Mathematical Description of Waves

Let us consider a wave progressing along the X-axis as shown in Figure I.

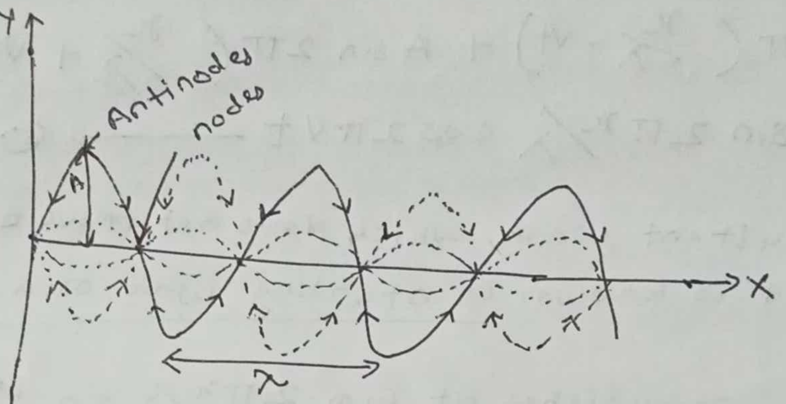


Figure 1. Standing harmonic wave

This wave motion can be described quantitatively by the differential equation

$$\frac{\delta^2 \varphi}{\delta x^2} = \frac{1}{c^2}\frac{\delta^2 \varphi}{\delta t^2} \longrightarrow (1)$$

The value 'φ' is the amplitude function and is a measure of the variation of displacement along the Y-axis at a particular distance along the X-axis, 'c' is the velocity of the travelling wave and 't' is the time.

Wave travelling from left to right

One of the solutions in terms of the sine function is

$$\varphi = A \sin 2\pi \left(\frac{x}{\lambda} - vt\right) \longrightarrow (2)$$

where λ = wavelength, v = frequency, A = Amplitude.

If two waves φ_1 & φ_2 cross each other, then the resultant amplitude is the sum of the amplitudes of each separate wave at the point of crossing. Mathematically

$$\varphi = a_1 \varphi_1 + a_2 \varphi_2 \longrightarrow (3)$$

where a_1 & a_2 are arbitrary constants. This is an example of the principal of superposition.

Wave travelling from right to left

$$\varphi = A \sin 2\pi \left(\frac{x}{\lambda} + vt\right) \longrightarrow (4)$$

When two waves of the form of eqn ② travel with equal speed but in opposite direction, then their resultant amplitude by the principal of superposition will be

$$\varphi = A \sin 2\pi \left(\frac{x}{\lambda} - vt \right) + A \sin 2\pi \left(\frac{x}{\lambda} + vt \right)$$

$$= 2A \sin 2\pi x/\lambda \cos 2\pi v t \longrightarrow ⑤$$

the new resultant wave, which does not move either forward or backward is known as standing wave or a stationary wave.

From eqn ⑤ φ vanishes at $\sin 2\pi x/\lambda = 0$ at $x = 0, \frac{\lambda}{2}, 2\frac{\lambda}{2} \ldots n\lambda/2$. These points are known as nodes (minimum amplitude)

The distance between two successive nodes is $\frac{\lambda}{2}$ and midway between two nodes are the positions of maximum amplitude or antinodes.

The schrodinger time independent wave equation

(1926) The differential equation correlating the energy of a microsystem to its space coordinates. For a particle of mass m moving in one-dimension with energy E this is given by

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

where ψ is a function of x and is called a wavefunction $V(x)$ is the potential energy of the particle at a point x.

Let us consider an electron wave moving along X-axis and behaving like a standing wave.

The amplitude function for this wave from ⑤ can be written as $\varphi(x,t) = 2A \sin 2\pi x/\lambda \cdot \cos 2\pi v t$

$$= \psi(x) f(t) = \psi(x) \cos 2\pi v t \longrightarrow ⑥$$

$\psi(x)$ is a function of x-coordinates only.
$f(t)$ is a function of t-coordinate only.

simple differentiation of eqn ⑥ gives

$$\frac{\delta^2 \psi}{\delta x^2} = \cos 2\pi v t \cdot \frac{d^2\psi(x)}{dx^2}$$

$$\frac{\delta \psi}{\delta t} = -\psi(x) \cdot 2\pi v \sin 2\pi v t$$

$$\frac{\delta^2 \psi}{\delta t^2} = -\psi(x)\, 4\pi^2 v^2 \cos 2\pi v t$$

substituting these values in eqn ①, we get

$$\cos \cancel{2\pi v t}\, \frac{d^2\psi(x)}{dx^2} = -\frac{1}{c^2}\psi(x)\, 4\pi^2 v^2 \cos \cancel{2\pi v t}$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{1}{c^2} 4\pi^2 v^2 \psi(x) \longrightarrow ⑦$$

$\boxed{\text{since, } c = \lambda v}$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{1}{\lambda^2 \cancel{v^2}} 4\pi^2 \cancel{v^2} \psi(x)$$

$$= \frac{-4\pi^2}{\lambda^2}\psi(x) \longrightarrow ⑧$$

For microparticles,

de Broglie equation for matter waves is

$$\boxed{\lambda = \frac{h}{mv}}$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi^2 m^2 v^2}{h^2}\psi(x) \longrightarrow ⑨$$

Total energy (E) = Kinetic energy (T) + potential energy (V).

$$T = \frac{1}{2}mv^2 = E - V \Rightarrow m^2v^2 = 2(E-V)m$$

substituting this value in equation ⑨, we obtain

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h}(E-V)\psi = 0} \longrightarrow ⑩$$

This is the Schrodinger equation for a single particle of mass m moving in one dimension.

For three dimensions,

$$\boxed{\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0} \longrightarrow (11)$$

Where ψ & V are functions of coordinates x, y, z & ψ is known as the wave function.

The schrodinger equation for a one-particle system is generally written in the form

$$\boxed{-\frac{h^2}{8\pi^2 m}\left[\frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2}\right]\psi + V\psi = E\psi} \longrightarrow (12)$$

Interpretation of the wave Function

According to Born, $|\psi|^2$ is proportional to the probability of finding a particle at a point at any given moment.

Since the probability of finding a particle at a given point in space must be real, more generally $\psi^*\psi$ is taken as the measure of the probability of finding a particle at any point, if ψ is a complex function. The function ψ^* is the complex conjugate of ψ & their product will always be a real non-negative quantity.

Example $\psi = a + ib$, where $i = \sqrt{-1}$

$\psi^* = a - ib$

$\psi^*\psi = a^2 + b^2$ = a real non-negative quantity. If ψ is a real function, then $\psi = \psi^*$

Born postulate for one-dimensional system

If the wavefunction of a particle has a value ψ at some point x, the probability (P) of finding the particle between x and $x + dx$ (within the infinitesimal distance element dx) is proportional to $|\psi|^2 dx$.

$$P \propto |\psi|^2 dx \longrightarrow (1)$$

If the wavefunction of a particle has value ψ at some point 'M' with coordinates (x, y, z) the probability (P) of finding the particle between x & $x+dx$, y & $y+dy$ & $z+dz$ (ie. within the infinitesimal volume element $d\tau = dx\,dy\,dz$) is proportional to $|\psi|^2 dx\,dy\,dz$ ie

$$P \propto |\psi|^2 dx\,dy\,dz = |\psi|^2 d\tau$$

Graphically the probability $|\psi|^2 dx$ & the probability density distribution function $|\psi|^2$ for one-dimensional system are shown in Figure ②

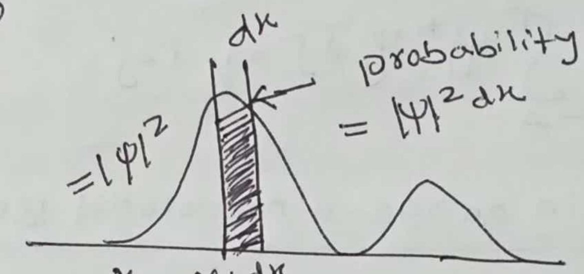


Figure ② the probability density $|\psi|^2$. The probability of finding the particle in a region between x & $x+dx$ is $|\psi|^2 dx$.

Properties of wave Function

① ψ must be single-valued

② ψ & its first derivative must be continous

③ ψ must be finite for all physically possible values of x, y, z in the sense that $\int \psi^* \psi \, d\tau$ exists.

When a wave function satisfies these three conditions, the function is called a wave-behaved function.

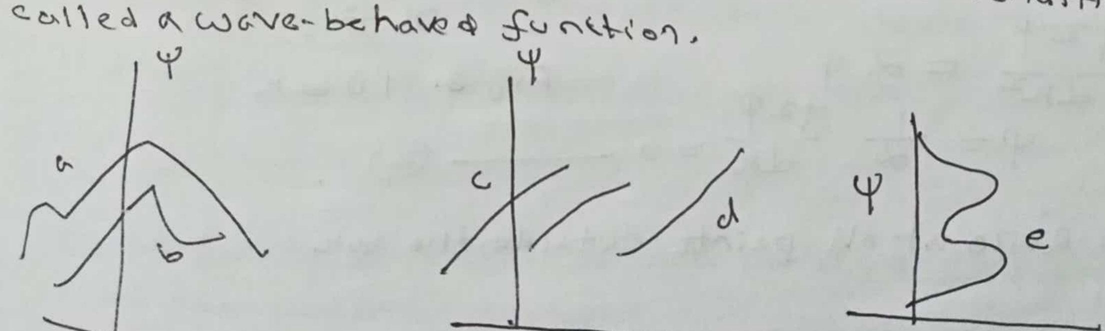


Figure ③ (a) Function (a) is continous and its first derivative also continous, Function (b) is continous but its first derivative has a discontinuity, Function (c) is discontinous. (d) Function approaches infinity (e) is multivalued

Normalised and Orthogonal Functions

When ψ_i & ψ_j of a system satisfy the condition of orthogonality

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, d\tau = 0, \quad i \neq j$$

& that of normalization

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, d\tau = 1, \quad i = j$$

A Particle in an one-dimensional Box

Let us consider that a particle of mass 'm' confined in a box of length 'a' and moving along the x-direction. The potential energy outside the box is infinite but inside the box its value is zero

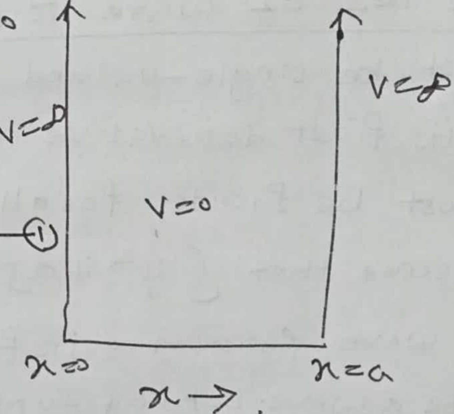


Fig 3. 1D box

Outside the box, $V = \infty$

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

for finite values of energy E, $E = 0$

$$\frac{d^2\psi}{dx^2} = \infty \psi$$

$$\psi = \frac{1}{\infty}\frac{d^2\psi}{dx} = 0 \quad \text{—— (2)}$$

Thus, ψ is zero at all points outside the box

Inside the box $\quad x = 0, \& \, x = a, \, V = 0$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E\psi = 0 \quad \text{—— (3)}$$

Let $K^2 = \frac{8\pi^2 m}{h^2} E$ ——— (4)

where k is a constant, and is independent of x

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \text{——— (5)}$$

The general solution of this equation is

$$\psi = A \sin kx + B \cos kx \quad \text{——— (6)}$$

A & B are arbitrary constants.

At $x = 0$, $\psi = 0$

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

$$0 = B$$

substitute this value in (6)

$$\psi = A \sin kx + 0 \Rightarrow \psi = A \sin kx \longrightarrow (7)$$

At the other wall, $x = a$, $\psi = 0$

$$0 = A \sin k.a$$

$\cancel{A = 0}$, or $\sin ka = 0$

Not acceptable

$$\sin ka = 0 = \sin n\pi$$

$$ka = n\pi \Rightarrow k = \frac{n\pi}{a} \quad \text{——— (8)}$$

where n is an integer, having values 0, 1, 3 . . .

∴ The wavefunction of the particle inside the box is

$$\boxed{\psi_n = A \sin\left(\frac{n\pi x}{a}\right)} \quad \text{——— (9)}$$

Substituting k value in eqn (4), the translational kinetic energy of the particle is given by

$$K^2 = \frac{8\pi^2 m}{h^2} E \Rightarrow \left(\frac{n\pi}{a}\right)^2 = \frac{8\pi^2 m}{h^2} E_n$$

$$\boxed{E_{zero point} = \frac{h^2}{8ma^2}}$$

$$\Rightarrow \boxed{E_n = \frac{n^2 h}{8ma^2}} \quad n = 1, 2, 3 . . . . .$$

//.

<u>Normalization of the wave function</u> The probability that the particle is somewhere between $x=0$ and $x=a$ is unity because at all the times it is somewhere in the box

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

But $\sin^2 \frac{n\pi x}{a} = \frac{1}{2}\left(1 - \cos \frac{2n\pi x}{a}\right)$

So,

$$\int_0^a \psi_n^* \psi_n \, dx = A^2 \left[\frac{1}{2} \int_0^a dx - \frac{1}{2} \int_0^a \cos \frac{2n\pi x}{a} \, dx \right]$$

$$= A^2 \left[\frac{a}{2} - 0 \right] = 1 \Rightarrow A = \left(\frac{2}{a}\right)^{1/2}$$

Thus, the normalised wavefunction of a particle in a one dimensional box is given by

$$\boxed{\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a}}$$

<u>Example</u> π-electrons in conjugated polyenes may be treated as free particles moving in a 1D box of length equal to the sum of all the carbon-carbon bond lengths plus an additional C–C single bond.

<u>solution</u>

$V = \infty$ $\qquad V = 0 \qquad$ $V = \infty$

$CH_2 = CH - CH = CH_2$

$x = 0 \longrightarrow x = a$

Butadiene

considering

4π electrons of butadiene are moving in a box of assumed length.

Length of the box $= 2 \times C{=}C + 2 \times C{-}C$

$= 2 \times 0.134\,nm + 2 \times 0.154\,nm$

$= \underline{0.576\,nm}$

Therefore, the energy of the first three states are given by

$$E_1 = \frac{h^2}{8m(0.576\,nm)^2} = 1.817 \times 10^{-19}\,J$$

$$E_2 = \frac{4h^2}{8m(0.576\,nm)^2} = 7.271 \times 10^{-19}\,J$$

$$E_3 = \frac{9h^2}{8m(0.576\,nm)^2} = 16.359 \times 10^{-19}\,J$$

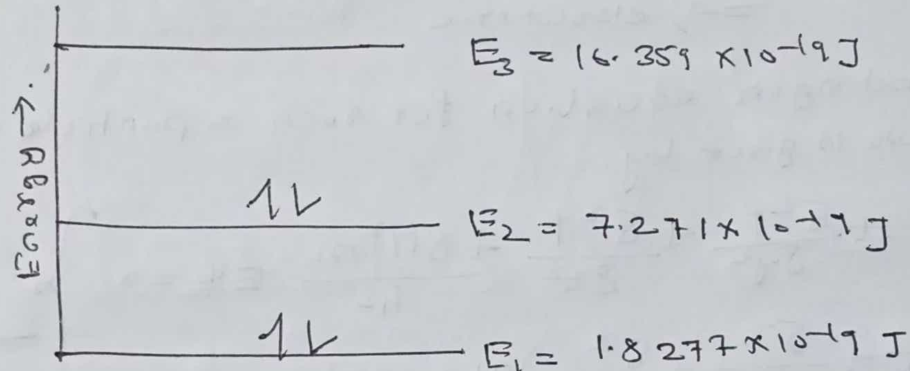
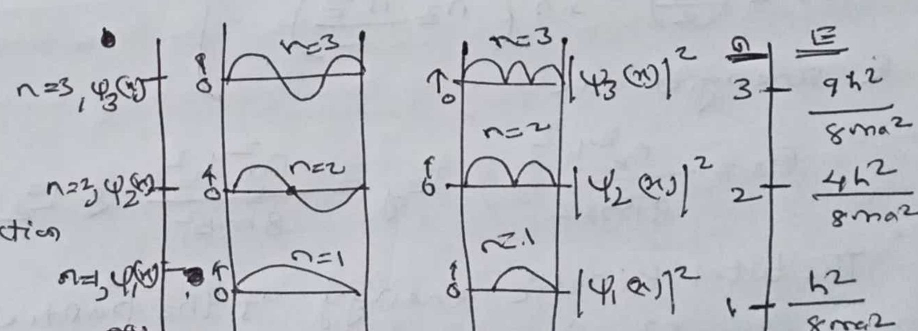


Fig: Energy diagram

<u>Graphical Interpretation</u> The graphs of the wavefunctions and the probability densities are shown in Figure ①

① Points at the boundaries of the box, points inside the box have wavefunction zero

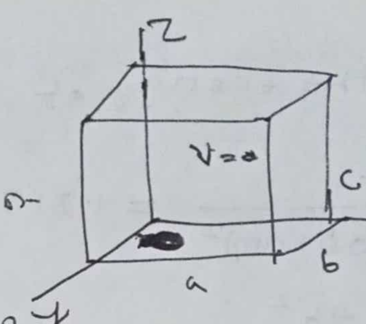


② The probability density, $[\psi]^2$ has the same number of maxima as the quantum number n.

Fig① ⓐ Wavefunction, ψ ⓑ probability density function $\psi^* \psi$.

③ As Energy levels increases with more nodes, the maxima and the minima probability curves come closer and ultimately becomes undetectable.

Particle in a 3D box



For a particle in three-dimensional box with edges of length a, b & c, the wavefunction ψ will be a function of all three space coordinates.

Potential energy, V=0 inside the box & V= ∞ outside the box.

$$V(x,y,z) = 0 \text{ for } 0 \le x \le a,\ 0 \le y \le b \ \& \ 0 \le z \le c$$
$$= \infty, \text{ elsewhere}$$

The Schrodinger equation for such a particle moving within box is given by

$$\frac{\delta^2\psi}{\delta x^2} + \frac{\delta^2\psi}{\delta y^2} + \frac{\delta^2\psi}{\delta z^2} + \frac{8\pi^2 m}{h^2}E\psi = 0$$

or $$\left(\frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2}\right)\psi + \frac{8\pi^2 m}{h^2}E\psi = 0 \quad \text{--- (1)}$$

The normalized wavefunctions are

$$\psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right)$$
$$\psi_N(y) = \left(\frac{2}{b}\right)^{1/2} \sin\left(\frac{n_y \pi y}{b}\right)$$
$$\psi_N(z) = \left(\frac{2}{c}\right)^{1/2} \sin\left(\frac{n_z \pi z}{c}\right) \quad \text{--- (2)}$$

& Energies are

$$E_x = \frac{n_x^2 h^2}{8ma^2},\ E_y = \frac{n_y^2 h^2}{8mb^2} \ \& \ E_z = \frac{n_z^2 h^2}{8mc^2}$$

∴ The total kinetic energy of the particle is given by

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \quad \text{--- (3)}$$

The complete wavefunction for the particle is given by

$$\psi(x,y,z) = (8/abc)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right) \cdot \sin\left(\frac{n_y \pi y}{b}\right) \cdot \sin\left(\frac{n_z \pi z}{c}\right) \quad \text{--- (4)}$$

Degeneracy

For a particle in 3D, if sides are equal $a=b=c$, then the total energy becomes

$$\boxed{E = \frac{h^2}{8ma^2}\left[n_x^2 + n_y^2 + n_z^2\right]}$$

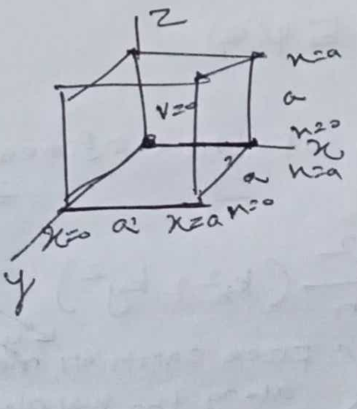
For lowest energy level, $n_x = n_y = n_z = 1$,

$$\text{Energy} = \frac{3h^2}{8ma^2}$$

* When energy levels of different states are the same, such energy levels are said to be degenerate. The number of different states belonging to the same energy level is known as the degree of degeneracy.

Table ① Energy levels and Degeneracy of various states

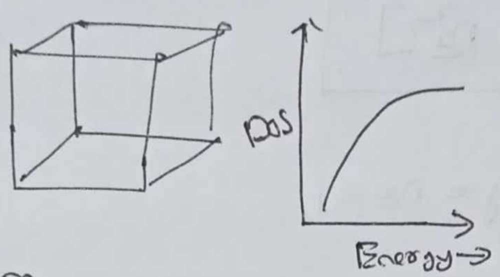
Quantum numbers & Number of states $(n_x n_y n_z)$	Energy Levels	Degree of Degeneracy
(1 1 1)	$3h^2/8ma^2$	Non-degenerate
(2 1 1), (1 2 1), (1 1 2)	$\frac{6h^2}{8ma^2}$	3-fold degenerate
(2 2 1), (1 2 2) (2 1 2)	$\frac{9h^2}{8ma^2}$	3-fold "
(3 1 1), (1 3 1), (1 1 3)	$\frac{11h^2}{8ma^2}$	3 " "
(2 2 2)	$\frac{12h^2}{8ma^2}$	Non-degenerate
(1 2 3), (1 3 2), (2 1 3), (3 2 1), (3 1 2), (2 3 1)	$\frac{14h^2}{8ma^2}$	six fold degenerate



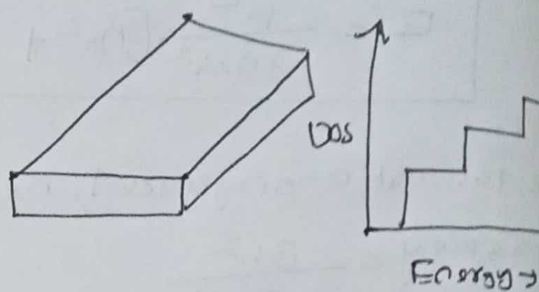
$\boxed{a=b=c=a}$ sides equal.

Density of States (DOS)

Density of States (DOS) Describes the number of electron states that are available in a system.

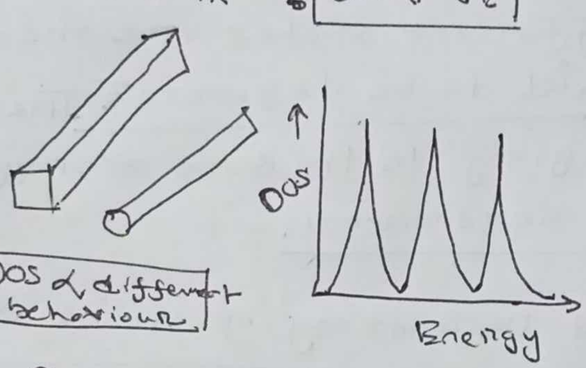


(a) 3D bulk $\boxed{DOS \propto \sqrt{E}}$



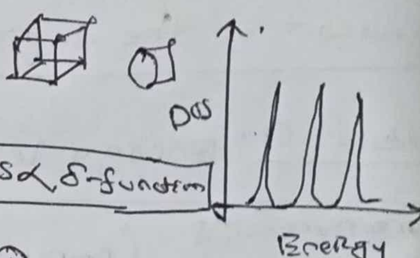
(b) 2D quantum well

$\boxed{DOS \propto \text{step function}}$



$\boxed{DOS \propto \text{different behaviour}}$

(c) 1D nanowire / quantum wire



$\boxed{DOS \propto \delta\text{-function}}$

(d) 0D quantum dot.

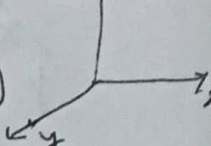
For nanoscale materials, the energy levels and DOS vary as a function of size resulting in dramatic changes in the material property.

The schrodinger eqn in nanoparticle

The allowed energy levels of the electrons can be found by solving the following schrodinger eqn

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + V(z)\right]\psi(z) = E\,\psi(z)$$

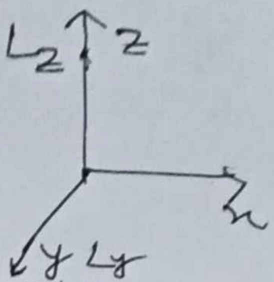
The allowed energy states of the confined electron in a quantum well (2D)



$$E_i(k_x, k_y) = \frac{h^2 i^2}{8mL_z^2} + \frac{\hbar^2}{2m}(k_x^2 + k_y^2)$$

(confinement in z-axis) (Free carrier movement along the x-y plane)

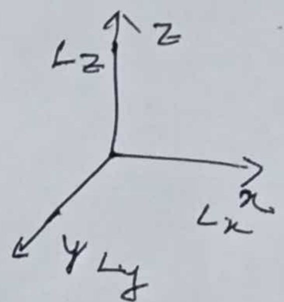
Quantum wires (1D system)



$$E_{i,j}(k_x) = \frac{h^2}{8m}\left(\frac{i^2}{L_z^2} + \frac{j^2}{L_y^2}\right) + \frac{\hbar^2 k_x^2}{2m}$$

(confinement in two axes) (free carrier movement along x-axis)

Quantum dots (0D system)



$$E_{i,j,k} = \frac{h^2}{8m}\left(\frac{i^2}{L_z^2} + \frac{j^2}{L_y^2} + \frac{k^2}{L_x^2}\right)$$

(confinement along all three axes (dimensions))