Syllabus

Photons and light waves - Electrons and matter waves –Compton effect - The Schrodinger equation (Time dependent and time independent forms) - meaning of wave function - Normalization –Free particle - particle in a infinite potential well: 1D,2D and 3D Boxes Normalization, probabilities and the correspondence principle.

Objectives

- Understand the importance of quantum physics.
- Knowledge on basic concept of dual nature of light.
- Understanding the time dependent and independent wave equation using Schrodinger equation.
- Understanding the role of free particle in 1D, 2D and 3D boxes.

Keywords: Compton effect, Schrodinger equation, particle in 1D,2D and 3D boxes.

4. 1 Introduction

- The most outstanding development in modern science is the conception of quantum mechanics. The quantum mechanics is better than Newtonian classical mechanics in explaining the fundamental physics.
- The fundamental concepts were not different from those of every day experience, such as particle, position, speed, mass, force, energy and even field. These concepts are referred as *classical*.
- The world of atoms cannot be described and understood with these concepts. For atoms and molecules, the ideas and concepts used in dealing with optics in day to day life is not sufficient. Thus, it needed new concepts to understand the properties of atoms.
- A group of scientist Neils Bohr W. Heisenberg, E. Schrodinger, P.A.M. Dirac, W. Pauli and M. Born conceived and formulated these new ideas in the beginning of 20^{th} century. This new formulation, a branch of physics, was named as ***quantum mechanics.***

Limitation of classical mechanics

- The classical mechanics deals with macroscopic phenomena which is identical and distinguishable. But it gives controversial results on certain microscopic studies such as black body radiation, photoelectric effect, emission of X-rays, etc.,
- In classical mechanics, a body which is very small in comparison with other body is termed as *particle* whereas in quantum mechanics, the body which cannot be divide further is termed as *particle*.

- The other main difference is the quantized energy state. In classical mechanics, an oscillating body can assume any possible energy. But on quantum mechanics, an oscillating body can have only discrete non-zero energy.

Need of quantum mechanics

- Classical mechanics successfully explained the motions of object which are observable directly or by instruments like microscopes. But it fails to explain the actual behaviour. Therefore, the classical mechanics cannot used to explain in atomic level, e.g. motion of an electron in an atom.
- The phenomena of black body radiation, photoelectric effect, emission of X-rays, etc., were explained by Max Planck in 1900 by introducing the formula
  $E = n\,h\,v$ (1)
  Where $n = 0, 1, 2,\ldots$
  h = Planck's constant = 6.626×10^{-34} J/s.
- This is known as *quantum hypothesis* and marked the beginning of modern physics. The whole microscopic world obeys the above formula.

4.2 Photons and light waves

The wave and particle duality of radiation is easily understood by knowing a difference between a wave and a particle.

Wave

- A wave originates due to oscillations and it is spread out over a large region of space. A wave cannot be located at a particular place and mass cannot be carried by a wave.
- Actually, a wave is a spread out disturbance specified by its amplitude A, frequency v, wavelength λ, phase δ and intensity I.
- The phenomenon of interference, diffraction and polarization require the presence of two or more waves at the same time and at the same position. It is very clear that two or more particles cannot occupy the same position at the same time. So one has to conclude that radiation behaves like waves.

Particle

- A particle is located at some definite point and it has mass. It can move from one place to another. A particle gains energy when it is accelerated and it losses energy when it is slowed down.
- A particle is characterized by mass m, velocity v, momentum p and energy E.
- Spectra of black body radiation, Compton effect, photoelectric effect, etc. could not be explained on wave nature of radiation. These phenomena established that radiant energy interacts with matter in the forms of *photons or quanta*. Therefore, Planck's quantum theory came to conclude that radiation behaves like particles.
- Thus, radiation sometimes behaves as a wave and at some other times as a particles. Now, wave – particle duality of radiation is universally accepted.

4.3 Wave – particle duality – electrons and matter waves

According to de-Broglie hypothesis, a moving particle is always associated with waves.

(i) Waves and particles are the only two modes through which energy can propagate in nature

(ii) Our universe is fully composed of light radiation and matter

(iii) Since nature loves symmetry, so matter and waves must be symmetric.

The waves associated with the matter particles are called *matter waves or de-Broglie waves.*

From Planck's theory, the energy of a photon of frequency υ is given by $E = h\upsilon$ (1)

According to Einstein's mass energy relation, $E = mc^2$ (2)

Where m – mass of a photon, c – velocity of a photon

Equating (1) and (2), we get

$$hv = mc^2 \quad (3)$$

$$\frac{hc}{\lambda} = mc^2$$

$$\lambda = \frac{h}{mc} \quad (4)$$

Since $mc=p$ momentum of photon, then

$$\lambda = \frac{h}{p} \quad (5)$$

According to de-Broglie hypothesis, the wavelength of de-Broglie wave associated with any moving particle of mass *'m'* with velocity *'v'* is given by

$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad (6)$$

In terms of Energy

We know that $E = \frac{1}{2}mv^2$

Multiply m by both sides $mE = \frac{1}{2}m^2v^2$

(or) $\sqrt{2mE} = mv$

(or) $\sqrt{2mE} = p$

We know that, $\lambda = \frac{h}{p}$ and hence (or) de-Broglie wavelength $\lambda = \frac{h}{\sqrt{2mE}}$

In terms of electrons

We know that kinetic energy in terms of electron volt is given by $eV = \frac{1}{2}mv^2$

Multiply m by both sides $meV = \frac{1}{2}m^2v^2$

(or) $\sqrt{2meV} = mv$

(or) $\sqrt{2meV} = p$

We know that, $\lambda = \frac{h}{p}$ and hence

(or) de-Broglie wavelength $\lambda = \frac{h}{\sqrt{2meV}}$

Properties of Matter

(i) Matter waves are not electromagnetic waves.

(ii) Matter waves are new kind of waves in which due to the motion of the charged particles, electromagnetic waves are produced.

(iii) Lighter particles will have high wavelength

(iv) Particles moving with less velocity will have high wavelength

(v) The velocity of matter wave is not a constant, it depends on the velocity of the particle.

(vi) If the velocity of the particle is infinite then the wavelength of matter wave is indeterminate(λ=0)

(vii) The wave and particle aspects cannot appear together

(viii) Locating the exact position of the particle in the wave is uncertain

4.4 Compton Effect

When a beam of monochromatic radiation such as X-rays, γ rays etc., of high frequency is allowed to fall on a fine scatterer, the beam is scattered into two components viz,

(i) One component having the same frequency (or) wavelength as that of the incident radiation so called **unmodified radiation,** and

(ii) The other component having lower frequency (or) higher wavelength compared to incident radiation, so called **modified radiation**.

This effect of scattering is called **Compton Effect and the change in wavelength of scattered X – rays is known as Compton shift.**

Thus as a result of Compton scattering, we get (i) Unmodified radiation (ii) Modified radiation and (iii) a recoil electron.

Theory of Compton Shift

Principle

In Compton scattering the collision between a photon and an electron is considered. Then by applying the laws of conservation of energy and momentum, the expression for Compton wavelength is derived.

Assumptions

1. The collision occurs between the photon and an electron in the scattering material.
2. The electron is free and is at rest before collision with the incident photon.

Now, let us consider a photon of energy 'hν' colliding with an electron at rest of mass m_0.

During the collision process, a part of energy is given to the electron, which in turn increases the kinetic energy of the electron and hence it recoils at an angle of Φ with mass 'm' and velocity 'v' as in fig. The scattered photon moves with an energy $h\nu'$ with longer wavelength than hν, at an angle θ with respect to the original direction.

Let us find the energy and momentum components before and after collision process.

Energy before collision

(i) Energy of the incident photon = $h\nu$

(ii) Energy of the electron at rest = m_0c^2

Where m_0 is the rest mass energy of the electron.

Total Energy before Collision = $h\nu + m_0c^2$ (1)

Energy after collision

(i) Energy of the scattered photon = $h\nu'$

(ii) Energy of the recoil electron = mc^2

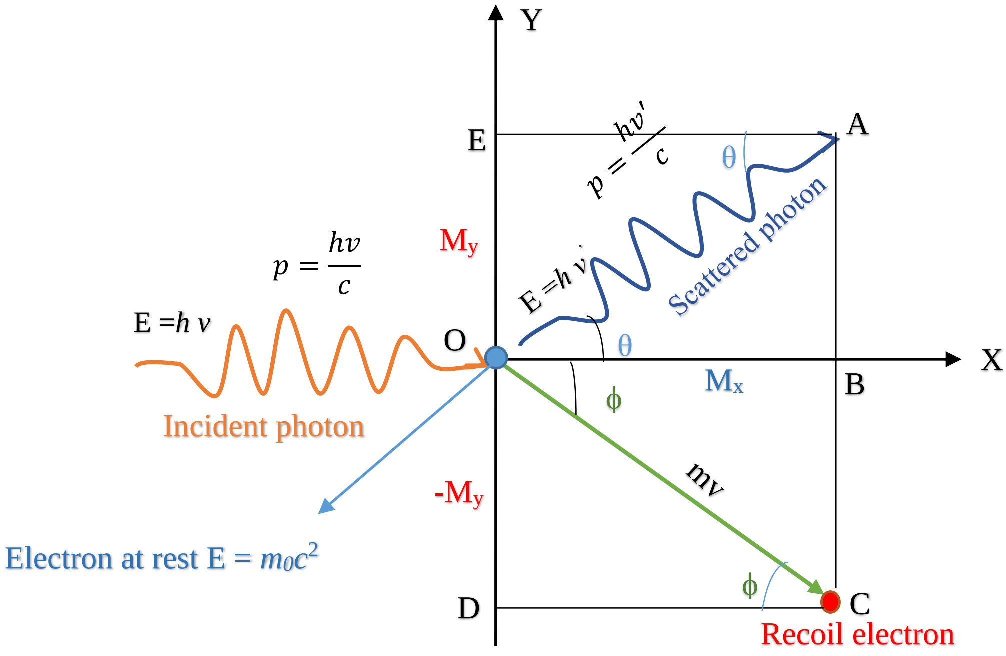
Where m is the mass of the electron moving with velocity 'v'

Total energy after collision = $h\nu' + mc^2$ (2)

We know according to the law of conservation of energy, Total energy before collision = Total energy after collision

Therefore Equation (1) = Equation (2)

(i.e.,) $h\nu + m_0c^2 = h\nu' + mc^2$ (or) $h(\nu - \nu') + m_0c^2 = mc^2$ (3)



X-component of Momentum before collision

(i) X-component momentum of the incident photon = $\frac{h\nu}{c}$

(ii) X-component momentum of the electron at rest = 0

$\therefore$ **Total X-Component of momentum before collision =** $\frac{h\nu}{c}$ (4)

X-component of Momentum after collision

(i) X-component momentum of the scattered photon can be calculated from fig. 4.11

In ΔOAB $\cos\theta = \frac{M_x}{h\nu'/c}$

$\therefore$ X-component momentum of the scattered photon = $\frac{h\nu'}{c}\cos\theta$

(ii) X-component momentum of the recoil electron can be calculated from figure.

(iii) In ΔOBC $\cos\phi = \frac{M_x}{mv}$

$\therefore$ X-component momentum of the recoil electron $(M_y) = mv\cos\phi$

Total X-component of momentum after collision = $\frac{hv'}{c}\cos\theta + mv\cos\phi$ (5)

We know according to the law of conservation of momentum,

Total momentum before collision = Total momentum after collision

i.e., Equation (4) = Equation (5)

$$\frac{hv}{c} = \frac{hv'}{c}\cos\theta + mv\cos\phi \qquad (6)$$

Y-component of momentum before collision

(i) Y-component momentum of the incident photon = 0

(ii) Y-component momentum of the electron at rest = 0

Total Y-Component of momentum before collision = 0 (7)

Y-component of momentum after collision

(i) Y-component momentum of the scattered photon can be calculated from fig. 4.11.

In ΔOAE , $\sin\theta = \frac{M_y}{hv'/c}$

Y-component momentum of the scattered photon= $\frac{hv'}{c}\sin\theta$

(ii) Y-component momentum of the recoil electron can be calculated from figure.

(iii) In ΔOCD, $\sin\phi = \frac{-M_y}{mv}$

Y-component momentum of the recoil electron = $-mv\ sin\ \phi$

Total Y-component of momentum after collision = $\frac{hv'}{c}\sin\theta - mv\sin\phi$ (8)

According to the law of conservation of momentum,

Total momentum before collision = Total momentum after collision i.e., Equation (7) = Equation (8)

$$0 = \frac{hv'}{c}\sin\theta - mv\sin\phi \qquad (9)$$

From equation (6), we can write $\frac{hv}{c} - \frac{hv'}{c}\cos\theta = mv\cos\phi$

(or) $mvc\cos\phi = h(v - v'\cos\theta)$ (10)

from equation (9) we can write

$$hv'\sin\theta = mcv\sin\phi \qquad (11)$$

Squaring equation (10)

$$h^2(v - v'\cos\theta)^2 = m^2c^2v^2\cos^2\phi$$

$$h^2v^2 + h^2v'^2\cos^2\theta - 2h^2(vv'\cos\theta) = m^2c^2v^2\cos^2\phi \qquad (12)$$

Squaring equation (11), we get

$$h^2v'^2\sin^2\theta = m^2c^2v^2\sin^2\phi \qquad (13)$$

Equation (12) + (13) $\Rightarrow$

$$h^2v^2 + h^2v'^2\cos^2\theta + h^2v'^2\sin^2\theta - 2h^2(vv'\cos\theta) = m^2c^2v^2\cos^2\phi + m^2c^2v^2\sin^2\phi$$

(or) $h^2v^2 + h^2v'^2 - 2h^2(vv'\cos\theta) = m^2c^2v^2$ (14)

While adding Eqn. (12) & (13), $\cos^2\phi + \sin^2\phi = 1$ (RHS) and $h^2v'^2\sin^2\theta + h^2v'^2\cos^2\theta = h^2v'^2$ (LHS)

Squaring equation (3) on both sides ($h(v - v') + m_0c^2 = mc^2$), we have

$$h^2(v - v')^2 + m_0^2c^4 + 2h(v - v')m_0c^2 = m^2c^4$$

$$h^2v^2 + h^2v'^2 - 2h^2vv' + m_0^2c^4 + 2h(v - v')m_0c^2 = m^2c^4 \qquad (15)$$

Subtracting equation (15) from equation (14) we get

$$-2h^2vv'(1 - \cos\theta) + 2h(v - v')m_0c^2 + m_0^2c^4 = m^2c^2(c^2 - v^2) \qquad (16)$$

From the theory of relativity, the relativistic formula for the variation of mass with velocity of the electron is given by

$$m = \frac{m_0}{\sqrt{1-\frac{v^2}{c^2}}} \quad \text{(or)} \quad m^2 = \frac{m_0{}^2 c^2}{(c^2 - v^2)}$$

$$m^2(c^2 - v^2) = m_0{}^2 c^2 \qquad (17)$$

Now let us multiply c^2 on both sides of this equation to make it similar to equation (15)

$$m^2 c^2 (c^2 - v^2) = m_0{}^2 c^4 \qquad (18)$$

Substitute the value of (18) and (16)

$$-2h^2 vv^{'}(1-\cos\theta) + 2h(v - v^{'})m_0 c^2 + m_0{}^2 c^4 = m_0{}^2 c^4$$

$$-2h^2 vv^{'}(1-\cos\theta) + 2h(v - v^{'})m_0 c^2 + \cancel{m_0{}^2 c^4} = \cancel{m_0{}^2 c^4}$$

$$\text{(or)} \ 2h(v - v^{'})m_0 c^2 = 2h^2 vv^{'}(1-\cos\theta)$$

$$\text{(or)} \ \cancel{2}\cancel{h}(v - v^{'})m_0 c^2 = \cancel{2}h^{\cancel{2}} vv^{'}(1-\cos\theta)$$

$$\text{(or)} \ \frac{(v - v^{'})}{vv^{'}} = \frac{h}{m_0 c^2}(1-\cos\theta)$$

$$\text{(or)} \ \frac{v}{vv^{'}} - \frac{v^{'}}{vv^{'}} = \frac{h}{m_0 c^2}(1-\cos\theta)$$

$$\text{(or)} \ \frac{1}{v^{'}} - \frac{1}{v} = \frac{h}{m_0 c^2}(1-\cos\theta)$$

$$\text{(or)} \ \frac{c}{v^{'}} - \frac{c}{v} = \frac{h}{m_0 c}(1-\cos\theta)$$

$$\text{(or)} \ \lambda^{'} - \lambda = \frac{h}{m_0 c}(1-\cos\theta) \qquad \left(\because \lambda = \frac{c}{v}\right) \qquad (19)$$

$$\text{(or)} \ \Delta\lambda = \frac{h}{m_0 c}(1-\cos\theta) \qquad (20)$$

Equation (20) represents the shift in wavelength, i.e. Compton shift which is independent of the incident radiation as well as the nature of the scattering substance.

Thus the shift in wavelength or Compton shift purely depends on the angle of scattering.

Special cases

Case (i) when θ = 0; cos θ = 1

Equation (18) becomes Δλ = 0 .This implies that at θ = 0 the scattering is absent and the out coming radiation has the same wavelength or frequency as that of the incident radiation. Thus the output will be a single peak as shown in figure 4.12 (a).

Case (i) when θ = 90^0; cos θ = 0

Equation (18) becomes $\lambda = \frac{h}{m_o C}$ Substituting h, m_o *and* C, $\Delta\lambda = 0.02424 A^o$

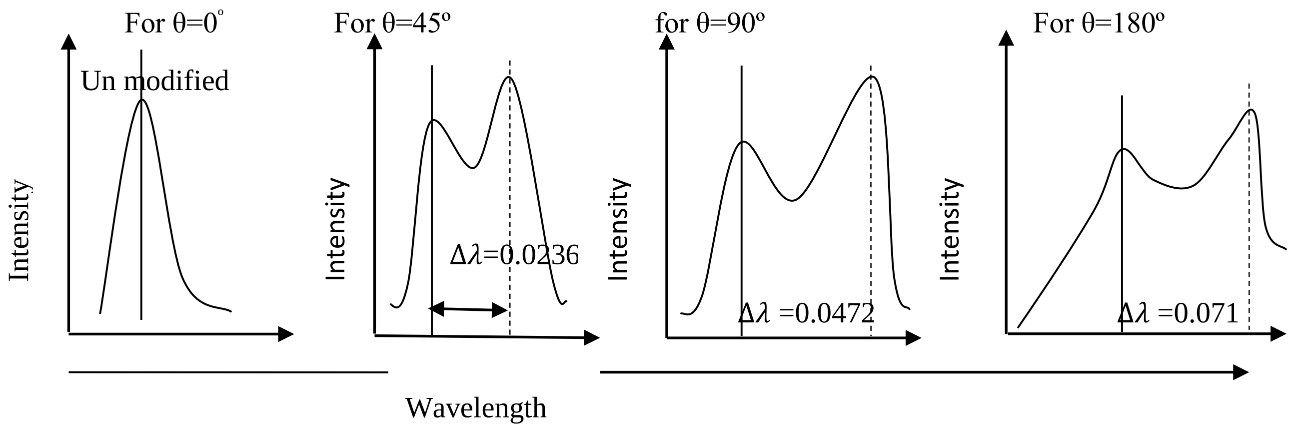
This wavelength is called COMPTON WAVELENGTH, which has a good agreement with the experimental results as shown in fig.4.12(c)

Case (i) when θ = 180^0; cos θ = -1

Equation (18) becomes $\lambda = \frac{h}{m_o C}\left[1-(-1)\right] = \frac{2h}{m_o C}$

Substituting h, m_o *and* C, $\Delta\lambda = 0.04848 A^o$

Thus for θ = 180^0 the shift in wavelength is found to be maximum as shown in fig 4.12(d).



EXPERIMENTAL VERIFICATION OF COMPTON EFFECT:

Principle

When a photon of energy 'hv' collides with a scattering element, the scattered beam has two components, viz, one of the same frequency (or) wavelength as that of the incident radiation and the other has lower frequency (or) higher wavelength compared to incident frequency (or) wavelength. This effect is called Compton effect and the shift n wavelength is called Compton shift.

Construction

It consists of an X-ray tube for producing X-rays. A small block of carbon C (scattering element) is mounted on a circular table as in figure. A Bragg's spectrometer (B_s) is allowed to freely swing in an arc about the scattering element to catch the scattered photons. Slits S_1 and S_2 helps to focus the X-rays onto the scattering element.

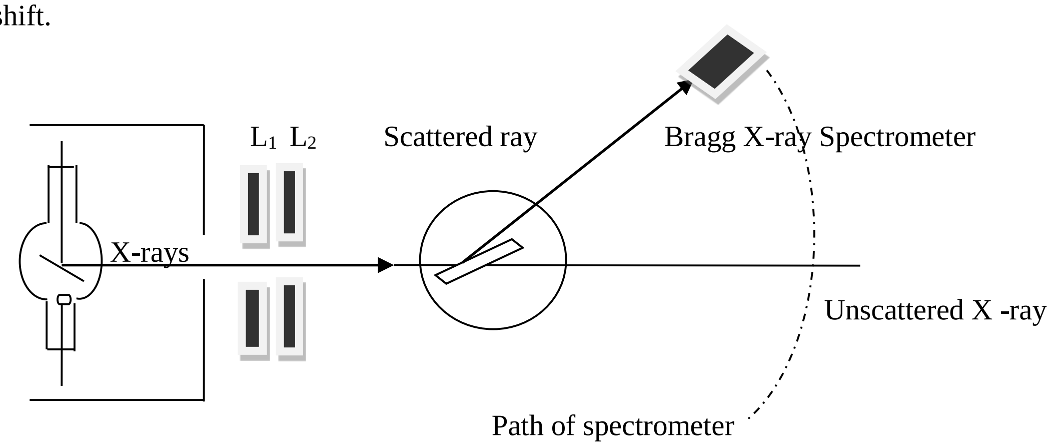
Working

X-rays of monochromatic wavelength 'λ' is produced from an X-ray tube and is made to pass through the slits S_1 and S_2. These X-rays are made to fall on the scattering element. The scattered X-rays are received with the help of the Bragg's spectrometer and the scattered wavelength is measured .Now an ionization energy is replaced at the target to measure the intensity for the corresponding wavelength.

The experiment is repeated for various scattering angles and the scattered wavelengths and the corresponding intensities are measured. The experimental results are plotted as in figure

In this fig. when the scattering angle $\theta = 0^0$, the scattered radiation peak will be the same as that of the incident radiation peak 'A'. Now when the scattering angle is increased, for one incident radiation peak A of wavelength (λ) we get two scattered peaks A and B. Here the peak 'A' is found to be of same wavelength as that of the incident wavelength and the peak B is of greater wavelength than the incident radiation. The shift in wavelength (or) difference in wavelength (Δλ) of the two scattered beams is found to increase with respect to the increase in scattering angle.

At $\theta = 90^0$, Δλ is found to be 0.0236 ≈ 0.02424, which has good agreement with the theoretical results. Hence this wavelength is called Compton wavelength and the shift in wavelength is called Compton shift.



4.5 Schrödinger wave equations

Schrödinger describes the wave nature of a particle in mathematical form and it is known as Schrödinger wave equation. There are two types: time dependent and independent wave equations.

Schrödinger Time Dependent wave function

A particle can behave as a wave only under motion. So, it must be accelerated by a potential field

∴ Total energy (E) = Potential Energy (V) + Kinetic Energy

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

(or) $E = V + \frac{1}{2}\frac{m^2v^2}{m}$

(or) $E = V + \frac{p^2}{2m}$ [Since p = mv] (or) $E\Psi = V\Psi + \frac{p^2}{2m}\Psi$ (1)

According to classical mechanics if '*x*' is the position of the particle moving with the velocity '*v*', then the displacement of the particle at any time '*t*' is given by

$$y = Ae^{-i\omega\left(t-\left(\frac{x}{v}\right)\right)}$$

Where ω is the angular frequency of the particle

Similarly in quantum mechanics the wave equation Ψ (x, y, z, t) represents the position (x, y, z) of a moving particle at any time't' and is given by

$$\Psi(x,y,z,t) = Ae^{-i\omega\left(t-\left(\frac{x}{v}\right)\right)} \quad (2)$$

We know that angular frequency ω = 2πν

∴ Equation (2) becomes

$$\Psi(x,y,z,t) = Ae^{-i2\pi\left(\nu t-\left(\frac{x\nu}{v}\right)\right)} \quad (3)$$

We know $E = h\nu$ (or) $\nu = \frac{E}{h}$ (4)

Also, if '*v*' is the velocity of the particle behaving as a wave,

Then the frequency $\nu = \frac{v}{\lambda}$ (or) $\frac{\nu}{v} = \frac{1}{\lambda}$ (5)

Substituting equations (4) & (5) in equation (3), we get

$$\Psi(x,y,z,t) = Ae^{-i2\pi\left(\left(\frac{Et}{h}\right)-\left(\frac{x}{\lambda}\right)\right)} \quad (6)$$

If 'p' is the momentum of the particle, then the de-Broglie wavelength

is given by $\lambda = \frac{h}{mv} = \frac{h}{p}$ (7)

Substituting equation (7) in (6) we get

$$\Psi(x,y,z,t) = Ae^{-i2\pi\left(\left(\frac{Et}{h}\right)-\left(\frac{px}{h}\right)\right)}$$

(or) $\Psi(x,y,z,t) = Ae^{-i\frac{2\pi}{h}(Et-px)}$

Since $\hbar = \frac{h}{2\pi}$ we can write $\Psi(x,y,z,t) = Ae^{-\frac{i}{\hbar}(Et-px)}$ (8)

Differentiating equation (8) partially with respect to 'x' we get

$$\frac{\partial \Psi}{\partial x} = Ae^{-\frac{i}{\hbar}(Et-Px)}\left(\frac{ip}{\hbar}\right)$$

Differentiating once again partially with respect to ‘x’ we get

$$\frac{\partial^2 \Psi}{\partial x^2} = Ae^{-\frac{i}{\hbar}(Et-Px)}\left(\frac{i^2 p^2}{\hbar^2}\right)$$

Since $\Psi(x,y,z,t) = Ae^{-\frac{i}{\hbar}(Et-px)}$ and $i^2 = -1$, we can write

$$\frac{\partial^2 \Psi}{\partial x^2} = \Psi(x,y,z,t)\left(\frac{-p^2}{\hbar^2}\right)$$

(or) $p^2\Psi = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2}$ (9)

Differentiating equation (8) partially with respect to ‘*t*’ we get

$$\frac{\partial \Psi}{\partial t} = Ae^{-\frac{i}{\hbar}(Et-Px)}\left(\frac{-iE}{\hbar}\right)$$

(or) $\frac{\hbar}{-i}\frac{\partial \Psi}{\partial t} = \Psi(x,y,z,t)E \qquad \left[\because \Psi(x,y,z,t) = Ae^{-\frac{i}{\hbar}(Et-px)}\right]$

(or) $E\Psi = i\hbar\frac{\partial \Psi}{\partial t}$ (10)

Substituting equations (9) & (10) in equation (1), we get

$$i\hbar\frac{\partial \Psi}{\partial t} = V\Psi - \frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2}$$

(or) $i\hbar\frac{\partial \Psi}{\partial t} = \left[V - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right]\Psi$ (11)

Equation (11) represents the one dimensional Schrodinger time dependent wave equation along ‘x’ direction. Also the wave function Ψ (x, y, z, t) depends on both the position (x, y, z) and time (t)

Similarly for three dimensional Schrodinger time dependent wave equation can be written as

$i\hbar\frac{\partial \Psi}{\partial t} = \left[V - \frac{\hbar^2}{2m}\nabla^2\right]\Psi$ (12)

Where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Equation (12) can also rewritten as $E\Psi = H\Psi$

Where E is an energy operator given by $E = i\hbar \frac{\partial}{\partial t}$ &

H is called Hamiltonian operator, given by $H = V - \frac{\hbar^2}{2m}\nabla^2$

4.6 Schrödinger time independent wave equation

In Schrödinger time dependent wave equation the wave function 'Ψ' depends on time, but in Schrodinger time independent wave function 'Ψ' does not depend on time & hence it has many applications.

We know that time dependent wave function

$$\Psi(x,y,z,t) = Ae^{-\frac{i}{\hbar}(Et-px)}$$

Now, splitting the RHS of this equation in to (i) Time dependent factor & (ii) Time independent factor, we get

$$\Psi(x,y,z,t) = Ae^{\frac{-iEt}{\hbar}} e^{\frac{ipx}{\hbar}}$$

(or) $$\Psi(x,y,z,t) = A\psi e^{\frac{-iEt}{\hbar}} \quad (1)$$

Where 'ψ' represents the time independent wave function. i.e., $\psi = e^{\frac{ipx}{\hbar}}$

Differentiating equation (1) partially with respect to 't' we get $\frac{\partial\Psi}{\partial t} = A\psi e^{\frac{-iEt}{\hbar}}\left[\frac{-iE}{\hbar}\right]$ (2)

Differentiating equation (1) partially with respect to 'x' we get, $\frac{\partial\Psi}{\partial x} = Ae^{\frac{-iEt}{\hbar}}\frac{\partial\psi}{\partial x}$

Differentiating once again partially with respect to 'x' we get, $\frac{\partial^2\Psi}{\partial x^2} = Ae^{\frac{-iEt}{\hbar}}\frac{\partial^2\psi}{\partial x^2}$ (3)

We know the time dependent wave equation for 1-dimension is

$$i\hbar\frac{\partial\Psi}{\partial t} = V\Psi - \frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} \quad (4)$$

We can get the Schrödinger time dependent wave equation, just by substituting equations (1),(2) & (3), which has relation between the time dependent wave function (Ψ) and time independent wave Function (ψ) in equation (4)

Thus, substituting equations (1),(2) & (3) in equation (4) , we get

$$i\hbar A\psi e^{\frac{-iEt}{\hbar}}\left[\frac{-iE}{\hbar}\right] = VA\psi e^{\frac{-iEt}{\hbar}} - \frac{\hbar^2}{2m}Ae^{\frac{-iEt}{\hbar}}\frac{\partial^2\psi}{\partial x^2}$$

(or) $i\hbar\psi\left[\frac{-iE}{\hbar}\right] = V\psi - \frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$

(or) $(-i)^2 E\psi = V\psi - \frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$ (or) $E\psi - V\psi = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2}$

(or) $\frac{\partial^2\psi}{\partial x^2} = \frac{-2m}{\hbar^2}\left[E\psi - V\psi\right]$

(or) $\frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}\left[E - V\right]\psi = 0$ (5)

Equation (5) represents the Schrodinger time independent wave function in one dimension along 'x' direction. Here the wave function is independent of time .Similarly for 3 – dimension, the Schrodinger time independent wave function is given by $\nabla^2\psi + \frac{2m}{\hbar^2}\left[E - V\right]\psi = 0$ (6)

Where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

4.7 Physical Significance of a wave function [Ψ]

Wave function

It is the variable quantity that is associated with a moving particle at any position (x, y, z) and at any time t and it relates the probability of finding the particle at that point and at that time

(i) It gives the relation between the particle and wave nature of the matter statistically

i.e., $\Psi = \psi e^{-i\omega t}$

(ii) Wave function gives the information about the particle behavior

(iii) Ψ is a complex quantity and does not have any physical meaning

Normalization

(iv) $|\psi|^2 = \psi^*\psi$ is real & positive. This concept is similar to light. In light amplitude may be (+ve) or (-ve) but the square of intensity of light is +ve & measurable

(v) $|\psi|^2$ represents the probability density of finding the particle per unit volume which is called Normalization of a wave function.

(vi) for a given volume $d\tau$, the probability of finding the particle is given by Probability $P = \iiint_v |\psi|^2 \, d\tau$ where $d\tau = dx \times dy \times dz$

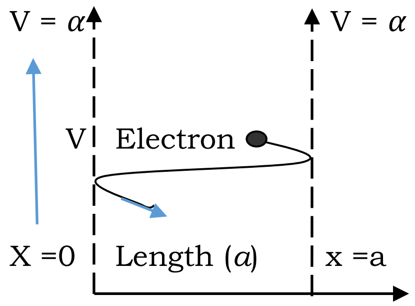
(vii) The probability will have any values between 0 & 1

- If P =0 , then there is no particle within the given limits
- If P = 1 ,the particle is definitely present within the given limits

- If P = 0.7, then there is 70% chance of finding the particle within the given limits. Also there is 30% of no chance of finding the particle.

4.8 Application of Schrodinger wave equation to a particle (electron) enclosed in a one dimensional infinite potential well (or) box

Let us consider a particle (electron) of mass 'm' moving along x- axis, enclosed in a one dimensional potential box as shown in figure. Since the walls are of infinite potential the particle does not penetrate out from the box



Also, the particle is confined between the lengths 'a' of the box and has elastic collisions with the Walls. Therefore the potential energy of the electron inside the box is constant and can be taken as zero for simplicity

∴ Outside the box and on walls of the box, the potential energy V of the electron is α. Inside the box the potential energy of the electron is zero

i.e., the boundary condition is $V(x) = 0 \; when \; 0 < x < a$

$$V(x) = \alpha \; when \; 0 \geq x \geq a$$

Since the particle cannot exist outside the box and thus wave function ψ = 0 at $0 \geq x \geq a$

Now, Consider the Schrodinger one dimensional time independent wave function

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

Since the potential energy inside the wall is zero, the particle has kinetic energy alone. Hence it is called free particle (electron), now the above equation becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}E\psi = 0$$

(or) $$\frac{\partial^2 \psi}{\partial x^2} + k^2\psi = 0 \quad (1)$$

Where $$k^2 = \frac{2mE}{\hbar^2} \quad (2)$$

The second order differential equation of equation (1) has two arbitrary constants

∴ The solution of equation (1) is $\psi(x) = A\sin kx + B\cos kx$ (3)

Where A & B are arbitrary constants which can be found by applying the boundary conditions

Condition (i) at x =0, potential energy V = α. Hence there is no particle at the walls of the box,

Therefore ψ(x) = 0 Equation (3) becomes $0 = A\sin 0 + B\cos 0$

$= 0 + B(1)$

$\therefore B = 0$

Condition (ii) at x = a, potential energy V =α there is no particles at the walls of box ∴ ψ(x) = 0

Now, Equation (3) becomes $0 = A\sin ka + B\cos ka$

(or) $0 = A\sin ka + 0$ [∵B =0 from condition (i)]

Also A is a Constant & hence $A \neq 0; \sin ka = 0$

Thus, we can write as $\sin n\pi = 0$

Comparing these two equations we can write $ka = n\pi$, where 'n' is a integer

(or) $$k = \frac{n\pi}{a} \qquad (4)$$

Substituting the value of B & k in equation (3)

The wave function in one dimensional box is $$\psi(x) = A\sin\left(\frac{n\pi x}{a}\right) \qquad (5)$$

Energy of the particle (electron)

Equation (2) can be rewritten as $k^2 = \dfrac{2mE}{\left(\dfrac{h^2}{4\pi^2}\right)}$ $\left[\because \hbar = \dfrac{h}{2\pi}\right]$

(or) $$k^2 = \frac{8\pi^2 mE}{h^2} \qquad (6)$$

Squaring equation (4), we get $$k^2 = \frac{n^2\pi^2}{a^2} \qquad (7)$$

Equating equation (6) & (7) we get

$$\frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{a^2}$$

∴ The Energy of the particle (electron) $$E_n = \frac{n^2h^2}{8ma^2} \qquad (8)$$

From equation (5) & (8) we can say that for each value of 'n' there is energy

Level with the corresponding wave function and hence each E_n is said to be *Eigen value* corresponding to the *Eigen function* ψ_n

Energy levels of an electron:

The ground energy state can be calculated by substituting n = 1 in equation (8), we get, $E_1 = \dfrac{h^2}{8ma^2}$

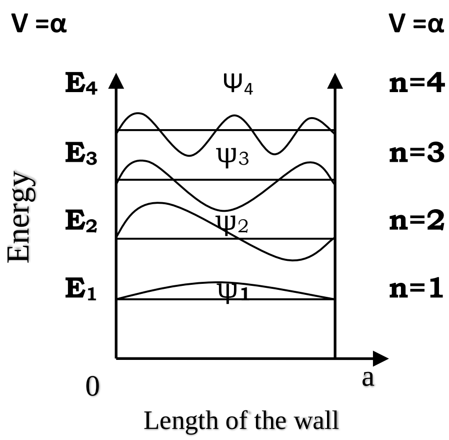
For n=2, $E_2 = \dfrac{2^2 h^2}{8ma^2} = 4E_1$; For n=3, $E_3 = \dfrac{3^2 h^2}{8ma^2} = 9E_1$, etc.,

Similarly we can calculate 'n' number of energy levels by substituting n=1, 2, 3… n.

In general we can write $E_n = n^2 E_1 \quad E_n = n^2 E_1$ (9)

From these levels, it is found that each energy level of an electron are discrete

The various Eigen values corresponding to their Eigen function is shown in figure



Normalization of the wave function

It is process by which the probability (P) of finding the particle (electron) inside the box

We know that if (P) = 1 then the particle lies inside the box

∴ Probability of 1 – D box of length 'a' is $$P = \int_0^a |\psi^2| dx = 1 \tag{10}$$

[∵ *the particle lies between* 0 *and* l]

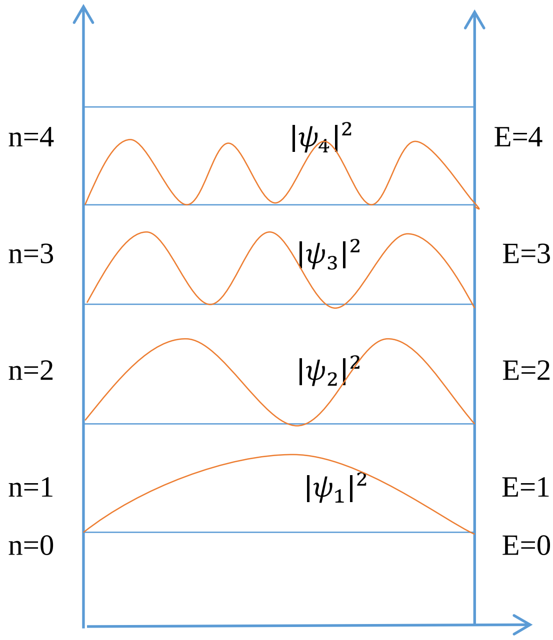
Substituting equation (5) in equation (10) we get

$$P = \int_0^a A^2 \sin^2 \frac{n\pi x}{a} dx = 1$$

$$\text{(or) } P = A^2 \int_0^a \left\{ \frac{1 - 2\cos\left(\frac{n\pi x}{a}\right)}{2} \right\} dx = 1$$

$$\text{(or) } P = A^2 \left[\left(\frac{x}{2}\right) - \left(\frac{1}{2}\right) \frac{\sin\left(\frac{2\pi n x}{a}\right)}{\left(\frac{2n\pi}{a}\right)} \right]_0^a = 1$$

$$\text{(or) } P = A^2 \left[\left(\frac{a}{2}\right) - \left(\frac{1}{2}\right) \frac{\sin\left(\frac{2\pi n a}{a}\right)}{\left(\frac{2n\pi}{a}\right)} \right] = 1$$



$$\text{(or) } P = A^2 \left[\left(\frac{a}{2}\right) - \left(\frac{1}{2}\right) \frac{\sin(2\pi n)}{\left(\frac{2n\pi}{a}\right)} \right] = 1 \qquad (11)$$

We know that $\sin n\pi = 0 \therefore \sin 2n\pi = 0$

Equation (11) can be rewritten as $\frac{A^2 a}{2} = 1$

$$\text{(or) } A^2 = \frac{2}{a}$$

$$\text{(or) } A = \sqrt{\frac{2}{a}}$$

Substituting the value of 'A' in equation (5), we get

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \qquad (12)$$

Equation (12) is said to be *normalized wave function*

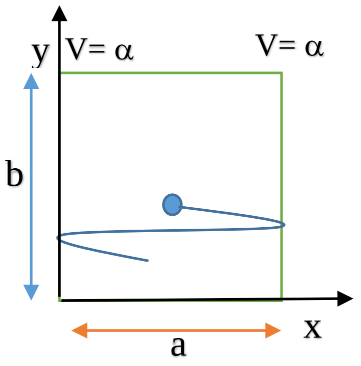
4.9 Particle in a two dimensional potential box (2D)

The solution of one dimensional box can be extended for a two dimensional potential box. In a two dimensional potential box, the particle (electron) can move in *x* and *y* directions. Therefore instead of one quantum number *n*, we have to use quantum numbers n_x and n_y corresponding the two coordinate axis (i.e.,) *x* and *y* respectively.

Let us consider a particle enclosed in a 2-D potential box of length *a* and *b* along *x* and *y* axis respectively as shown in figure. Since the particle inside the 2D box has elastic collision with the walls, the potential energy of the electron inside the box is constant and can be taken as zero for simplicity.

Therefore, we can say that outside the box and on the wall of the box, the potential energy is α. Therefore the boundary conditions are

Sl.No	Boundary conditions	Inference
1	V(*x, y*) = 0 when 0 < *x* < *a* V(*x, y*) = 0 when 0 < *x* < *b*	Within this boundary the particle exist and we need to find the energy values and wave function
2	V(*x, y*) = α when 0 ≥ *x* ≥ *a* V(*x, y*) = α when 0 ≥ *x* ≥ *b*	In this area the particle does not exist and therefore the wave function = 0



To find the wave function of the particle within the boundary Conditions (1). Let us consider the 2-D Schrodinger time independent Wave equations.

i.e., $$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{2m}{\hbar^2}[E-V]\psi=0 \qquad (3)$$

Since V = 0 (for a free particle), we can write equation (3) as

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{2m}{\hbar^2}E\psi=0 \qquad (4)$$

Equation (4) is a partial differential equation, in which ψ is a function of two variables, *x* and *y*

We can solve this using method of separation of variables. The solution for equation (4) can be written as $\psi(x,y)=X(x)Y(y)$

Which means ψ is a function of *x and* y and is equal to product of 2 functions *X* and *Y*. where X is a function of *x* only and Y is a function of *y* only.

Therefore, we can say that the solution for equation (4) is $\psi = XY$ (5)

Differentiating equation (5) partially with respect to *x* twice, we get

$$\frac{\partial\psi}{\partial x}=Y\frac{dX}{dx}$$

$$\frac{\partial^2\psi}{\partial x^2}=Y\frac{d^2X}{dx^2} \qquad (6)$$

Similarly, differentiating equation (5) partially with respect to *y* twice, we get

$$\frac{\partial\psi}{\partial y}=X\frac{dY}{dy}$$

$$\frac{\partial^2\psi}{\partial y^2}=X\frac{d^2Y}{dy^2} \qquad (7)$$

Substituting equations (5), (6) and (7) in equation (4), we get

$$Y\frac{d^2X}{dx^2}+X\frac{d^2Y}{dy^2}+\frac{2m}{\hbar^2}EXY=0$$

(or) $Y\frac{d^2X}{dx^2}+X\frac{d^2Y}{dy^2}=-\left[\frac{2m}{\hbar^2}E\right]XY$ (8)

Dividing equation (8) by *XY* on both sides we get

$$\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}=-\left[\frac{2m}{\hbar^2}E\right] \quad (9)$$

(or) $\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}=-\left[k_x^2+k_y^2\right]$ (10)

Where $\frac{2m}{\hbar^2}E=k_x^2+k_y^2$ (11)

In equation (10), LHS is independent of each other and is equal to a constant in RHS. Therefore, we can equate each term of LHS to each constant in RHS

Therefore, we can write

$$\frac{1}{X}\frac{d^2X}{dx^2}=-k_x^2 \text{ (or) } \frac{d^2X}{dx^2}=-k_x^2X \text{ (or) } \frac{d^2X}{dx^2}+k_x^2X=0 \quad (12)$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2}=-k_y^2 \text{ (or) } \frac{d^2Y}{dy^2}=-k_y^2Y \text{ (or) } \frac{d^2Y}{dy^2}+k_y^2Y=0 \quad (13)$$

Equations (12) & (13) represents the differential equations in *x* and *y* co-ordinates. The solution for equation (13) can be written as

$$X(x)=A_x\sin k_xx+B_x\cos k_xx \quad (14)$$

Where A and B are arbitrary constants, which can be found by applying boundary conditions.

Boundary conditions

(i) **When *x* = 0: *X* = 0**

Equation (14) becomes, $0 = 0 + B_x$

Therefore $\boldsymbol{B_x = 0}$ (15)

(ii) when *x* = *a*; *X* = 0,

Equation (14) becomes $0 = A_x \sin k_x a$.

Since $A_x \neq 0$ (because if $A_x = 0$, then *X(x)* becomes zero and the particle is not there)

$\therefore \sin k_xa=0$

We know that $\sin n_x\pi=0$

Comparing the above two equations we can write, $k_xa=n_x\pi$

(or) $k_x=\frac{n_x\pi}{a}$ (16)

Substituting equations (15) & (16) in equation (14) we get

$$X(x) = A_x \sin\frac{n_x \pi x}{a} \qquad (17)$$

Equation (17) represents the un-normalized wave function

Normalization

Equation (17) can be normalized by integrating it within the boundary conditions limit. i.e., 0 to *a*

Therefore, we can write $\int_0^a |X(x)|^2 dx = 1$

(or) $\int_0^a A_x^2 \sin^2 \frac{n_x^2 \pi x}{a} dx = 1$

Solving the above equation, we get $\frac{A_x^2 a}{2} = 1$ (or) $A_x = \sqrt{\frac{2}{a}}$ (18)

Then, equation (17) becomes $X(x) = \sqrt{\frac{2}{a}} \sin\frac{n_x \pi x}{a}$ (19)

Similarly by solving equation (13) with the boundary condition *0* to *b*, we can write

$$Y(y) = \sqrt{\frac{2}{b}} \sin\frac{n_y \pi y}{b} \qquad (20)$$

Eigen functions

The complete wave function for equation (4) can be written as

$$\psi(x,y) = X(x)Y(y)$$

Substituting equations (19) and (20) in the above equation, we get

$$\psi_{n_x n_y} = \frac{2}{\sqrt{a}} \sin\frac{n_x \pi x}{a} \frac{2}{\sqrt{a}} \sin\frac{n_y \pi y}{b}$$

$$\therefore \psi_{n_x n_y} = \frac{2}{\sqrt{ab}} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} \qquad (21)$$

Equation (21) represents the Eigen function for an electron in a 2D-box.

Eigen values

From Equation (11) we can write $\frac{2m}{\hbar^2} E = k_x^2 + k_y^2$

$$\therefore E = \frac{\hbar^2}{2m}[k_x^2 + k_y^2] \qquad (22)$$

From equation (16), we can write $k_x^2 = \frac{n_x^2 \pi^2}{a^2}$

Similarly, $k_y^2 = \frac{n_y^2 \pi^2}{b^2}$

Substituting these equation in (22), we get $\therefore E = \frac{\hbar^2}{2m}\left(\frac{n_x^2\pi^2}{a^2} + \frac{n_y^2\pi^2}{b^2}\right)$

(or) $\therefore E = \frac{h^2 \times \pi^2}{4\pi^2 \times 2m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$

(or) $E_{n_x n_y} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$ (23)

This the energy eigen values of an electron in a 2D-rectangular box.

Square box

For a square box $a = b$

Therefore, we can write equation (23) as $E_{n_x n_y} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2\right)$ (24)

Corresponding normalized wave function of an electron in a square box can be obtained from equation (21) as $\therefore \psi_{n_x n_y} = \sqrt{\frac{2}{a} \times \frac{2}{a}} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{a}$

Therefore, $\therefore \psi_{n_x n_y} = \frac{2}{a} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{a}$ (25)

These equations (24) and (25) can lead to several combination of two quantum numbers (n_x *and* n_y) leads to different energy eigen values and eigen functions.

Example

(i) if $n_x = n_y = 1$; $E_{11} = \frac{2h^2}{8ma^2}$ (26)

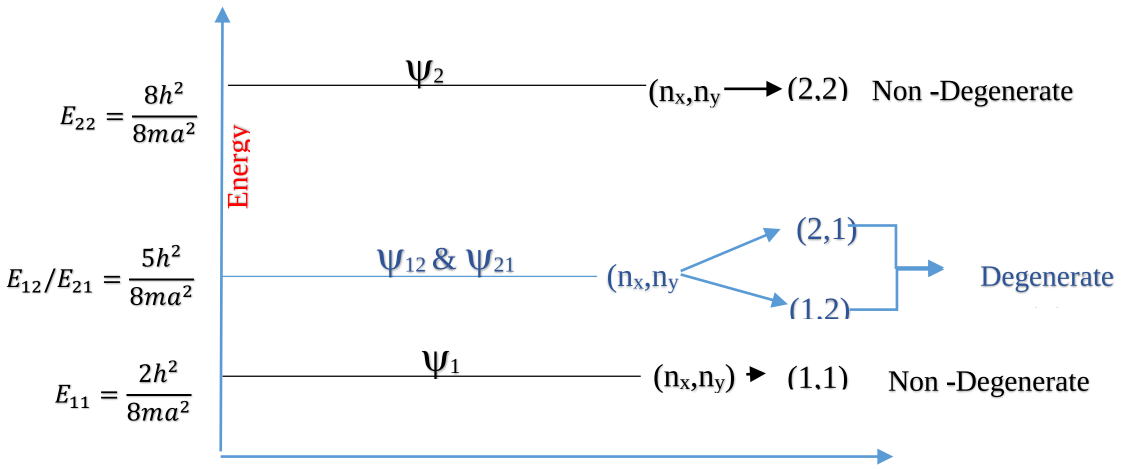
The corresponding wave function is $\psi_{11} = \frac{2}{a} \sin\frac{\pi x}{a} \sin\frac{\pi y}{a}$ (27)

(2) if $n_x = 1$; $n_y = 2$; $E_{12} = E_{21} = \frac{5h^2}{8ma^2}$ (28)

The corresponding wave function is $\psi_{12} = \frac{2}{a} \sin\frac{\pi x}{a} \sin\frac{2\pi y}{a}$

$$\psi_{21} = \frac{2}{a} \sin\frac{2\pi x}{a} \sin\frac{\pi y}{a} \quad (29)$$

Thus, from equations (26) & (28) we can say that the energy Eigen values are discrete and are quantized as shown in figure



4.10. Particle in a three dimensional potential box

The solution of one-dimensional potential box can be extended for a three dimensional potential box. In a three dimensional potential box, the particle (electron) can move in any direction in space. Therefore instead on one quantum number we have to use three quantum number n_x, n_y and n_z corresponding to the three coordinate axis (i.e.,) x, y and z respectively.

Let us consider a particle enclosed in a 3 – dimensional potential box of length *a*, *b* and *c* long *x*, *y* nd *z* axis respectively. Since particle inside the 3D box has elastic collisions with the walls, the potential energy of the electron inside the box is constant and can be taken as zero for simplicity.

Therefore, we can say that outside the box and on the wall of the box, the potential energy is α. Therefore, boundary conditions are:

Sl.No	Boundary conditions	Inference
1	$V(x, y, z) = 0$ when $0 < x < a$ $V(x, y, z) = 0$ when $0 < x < b$ $V(x, y, z) = 0$ when $0 < x < c$	Within this boundary the particle exist and we need to find the energy values and wave function
2	$V(x, y, z) = \alpha$ when $0 \geq x \geq a$ $V(x, y, z) = \alpha$ when $0 \geq x \geq b$ $V(x, y, z) = 0$ when $0 < x <$ c	In this area the particle does not exist and therefore the wave function = 0

To find the wavefunctions of the particle within the boundary conditions (1), let us consider the 3-D Schrodinger wave equation

i.e., $$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{2m}{\hbar^2}[E-V]\psi=0 \qquad (3)$$

Since V = 0 (for a free particle), we can write equation (3) as

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{2m}{\hbar^2}E\psi=0 \qquad (4)$$

Equation (4) is a partial differential equation, in which ψ is a function of three variables, x, y and z

We can solve this using method of separation of variables. The solution for equation (4) can be written as $\psi(x,y,z) = X(x)Y(y)Z(z)$

Which means ψ is a function of x, y, z and is equal to product of 3 functions X, Y and Z. where X is a function of x only, Y is a function of y only and Z is a function of z only.

Therefore, we can say that the solution for equation (4) is $\psi = XYZ$ (5)

Differentiating equation (5) partially with respect to x twice, we get

$$\frac{\partial\psi}{\partial x} = YZ\frac{dX}{dx}$$

$$\frac{\partial^2\psi}{\partial x^2} = YZ\frac{d^2X}{dx^2} \qquad (6)$$

Similarly, differentiating equation (5) partially with respect to y twice, we get

$$\frac{\partial\psi}{\partial y} = XZ\frac{dY}{dy}$$

$$\frac{\partial^2\psi}{\partial y^2} = XZ\frac{d^2Y}{dy^2} \qquad (7)$$

Similarly, differentiating equation (5) partially with respect to z twice, we get

$$\frac{\partial\psi}{\partial z} = XY\frac{dZ}{dz}$$

$$\frac{\partial^2\psi}{\partial y^2} = XY\frac{d^2Z}{dz^2} \qquad (8)$$

Substituting equations (5), (6) and (7) in equation (4), we get

$$YZ\frac{d^2X}{dx^2} + XZ\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{dz^2} + \frac{2m}{\hbar^2}EXYZ = 0$$

(or) $$YZ\frac{d^2X}{dx^2} + XZ\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{dz^2} = -\left[\frac{2m}{\hbar^2}E\right]XYZ \qquad (9)$$

Dividing equation (8) by XYZ on both sides we get

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = -\left[\frac{2m}{\hbar^2}E\right] \qquad (10)$$

(or) $$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Y}{dz^2} = -\left[k_x^2 + k_y^2 + k_z^2\right] \qquad (11)$$

Where $\frac{2mE}{\hbar^2} = k_x^2 + k_y^2 + k_z^2$ (12)

In equation (10), LHS is independent of each other and is equal to a constant in RHS. Therefore, we can equate each term of LHS to each constant in RHS

Therefore, we can write

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k_x^2 \text{ (or) } \frac{d^2X}{dx^2} = -k_x^2 X \text{ (or) } \frac{d^2X}{dx^2} + k_x^2 X = 0 \qquad (13)$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = -k_y^2 \text{ (or) } \frac{d^2Y}{dy^2} = -k_y^2 Y \text{ (or) } \frac{d^2Y}{dy^2} + k_y^2 Y = 0 \qquad (14)$$

$$\frac{1}{Z}\frac{d^2Z}{dz^2} = -k_z^2 \text{ (or) } \frac{d^2Z}{dz^2} = -k_z^2 Z \text{ (or) } \frac{d^2Z}{dz^2} + k_z^2 Z = 0 \qquad (15)$$

Equations (12) , (13) and (14) represents the differential equations in *x, y* and *z* co-ordinates. The solution for equation (13) can be written as

$$X(x) = A_x \sin k_x x + B_x \cos k_x x \qquad (16)$$

Where A and B are arbitrary constants, which can be found by applying boundary conditions.

Boundary conditions

(i) **When $x = 0$: $X = 0$**

Equation (14) becomes, $0 = 0 + B_x$

Therefore $\mathbf{B_x = 0}$ (17)

(ii) when $x = a$; $X = 0$,

Equation (14) becomes $0 = A_x \sin k_x a$.

Since $A_x \neq 0$ (because if $A_x = 0$, then $X(x)$ becomes zero and the particle is not there)

$$\therefore \sin k_x a = 0$$

We know that $\sin n_x \pi = 0$

Comparing the above two equations we can write, $k_x a = n_x \pi$

$$\text{(or) } k_x = \frac{n_x \pi}{a} \qquad (18)$$

Substituting equations (15) & (16) in equation (14) we get

$$X(x) = A_x \sin \frac{n_x \pi x}{a} \qquad (19)$$

Equation (17) represents the un-normalized wave function

Normalization

Equation (17) can be normalized by integrating it within the boundary conditions limit. i.e., 0 to *a*

Therefore, we can write $\int_0^a |X(x)|^2 dx = 1$

(or) $\int_0^a A_x^2 \sin^2 \frac{n_x \pi x}{a} dx = 1$

Solving the above equation, we get $\frac{A_x^2 a}{2} = 1$ (or) $A_x = \sqrt{\frac{2}{a}}$ (20)

Then, equation (17) becomes $X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a}$ (21)

Similarly by solving equations (13) and (14) with the boundary condition *0* to *b* and *0* to *c*, we can write

$$Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \quad (22)$$

$$Z(z) = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c} \quad (23)$$

Eigen functions

The complete wave function for equation (4) can be written as

$$\psi(x,y,z) = X(x)Y(y)Z(z)$$

Substituting equations (19) and (20) in the above equation, we get

$$\psi_{n_x n_y n_z} = \frac{2}{\sqrt{a}} \sin \frac{n_x \pi x}{a} \frac{2}{\sqrt{b}} \sin \frac{n_y \pi y}{b} \frac{2}{\sqrt{c}} \sin \frac{n_z \pi z}{c}$$

$$\psi_{n_x n_y n_z} = \frac{2\sqrt{2}}{\sqrt{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \quad (24)$$

Equation (24) represents the Eigen function for an electron in a 3D-box.

Eigen values

From Equation (11) we can write $\frac{2m}{\hbar^2} E = k_x^2 + k_y^2 + k_z^2$

$$\therefore E = \frac{\hbar^2}{2m}[k_x^2 + k_y^2 + k_z^2] \quad (25)$$

From equation (16), we can write $k_x^2 = \frac{n_x^2 \pi^2}{a^2}$

Similarly, $k_y^2 = \frac{n_y^2 \pi^2}{b^2}$, $k_z^2 = \frac{n_z^2 \pi^2}{c^2}$

Substituting these equation in (25), we get $\therefore E = \frac{\hbar^2}{2m}\left(\frac{{n_x}^2\pi^2}{a^2} + \frac{{n_y}^2\pi^2}{b^2} + \frac{{n_z}^2\pi^2}{c^2}\right)$

(or) $\therefore E = \frac{h^2 \times \pi^2}{4\pi^2 \times 2m}\left(\frac{{n_x}^2}{a^2} + \frac{{n_y}^2}{b^2} + \frac{{n_z}^2}{c^2}\right)$

(or) $E_{n_x n_y} = \frac{h^2}{8m}\left(\frac{{n_x}^2}{a^2} + \frac{{n_y}^2}{b^2} + \frac{{n_z}^2}{c^2}\right)$ (26)

This the energy eigen values of an electron in a 3D-rectangular box.

Cubical box

For a cubical box, $a = b = c$,

Therefore, we can write equation (26) as $E_{n_x n_y n_z} = \frac{h^2}{8ma^2}\left({n_x}^2 + {n_y}^2 + {n_z}^2\right)$ (24)

Corresponding normalized wave function of an electron in a cubical box can be obtained from equation (24) as $\therefore \psi_{n_x n_y n_z} = \sqrt{\frac{2}{a} \times \frac{2}{a} \times \frac{2}{a}} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{a} \sin\frac{n_z \pi z}{a}$

$\therefore \psi_{n_x n_y n_z} = \sqrt{\frac{8}{a^3}} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{a} \sin\frac{n_z \pi z}{a}$ (27)

These equations (26) and (27) can lead to several combination of three quantum numbers (n_x, n_y *and* n_z) leads to different energy eigen values and eigen functions.

Example

(i) if $n_x = n_y = n_z = 1$; $E_{111} = \frac{2h^2}{8ma^2}$ (28)

The corresponding wave function is $\psi_{111} = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{\pi z}{a}$ (29)

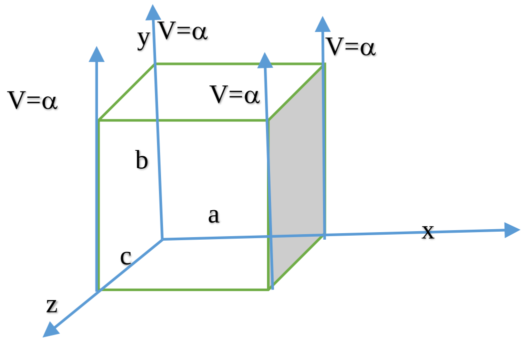
(2) if $n_x = 1$; $n_y = 1$; $n_z = 2$; $E_{112} = E_{121} = E_{211} \frac{6h^2}{8ma^2}$ (30)

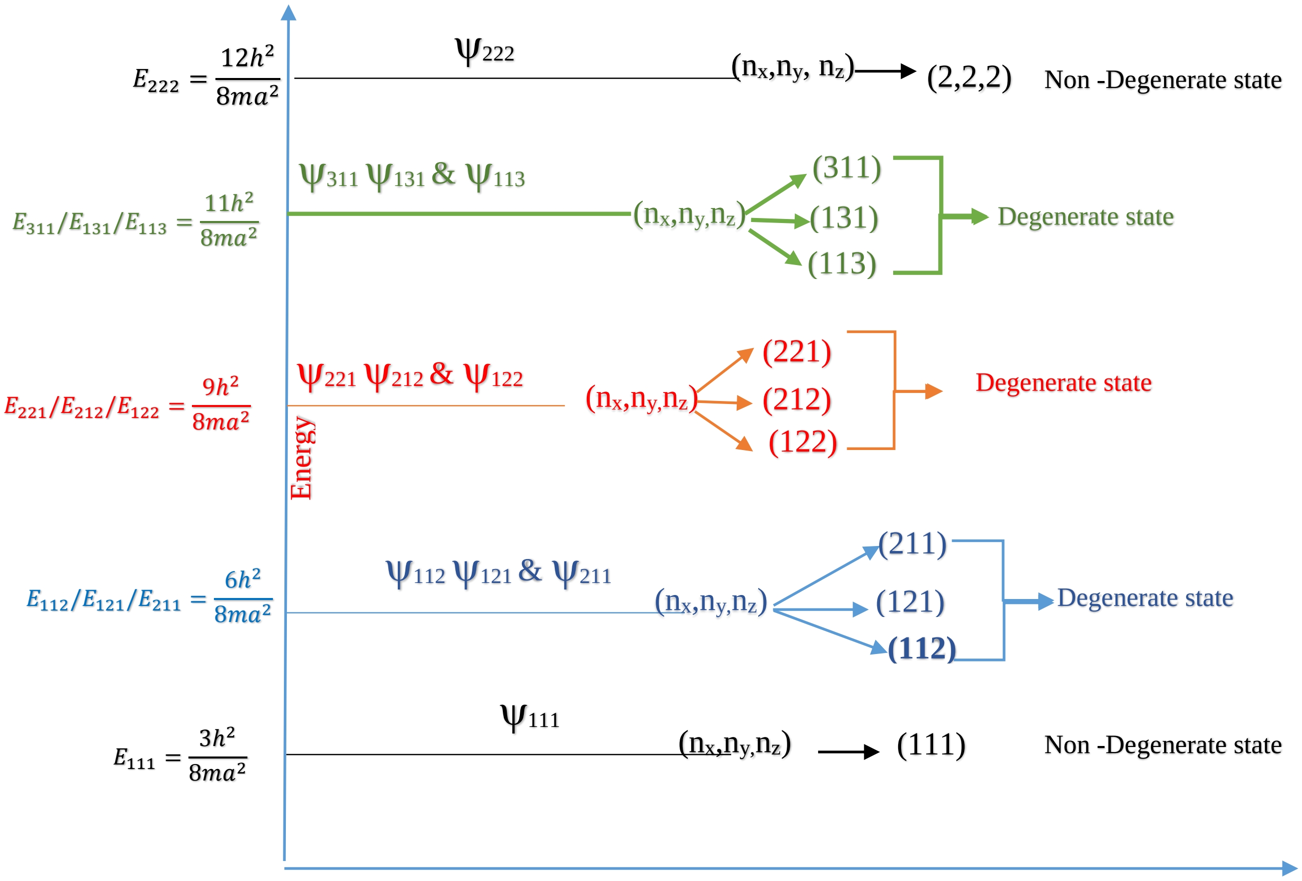
The corresponding wave function is $\psi_{112} = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{2\pi z}{a}$

$$\psi_{121} = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{2\pi y}{a} \sin\frac{\pi z}{a}$$

$$\psi_{211} = \sqrt{\frac{8}{a^3}} \sin\frac{2\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{\pi z}{a} \quad (31)$$

The energy values for various set of quantum number combination is shown in figure. Therefore, we can say that the energy Eigen values are discrete and are quantized.





Degeneracy and Non – Degeneracy

Degeneracy

It is seen from equations (30) & (31) for several combination of quantum numbers we have same energy eigen values but different eigen functions. Such states and energy levels are called Degenerate states. The three combination of quantum numbers (112), (121) and (211) which gives same eigen value but different eigen functions are called *3 – fold degenerate state.*

Non – degeneracy

For various combinations of quantum number if we have same energy eigen value and same eigen function (one) then such states and energy levels are called *non – degenerate state.*

4.11. Probabilities and correspondence principle

According to Neils Bohr, any new theory (or) any new description of nature must agree with the old theory, wherein we get correct results. This conceptual thinking exactly matches witht e classical theory and quantum theory.

Correspondence principle

According to correspondence principle *"For large value of principal quantum number 'n' the quantum mechanics merges with classical mechanics"* i.e., the classical theory and quantum theory will have same results.

In other words, we can say that the quantum mechanics under certain limits like high energy (or) high mass (or) high length (or) higher quantum number etc. it approaches classical mechanics.

Quantum mechanics ⇒ certain limits ⇒ Classical mechanics

Example

For a particle enclosed in one dimensional potential well, according to correspondence principle, the quantum theory merges with the classical theory, for large value of n and inturn for large value of Energy values (E).

Using Eigen value (Proof 1)

Let us discuss how the quantum mechanics merges with classical mechanics for a particle enclosed in a one dimensional potential well. We know that the energy eigen value for a particle in the nth level, enclosed in a one dimensional potential well is $E_n = \frac{n^2h^2}{8ma^2}$ (1)

The energy eigen value for a particle in $(n+1)^{th}$ level is $E_{n+1} = \frac{(n+1)^2h^2}{8ma^2}$ (2)

Let us find the difference (or) change in energy from $(n+1)^{th}$ energy level to n^{th} energy level

Therefore, change in energy $\Delta E = E_{n+1} - E_n$ (3)

Substituting equation (1) and equation (2) in equation (3) we get

$$\Delta E = \frac{(n+1)^2h^2}{8ma^2} - \frac{n^2h^2}{8ma^2}$$

(or) $$\Delta E = \frac{h^2}{8ma^2}((n+1)^2 - n^2)$$

(or) $$\Delta E = \frac{h^2}{8ma^2}(n^2 + 2n + 1 - n^2)$$

(or) $$\Delta E = \frac{h^2}{8ma^2}(2n+1) \quad (4)$$

To find $\frac{\Delta E}{E}$

From equations (4) & (1), we get $\frac{\Delta E}{E} = \frac{\frac{h^2}{8ma^2}(2n+1)}{\frac{n^2h^2}{8ma^2}}$

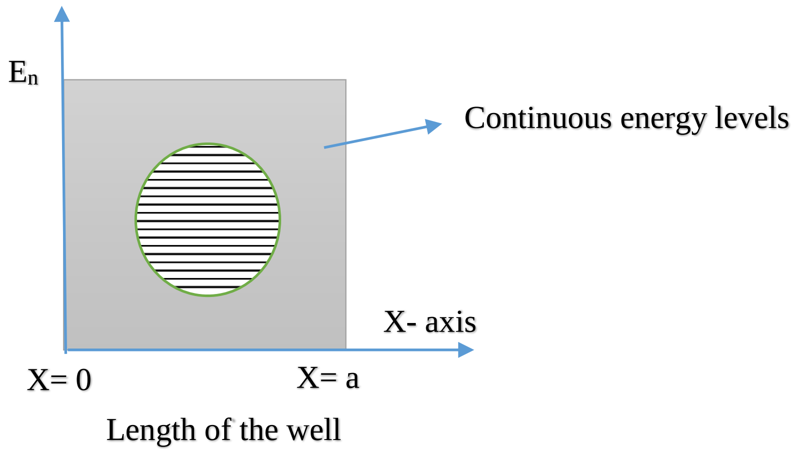
(or) $\frac{\Delta E}{E} = \frac{(2n+1)}{n^2} = \frac{2n}{n^2} + \frac{1}{n^2}$ (or) $\frac{\Delta E}{E} = \frac{2}{n} + \frac{1}{n^2}$ (5)

For large values of 'n' i.e., If n is ∞, equation (5) becomes $\frac{\Delta E}{E} = \frac{2}{\infty} + \frac{1}{\infty^2}$

(or) $\frac{\Delta E}{E} = \frac{1}{\infty}$

$\therefore \frac{\Delta E}{E} = 0$ **(6)**

The above equation (6) indicates that for large values of *n* the difference between the energy levels approaches zero and hence we can say that for large values of *n*, the energy values are continuous rather than discrete.



Using Eigen function (Proof 2)

We can also verify the same using the Eigen functions by finding probability of wave function.

Probabilities

We know that the wave function for a particle enclosed in a one dimensional potential well is

$$\psi_n = \sqrt{\frac{2}{a}} \sin\frac{n\pi x}{a} \quad (7)$$

The probability of the wave function for n^{th} state shall be written as $|\psi_n|^2$.

For *n* = *1*

For ground state, i.e., for n = 1, we get the normalised wave function in which the probability of finding the particle is maximum at middle

For n = 2

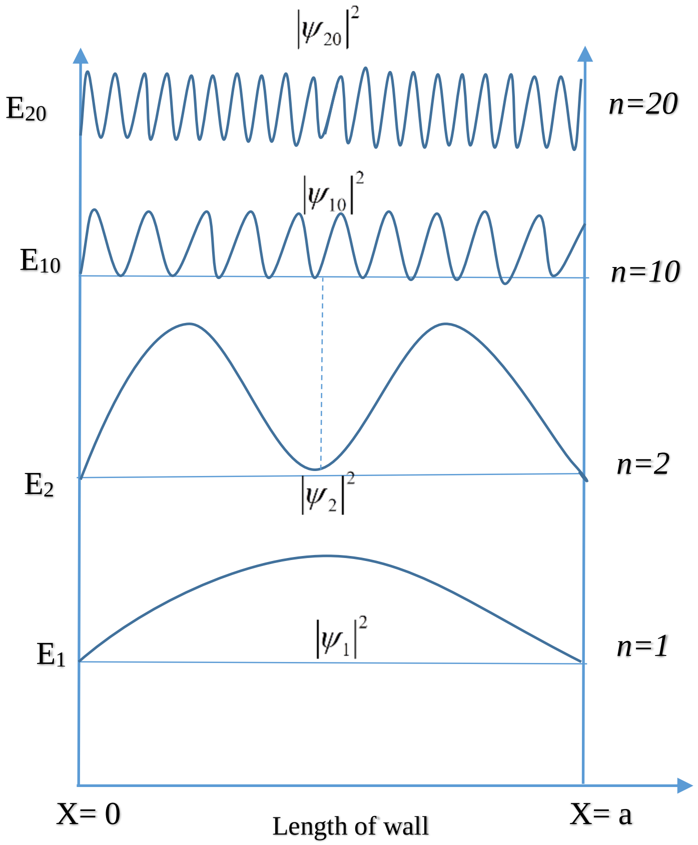
For the first excited state i.e., n = 2, we get the normalised wave function in which the probability of finding the particle is minimum at the middle.

For n = 10

For the 9th excited state, we get the normalized wave function in which the probability of finding the particle increases in all areas of the well.

For n = 20

For higher values of energy such as (E_{20}), (E_{30}), i.e., n = 20, 30, etc., the probability of finding the particle is same (or) constant throughout the particular energy level.



Classical Proof

If we see the energy level of the particle classically, then the probability of finding that particle is constant. Therefore, my merging the quantum wave functions for n = 20 and classical wave functions for $n = 20$, we can see that the probability of finding the particle in a quantum wave function is almost the same as that of the probability of finding the particle in a classical wave function.

Conclusion

Thus for large values of *n* (or) for large value of energies (E), the normalized quantum wavefunctions merges with classical wave functions. i.e., Quantum mechanics merges with classical mechanics. Hence correspondence principle is proved.

Part – A Question and Answer

1. What is Compton Wavelength?

The shift in wavelength corresponding to the scattering angle of 90° is called Compton wavelength.

W.K.T Compton shift $(\Delta\lambda) = \frac{h}{m_0 C}(1 - \cos 90°) = \frac{6.626 \times 10^{-34}}{9.11 \times 10^{-31} \times 3 \times 10^{-8}} = 0.02424 A°$

2. State De-Broglie's Hypothesis (or) explain the concept of wave nature? (or) What is meant by matter waves? Give the origin of concept?

The light exhibit dual nature such as a particle & wave. De-Broglie suggested that an electron, which is a particle, can also behave as a wave and exhibit the dual nature. Thus the wave associated with the material particle are called matter waves $\therefore De - Broglie\ wavelength\ (\lambda) = \frac{h}{mv}$

3. What is the physical significance of a wave function?

(i) The probability of finding the particle in space at any given instant of time is characterized by a function ψ (x,y,z) called wave function

(ii) It relates the particle and the wave statistically

(iii) It gives the information about the particle behavior

(iv) It is a complex quantity

(v) $\psi\psi^*$ is a probability density of the particle , which is real and positive.

4. What is meant by photon? Give any two properties?

Photons are discrete energy values in the form of small quanta's of definite frequency (or) wavelength.

Properties:

(i) They does not have any charge and they will not intense

(ii) The energy & momentum of the photon is given by E = hυ and p = mc

5. Define Compton effect and Compton shift?

When a photon of energy "hυ" collides with a scattering element. The scattering beam has two components as one of them have same frequency (or) wavelength as that of incident radiation and the other have lower frequency (or) higher wavelength . This effect is called Compton effect. The shift in wavelength due to scattered x- rays is called Compton shift.

6. Define Eigen value and Eigen function?

Energy of a particle moving in one dimensional box of width 'a' is $E_n = \frac{n^2 h^2}{8ma^2}$.for each value of 'n' there is a energy level. Where E_n is called Eigen value.

For every quantum state, there is a corresponding wave function 'ψ_n' called Eigen function given by $\psi_n = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$

7. What is meant by degenerate (or) non – degenerate state?

For various combinations of quantum numbers if we get some Eigen value at different eigen functions, then it is called degenerate state.

For various combinations of quantum numbers if we get same eigen values & eigen functions, then it is called non-degenerate state.

8. What are the properties of matter waves?

(ix) Matter waves are not electromagnetic waves.

(x) Matter waves are new kind of waves in which due to the motion of the charged particles, electromagnetic waves are produced.

(xi) Lighter particles will have high wavelength

(xii) Particles moving with less velocity will have high wavelength

(xiii) The velocity of matter wave is not a constant, it depends on the velocity of the particle.

(xiv) If the velocity of the particle is infinite then the wavelength of matter wave is indeterminate(λ=0)

(xv) The wave and particle aspects cannot appear together

(xvi) Locating the exact position of the particle in the wave is uncertain.

9. For a free particle moving with a one dimensional potential box, the ground state energy cannot be zero, why?

For a free particle moving within a one dimensional potential box, when *n=0* the wave function is zero for all values of *x* i.e., it is zero even within the potential box. This would mean that the particle is not present within the box. Therefore the state with *n=0* is not allowed.

10. How de-Broglie justified his concept?

Our universe is fully composed of light and matter

Nature loves symmetry. If radiation like light can act like wave and particle, then material particles (Eg: proton, neutron, etc.,) should also act as particle and wave

Every moving particle has always associated with a wave.

Part – B

1. Define Compton effect. Derive an expression for the wavelength of the scattered photon. Also briefly explain the experimental verification
2. Derive Schrodinger time dependent and independent wave equation for one dimensional box.
3. Arrive Schrodinger wave equation and apply the same to determine the particle in 1-D box and arrive the corresponding Eigen values and functions.
4. Derive the time independent wave equation and apply the same for a particle in a 2-D rectangular box to obtain the corresponding Eigen values and eigen functions.
5. Derive the time independent wave equation and apply the same for a particle in a 3-D rectangular box to obtain the corresponding Eigen values and eigen functions.
6. State prove correspondence principle using Eigen values and Eigen functions.