MODULE-1
QUANTUM MECHANICS

Introduction

In classical mechanics, the future history of a particle is completely determined by its initial position and momentum together with the forces that act upon it. In everyday world, these quantities can all be determined well enough for the predictions of Newtonian mechanics to agree with what we find. Quantum mechanics also arrives at relationships between observable quantities, but the uncertainty principle suggests that the nature of an observable quantity is different in the atomic realm.The quantities whose relationships quantum mechanics explores are probabilities instead of asserting for exactness.

However classical mechanics turns out to be just an approximate version of quantum mechanics, the certainties of classical mechanics are illusory and their apparent agreement with experiment occurs because ordinary objects consists of so many individual atoms that departs from average behavior which are unnoticeable.

The application of quantum mechanics to problems involving nuclei, atoms,

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molecules, and matter in the solid state made it possible to understand a vast body of data which is vital for any theory leading to predictions of remarkable accuracy. Quantum mechanics has survived every experimental test thus far of even its most unexpected conclusions.

Wave-Particle Dualism

In the year 1924 Louis de Broglie speculated that the particle may show the wave behavior, almost after two decades of discovery of particle nature of wave by Einstein's photo-electric effect and Compton effect in the year 1905. de-Broglie proposed that moving objects have wave as well as particle characteristics and postulated that the particle like electrons, protons in motion can be associated with waves whose wavelength is related to their momentum. The existence of de-Broglie waves was experimentally demonstrated by Davisson and Germer's experiment in the year 1927 and the duality principle thus provided the starting point of Heisenberg uncertainty principle leading towards the development of quantum mechanics.

de-Broglie Wavelength

Consider a particle of mass 'm' moving with the velocity of light, then according to Einstein's mass-energy relation the equation for particle can be

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written as,

$$E = mc^2 \tag{1}$$

From Planck's law the energy equation for the light can be written as,

$$E = h\nu \tag{2}$$

comparing equation (1)and (2)we get

$$mc^2 = h\nu$$
$$mc^2 = \frac{hc}{\lambda}$$
$$or\ \lambda = \frac{h}{mc} \tag{3}$$

Equation (3) is valid only for photon,

therefore for all other particles whose velocity is less than the velocity of light

$$\boxed{\lambda = \frac{h}{mv}\ or\ \lambda = \frac{h}{p}} \tag{4}$$

equation (4) represents the de-Broglie wavelength.

where h is the Planck's constant $(6.625 \times 10^{-34} Js)$.

v is the velocity associated with the particle.

m is the mass of the particle.

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Other Forms of de-Broglie Wavelength

$$\lambda = \frac{h}{\sqrt{2mE_k}}$$
$$\lambda = \frac{h}{\sqrt{2meV}}$$

de-Broglie's Wavelength for Electron

Consider the kinetic energy relation $E_k = \frac{1}{2}mv^2$

Multiply and divide by 'm' on RHS in the above equation

$\implies E_k = \frac{m^2v^2}{2m}$ or $E_k = \frac{p^2}{2m}$

$\implies p = \sqrt{2mE_k}$

Substituting for p in de-Broglie's equation, we get

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

But the kinetic energy with which the electron moves is given by,

$E_k = eV$

$$\implies \boxed{\lambda = \frac{h}{\sqrt{2meV}}}$$

Matter Waves

Matter waves are the waves associated with moving particle.

Characteristics of Matter Waves

1. Matter waves are not electromagnetic in nature since they do not depend on the charge of the particle.
2. Lighter the particle, greater is the wavelength associated with because

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$\lambda \propto \frac{1}{m}$

3. Greater is the velocity of the particle, smaller is the wavelength associated with it because $\lambda \propto \frac{1}{v}$

4. The velocity of matter waves is greater than the velocity of light. This indicates that matter waves are probability waves.

Wave Packet, Phase velocity and Group Velocity

Wave Packet: If two or more waves which has slightly different wavelength superimposed on each other then the resultant pattern emerges as a variation in amplitude, this variation represents wave group and is called as wave packet.

Group Velocity: Group velocity is the velocity with which the wavepacket propagates which is formed due to superimposition of two or more waves with slightly different wavelength. The group velocity of a particle associated with wave is represented as,

$$v_{group} = \frac{d\omega}{dk}$$

Phase velocity: If a point is marked on a travelling wave then that point becomes the representative point for that particular phase , then the velocity with which this phase difference of a matter waves is propagated is called as

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phase velocity. The phase velocity of a particle wave is represented as,

$$v_{phase} = \frac{\omega}{k}$$

Heisenberg's uncertainty principle and its physical significance

Heisenberg's Uncertainty Principle states that " It is impossible to measure simultaneously both the position and momentum of a particle accurately". If we make an effort to measure very accurately the position of a particle, it leads to large uncertainty in the measurement of momentum and vice versa". And the uncertainty relations are given by,

$$\boxed{\triangle p.\triangle x \geq \frac{h}{4\pi}}$$

$$\boxed{\triangle E.\triangle t \geq \frac{h}{4\pi}}$$

$$\boxed{\triangle L.\triangle \theta \geq \frac{h}{4\pi}}$$

where,

$\triangle$x=Uncertainty in measurement of position

$\triangle$p=Uncertainty in measurement of momentum

$\triangle$E=Uncertainty in measurement of energy

$\triangle$t= Uncertainty in measurement of time

$\triangle$L=Uncertainty in measurement of angular momentum

$\triangle\theta$=Uncertainty in measurement of angular displacement

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Physical significance

One should not think of exact position or an accurate value for momentum of a particle. Instead, one should think of the probability of finding the particle at a certain position. Thus in quantum mechanics the word Exactness is replaced by Probability.

Application of Heisenberg's Uncertainty Principle

Non-existence of Electron Inside the Nucleus

Considering the Heisenberg's uncertainty equation,

$\triangle p. \triangle x \geq \frac{h}{4\pi}$

where $\triangle x \leq 10^{-14}\ m$

i.e, the maximum uncertainty of finding the electron inside the nucleus is equal to 1 Fermi or $10^{-14} m$ using this in uncertainty equation, we have

$\triangle p_x \geq \frac{6.623 \times 10^{-34}}{4\pi \times 10^{-14}}$

$\triangle p_x \geq 5.27 \times 10^{-21}\ kg\ m/s$

since $\triangle x$ is the maximum uncertainty in determining the position of a electron inside the nucleus, then $\triangle p$ becomes the minimum uncertainty in determining the momentum of a electron.

Therefore $\triangle p_{min} = p_{min} \geq 5.27 \times 10^{-21}\ kg\ m/s$

Then using the kinetic energy equation in terms of momentum we shall find the minimum energy required for an electron to exist inside the nucleus.

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$$E = \frac{p^2}{2m}$$

$$E = \frac{(5.27 \times 10^{-21})^2}{2 \times 9.1 \times 10^{-31}}$$

$$E_{min} = 95 \times 10^6 \ eV \ = 95 \ MeV$$

Conclusion: For an electron to exist inside the nucleus it should posses the minimum energy of 95 MeV, but the experimental investigations on β decay process reveal that the maximum kinetic energy of β particle (electron) is found to be 3 to 4 MeV. This clearly indicates that the electron cannot exist inside the nucleus.

Principle of Complimentarity

Statement:Bohr stated as "In a situation where the wave aspect of a system is revealed, its particle aspect is concealed, and in a situation where the particle aspect is revealed its wave aspect is concealed. Revealing both simultaneously is impossible, the wave and particle aspect are complimentarity".

Correlation Between de-Broglie's wavelength, Uncertainty principle and Wave packet

The consequence of uncertainty principle is both the wave and particle nature of the matter cannot be measured simultaneously. In other words we cannot precisely describe the dual nature of light.

If an experiment is designed to measure the particle nature of the wave, during this experiment errors of measurement of both position and the time

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coordinates must be zero and hence the momentum, energy and the wave nature of the matter are completely unknown and which is true in either case also.

Therefore we can conclude that when the particle nature of the matter is measured or displayed, the wave nature of the matter is neccessarily suppressed and vice versa.

Wave function (ψ)

Wave function describes the state of a quantum mechanical system. It is represented by the symbol ψ. Wave function contains the information about the system and it accounts for wave like properties of a particle. It is obtained by solving a fundamental equation called Schrodinger wave equation.

In general, the wave function ψ is a complex quantity and can be written as $\psi = a + ib$ where a and b are real. The probability of finding the particle is positive and it lies between 0 and 1. But ψ can be positive or negative or complex. Thus ψ itself has no physical significance. The amplitude can be –ve or +ve and –ve probability is meaningless.

According to Max Born's interpretation, the probability of finding a particle at any instant of time t is proportional to $|\psi|^2$. Thus if ψ is the wave function in a given region of volume dV=dx dy dz, then $|\psi|^2$ dV gives the probability of finding the particle within the region dV at a given instant of time t. $|\psi|^2$ dV is referred to as 'probability density' and is given by,

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$|\psi|^2 = \psi\psi^*$

where $\psi^* = a–ib$, represents the complex conjugate of ψ. As the particle has to exist somewhere in space, the total probability of finding the particle is 1.

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

The above equation is called Normalization condition.

Properties of Wave function

1. ψ is single valued everywhere.
2. ψ is finite everywhere.
3. ψ and its first derivatives w.r.t its variable are continuous everywhere .
4. For bound states, ψ must vanish at infinity. If ψ is a complex function, then $\psi\psi^*$ must vanish at Infinity.

Eigen functions and Eigen values

The wave functions which are single valued, finite and their first derivatives w.r.t their variables are continues are called eigen functions. The solution of the schrödinger wave equation gives the wave function ψ. With the knowledge of ψ, we can determine the energy of the given system. Since all wave function are not acceptable, all the values of energies are not acceptable. Only those values of energy corresponding to the eigen functions are acceptable and are called eigen values.

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Time Independent Schrödinger wave equation:

Consider a particle of mass m, moving with a velocity 'v'. According to de-Broglie's hypothesis wave length of the wave associated with the particle is given by,

$$\lambda = \frac{h}{mv} \tag{1}$$

A wave travelling along x-axis can be represented by the equation

$$\Psi = Ae^{i(\omega t - kx)} \tag{2}$$

where Ψ is the wave function and 'A' is the amplitude.

The time independent part of equation (2) is,

$$\psi = Ae^{-ikx} \tag{3}$$

$$Then\ equation\ (2) \implies \Psi = \psi e^{i\omega t} \tag{4}$$

differentiating equation (4) twice w.r.t 'x' we get,

$$\frac{d\Psi}{dx} = \frac{d\psi}{dx}\, e^{i\omega t}$$

$$\frac{d^2\Psi}{dx^2} = \frac{d^2\psi}{dx^2}\, e^{i\omega t} \tag{5}$$

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differentiating equation (4) twice w.r.t 't' we get,

$$\frac{d\Psi}{dt} = \psi\ i\omega\ e^{i\omega t}$$
$$\frac{d^2\Psi}{dt^2} = \psi\ (i\omega)^2\ e^{i\omega t}$$
$$\frac{d^2\Psi}{dt^2} = -\omega^2\ \psi\ e^{i\omega t} \tag{6}$$

We have the equation for a travelling wave as,

$$\frac{d^2y}{dx^2} = \frac{1}{v^2}\frac{d^2y}{dt^2}$$

where 'y' is the displacement and 'v' is the velocity of the wave.

By analogy, we can write the wave equation for de Broglie's wave for the motion of a free particle as

$$\frac{d^2\Psi}{dx^2} = \frac{1}{v^2}\frac{d^2\Psi}{dt^2} \tag{7}$$

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substituting for $\frac{d^2\Psi}{dx^2}$ and $\frac{d^2\Psi}{dt^2}$ in the above equation from equation (5) and (6)

$$\frac{d^2\psi}{dx^2}\, e^{i\omega t} = \frac{-\omega^2}{v^2}\, \psi\, e^{i\omega t}$$

$$\frac{d^2\psi}{dx^2} = \frac{-\omega^2}{v^2}\, \psi$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2\nu^2}{\nu^2\lambda^2}\, \psi$$

$$since\ \omega = 2\pi\nu,\ v = \nu\lambda$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\, \psi$$

$$\frac{1}{\lambda^2} = -\left(\frac{1}{4\pi^2}\right)\left(\frac{1}{\psi}\right)\frac{d^2\psi}{dx^2} \tag{8}$$

The kinetic energy equation is given by,

$$E_k = \frac{p^2}{2m} \tag{9}$$

From equation(1) we have

$$\lambda = \frac{h}{p}$$

$$\Longrightarrow p^2 = \frac{h^2}{\lambda^2} \tag{10}$$

substituting for p^2 from equation (10) in equation(9)

$$E_k = \frac{h^2}{2m\lambda^2} \tag{11}$$

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substituting for $\left(\frac{1}{\lambda^2}\right)$ from equation (8) in equation(11)

$$E_k = \frac{h^2}{2m}\left[-\left(\frac{1}{4\pi^2}\right)\left(\frac{1}{\psi}\right)\frac{d^2\psi}{dx^2}\right]$$

$$E_k = -\frac{h^2}{8m\pi^2}\left(\frac{1}{\psi}\right)\frac{d^2\psi}{dx^2} \tag{12}$$

The total energy of the particle is given by,

$$E = E_k + V \tag{13}$$

where 'V' is the potential energy of a particle

substituting for kinetic energy from equation(12) in equation(13)

$$E = -\frac{h^2}{8m\pi^2}\left(\frac{1}{\psi}\right)\frac{d^2\psi}{dx^2} + V$$

$$(E - V) = -\frac{h^2}{8m\pi^2}\left(\frac{1}{\psi}\right)\frac{d^2\psi}{dx^2}$$

$$\frac{8m\pi^2}{h^2}(E - V)\psi = -\frac{d^2\psi}{dx^2}$$

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{8m\pi^2}{h^2}(E - V)\psi = 0} \tag{14}$$

Equation(14) represents the time-independent Schrödinger wave equation.

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Application of Schrödinger wave equation:

Particle in a one dimensional box

Consider a box of width 'a' with infinitely high walls. The particle is restricted to move along x-axis only in the region from x=0 to x=a.(see fig 1)

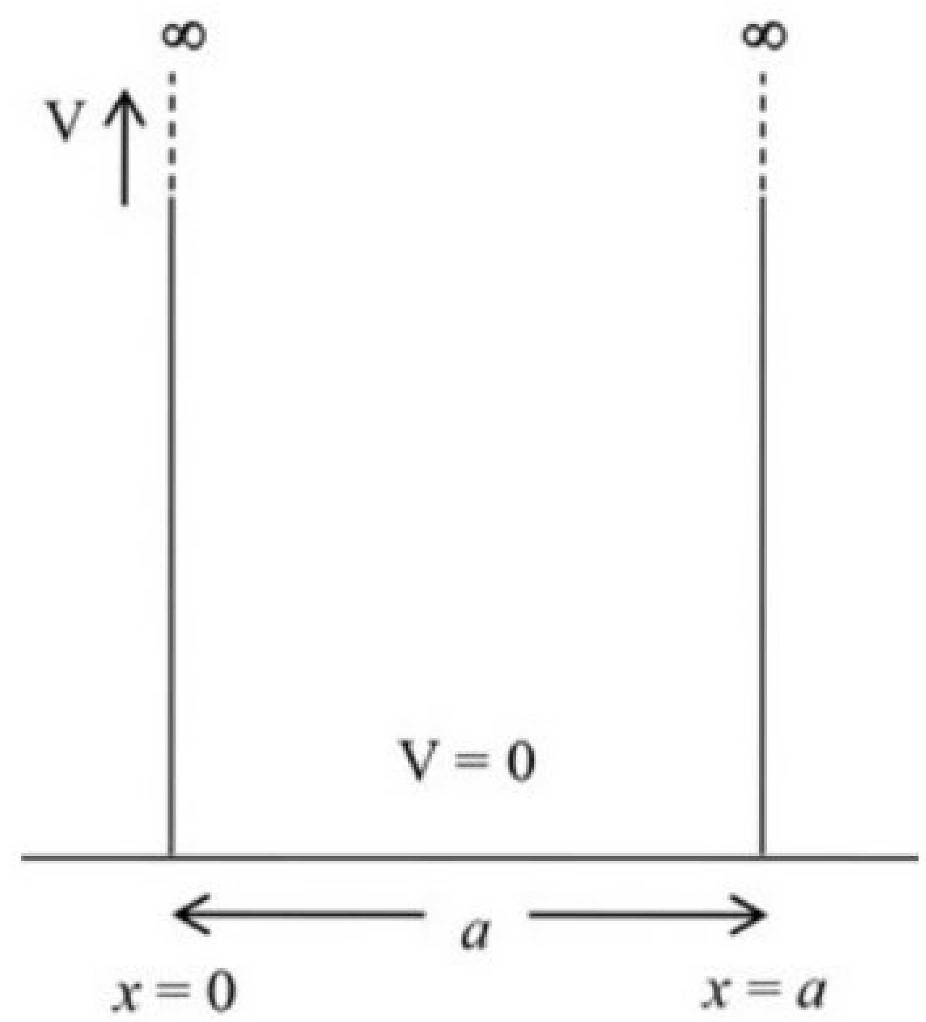

Figure 1

Since the particle is a free particle, the potential energy is taken to be zero inside the box. Since the particle cannot have infinite energy it cannot be seen at points x=0 and x=a. The value of ψ outside the box is zero.

$i.e$, $\psi = 0$ for x=0 and x=a

$\therefore$ The Schrödinger equation inside the box, is given by

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

$$\frac{d^2\psi}{dx^2} + \frac{8m\pi^2 E}{h^2}\psi = 0 \quad (1)$$

$$since\ V = 0$$

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This equation is of the form

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \tag{2}$$

$$where\ \ k^2 = \frac{8m\pi^2 E}{h^2} \tag{3}$$

The solution of (2) is of the form

$$\psi = A\ sinkx + B\ coskx \tag{4}$$

where A and B are constants.

Case 1: At x=0, ψ=0

$$Equation(4) \implies Asin0 + Bcos0 = 0$$

$$B = 0 \tag{5}$$

Case 2: At x=a, ψ=0

$$Equation(4) \implies Asin(ka) + Bcos(ka) = 0, since\ B = 0$$

$$\therefore Asin(ka) = 0, where\ A \neq 0$$

$$since\ sin\pi = 0, sin2\pi = 0, sin3\pi = 0..........sinn\pi = 0$$

$$\therefore sin(ka) = sin(n\pi) \implies ka = n\pi$$

$$k = \frac{n\pi}{a} \tag{6}$$

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substituting(6) in equation(3), we get

$$\frac{n^2\pi^2}{a^2} = \frac{8m\pi^2 E}{h^2}$$
$$\boxed{E_n = \frac{n^2h^2}{8ma^2}} \quad (7)$$

Equation (7) represents energy eigenvalue value of a free particle in a potential well of infinite depth.

Normalization of A : Substituting (5) and (6) in equation (4)

$$\implies \psi = A\ sin(ka)x + B\ cos(ka)x \quad (8)$$

$$since\ B = 0$$

$$\psi = Asin\left(\frac{n\pi}{a}\right)x \quad (9)$$

from normalization equation we have,

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

substituting for ψ we get,

$$\int_0^a A^2 \left[sin^2\left(\frac{n\pi}{a}\right)x\right] dx = 1$$
$$but\ sin^2 x = \frac{1 - cos2x}{2}$$

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

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

$$\frac{A^2}{2}[a-0] = 1$$

$$A = \sqrt{\frac{2}{a}} \tag{10}$$

substituting equation (10) in equation (9),we obtain

$$\boxed{\psi_n = \sqrt{\frac{2}{a}} sin\left(\frac{n\pi}{a}\right)x} \tag{11}$$

Equation (11) represents the energy Eigen function of a free particle in a box.

Wave function, probability density and energy of the particle in different energy levels.

1. For ground state or zeroth energy state n=1

$$E_n = \frac{n^2h^2}{8ma^2} \Longrightarrow E_{n=1} = \frac{h^2}{8ma^2}$$

$$Then\ \ \psi_{n=1} = \sqrt{\frac{2}{a}} sin\left(\frac{\pi}{a}\right)x$$

$i.e,\ \psi$ is minimum at x=0 and x=a and maximum at x=0

$\Longrightarrow$ The probability of finding a particle at ground state is maximum at the center of the box.

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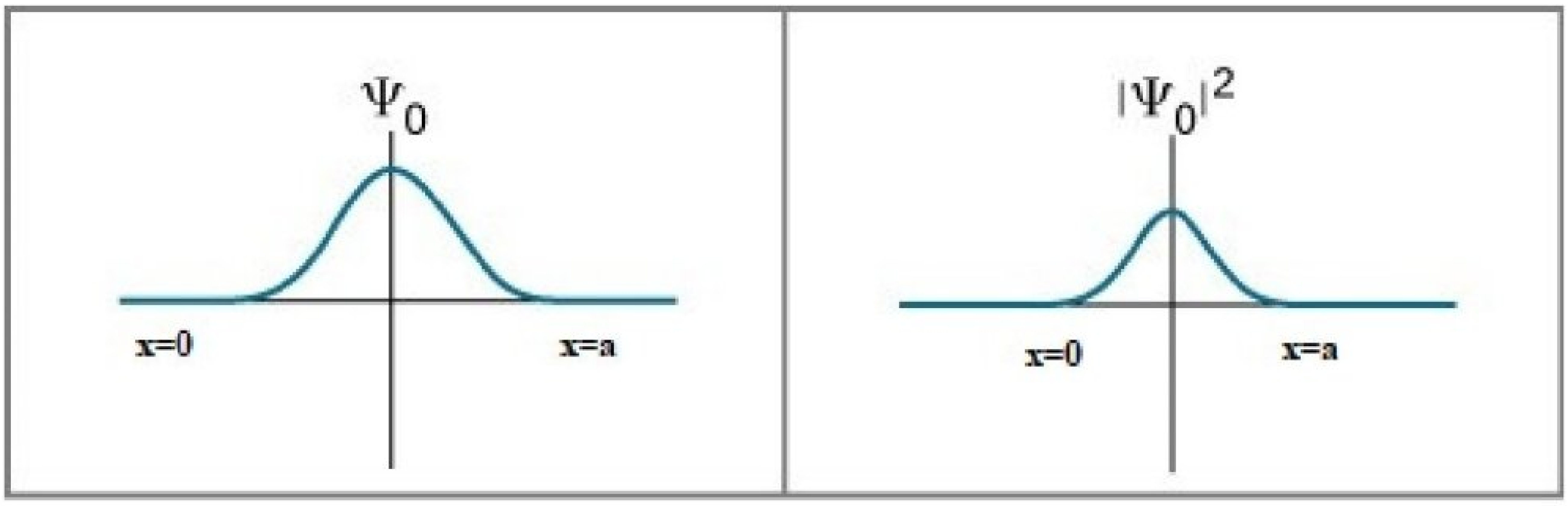
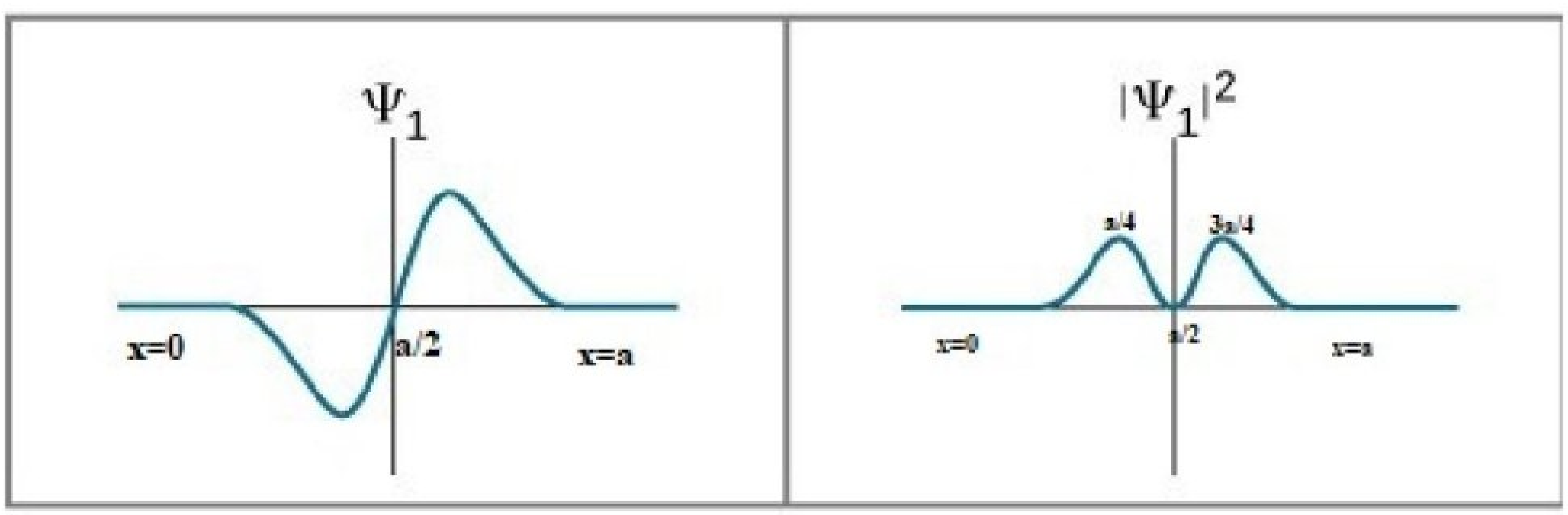


2. For 1st excited state n=2

$$E_n = \frac{n^2h^2}{8ma^2} \implies E_{n=2} = \frac{4h^2}{8ma^2}$$
$$Then\ \psi_{n=2} = \sqrt{\frac{2}{a}} sin\left(\frac{2\pi}{a}\right) x$$

i.e, ψ is minimum at x=0, x=a/2 and x=a and maximum at x=a/4, 3a/4

$\implies$ The probability of finding a particle in a box at 1st excited state is maximum at a/4 and 3a/4 .



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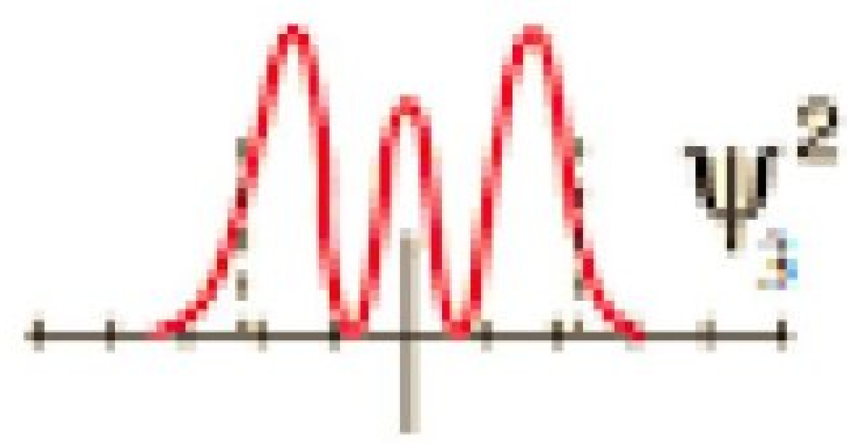
3. <u>For 2nd excited state n=3</u>

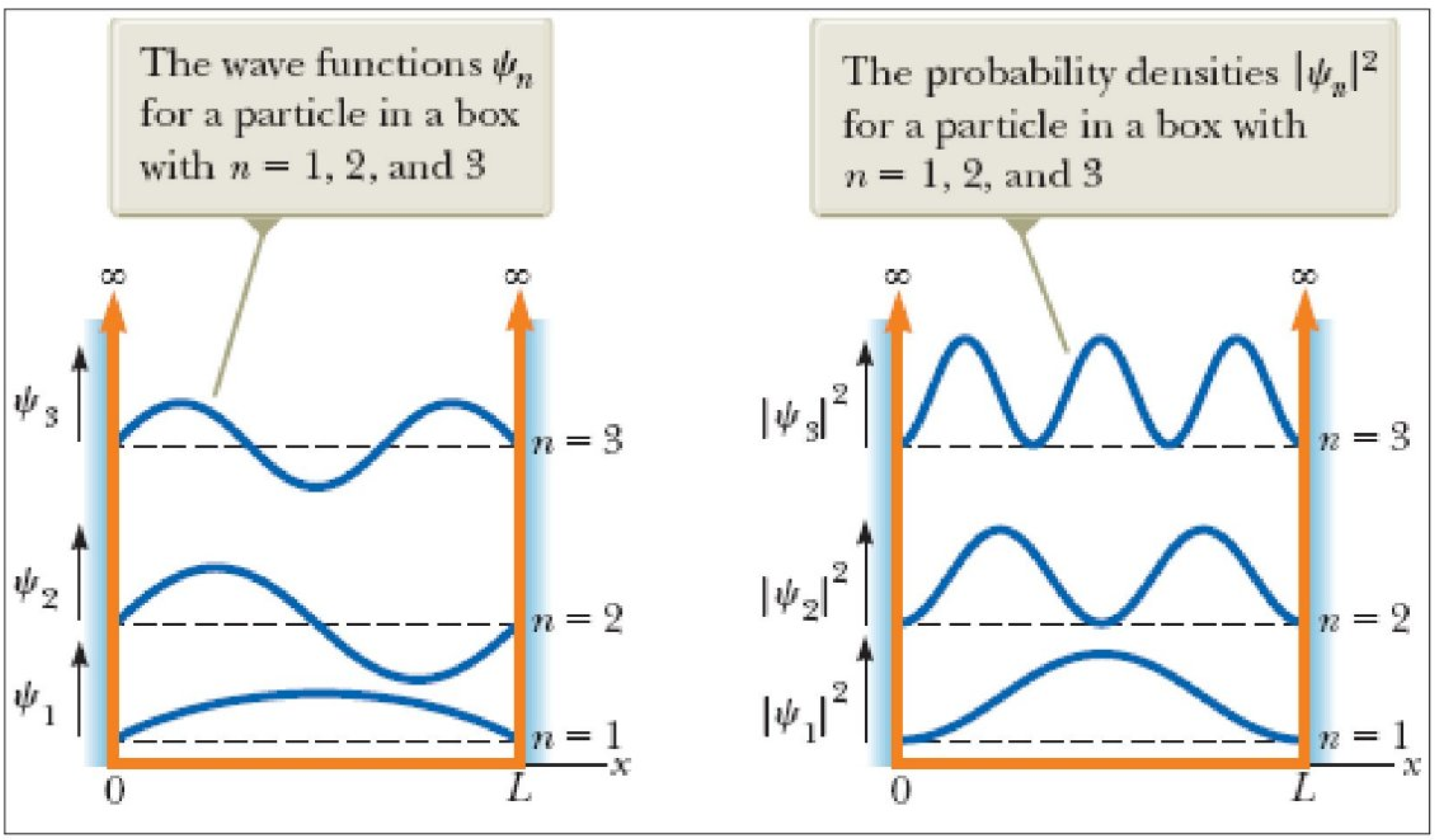
$$E_n = \frac{n^2h^2}{8ma^2} \implies E_3 = \frac{9h^2}{8ma^2}$$

$$Then\ \ \psi_{n=3} = \sqrt{\frac{2}{a}} sin\left(\frac{3\pi}{a}\right)x$$

i.e, ψ is minimum at x=0, x=a/3, x=2a/3 and x=a

$\implies$ The probability of finding a particle in a box at 2nd excited state is maximum at x=a/6, x=a/2 and 5a/6 .





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