PARTICLE IN 1-D BOX

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- Let us write the Schrodinger wave equation in one
- dimension.
- $-h^2/8\pi^2 m.\ d^2\Psi\ /dx^2 + U\Psi = E\ \Psi$……(1)
- If we consider an electron of mass m in a box of 1-
- dimension whose length is a.
- The particle can exist anywhere between x=0 to x=a.
- Let the potential energy of the particle be zero inside
- this potential energy well and let the potential
- energy at x=0 and x=a as well as outside the box be
- ∞.

Thus the particle is unable to cross this energy barrier and go outside the box.

We can write the Schrodinger wave equation outside the box:

$$-h^2/8\pi^2 m.\ d^2\Psi /dx^2 + \infty\Psi = E\ \Psi ....(2)$$

Multiplying this equation (2) by $-8\pi^2 m/h^2$, we get

$$d^2\Psi /dx^2 - 8\pi^2 m/h^2\ \infty\Psi = -8\pi^2 m/h^2\ E\ \Psi$$

This equation can be rearranged as

$$d^2\Psi /dx^2 = 8\pi^2 m/h^2\ \infty\Psi - 8\pi^2 m/h^2\ E\ \Psi$$

$$= 8\pi^2 m/h^2\ (\infty - E)\ \Psi ....(3)$$

- For finite values of energy, equation (3) can be written as $d^2\Psi / dx^2 = \infty \Psi$......(4)
- The left hand side of this equation has to be finite (Ψ is a well behaved wave function), so the right hand side has to be finite which is possible only if $\Psi=0$.
- Thus $\Psi=0$ for all points outside the box and the particle cannot exist outside the box at all.

When the particle is inside the box, the potential energy is 0. Therefore the Schrodinger wave equation inside the box is :

$$-h^2/8\pi^2 m.\ d^2\Psi\ /dx^2 = E\ \Psi \ldots\ldots..(5)$$

Or $$d^2\Psi\ /dx^2 + 8\pi^2 mE\ \Psi/h^2 = 0 \ldots\ldots\ldots(6)$$

Let $$k^2 = 8\pi^2 mE/h^2 \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Thus, rewriting we have

$$d^2\Psi\ /dx^2 + k^2\Psi = 0 \ldots\ldots\ldots\ldots(8)$$

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$$d^2\Psi /dx^2 + k^2\Psi = 0 \ ....(8)$$

This is a second order differential equation whose solution is of the form

$$\Psi = A.\sin kx + B.\cos kx \ ...(9)$$

where A and B are arbitrary constants.

The values of these constants can be calculated using the boundary conditions.

Since the wave function is 0 outside the box,

It must also be 0 at the walls of the box as there must be a continuity in the values of Ψ at the walls of the box.

Thus Ψ must be 0 at $x=0$ and $x=a$.

Thus at $x=0$ the equation (9) becomes:

$0= A\sin k.0+B\cos k.0$

$0=B\cos k.0$

Since $\cos k.0=1$, therefore $B=0$

Thus equation (9) is reduced to

$\Psi=A\sin kx$ ………..(10)

At the point $x=a$, equation (9) becomes:

$$0 = A \sin ka$$

For this to be true, either $A=0$ or $\sin ka=0$

If $A=0$, the wave function will become 0 everywhere inside the box which is not acceptable, so $\sin ka=0$

Since $\sin ka$ can be zero for all values of $\sin n\pi$

Therefore $\sin ka = \sin n\pi$

$$\text{Or } ka = n\pi$$

Or $k = n\pi/a$ ....(11)

Where n is an integer having values 0,1,2,3…

Finally, the wave function for the particle inside the box becomes

$\Psi = A \sin n\pi x/a$ ………(12)

Using equation (7) and (11), we get

$(n\pi/a)^2 = 8\pi^2 mE/h^2$

or $n^2\pi^2/a^2 = 8\pi^2 mE/h^2$

or **$E_n = n^2 h^2/8ma^2$ ……….(13)**

For a particle moving between two points , the energy is quantized.

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n	$E_n = n^2h^2/8ma^2$
1	$h^2/8ma^2$
2	$4h^2/8ma^2$
3	$9h^2/8ma^2$
4	$16h^2/8ma^2$

No such discrete levels are expected from classical mechanics.

Although n=0 is permitted but it is not acceptable as it would make the wave function 0 everywhere inside the box.

Thus, lowest energy is obtained by substituting n=1 in equation (13).

This energy is known as the Zero point energy.

$$\mathbf{E_{zero\ point} = h^2 / 8ma^2}$$

The salient features of the particle in a box problem are summarized below.

1) The particle is not at rest even at 0 Kelvin.

Therefore, the position of the particle cannot be precisely known.

In such a situation, only the mean value of the kinetic energy can be known. Therefore, the momentum of the particle is also not known precisely.

The occurrence of zero point energy is in accordance with Heisenberg’s Uncertainty Principle.

2) The allowed integral values of n come naturally as a consequence of the solution and not as an arbitrary postulate as given by Bohr.

‘n’ is called a quantum number.

3) The energies of the electron are quantized. The only permitted values are as given in the table.

4) Plots of Ψ and Ψ^2 for different values of n are as shown.

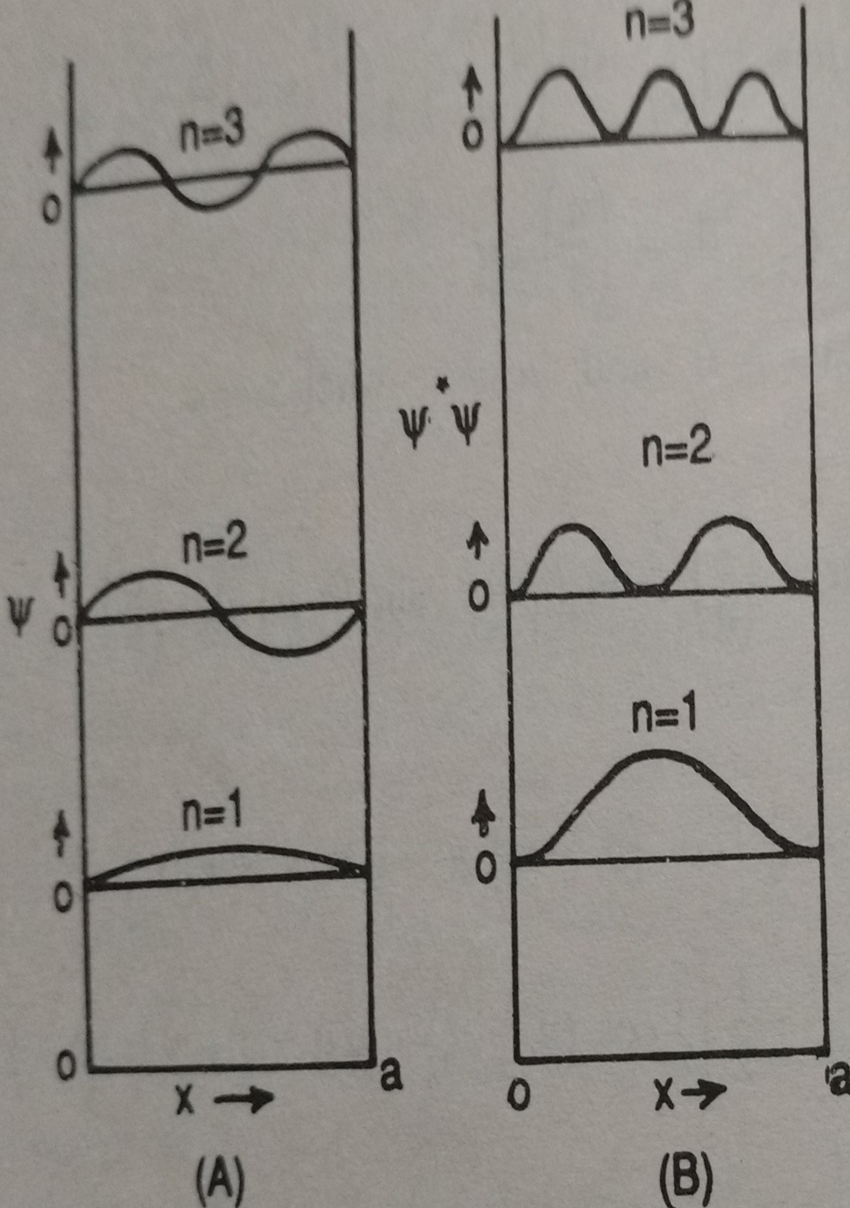

Fig. 3.5 (A) Wave function ψ and (B) probability density function $\psi^*\psi$ for the lowest three energy levels for a particle in a box

The plots of Ψ and Ψ^2 for different values of n are as shown. The appearance of nodes and antinodes in the wave function is another striking feature of this problem.

The plots of Ψ versus x show that there are n-1 nodes (regions of zero amplitude and zero probability) in each wave function. The antinodes are regions of high probability e.g. at x=a/2, in case of Ψ_1 and at x=a/4 and 3a/4 in case of Ψ_2.

There are nodal points in between positions other than x=0 and x=a

5) The probability density Ψ^2 has the same number of maxima as the quantum number 'n'.

For n=2, the probability of finding the particle at the centre of the box is zero, which is quite different from the classical result.

6) As we go to higher energy levels with more nodes, the maxima and minima of probability curves come closer together and the variations in probability along the 1-d box become undetectable.

For higher quantum numbers, we approach the results of uniform probability density.

This is in agreement with ‘Bohr Correspondence Principle’. According to this principle, the quantum mechanical result must go over to classical mechanics when the quantum number describing the system becomes very large.

7) The energy expression $E_n = n^2 h^2/8ma^2$ shows that energy is inversely proportional to a^2 i.e., square of the length of the box.

Longer the box, lower will be its energy.

More localized the electron, higher will be its energy.

In chemical systems , larger the extent of delocalization, more stable is the system energetically. (For example, benzene and other conjugated systems.)

8) At a first glance, the energy expression is inversely proportional to the mass of the particle. It seems to contradict the fact that kinetic energy is proportional to mass of the particle.

However, if we understand that submicroscopic particles travel close to the speeds of light, we can understand this contradiction.

The energy expression suggests that the lighter particles will have velocities close to the velocity of light and heavier particles will have lower velocities.

This would suggest that β-rays would have higher velocities than α- rays.