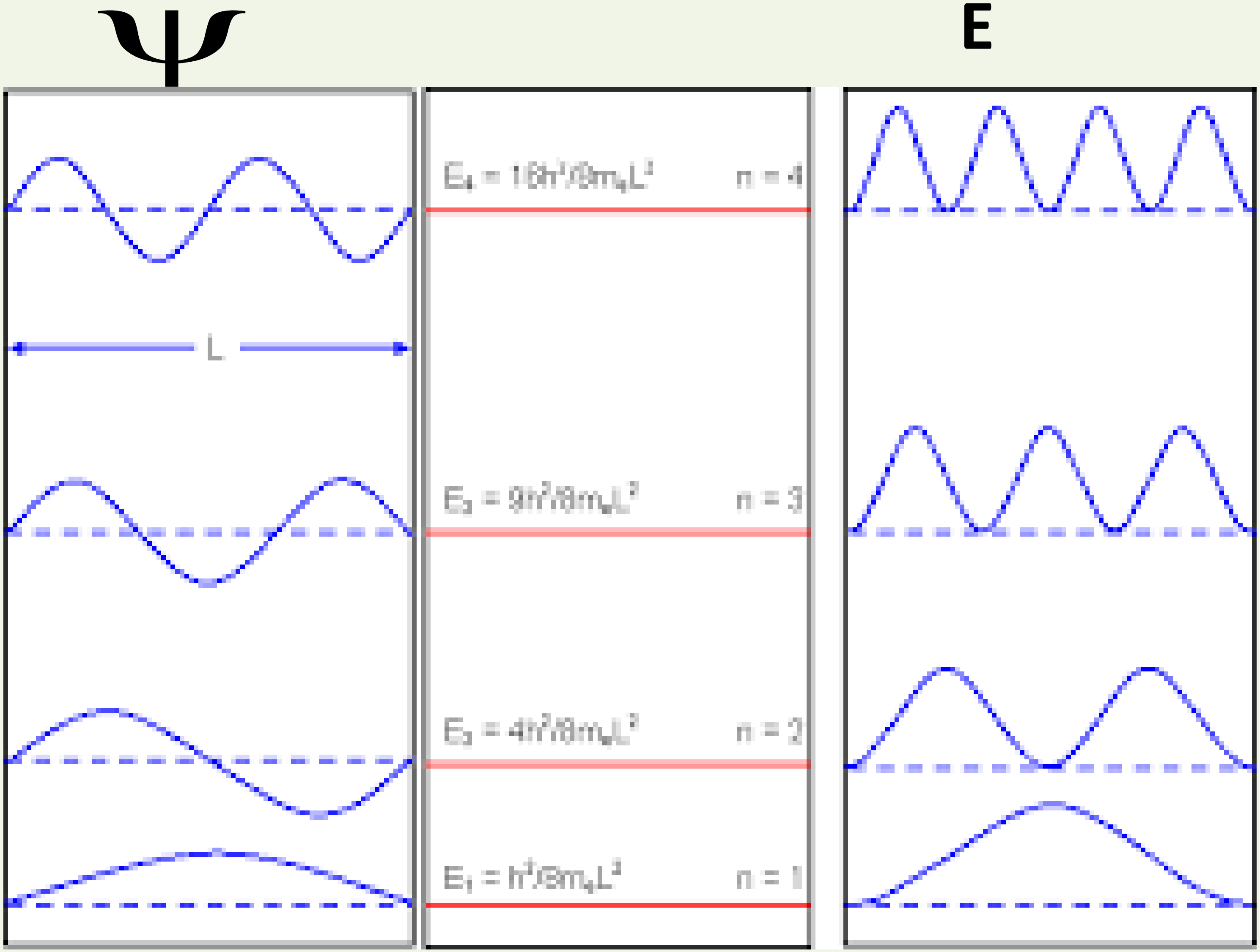
$$k^2 = \frac{2mE}{\hbar^2} \rightarrow E = \frac{k^2\hbar^2}{2m}$$

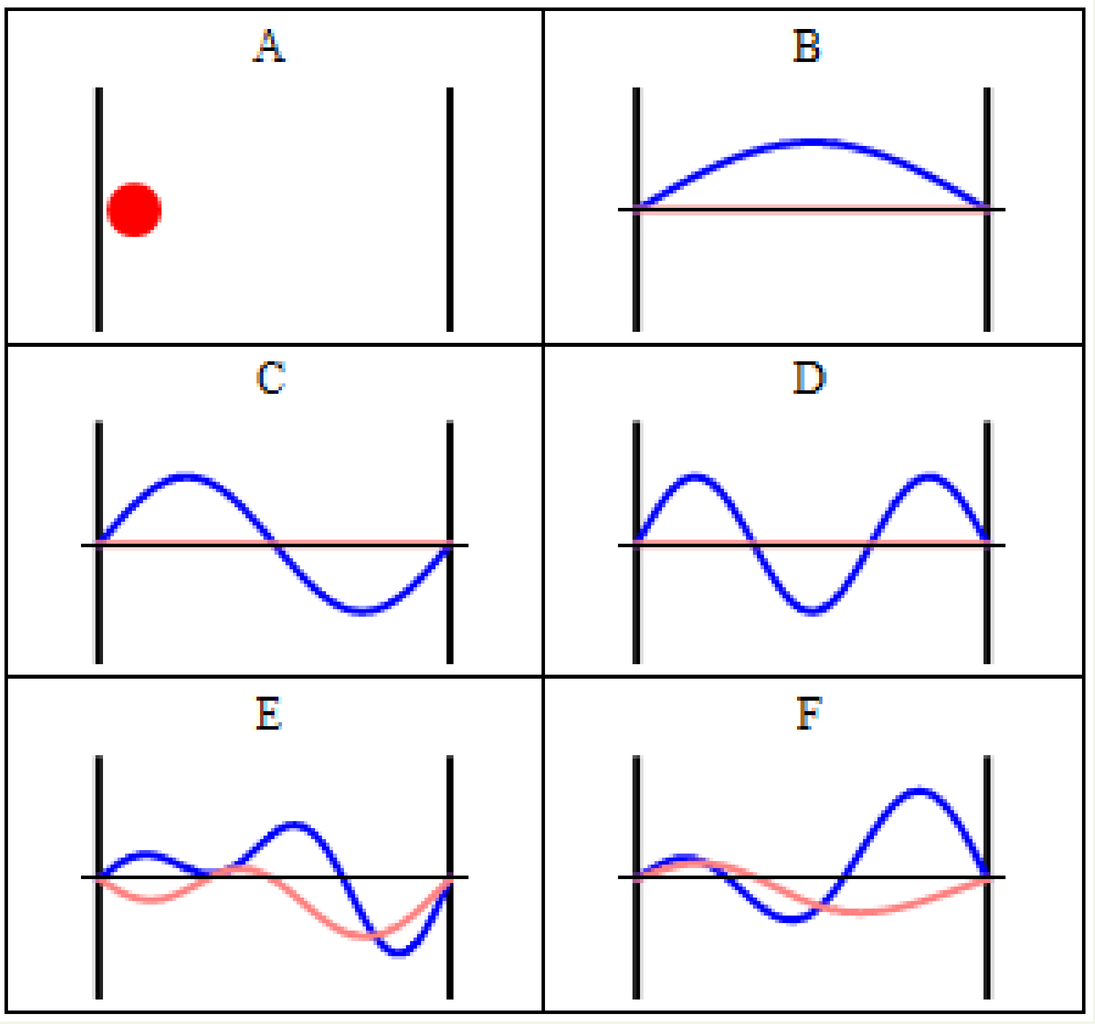
$$E = \frac{\left(\frac{n\pi}{L}\right)^2\left(\frac{h}{2\pi}\right)^2}{2m}$$

$$where,.k = \frac{n\pi}{L} \,\&\, \hbar = \frac{h}{2\pi}$$

$$E = \frac{n^2h^2}{8mL^2}$$

The wave functions Ψ_n and the corresponding energies E_n which are called Eigen functions and Eigen values, of the quantum particle.


Ψ
E
E4 = 16h²/8meL²
n = 4
L
E3 = 9h²/8meL²
n = 3
E2 = 4h²/8meL²
n = 2
E1 = h²/8meL²
n = 1


A
B
C
D
E
F