

Advanced Engineering Physics

UNIT – III Quantum Mechanics

Syllabus

Introduction, de-Broglie hypothesis, Heisenberg uncertainty principle, postulates of quantum mechanics: operators in quantum mechanics, eigen values and eigen functions, expectation value; physical significance of wave function, Schrödinger's time independent wave equation, particle in a 1D box, Bloch's theorem (qualitative), Kronig-Penney model (qualitative): E-k diagram, Concept of phase and group velocity; formation of energy bands, origin of bandgap, classification of solids, concept of discrete energy levels and quantum confinement in nanomaterials.

Failures of Classical Mechanics:

Classical mechanics (Newtonian mechanics) successfully explains the motion of macroscopic bodies — such as planets, projectiles, and machines.

However, when the same principles were applied to microscopic particles like electrons, atoms, or photons, they failed to describe their actual behaviour.

Wave-Particle Duality:

Classical mechanics treats particles and waves as separate entities. But experiments (like the photoelectric effect and electron diffraction) show that particles exhibit wave-like behaviour, and waves exhibit particle-like behaviour — something classical physics cannot explain.

Discrete Energy Levels:

Classical theory predicts that an electron revolving around a nucleus could have any energy. However, atomic spectra show that only specific (quantized) energy levels exist — a clear contradiction.

Radiation Problem:

According to classical electrodynamics, an accelerating charged particle (like an electron in orbit) should continuously radiate energy and spiral into the nucleus — meaning atoms should collapse. But atoms are stable, proving classical predictions wrong.

de-Broglie's hypothesis

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

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

Where 'm' is the mass of material particle, v is its velocity and p is its momentum.

Derivation for de-Broglie's wavelength

According to Planck's theory of radiation of energy of a photon is given by

$$E = h \nu = \frac{hc}{\lambda} \text{ ----- (1)}$$

Where 'c' is velocity of light.

According to Einstein mass-energy relation

$$E = mc^2 \text{ ----- (2)}$$

Using equation (1) and (2) we get,

$$mc^2 = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{h}{mc} \text{ ----- (3)}$$

where $mc = P$ (momentum associated with photon.)

For a material particle of mass m and moving with velocity v , the wavelength associated with this particle is given by

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

i) If 'E' is the kinetic energy of the material particle, then

$$E = \frac{1}{2} mv^2 \Rightarrow 2E = mv^2 \Rightarrow 2mE = m^2 v^2 \Rightarrow 2mE = p^2$$

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

$\therefore$ deBroglie wavelength

$$\lambda = \frac{h}{\sqrt{2mE}} \text{ ----- (5)}$$

ii) When a charged particle of charge q is accelerated by a potential difference V , then wavelength is

$$\lambda = \frac{h}{\sqrt{2mqV}} \text{ ----- (6)}$$

iii) When a material particle of is in thermal equilibrium at a temperature T , then $E = \frac{3}{2} kT$

Where $K = 1.38 \times 10^{-23}$ J/K is Boltzmann's constant

$$\lambda = \frac{h}{\sqrt{3mkT}} \text{ ----- (7)}$$

iv) de Broglie wavelength associated with electron:

let us consider the case of an electron of mass m and charge 'e' which is accelerated by a potential V , then $\frac{1}{2} mv^2 = eV$ where $e = 1.6 \times 10^{-19}$ C mass of electron, $m = 9.1 \times 10^{-31}$ kg

$$\Rightarrow v = \sqrt{\frac{2eV}{m}}$$

$$\Rightarrow \lambda = \frac{h}{mv} = \frac{h}{\sqrt{2eVm}}$$

$$\lambda = \frac{12.26}{\sqrt{V}} \text{ A}^0 \text{ ----- (8)}$$

If $V = 100$ volts then $\lambda = 1.226 \text{ A}^0$

Properties of matter waves:

- i) Lighter is the particle, greater is the wavelength associated with it.
- ii) Smaller is the velocity of the particle, greater the wavelength associated with it.
- iii) When $v = 0$ then $\lambda = \infty$, i.e., the wave becomes indeterminate and $v = \infty$ then $\lambda = 0$. This shows that matter waves are generated by the motion of particles. These facts that matter waves are not electromagnetic waves.

iv) The velocity of matter wave is greater than the velocity of light.

A particle in motion with associated matter wave has two different velocities: one referring to mechanical motion of the particle represented by v and second related to the propagation of the wave represented by w .

We know that $E = h \nu$ and $E = mc^2$

$$\Rightarrow v = mC^2/h$$

$$\text{the wave velocity, } w = v \times \lambda \quad \text{since} \quad \lambda = \frac{h}{mv}$$

$$w = (mC^2/h) \left(\frac{h}{mv} \right)$$

$$w = C^2/v$$

$$\Rightarrow w > C$$

As a particle velocity v cannot exceed the velocity of light.

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

Heisenberg's Uncertainty principle.

In classical mechanics, physical quantities such as position, momentum, energy, and time can be measured simultaneously and accurately.

However, in the microscopic world (for particles like electrons, protons, neutrons, and photons), such precise measurements are not possible.

According to Werner **Heisenberg (1927)**, it is impossible to determine simultaneously the exact position and exact momentum of a microscopic particle with absolute accuracy.

If Δx is the uncertainty associated with the position of a particle and Δp the uncertainty associated with its momentum, then the product of these uncertainties will always be equal or greater than $h/4\pi$.

$$\Delta x. \Delta p \geq h/4\pi$$

Other Forms of the Principle

$$\Delta \theta. \Delta J \geq h/4\pi$$

$$\Delta t. \Delta E \geq h/4\pi$$

Where, $\Delta \theta$ = uncertainty in angular position, ΔJ = uncertainty in angular momentum, ΔE = uncertainty in Energy, and Δt = uncertainty in time

The postulates of quantum mechanics

The postulates of quantum mechanics are the basic rules that form the foundation of the theory. They explain how quantum systems such as electrons or atoms behave. These postulates describe how the state of a system is represented, how physical quantities like energy and momentum are expressed, what happens during a measurement, and how a system changes with time. Generally, there are five or six main postulates that together define the mathematical framework and physical meaning of quantum mechanics.

1. State of the system

The state of a quantum mechanical system is described by a complex-valued wave function, $\Psi(\vec{r}, t)$. This function contains all accessible information about the system and must be:

- **Single-valued:** To ensure a unique probability of finding a particle in any given state.
- **Continuous and differentiable:** So that quantum operators, which involve derivatives, can be applied to it.
- **Square-integrable:** So that the total probability of finding the particle somewhere in space is equal to one. The quantity $|\Psi(\vec{r}, t)|^2$ represents the probability density of finding the particle at position $\vec{r}$ and time t .

2. Operators for observables

Every measurable physical quantity (an "observable") in classical mechanics has a corresponding linear, Hermitian operator in quantum mechanics. This ensures that the eigenvalues, which are the possible results of a measurement, are always real numbers. Examples include:

- **Position operator:** $\hat{x}$
- **Momentum operator:** $\hat{p} = -i\hbar \frac{\partial}{\partial x}$
- **Total energy (Hamiltonian) operator:** $\hat{H} = -\hbar^2 / 2m \nabla^2 + V(x)$

3. Measurement outcomes

When you measure an observable, the only possible result you can obtain is one of the eigenvalues of the corresponding operator.

- **Eigenvalue equation:** For an operator $\hat{A}$ and its corresponding observable A , the possible measurement values a are given by the eigenvalue equation $\hat{A}\Psi = a\Psi$, where Ψ is the eigenfunction.
- **Quantization:** This postulate explains why certain physical quantities are quantized, or limited to a discrete set of values.

4. Expectation values

If a system is in a state described by a normalized wave function Ψ , the average (or "expectation") value of a physical quantity is given by the integral:

$$\langle A \rangle = \int \Psi^* \hat{A} \Psi d\tau$$

where Ψ^* is the complex conjugate of the wave function.

5. Time evolution

The time evolution of the wave function is governed by the time-dependent Schrödinger equation:

$$\hat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Here, $\hat{H}$ is the Hamiltonian operator representing the total energy of the system. This postulate is the quantum mechanical equivalent of Newton's second law in classical mechanics.

Schrodinger Time – Independent wave equation:

According to de-Broglie theory, a particle of mass ‘m’ is always associated with a wave whose wavelength $\lambda = \frac{h}{mv}$. Consider a system of stationary waves associated with a particle. Let (x, y, z) be the coordinates of the particle, and ψ , the displacement for the de-Broglie at any time t. ψ is called as wave function.

The classical differential equation of a wave motion is given by

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) \\ = v^2 \nabla^2 \psi \text{ ----- (1)}$$

Where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is called Laplace operator, and v is called wave velocity.

$$\Psi = \psi_0 \sin \omega t = \psi_0 \sin 2\pi \nu t \text{ ----- (2)}$$

$$\frac{\partial \Psi}{\partial t} = \psi_0 (2\pi \nu) \cos 2\pi \nu t$$

$$\frac{\partial^2 \Psi}{\partial t^2} = -\psi_0 (2\pi \nu)^2 \sin 2\pi \nu t = -4\pi^2 \nu^2 \Psi \quad \text{Since } v = \nu \lambda \Rightarrow \nu = \frac{v}{\lambda}$$

$$\frac{\partial^2 \Psi}{\partial t^2} = -\frac{4}{\lambda^2} \pi^2 v^2 \Psi \text{ ----- (3)}$$

Substituting (3) in (1)

$$v^2 \nabla^2 \psi = -\frac{4}{\lambda^2} \pi^2 v^2 \Psi \quad \text{Since } \lambda = \frac{h}{mv}$$

$$\nabla^2 \psi + \frac{4}{\lambda^2} \pi^2 \Psi = 0$$

$$\nabla^2 \psi + \frac{4}{h^2} \pi^2 m^2 v^2 \Psi = 0 \text{ ----- (4)}$$

If E be the total energy and V is potential energy, then its kinetic energy $\frac{1}{2} mv^2 = E - V$

$$\Rightarrow mv^2 = 2(E - V)$$

$$\Rightarrow m^2 v^2 = 2m(E - V) \text{ ---- (5)}$$

Using (5) in (4)

$$\Rightarrow \nabla^2 \psi + \frac{4}{h^2} \pi^2 2m(E - V) \psi = 0$$

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

This equation is called Schrodinger Time-Independent wave equation.

For a free particle, $V = 0$, the Schrodinger wave equation for a free particle is given by

$$\Rightarrow \nabla^2 \psi + \frac{2mE}{h^2} \psi = 0$$

Wave function:

Wave function is a mathematical complex quantity which describes the quantum state of a system. Wave function can characterize the behavior of the particles.

Physical significance of a wave function:

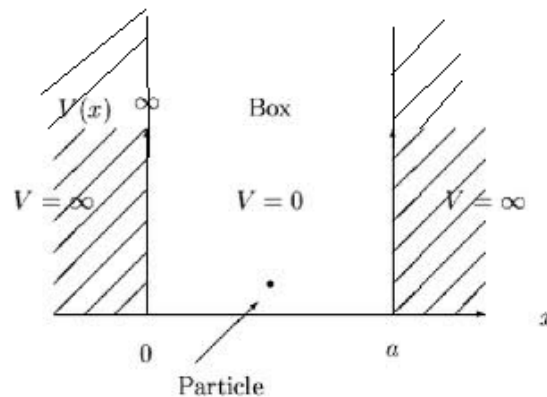
1. The wave function ψ has no direct physical meaning. It is a complex quantity representing the variation of matter wave. It connects the particle nature and its associated wave nature statistically.

2. $\Psi \cdot \psi^*$ or $|\psi|^2$ is the probability density function. $\Psi \cdot \psi^* dx dy dz$ gives the probability of finding the electron in the region of space.

If the particle is present $\int_{-\infty}^{\infty} \psi \psi^* dx dy dz = 1$ is called Normalization which was given by Max Born.

3. The wave function ψ can be considered as probability amplitude since it is used to find the location of the particle.

Particle in Three – Dimensional potential box of infinite height:



Let us consider the case of a particle of mass 'm' moving along x-direction between two rigid walls at $x = 0$ and $x = a$. The particle is free to move between the walls. The potential energy of the particle between the walls is constant because no force is acting on the particle. The constant potential energy is taken as zero. When the particle strikes any one of the walls, it is reflected back immediately. Now the force acting on the particle abruptly changes from zero to infinity.

The potential function $V(x)$ is defined as

$$V(x) = 0 \quad \text{for} \quad 0 < x < a \quad \text{and} \quad \text{-----} (1)$$

$$V(x) = \infty \quad \text{for} \quad x \leq 0 \quad \text{and} \quad x \geq a$$

The Schrodinger wave equation for a particle is given by

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

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

As $V = 0$ between the walls, hence equation turns to

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{h^2} E \psi = 0 \quad \text{Let} \quad \frac{2m}{h^2} E = K^2$$

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

The solution of equation (2) is of the form $\sin Kx$ and $\cos Kx$

$$\therefore \psi(x) = A \sin kx + B \cos kx \text{ ----- (3)}$$

Where A and B are constants. These constants can be obtained by applying boundary conditions.

$$\text{i.e., } \psi = 0 \quad \text{at } x = 0 \text{ and } x = a$$

$$\text{for } x=0 \Rightarrow \psi = 0$$

$$(3) \Rightarrow 0 = A(0) + B(1)$$

$$\Rightarrow B = 0$$

$$\text{Again, for } x = a \Rightarrow \psi = 0 \Rightarrow 0 = A \sin ka + 0 \Rightarrow \sin ka = 0 \Rightarrow ka = n\pi \text{ for } n = 0, 1, 2, 3, 4, \dots$$

$$K = \frac{n\pi}{a} \text{ ----- (5)}$$

The wave function becomes $\psi(x) = A \sin kx$

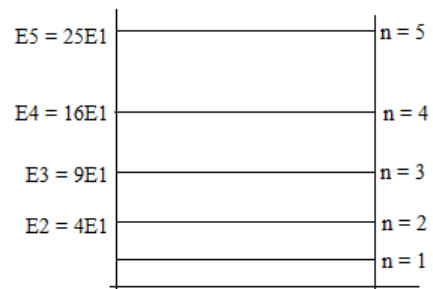
$$\psi(x) = A \sin \frac{n\pi x}{a} \text{ ----- (6)}$$

$$\text{from (5)} \quad k^2 = \frac{n^2 \pi^2}{a^2}$$

$$\text{from (5) and (4)} \quad \frac{n^2 \pi^2}{a^2} = \frac{2m}{\hbar^2} E$$

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

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



For Three dimension,

$$E_{n_x} = \frac{n_x^2 h^2}{8ma^2} \quad E_{n_y} = \frac{n_y^2 h^2}{8mb^2} \quad E_{n_z} = \frac{n_z^2 h^2}{8mc^2}$$

The allowed values of total energy are given by $E = E_x + E_y + E_z$

$$E = \frac{h^2}{8m} \left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right]$$

Where n_x, n_y, n_z denote any set of three positive numbers.

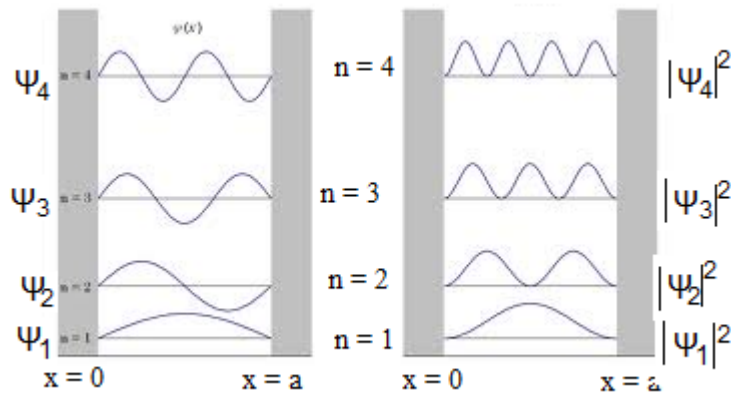
The constant A of equation (6) can be obtained by applying the normalization condition.

$$\int_0^a |\Psi(x)|^2 dx = 1 \Rightarrow \int_0^a A^2 \sin^2 \frac{n\pi x}{a} dx = 1$$

$$\Rightarrow A^2 \frac{1}{2} \int_0^a (1 - \cos \frac{2n\pi x}{a}) dx = 1$$

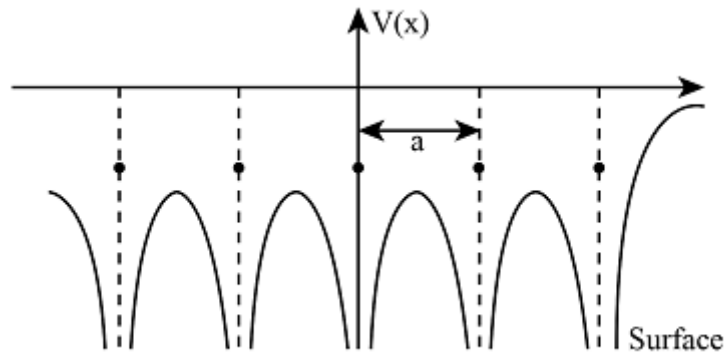
$$\Rightarrow A^2 \frac{1}{2} \left[\int_0^a dx - \int_0^a \cos \frac{2n\pi x}{a} dx \right] = 1 \Rightarrow \frac{A^2}{2} [a - 0] = 1 \Rightarrow A = \sqrt{\frac{2}{a}}$$

$$\text{The wave function } \Psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$



Band theory of solids

Band theory of solids was developed by Bloch in 1928. Band theory of solids is a quantum mechanical model that describes the range of energy levels (bands) that electrons can occupy in solid materials. According to this theory free electrons move in **periodic potential**. Periodic potential is the potential which arises due to the periodic arrangement of positive ion cores in lattice.



Since the lattice is a repetitive structure of the ion arrangement in a crystal, the type of variation of V also repeats itself. If a is the interionic distance, then, as we move in x -direction, the value of V will be same at all points which are separated by a distance equal to a .

$$V(x) = V(x+a)$$

where ' a ' is the periodicity of the lattice.

Bloch theorem

When an electron moves in periodic potential the solution of Schrodinger time independent equation must be of the form $\Psi(x) = U_k(x) e^{ikx}$, where e^{ikx} is plane wave which is modulated by a modulating function $U_k(x)$. $U_k(x)$ is also periodic function with the periodicity same as periodicity of the lattice, k is the propagation vector (wave vector), $k = \frac{2\pi}{\lambda}$.

According to Schrodinger time independent wave equation for a free particle with wave function ψ moving in a potential V is given by

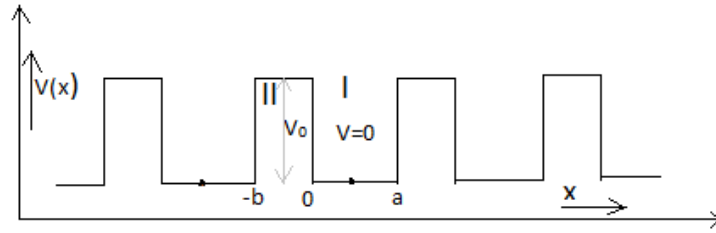
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi = 0 \quad \text{or} \quad \frac{d^2 \psi}{dx^2} + \frac{8\pi^2 m}{h^2} [E - V(x)] \psi = 0$$

The solution for the above equation was given by Bloch which is mathematically expressed as,

$$\Psi(x) = U_k(x) e^{ikx}$$

Kronig-Penney model

The Kronig-Penney model is a one-dimensional quantum mechanical model that describes the behaviour of electrons in a periodic potential. Kronig-Penney considered rectangular periodic potential for convenience and mathematical simplicity. The rectangular periodic potential can be divided into two regions as shown in the figure.



In region-I from 0 to 'a' where the potential of electron is zero and in region-II from '-b' to 0, the potential of electron is V_0 . Mathematically can be written as

$$V(x) = 0 \quad \text{for } 0 < x < a \text{ (Region-I)}$$

$$V(x) = V_0 \quad \text{for } -b < x < a \text{ (Region-II)}$$

Writing Schrodinger time independent wave equations for the above region-I and region-II are

$$\frac{d^2\psi_1}{dx^2} + \frac{8\pi^2m}{h^2} E \psi_1 = 0 \text{ ----- (1) for } 0 < x < a, \quad V(x) = 0$$

$$\frac{d^2\psi_2}{dx^2} + \frac{8\pi^2m}{h^2} (E - V_0) \psi_2 = 0 \text{ ----- (2) for } -b < x < 0, \quad V(x) = V_0$$

$$\text{Taking } \alpha^2 = \frac{8\pi^2m}{h^2} E \text{ ----- (3) and } \beta^2 = \frac{8\pi^2m}{h^2} (V_0 - E) \text{ ----- (4)}$$

The above Schrodinger time independent wave equations can be written as

$$\frac{d^2\psi_1}{dx^2} + \alpha^2 \psi_1 = 0 \text{ ----- (5)}$$

$$\frac{d^2\psi_2}{dx^2} - \beta^2 \psi_2 = 0 \text{ ----- (6)}$$

According to Bloch, when an electron moves in periodic potential the solution of Schrodinger time independent equation must be of the form

$$\Psi(x) = U_k(x) e^{ikx} \text{ ----- (7)}$$

Differentiating equation (7) twice with respect to 'x' and substituting the result into equations (5) and (6), two second-order differential equations are obtained. By applying the appropriate boundary conditions to these equations, four linear algebraic equations in the unknown constants are obtained. These four equations are then expressed in matrix form. On solving the above, we get

$$\frac{(\beta^2 - \alpha^2)}{2\alpha\beta} \sin h\beta b. \sin \alpha a + \cosh \beta b. \cos \alpha a = \cos k(a+b) \text{ ----- (8)}$$

The above equation is complicated. Kronig-Penney modified the above equation by taking the following assumptions.

When $b \rightarrow 0$ and $V_0 \rightarrow \infty$ such that bV_0 remains finite. Such a function is called as delta function.

Under these assumptions

$$\sin h\beta b \rightarrow \beta b$$

$$\cosh \beta b \rightarrow 1$$

$$\cos k(a+b) \rightarrow \cos ka$$

$$(\beta^2 - \alpha^2) = \frac{8\pi^2m}{h^2} (V_0 - E) - \frac{8\pi^2m}{h^2} E$$

$$(\beta^2 - \alpha^2) = \frac{8\pi^2 m}{h^2} (V_0 - 2E)$$

$V_0 \gg E$, $2E$ can be neglected

$$(\beta^2 - \alpha^2) = \frac{8\pi^2 m V_0}{h^2}$$

Substituting $\sin h\beta b \rightarrow \beta b$, $\cosh \beta b \rightarrow 1$ and $(\beta^2 - \alpha^2) = \frac{8\pi^2 m V_0}{h^2}$ in equation 8

$$\frac{8\pi^2 m V_0}{2\alpha\beta h^2} \beta b \cdot \sin \alpha a + \cos \alpha a = \cos ka$$

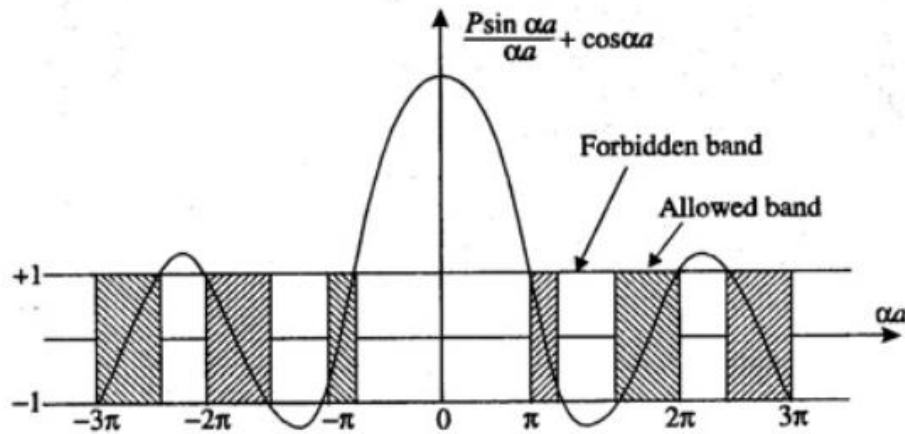
Multiplying and dividing by 'a'

$$\frac{4\pi^2 m V_0 ab}{\alpha a h^2} \sin \alpha a + \cos \alpha a = \cos ka$$

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \quad \text{----- (9)}$$

Where $P = \frac{4\pi^2 m V_0 ab}{h^2} = \frac{m V_0 ab}{\hbar^2}$ is the scattering power of the potential barrier and $V_0 b$ is called barrier strength.

The RHS term of equation 9 is bounded between -1 and +1. The left-hand side of the equation (9) is plotted as a function of αa for the value of $P = 3\pi/2$ which is shown in fig, the right-hand side one takes values between -1 to +1 as indicated by the horizontal lines in fig. Therefore, the equation (11) is satisfied only for those values of ka for which left hand side between ± 1 .



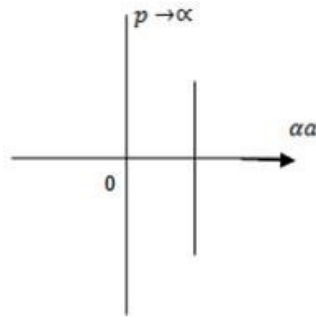
Conclusions given by Kronig-Penney from the graph.

1. From the graph it can be observed that, the allowed energy regions are shown by shaded portions i.e. motion of an electron in periodic potential is characterized energy bands and the energy bands are separated by forbidden bands.
2. As the value of ' αa ' increases, the width of the allowed energy bands also increases and the width of the forbidden band decreases.
3. With increasing P , i.e. with increasing potential barrier, the width of an allowed band decrease. As $P \rightarrow \infty$, the allowed energy becomes infinitely narrow and the energy spectrum is a line spectrum as shown in fig. When $P \rightarrow \infty$ Kronig-Penney model supports Quantum free electron theory.

If $P \rightarrow \infty$, then the equation (9) has solution

$$\text{for } P \rightarrow \infty \Rightarrow \sin \alpha a = 0 \Rightarrow \alpha a = \pm n\pi \Rightarrow \alpha = \pm \frac{n\pi}{a} \Rightarrow \alpha^2 = \frac{n^2 \pi^2}{a^2}$$

$$\Rightarrow \frac{2mE}{\hbar^2} = \frac{n^2 \pi^2}{a^2} \Rightarrow E = \frac{n^2 \hbar^2 \pi^2}{2ma^2} \Rightarrow E = \frac{n^2 h^2}{8ma^2}$$



4. With decreasing P

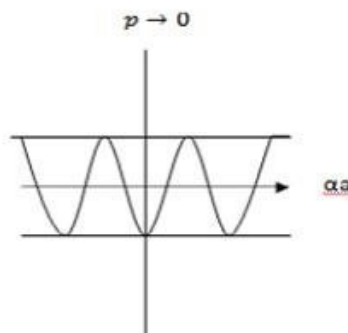
for $P = 0 \Rightarrow V_0 = 0$ i.e., $\cos \alpha a = \cos ka$

$$\Rightarrow \alpha a = ka \Rightarrow \alpha = k \Rightarrow \alpha^2 = k^2 \Rightarrow \frac{2mE}{\hbar^2} = \frac{4\pi^2}{\lambda^2}$$

$$\Rightarrow E = \frac{1}{2}mv^2$$

$$\text{since } k = \frac{2\pi}{\lambda}$$

$$\text{Since } \lambda = \frac{h}{mv} \Rightarrow \lambda^2 = \frac{h^2}{m^2v^2}$$



This shows that all the electrons are completely free to move in the crystal without any constraints. Hence, no energy level exists i.e. all the energy levels are continuous as shown in fig. When $P \rightarrow 0$ Kronig-Penney model supports the classical free electrons theory.

E-K diagram (Brillouin zones)

The electron moving in a periodic potential lattice can have energy values only between allowed regions or zones. With the help of equation

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

It is possible to plot the total energy of the electron (E) versus wave number or the propagation vector (k) and the plot is shown in the figure.

The RHS term $\cos Ka$ becomes ± 1 for values of $k = \frac{n\pi}{a}$ and hence the discontinuities in the E versus K graph occur at $k = \frac{n\pi}{a}$ where n takes the values of $\pm 1, \pm 2, \pm 3$, etc.

The dotted curve shows the parabola of free electron

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

In a periodic potential lattice, the energy values of electron are discontinuous, separated into allowed and forbidden zones occurring alternatively. We also notice that width of the forbidden band increases with E. Also, we find that as P decreases, the discontinuous E-K graph will reduce to continuous parabolic graph as shown in dotted line and forbidden bands disappear.

This means that the energy values become practically continuous.

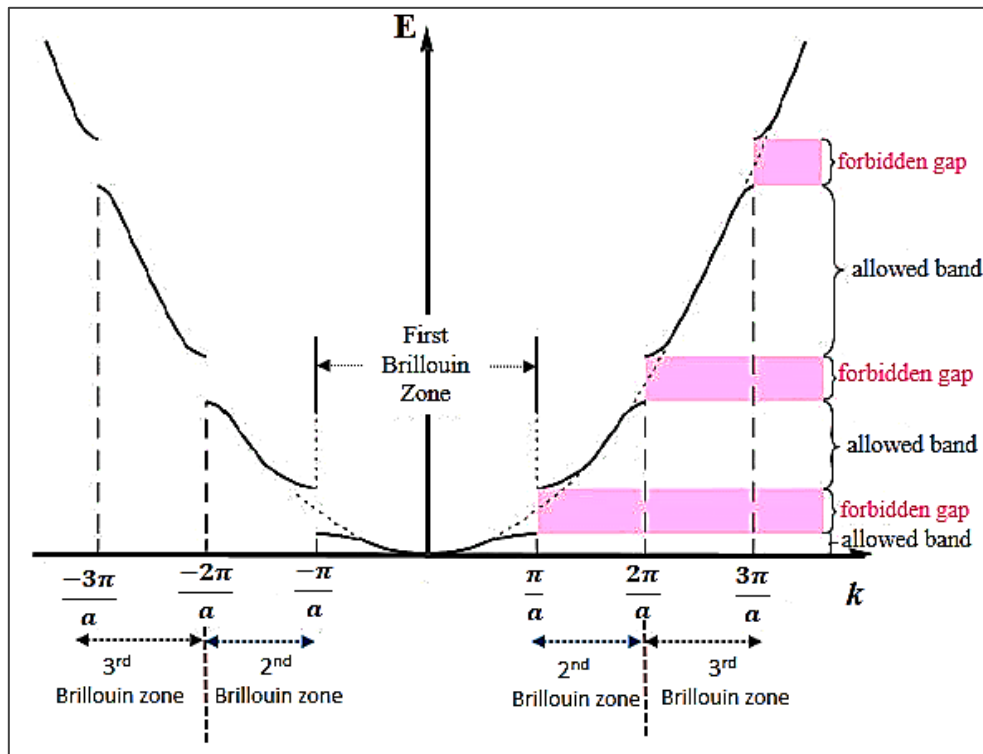
From the graph it can be observed that the electron has the allowed regions.

The allowed energy region which is extended from $-\frac{\pi}{a}$ to $+\frac{\pi}{a}$ ($k = -\frac{\pi}{a}$ to $+\frac{\pi}{a}$) is called first Brillouin zone.

The allowed energy region which is extended from $-\frac{2\pi}{a}$ to $-\frac{\pi}{a}$ and $+\frac{\pi}{a}$ to $+\frac{2\pi}{a}$ ($k = -\frac{2\pi}{a}$ to $-\frac{\pi}{a}$ and $+\frac{\pi}{a}$ to $+\frac{2\pi}{a}$) is called second Brillouin zone.

The allowed energy region which is extended from $-\frac{3\pi}{a}$ to $-\frac{2\pi}{a}$ and $+\frac{2\pi}{a}$ to $+\frac{3\pi}{a}$ ($k = -\frac{3\pi}{a}$ to $-\frac{2\pi}{a}$ and $+\frac{2\pi}{a}$ to $+\frac{3\pi}{a}$) is called third Brillouin zone.

In the same further Brillouin zones are continued.



Concept of phase velocity and group velocity

When waves propagate through a medium—such as electromagnetic waves, sound waves, or matter waves—they are typically composed of many sinusoidal components of different frequencies. To understand how these waves propagate, two important physical quantities are needed:

- Phase velocity
- Group velocity

These describe how individual wave phases and wave packets (wave groups) propagate in space.

Phase Velocity (V_p)

The phase velocity is the speed at which a single wave of a specific frequency (one component of the wave) travels.

For a wave of the form:

$$\psi(x, t) = A \sin(kx - \omega t)$$

Phase velocity is:

$$v_p = \frac{\omega}{k}$$

Where:

- ω = angular frequency
- k = wave number

It is the speed at which **crests, troughs**, or any fixed phase point moves.

It does **not** necessarily represent the speed of energy or information.

Example

Light in a medium with refractive index n :

$$v_p = \frac{c}{n}$$

where c is the speed of light in vacuum.

Group Velocity (V_g)

The group velocity is the speed at which a wave packet or group of waves travels. This wave packet carries energy and information.

Group velocity is:

$$v_g = \frac{d\omega}{dk}$$

It comes from considering two waves of slightly different frequencies that combine to form a wave packet.

Represents the speed of energy, signal, or information propagation.

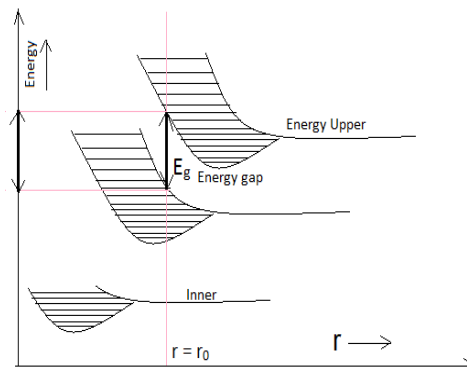
Determines how wave packets evolve in space.

Example

For matter waves (quantum mechanics):

$$v_g = \frac{p}{m} = v_{\text{particle}}$$

Formation of energy bands in solids:



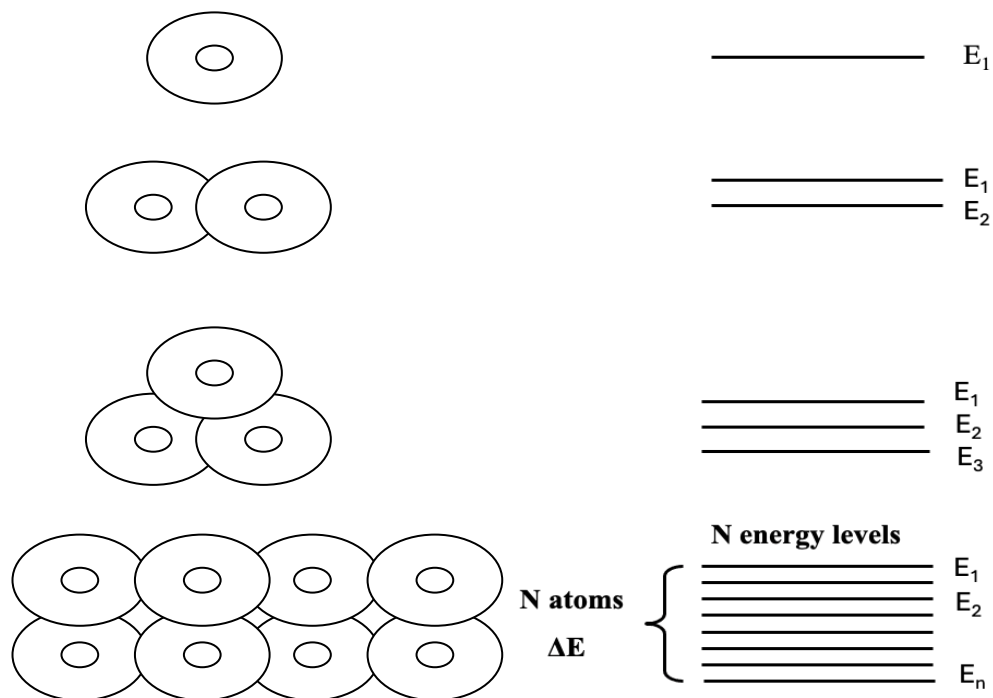
When the atoms are at large distances of separation as in case of gas molecules, the mutual interaction between the electron orbits of the neighbouring atoms can be neglected. When the atoms are brought to close to each other, the electrons respond to the influence of the other

nuclei, electron orbits of the atoms overlap when the atoms are brought still closer as in case of solid. Each energy level associated with the individual atom now repeats as many times as the number of atoms in the solid.

In the single atom, the energy broadens out into a large number of closely spaced levels of the atoms. Such a set of energy levels that has finite width is called an energy band.

At larger interatomic distances, the different energy levels have shown as discrete energy levels. But as the distance between the atoms reduced, it can be observed that each set of energy levels combines together to form a band of closely spaced levels under the influence of neighbouring atoms. The spreading of levels starts at different values of 'r' for different energy levels. The spreading of energy levels starts at larger distances for outer shells as the electrons in the outer shells interacts first with the neighbouring compare to inner shell electrons. At a particular distance ' r_0 ' each energy band separated by a finite energy gap ' E_g '.

- In a free atom, electrons occupy **discrete energy levels** (1s, 2s, 2p, etc.). Each electron level is sharply defined due to the absence of neighbouring atoms.
- When many atoms come close to form a solid (say N atoms), their outermost (valence) orbitals start to **overlap**.
- According to the **Pauli Exclusion Principle**, no two electrons can occupy the same quantum state. Therefore, the discrete atomic energy levels split into many closely spaced levels.



Valance Band

A valance band is an energy band formed by a series of closely spaced energy levels that contain the valence electrons of atoms in a solid. The valance band may be completely filled or partially filled with electrons, but it cannot be empty.

Conduction Band

The next higher permitted energy band above the valance band is the conduction band. The conduction band is generally empty or partially filled with electrons and cannot be completely

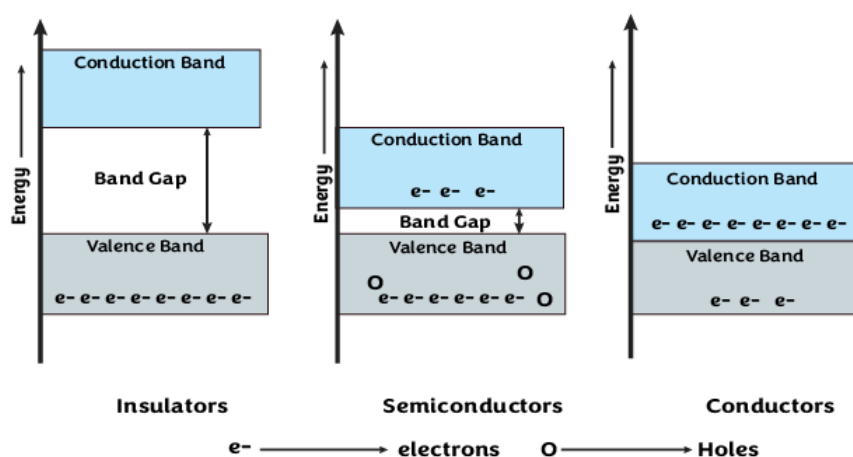
filled. Electrons in the conduction band are free to move within the solid, enabling electrical conduction.

Energy gap (band gap)

Energy gap (band gap) is the energy difference between the top of the valence band and the bottom of the conduction band in a solid. It represents a range of energies that electrons cannot occupy. The size of the energy gap determines whether a material is a conductor, semiconductor, or insulator.

$$E_g = E_c - E_v \text{ (eV)}.$$

Classification of solids into Metals, Semiconductors and Insulators



Insulators:

Large band gap (typically $> 5 \text{ eV}$).

Electrons cannot jump from valence band to conduction band easily.

Solid materials which do not conduct electric current under normal conditions are known as insulators. In insulators, the valence band is completely filled and it has no electrons in the conduction band. The forbidden energy gap will be very high when compared with conductor. The energy required to shift an electron from the valence band to the conduction band to make electrical conduction is very high. Hence it is not possible to provide enough energy by an ordinary electric field. We can achieve electric conduction in an insulator with very high voltage known as breakdown voltage.

Examples:

Rubber, Glass, Diamond, Plastic.

Semiconductors

Small band gap ($\approx 0.7 \text{ eV}$ to 3 eV).

At room temperature, some electrons gain energy to move from valence band to conduction band.

Semiconductors are materials whose electrical conductivity lies between that of conductors and insulators. The conductivity of semiconductors is in the order of 10^4 to $10^{-4} \text{ mho.m}^{-1}$. The magnitude of forbidden energy gap of a semiconductor lies in between the forbidden energy gap of insulators and conductors.

Examples:

Silicon (Si), Germanium (Ge), Gallium Arsenide (GaAs).

Conductors (Metals)

Valence band and conduction band overlap with each other.

Energy gap is zero.

A material which conducts electric current when a potential difference is applied across them is known as conductors. In case of conductors, the valence band is completely filled while conduction band is half filled as shown in figure. When a small potential difference is applied to a solid material, it provides sufficient energy to the electron in the valence band to shift to the conduction band. The shifting of electrons from the valence band to the unfilled conduction band results in the flow of current in the material.

Examples:

Copper, Silver, Gold.

Concept of Discrete Energy Levels and Quantum Confinement

In isolated atoms and molecules, electrons do not have continuous energy but occupy specific, fixed (discrete) energy levels. These levels arise from the quantum mechanical nature of electrons. When many atoms come together in a solid, their discrete levels split into closely spaced levels, forming energy bands. These bands appear continuous because of the large number of atoms.

Quantum confinement occurs when the size of a material is comparable to the de Broglie wavelength of an electron (typically a few nanometres). When particles are confined to extremely small spatial scales, their energy levels no longer form continuous energy bands, but rather exhibit quantized states, similar to discrete energy levels in an atom. Electrons confined in a small region behave like a particle in a box, giving rise to discrete energy states. When a material's dimension is extremely small (nano-size), The electron cannot move freely. Quantum confinement occurs.

Quantum confinement is a quantum mechanical effect that occurs when the size of a material is reduced to the nanoscale, typically less than 10 nanometres. At this size, the motion of electrons and electron-hole pairs (excitons) becomes physically restricted in one or more dimensions, leading to a change in the material's electronic and optical properties.

The primary consequences of quantum confinement include:

- **Discrete Energy Levels:** In bulk materials, electrons can have a continuous range of energy levels (energy bands). When confined, these energy levels become discrete, similar to those in an atom, which is why quantum dots are often called "artificial atoms".
- **Size-Dependent Band Gap:** The energy gap between the highest occupied molecular orbital (valence band) and the lowest unoccupied molecular orbital (conduction band) increases as the particle size decreases.
- **Tunable Optical Properties:** This size-dependent band gap means that materials can absorb or emit light of different energies (colors) depending on their size. For example, smaller semiconductor quantum dots emit blue light (higher energy), while larger ones emit red light (lower energy).