UNIT – II

Quantum mechanics

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Introduction:

- **WAVE**

A wave is nothing but a disturbance which is occurred in a medium and it is specified by its frequency, wavelength, phase, amplitude and intensity.

- **PARTICLE**

A particle or matter has mass and it is located at a some definite point and it is specified by its mass, velocity, momentum and energy.

Photon

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Photons are quanta or smallest packet of energy of electromagnetic radiation which can not be further subdivided.
Photons **travel with velocity equal to velocity of light** and their **rest mass is zero.**

Properties of Photon

1. Energy of photon= **h ν**

2. Rest mass of photon = Zero

Mass, m = $\dfrac{E}{c^2} = \dfrac{h\nu}{c^2} = \dfrac{hc}{\lambda c^2} = \dfrac{h}{\lambda c}$

3. Momentum, p= $\dfrac{h}{\lambda}$

4. Photons have no charge and so they are not affected by electric and magnetic fields.

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Classical Mechanics and Quantum Mechanics

- Classical mechanics can explain macroscopic phenomena such as motion of billiard balls or rockets.
- Quantum mechanics is used to explain microscopic phenomena such as photon-atom scattering and flow of the electrons in a semiconductor.
- Quantum Mechanics is a collection of postulates based on a huge number of experimental observations.

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Classical Mechanics:
Applicable to particles of macroscopic size
Deals with problems in terms of certainties
simultaneous determinations of the position and momentum of a particle is possible.
Energy is continuous.

Quantum Mechanics:
Applicable to particles of microscopic size
Deals with the problems in terms of probabilities
Simultaneous determination of the position and the momentum of a particle is not possible
Energy is quantized.

Importance Quantum Mechanics

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▶ opens new field – subatomic world

▶ Explains how transistor, micro devices works

▶ Why copper conduct electricity but glass does not

▶ Without Quantum Mechanics, we could never have designed and built:

  ▶ semiconductor devices

    ▶ computers, cell phones, etc.

  ▶ lasers

    ▶ CD/DVD players, bar-code scanners, surgical applications

  ▶ MRI (magnetic resonance imaging) technology

  ▶ nuclear reactors

  ▶ Artificial Intelligence

Wave Particle duality

- Light has dual nature – particle nature and wave nature
- Experiments – propagation experiments

    - Interaction experiments

Light behaves like wave while propagating

and behaves like a particle when it interacts with matter.

Interference and diffraction can be explained by wave nature

Photoelectric effect can be explained by particle nature.

Cont..

- In 1924 – Louis de Broglie put forward the wave – particle duality
- Nature has symmetry – universe is totally composed of light and matter
- When light has dual nature – why not matter ?
- Matter also exhibit dual nature – wave and particle
- Electrons, protons etc., also behave like particle and wave – possess mass as well as wavelength
- Introduced the concept of **Matter waves**

de Broglie Hypothesis

- **According to de Broglie just as light has dual characteristics (i.e. it acts as both wave as well as particle), there is a possibility that in a similar way moving particles such as electrons, protons, atoms etc. also exhibit dual characteristics i.e. they may have a wave character associated with them.**

- Such waves associated with material particles are called matter waves or de Broglie waves, whose wavelength is given by:

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

where m is mass of the particle
v is velocity of particle
h is Planck's constant = 6.62 X 10^{-34} J-s

> **De Broglie wavelength is more significant for small masses travelling at high speeds rather than large masses travelling at low speeds.**

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Proof of de-Broglie wave equation

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Acc. to Quantum Theory

$$E = h \nu \rule{4cm}{0.4pt} (1)$$

where ν is frequency of photon
If photon has mass m, then its energy is given by

$$E = mc^2 \rule{4cm}{0.4pt} (2)$$

Equating (1) and (2)

$$mc^2 = h \nu$$

$$mc = \frac{h \nu}{c} = \frac{h}{\lambda}$$

or $\lambda = \frac{h}{mc} = \frac{h}{p} \rule{4cm}{0.4pt} (3)$

where p = mc = momentum of photon

de Broglie assumed that this equation can be equally applicable to both photons and other material particles.
If m and v are the mass and velocity of moving particle, then its momentum

$$p = mv$$

and de Broglie equation is given by

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

Special cases:

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❖ **If E = K.E of material particle**

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

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

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

❖ **If a charged particle having charge 'e' is accelerated through a potential difference 'V' volts**

$$E = eV$$

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

$$\lambda = \frac{12.27\text{Å}}{\sqrt{V}} \text{ (for electron)}$$

❖ **Acc. to Kinetic theory of gases, average K.E of material particle is given by:**

$$E = \frac{1}{2}mv^2 = E = \frac{3}{2}kT$$

$$p = 3mkT$$

$$\lambda = \frac{h}{\sqrt{3mkT}}$$

Characteristics of Matter waves

- **Lighter particles have greater wavelength than the heavier particles**

- **Smaller the velocity of the particle, the greater is the wavelength associated with it.**

- **If velocity is zero, then corresponding wavelength is infinity. If velocity is infinity, then the wavelength is zero. This implies that the matter waves are always generated only when the particles are in motion.**

- **Matter waves are independent of the charge. They are produced by charged and also uncharged particles. This shows that the matter waves are not electromagnetic waves.**

- **Velocity of matter waves is not constant. It depends only on the velocity of particle, while the velocity of the electromagnetic wave is constant.**

- **The velocity of matter waves may be greater that the velocity of light.**

Differentiate Matter waves and EM Waves

Matter Waves	Electromagnetic Waves
Associated with moving particles	Oscillating charged particles give rise to em wave
λ depends on m and v	λ depends on energy
Can travel with velocity >c	Travels with velocity of light
Not electromagnetic in nature	Electric and magnetic fields vary periodically

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Wave Packet

- Wave packet is the resultant of the group of waves with slightly different velocity and wavelength, with such phase and amplitude that they interfere constructively over a small region of space where the particle can be located. Outside this region, they interfere destructively so that the amplitude reduces to zero.

> **Velocity of wave packet is called Group velocity (v_g)**
> **Velocity of individual waves is called Phase velocity (v_p)**

wave packet

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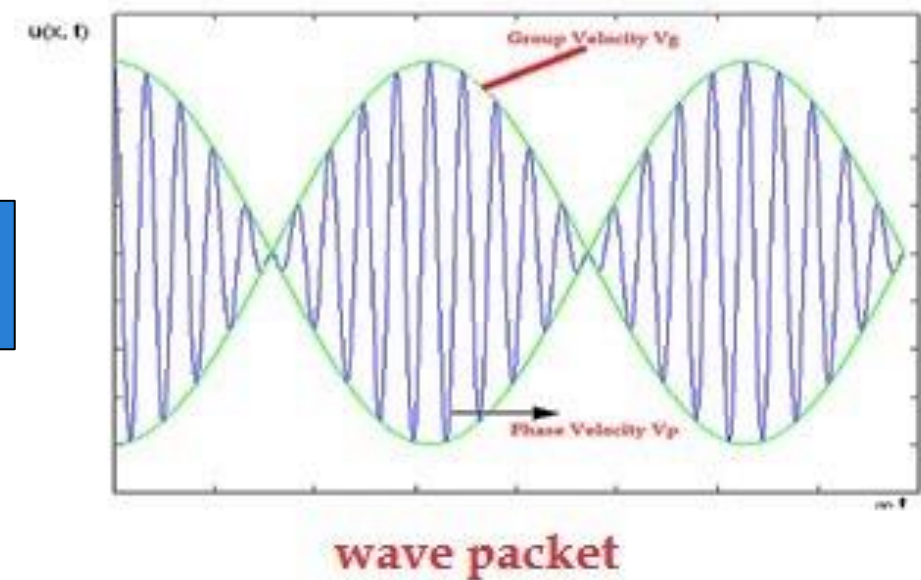
Group Velocity (v_g)
The velocity with which center of mass of wave packet moves is called group velocity.
The significance of group velocity lies in the fact that this is the velocity with which energy in the wave packet is transmitted.

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

Phase Velocity (v_p)
The velocity with which a monochromatic wave propagates through a medium is called phase velocity.

$$v_p = \frac{c^2}{v}$$

$$\text{or } v_p = \frac{\omega}{t}$$

$$v_g = v_p + k\frac{dv_p}{dk}$$

Heisenberg Uncertainty Principle

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Heisenberg Uncertainty principle states that it is impossible to measure accurately and simultaneously both the position of a particle along a particular direction (say x) and momentum of the particle in the same direction (i.e. p_x).

➤ **If Δx is the uncertainty in the measurement of position along x-direction and**
Δp_x is the uncertainty in the measurement of momentum along the same direction, then their product will be

$$\Delta x.\ \Delta p_x = \hbar$$
$$or$$
$$\Delta x.\ \Delta p_x \geq \frac{\hbar}{2}$$

where $\hbar$ = h/2π

❖ **Energy-time uncertainty relation: ΔE. Δt ≥ $\frac{\hbar}{2}$**

❖ **Angular position and angular momentum uncertainty relation:**

$$\Delta J.\ \Delta\Theta \geq \frac{\hbar}{2}$$

Wave Function $\psi\,(\vec{r},t)$

- Wave function is a variable quantity that mathematically describes the wave characteristics of a particle.
- Wave function provides the quantum mechanical description of the behavior of a particle or a system of mass m, potential energy V at a position vector r and time t.

- It is complex quantity and a function of space and time.

- It gives an idea for probability of finding particle in a particular region of space.

- The region where magnitude of ψ is large, probability of finding particle is more and vice versa.

$|\psi\,(\vec{r},t)| \longrightarrow$ large $\longrightarrow$ probability more

$|\psi\,(\vec{r},t)| \longrightarrow$ small $\longrightarrow$ probability less

Probabilty density $P\,(\vec{r},t)$

- **Product of $\psi\,(\vec{r},t)$ and its complex conjugate $\psi^*\,(\vec{r},t)$ gives position probability density $P(\vec{r},t)$.**

$$P(\vec{r},t) = \psi\,(\vec{r},t)\,\psi*(\vec{r},t) = |\psi\,(\vec{r},t)|^2$$

- **It is complex quantity and a function of space and time.**

- **It gives an idea for probability of finding particle in a particular region of space.**

$$\int_{-\infty}^{+\infty} |\psi\,(\vec{r},t)|^2 \; dV = 1$$

Since, the probability of finding the particle in given region of space is unity.

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Properties of wave function

- Ψ *must be* <u>*continuous*</u> *and* <u>*single valued*</u> *everywhere.*

- $\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}$ and $\frac{\partial \psi}{\partial z}$ *must be* <u>*continuous*</u> *and* <u>*single valued*</u> *everywhere.*

- Ψ *must be* <u>*normalizable*</u> *i.e.* Ψ *must go to zero as* $x \to \pm\infty, y \to \pm\infty, z \to \pm\infty$

Time dependent Schrodinger Wave Equation

For a particle moving in $+x$ direction, wave function ψ is given by

$$\Psi(x,t) = A\, e^{\frac{i}{\hbar}(px-Et)} \qquad \underline{\hspace{3cm}} (1)$$

Differentiating eqn. (1) w.r.t. x

$$\frac{\partial \Psi(x,t)}{\partial x} = A e^{\frac{i}{\hbar}(px-Et)} \left(\frac{i}{\hbar}\right)(p) \qquad \underline{\hspace{3cm}}(2)$$

$$\frac{\partial \Psi(x,t)}{\partial x} = \frac{ip}{\hbar}\, \Psi(x,t)$$

$$p\Psi(x,t) = -i\,\hbar\, \frac{\partial \Psi(x,t)}{\partial x} \qquad \underline{\hspace{3cm}}(3)$$

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Differentiating eqn. (2) w.r.t. x

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

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

$$\boldsymbol{p^2 \Psi(x,t) = -\hbar^2 \frac{\partial^2 \Psi(x,t)}{\partial x^2}} \qquad \underline{\qquad\qquad} (4)$$

Differentiating eqn. (1) w.r.t. t

$$\frac{\partial \Psi(x,t)}{\partial t} = Ae^{\frac{i}{\hbar}(px-Et)}\left(\frac{-i}{\hbar}\right)(E)$$

$$\mathbf{E\ \Psi(x,t) = i\,\hbar\,\frac{\partial \Psi(x,t)}{\partial t}} \qquad \underline{\qquad\qquad}(5)$$

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At speed << speed of light

$$E = \frac{p^2}{2m} + V(x,t)$$

Multiply both sides of above equation with Ψ

$$E\,\Psi(x,t) = \frac{p^2}{2m}\,\Psi(x,t) + V(x,t)\,\Psi(x,t)$$

Substituting values of eqn. (4) and (5) in above equation, we get

$$i\,\hbar\,\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\,\Psi(x,t \qquad \underline{\hspace{2cm}}(6)$$

This is time dependent Schrodinger Wave Equation (SWE)

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In 3-Dim.

$$i\,\hbar\,\frac{\partial\Psi(\vec{r},t)}{\partial t} = -\hbar^2\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right) + V(\vec{r},t)\,\Psi(\vec{r},t)$$

$$i\,\hbar\,\frac{\partial\Psi(\vec{r},t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\Psi(\vec{r},t)$$

$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)$ **is called <u>Hamiltonian operator</u> and is represented by H**

$$i\,\hbar\,\frac{\partial\Psi(\vec{r},t)}{\partial t} = H\,\Psi(\vec{r},t)$$

$$E\,\Psi(\vec{r},t) = H\,\Psi(\vec{r},t)$$

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Energy and Momentum Operators

In 1-Dim.

$$p_x = -i\,\hbar\,\frac{\partial}{\partial x}$$

$$p_x^2 = -\hbar^2\,\frac{\partial^2}{\partial x^2}$$

$$E = i\,\hbar\,\frac{\partial}{\partial t}$$

In 3-Dim

$$\vec{p} = -i\,\hbar\,\vec{\nabla}$$

$$p^2 = -\hbar^2\nabla^2$$

$$E = i\,\hbar\,\frac{\partial}{\partial t}$$

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Time independent Schrodinger Wave Equation

In some of the cases, P.E (V) of a particle does not depend on time t, it varies with position of particle only and the field is said to be stationary.

In stationary problems Schrodinger Equation can be simplified by separating out time and position dependent parts.

So, we can write wave function as

$$\Psi(x,t) = \Psi(x)\ \varphi(t)$$ _____(1)

Sicne, we have

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

Using (1) in above equation we get,

$$i\,\hbar\frac{\partial}{\partial t}(\Psi\,\varphi) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}(\Psi\,\varphi) + V\,\Psi\,\varphi$$

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

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Dividing throughout by (Ψ φ), we get

$$i\hbar \frac{1}{\varphi} \frac{\partial \varphi}{\partial t} = -\frac{\hbar^2}{2m} \frac{1}{\Psi} \frac{\partial^2 \Psi}{\partial x^2} + V$$

Since, V is a function of x only, so R.H.S of above equation is a function of x and L.H.S is a function of *t* only. Since, *x* and *t* are independent variables, both functions of *x* and *t* must be equal to a constant. *i.e.*

$$i\hbar \frac{1}{\varphi} \frac{\partial \varphi}{\partial t} = E$$

$$-\frac{\hbar^2}{2m} \frac{1}{\Psi} \frac{\partial^2 \Psi}{\partial x^2} + V = E$$

_____ (2)

Equation (2) can be rewritten as

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = E \Psi$$

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The above equation involves only the space co-ordinates and is called **time-independent Schrodinger wave equation.**

Eqn. (3) can be rewritten as
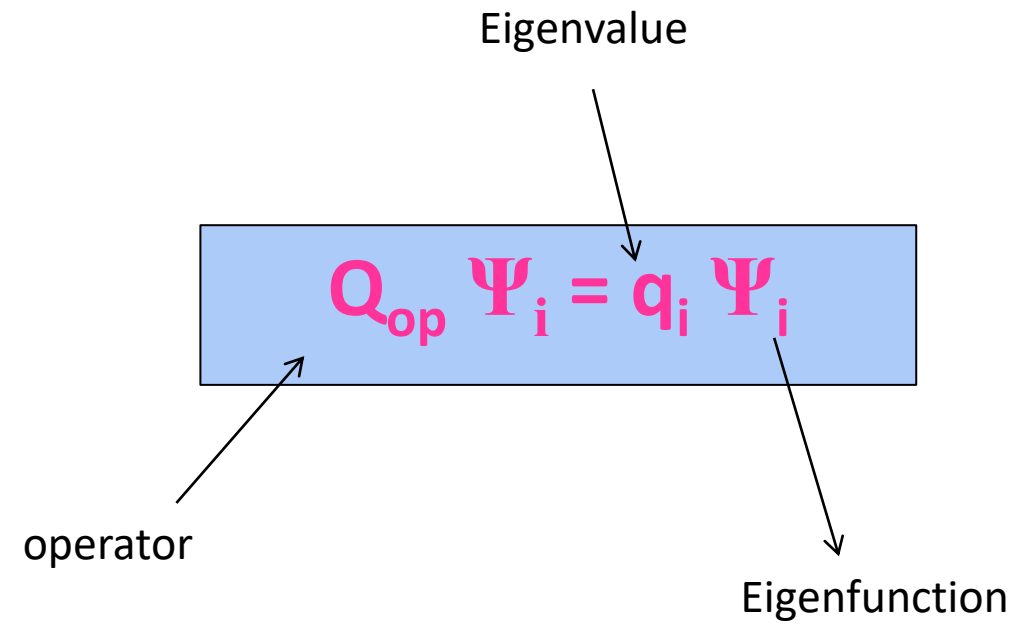
$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = (E-V)\,\Psi$$

$$\frac{\partial^2\Psi}{\partial x^2} = \frac{-2m}{\hbar^2}(E-V)\,\Psi$$

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{2m}{\hbar^2}(E-V)\,\Psi = 0$$

This is time-independent Schrodinger wave equation

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Eigenvalue

$$Q_{op} \Psi_i = q_i \Psi_i$$

operator

Eigenfunction

Schrodinger wave equation for a particle in 1-D box (Infinite Potential Well)

- Consider a particle of mass *m* restricted to move along x-axis between x=0 and x=L by ideally reflecting high walls of infinite high potential well, as shown in figure. Suppose that _P.E (V) of particle is zero_ inside the box and rises to infinity outside the box.

$$V(x) = 0 \qquad for \qquad 0 < x < L$$
$$\quad = \infty \qquad for \qquad x < 0, x > L$$

Outside box
$V(x) = \infty$

Inside box
$V(x) = 0$

Outside box
$V(x) = \infty$

$x = 0$ $x = L$
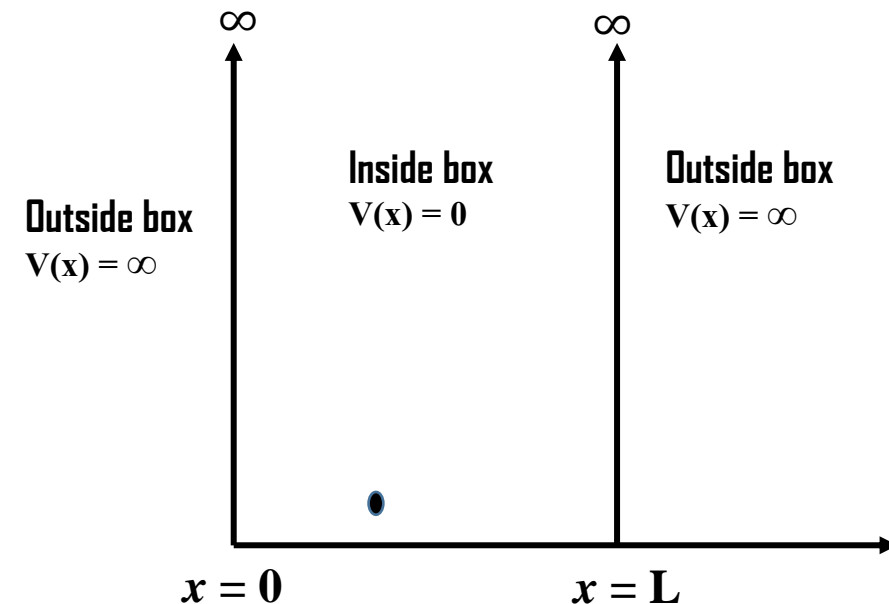
Schrodinger wave equation (for 1-dim.) is given as

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

For a particle trapped in 1-dim. box, V = 0,

So, the Schrodinger wave equation (S.W.E) is given by:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} E\, \psi = 0 \qquad \rule{3cm}{0.4pt} (1)$$

Put
$$k^2 = \frac{2mE}{\hbar^2} \qquad \rule{2.5cm}{0.4pt} (2)$$

$$\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0$$

The general solution of above equation is given as

$$\psi(x) = A\, e^{ikx} + B\, e^{-ikx} \qquad \rule{3cm}{0.4pt} (3)$$

where A and B are arbitrary constants.

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The value of these constants can be determined by applying boundary conditions.

i. $\psi(x) = 0$ at $x = 0$

ii. $\psi(x) = 0$ at $x = L$

Using 1st boundary condition

$$0 = A + B$$

$$A = -B \qquad \underline{\qquad\qquad} (4)$$

Using 2nd boundary condition

$$A\,e^{ikL} + B\,e^{-ikL} = 0$$

$$A\,e^{ikL} - A\,e^{-ikL} = 0$$

$$2i\,A\,\frac{(e^{ikL} - e^{-ikL})}{2i} = 0$$

$$2iA \sin kL = 0$$

Above equation is satisfied if either A = 0 or $\sin kL = 0$

But A ≠ 0 because it will also make B zero, which will make ψ = 0, and that's not possible.

Therefore, $\sin kL = 0$

$$kL = n\pi$$

$$k = \frac{n\pi}{L} \qquad _____ (5) \text{ where } n = 1, 2, 3\_\_\_\_ \text{ but n} \neq 0$$

Energy Eigen values

From equation (5) $\qquad\qquad k^2 = \dfrac{n^2\pi^2}{L^2}$

Also from equation (2) $\qquad\qquad k^2 = \dfrac{2mE}{\hbar^2}$

Comparing, we get $\qquad\qquad \dfrac{2mE}{\hbar^2} = \dfrac{n^2\pi^2}{L^2}$

$$\boldsymbol{E = \frac{n^2\pi^2\hbar^2}{2mL^2}} \qquad _____ (6)$$

Above relation indicates that only discrete energy values are allowed.

➢ **For n = 1 i.e. Ground state**

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2}$$

This is called **Zero Point Energy**. This is the minimum energy possessed by the particle in box i.e. the particle can not have zero kinetic energy.

➢ **for n = 2, 1st excited state**

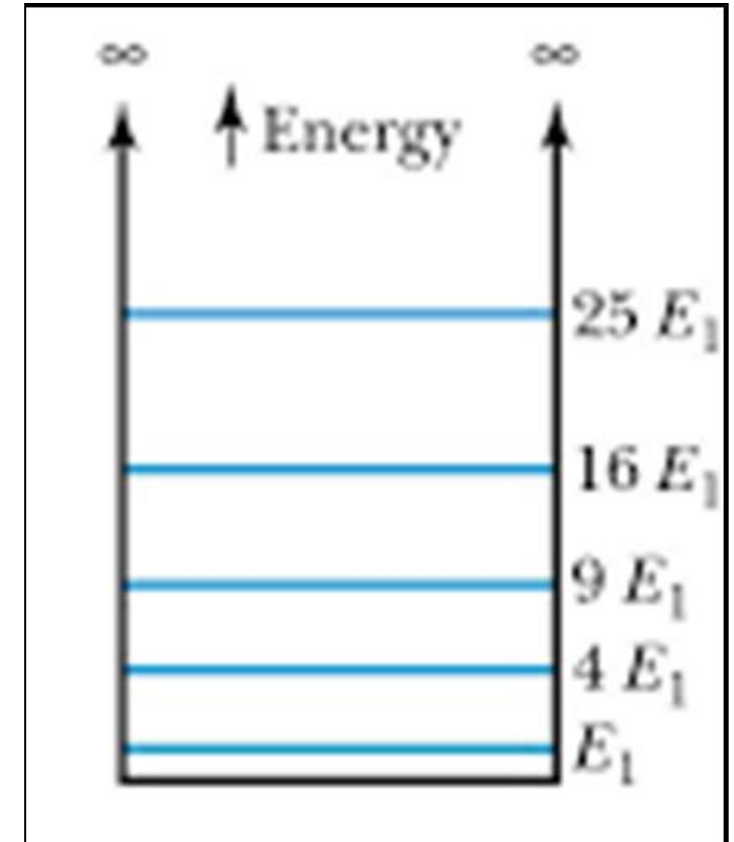$$E_2 = \frac{4\pi^2 \hbar^2}{2mL^2} = 4E_1$$

Similarly,

$E_3 = 9E_1$, 3rd excited state

$E_4 = 16 E_1$,

$E_5 = 25 E_1$ so on…….

i.e. $\boxed{E_n = n^2 E_1}$

Energy levels for a particle in 1-D box

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Spacing between Energy Levels

The spacing between (n+1) and nth energy level is given by

$$\Delta E = E_{(n+1)} - E_n = \frac{(n+1)^2 \pi^2 \hbar^2}{2mL^2} - \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

$$= (2n+1) \frac{\pi^2 \hbar^2}{2mL^2}$$

$$\Delta E = (2n+1)E_1$$

❖ *For a box of infinite length i.e L → ∞, the spacing between energy levels approaches to zero. Hence, energy spectrum becomes continuous and the particle behaves as it is free without au boundary condition..*

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Solution of equation (3) can be rewritten as

$$\psi(x) = A\left(e^{ikx} - e^{-ikx}\right)$$

$$\psi(x) = 2i\,A\,\frac{\left(e^{ikx} - e^{-ikx}\right)}{2i}$$

$$\psi(x) = 2iA\,\sin\frac{n\pi x}{L}$$

$$\psi(x) = |C|\,\sin\frac{n\pi x}{L} \quad _____ (6)$$

Evaluation of $|C|$:

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To evaluate $|C|,$ we will apply Normalization condition i.e.

$$\int |\psi\ (x)|^2\ dx = 1$$

$$|C|^2 \int_0^L sin^2 \frac{n\pi x}{L} dx = 1$$

$$\frac{1}{2} |C|^2 \int_0^L (1 - cos \frac{2n\pi x}{L}) dx = 1$$

$$\frac{1}{2} |C|^2 \left[x - \frac{sin \frac{2n\pi x}{L}}{\frac{2n\pi}{L}} \right]_0^L = 1$$

$$\frac{1}{2} |C|^2 (L - 0) = 0$$

$$|C|^2 = \frac{2}{L} \qquad \text{or} \qquad |C| = \sqrt{\frac{2}{L}}$$

Where C is the normalization constant

Therefore, the wavefunction (eqn. 6) becomes

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

Eigen Functions:

$$\psi_1(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}$$

$$\psi_2(x) = \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{L}$$

$$\psi_3(x) = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

$$\vdots$$
$$\vdots$$

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∞ ∞

$\psi_4(x)$ $n = 4$

$\psi_3(x)$ $n = 3$

$\psi_2(x)$ $n = 2$

$\psi_1(x)$ $n = 1$

$x = 0$ $x = L$
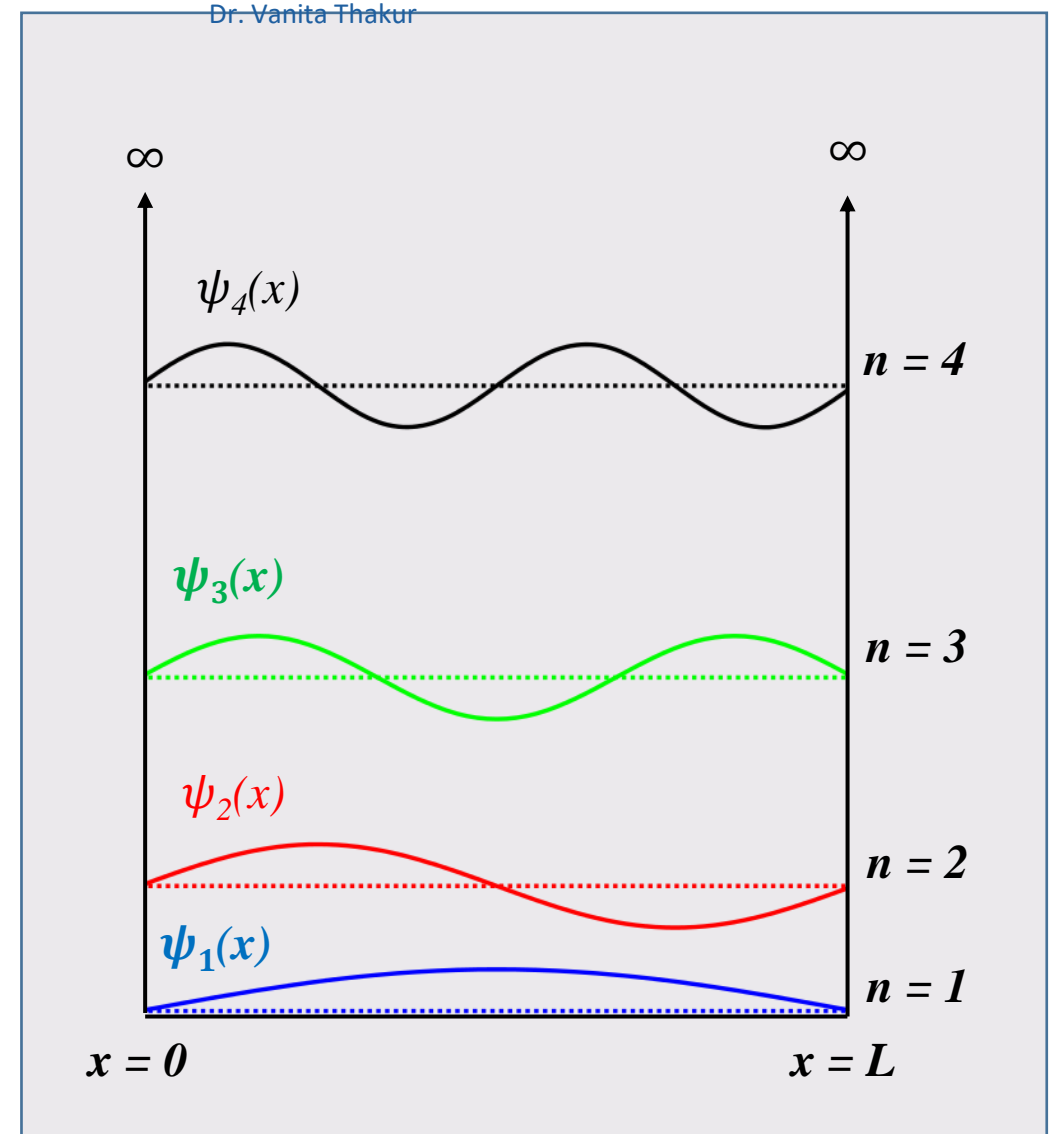
In the given diagram, points where the magnitude of wavefunction i.e. $\psi(x)$ **is zero** are called **NODES**.
Nodes are the points where the probability of finding the particle is zero.

$\psi_1(x)$ has 2-nodes: x=0 and x=L

$\psi_2(x)$ has 3-nodes: x=0, L/2 and L

$\psi_3(x)$ has 4-nodes: x=0, L/3, 2L/3 and L

Thus, $\psi_n(x)$ will have (n+1) nodes.

The points where the magnitude of wavefunction i.e.
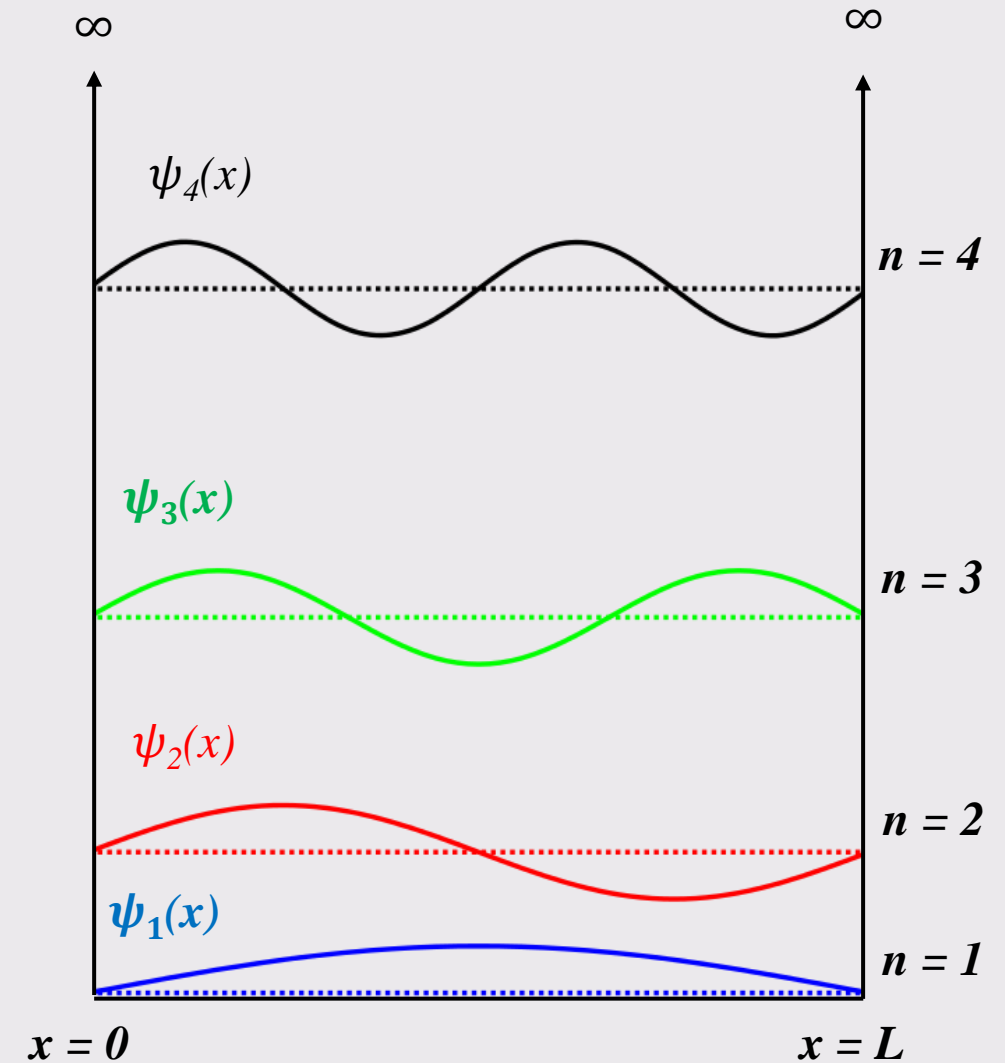$|\psi(x)|$ **is maximum** are called
ANTI-NODES.
Antinodes are the points where the probability of finding the particle is maximum.

$\psi_1(x)$ has 1-nodes: x=L/2

$\psi_2(x)$ has 2-nodes: x=L/4 and 3L/4

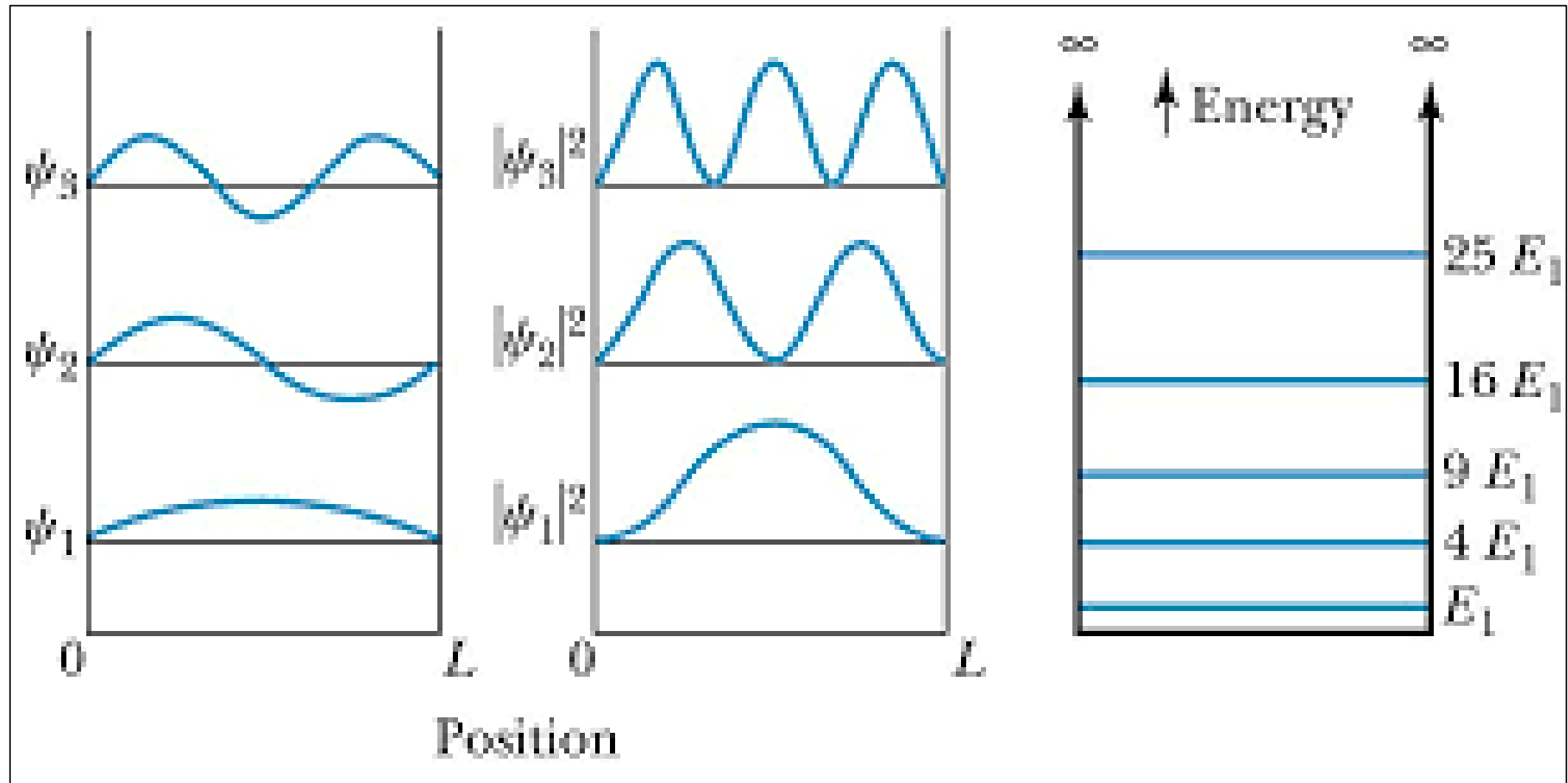*$\psi_3(x)$ has 3-nodes: x=L/6, 3L/6 and 5L/6*

And so on…..

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Probability of location of particle:

$P(x)dx = |\psi_n (x)|^2 dx$

$$= \left| \sqrt{\frac{2}{L}} \; sin \; \frac{n\pi x}{L} \right|^2 dx$$

$$= \frac{2}{L} sin^2 \; \frac{n\pi x}{L}$$

*So, for **n=1** the most probable position is at L/2.*
*For **n=2** the most probable positions are at x=L/4 and 3L/4.*
*For **n=3** the most probable positions are at x=L/6, 3L/6 and 5L/6*

$|\psi_3 (x)|^2$ *n=3*

$|\psi_2 (x)|^2$ *n=2*

$|\psi_1 (x)|^2$ *n=1*

x=0   *x=L*
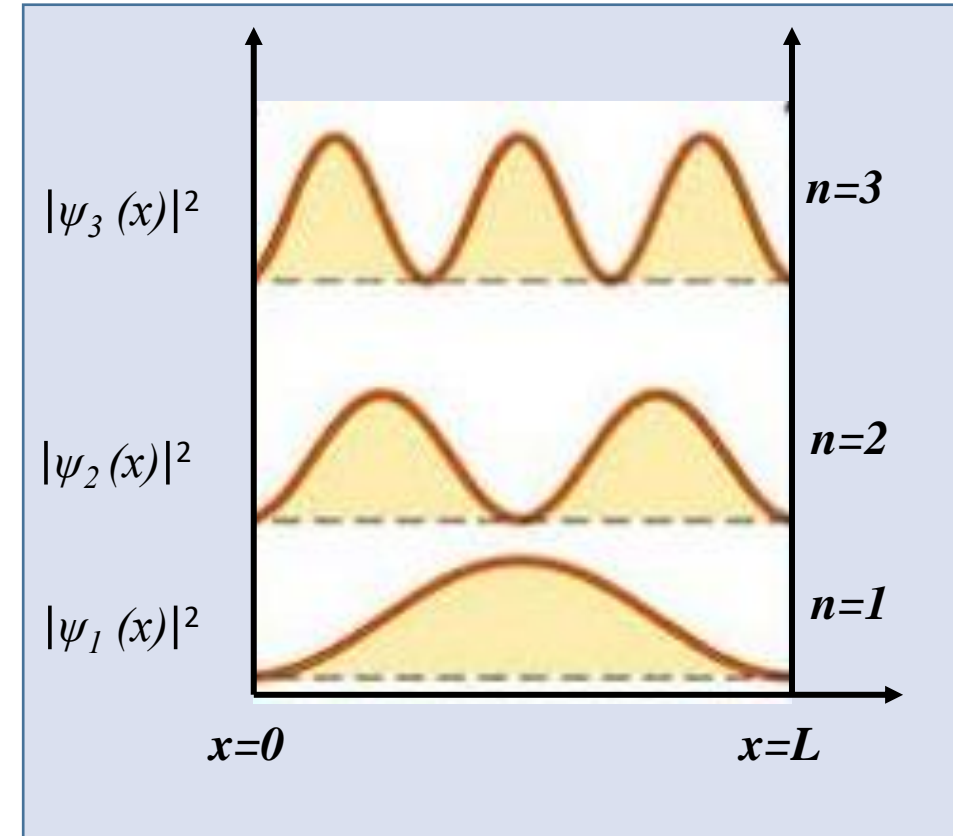
The Probability densities in 1-dim. Particle in a box.

Position

Comparison with Classical results

1. *Classically, a particle in a box can have any positive energy value.*
However, acc. to quantum theory, the particle is restricted to have only certain discrete energy values.

2. *Classically, a particle in a box can have even zero energy value.*
But acc. to quantum theory, the particle can not have zero energy. The minimum energy possessed by the particle is known as Zero point energy.

3. *Classical mechanics predicts that the probability of finding the particle anywhere in the well is same.*
However, as per quantum mechanics, the probability is different at different points. There are some points, where the particle is never found. Further, the probability of finding the particle is different in different energy states.

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Part-II

Solid State Physics

Introduction- to three different theories proposed

In order to understand the electronic properties of solids three different theories were proposed.

1. Classical free electron theory: The classical free electron theory was introduced by P. Drude in 1900 and developed by Lorentz in 1909 to explain electrical conduction in metals. This is also known as Drude and Lorentz theory. According to this theory, the free electrons in metals obey the laws of classical mechanics.

2. Quantum free electron theory: Quantum free electron theory was given by Sommerfeld in1928 and therefore is also known as Sommerfeld free electron theory. According to this theory, the free electrons in metals obey quantum mechanical laws.

3. Band theory of solids: Band theory of solids was given by F. Bloch in 1928. According to this theory, potential inside the crystal is considered to be periodic. This theory explained the concepts like band gap, effective mass etc. This is also known as Zone theory.

Classical Free Electron Theory

Assumptions/Postulates:

- The free electrons of a metal are like the molecules of a gas in a container.

- The free electrons are free to move in all possible directions about the whole volume of metals, thus, the resultant velocity of the free electron is zero.

- The electrons move in a completely <u>uniform potential field</u> due to ions fixed in the lattice.

- Since the electrons are assumed to be a perfect gas they obey classical kinetic theory of gases.

- Classical free electrons in the metal obey Maxwell-Boltzmann statistics.

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Classical Free Electron Theory

Drawbacks:

- This theory failed to explain the electronic specific heat and the specific heat capacity of metals.
- It failed to explain superconducting properties of metals.
- It also failed to explain the classification of materials into insulators, semiconductors and conductors.
- This model could not explain the positive Hall coefficient exhibited by some metals.
- It could not explain new phenomena like photo-electric effect, Compton effect, Black body radiation, etc.
- This theory failed to give a correct mathematical expression for thermal conductivity.
- Phenomenon of Ferromagnetism could not be explained by this theory.

Classical Free Electron Theory

Success:

- It successfully explained the electrical conductivity and thermal conductivity of metals.
- It verified Ohm's law.
- It also explained the optical properties of metals.
- It explained the Wiedemann - Franz law, according to which the ratio of thermal to electrical conductivityof a metal is proportional to the absolute temperature and the ratio is constant.

i.e. $$\frac{K}{\sigma} \propto T,$$

where K- thermal conductivity
and σ- electrical conductivity

Quantum Free Electron Theory

Quantum free electron theory was given by Sommerfeld in 1928. He retained the main features of classical free electron theory and added following two concepts in his quantum theory:
- Pauli's Exclusion Principle
- Fermi-Dirac statistics

Assumptions:
- The energies of free electrons are quantized.
- The distribution of electrons is as per the Pauli's exclusion principle.

The following assumptions of classical free electron theory holds good in quantum free electron theory also.
- The electrons travel with a constant potential inside the metal but confined within its boundaries.
- The attraction between the electrons and the lattice ions and the repulsion between the electrons themselves are ignored.

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# Quantum Free Electron Theory

Success:

- This theory successfully explained the specific heat of solids.
- This theory gave the successful explanation for the temperature dependence of electrical conductivity.
- It successfully explained the dependence of electrical conductivity on the electron concentration.
- This theory was able to provide the correct mathematical expression for the thermal conductivity of metals.
- This theory also successfully explained the photo electric effect, Compton Effect and block body radiation etc.

Failures

- This theory could not distinguish between metals, semiconductors and insulators.
- It could not provide an explanation for the positive value of Hall coefficient.
- This theory also failed to explain the negative temperature coefficient of resistivity.

Band Theory of Solids

- Band theory of solids was given by F. Bloch in 1928.
- According to this theory, potential inside the crystal is considered to be periodic i.e. the potential experienced by an electron in passing through the crystal lattice is periodic.
- The P.E of an electron in the field of positive ion is negative, so force between them is attractive.
- The potential is minimum at the positive ion sites and maximum in between the lattice ion positions.
- This periodicity extends up to infinity in all the directions within the crystal.
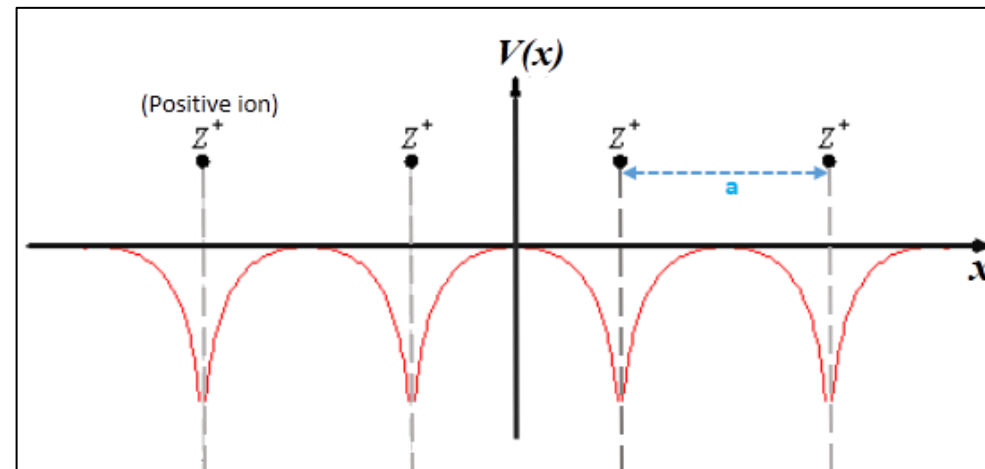
Kronig-Penney Model- Introduction to Origin of Band Gaps in Solids

- Kronig-Penney model tells us about the behavior of electrons in a periodic potential.
- According to this model, the potential filed of an electron in a linear arrangement of positive ions consists of periodically arranged rectangular potential wells separated by potential barriers.
- These potential wells are considered to be of zero potential and width 'a' and
- the potential barriers are of height 'V$_o$' and width 'b'.

This arrangement can be summarized as:
- Region I: $0 < x < a$, called Potential well region
- Region II: $-b < x < 0$, called Potential barrier region
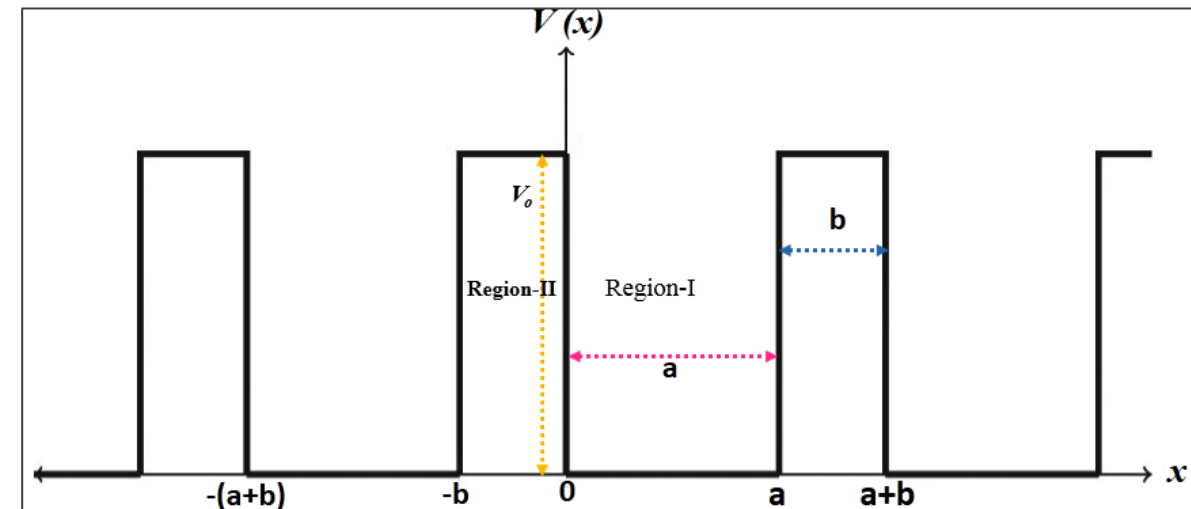
The Schrodinger Equations for the two regions are given as:

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\, E\, \psi = 0 \qquad\qquad 0 < x < a \qquad \text{-------- (1)}$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}\, (E - V_o)\, \psi = 0 \qquad\qquad -b < x < 0 \qquad \text{--------- (2)}$$

Assume E < V$_o$, and

Let

$$\alpha^2 = \frac{2m}{\hbar^2}\, E \qquad\qquad\qquad \text{----------- (3)}$$

$$\beta^2 = \frac{2m}{\hbar^2}\, (V_o - E) \qquad\qquad \text{-----------(4)}$$

Equations (1) and (2) become

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

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

The solution of wave equation for a periodic potential is given by

$$\psi(x) = e^{ikx} u_k(x) \qquad \text{----------- (7)}$$

where $u_k(x)$ is a periodic function in x.

The wave function of above type is known as <u>Bloch function</u>.

Substituting the above wave functions into the Schrodinger equations and solving it. After applying the periodic boundary condition, we get the following expression

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

where $P = \dfrac{maV_o b}{\hbar^2}$ is the measure of the area ($V_o b$) of the potential barrier.

Large value of P means, the electron is strongly bound to the potential well.

- The R.H.S of equation (8) can take values between +1 to -1. This equation can be satisfied only for those values of αa for which left side lies between +1 to -1.
- The plot below shows that Eq. (8) is satisfied only for only certain ranges of values of αa.

- The regions of allowed energy are called <u>bands</u> and they are separated by regions where there are no allowed energies (*forbidden regions*) and are called <u>*band gaps.*</u>

Conclusions:

1. Since, cos ka can have values between +1 and -1, so only those values of αa are allowed for which LHS if eqn. (8) is satisfied.

   So, allowed range of αa is given by
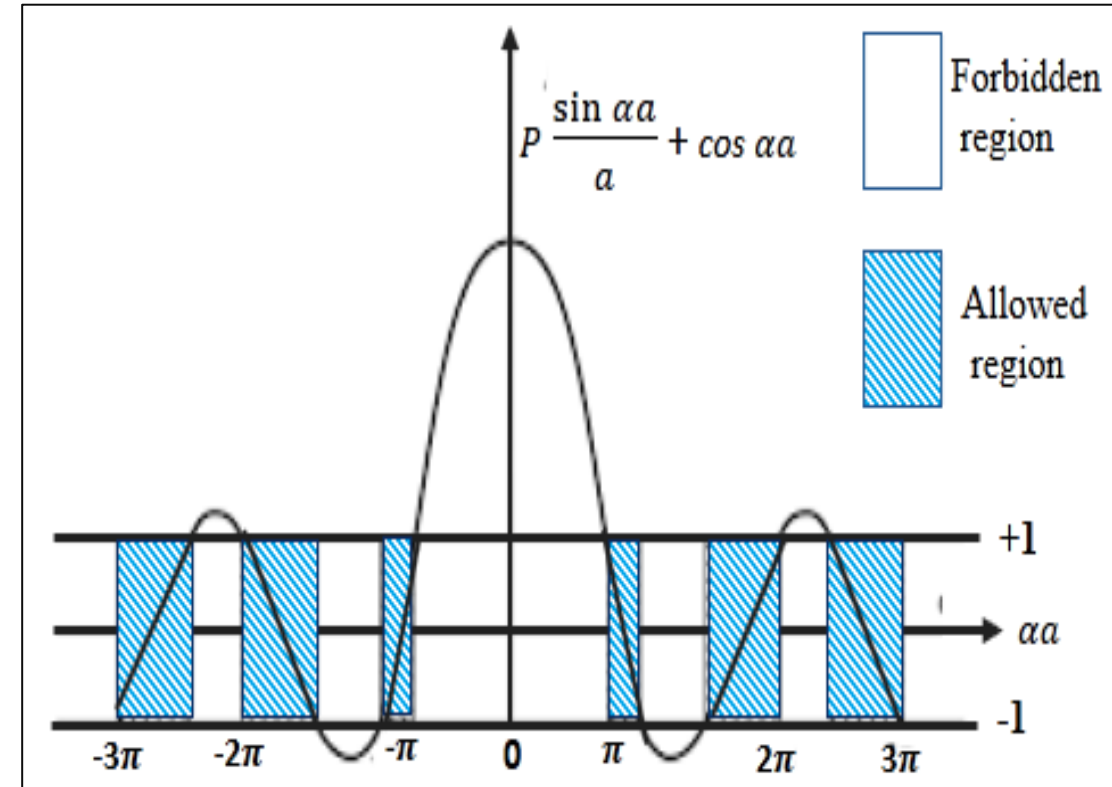
   $$\cos ka = \pm 1$$
   $$\cos ka = \cos n\pi$$
   $$k = \frac{\pm n\pi}{a} \qquad n = 0, 1, 2, 3\text{---}$$

The values of k define the boundaries of Brillouin zones.

2. The width of allowed energy bands go on increasing as value of αa increases.

3. As P gets larger, the height of the curve becomes very large and so the slope becomes steeper. Thus, <u>the bands become narrower</u>.

In the limit **P** → ∞, each band shrinks and are compressed to a line spectrum. So, equation 8 will have solution only if

$$\sin \alpha a = 0$$

$$\sin \alpha a = \sin n\pi$$

$$\alpha a = n\pi$$

$$\alpha = \frac{n\pi}{a}$$

$$\alpha^2 = \left(\frac{n\pi}{a}\right)^2$$

also
$$\alpha^2 = \frac{2m}{\hbar^2} E$$

Equating above two relations of α^2

$$\left(\frac{n\pi}{a}\right)^2 = \frac{2mE}{\hbar^2}$$

$$E = \frac{n^2 \pi^2 \hbar^2}{2ma^2}$$

which are the energies for an infinite square well.

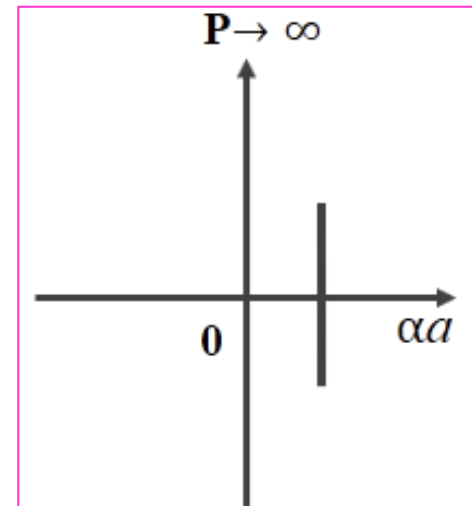4. In the limit **P** → **0** i.e. when there is no potential barrier, the energy band is broadened

$$\cos \alpha a = \cos ka$$

$$\alpha = k$$

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

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

This is the case for a free electron.

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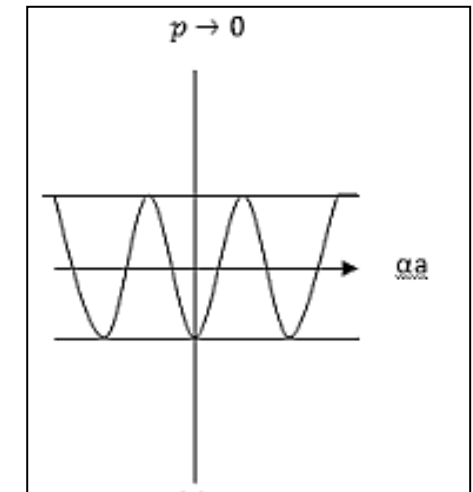
E-k Diagram

- Figure shown depicts the variation of energy (E) with wave number (k). The <u>parabolic relation between E and k</u> obtained in case of a free electron is interrupted at certain values of k.

- From the graph, it is clear that the electron has a allowed energy values in the region or zone from $k = \dfrac{-\pi}{a}$ to $k = \dfrac{+\pi}{a}$. This is called <u>first Brillouin zone</u>.

- After a break in energy values called *Forbidden energy gap*, there exists another allowed region of energy value from $k = \dfrac{-\pi}{a}$ to $\dfrac{-2\pi}{a}$ and from $k = \dfrac{+\pi}{a}$ to $\dfrac{+2\pi}{a}$. This is called <u>second Brillouin zone.</u> Similarly, another higher zones may be defined.

- The concept of allowed energy bands and forbidden gaps is clear from the figure shown.
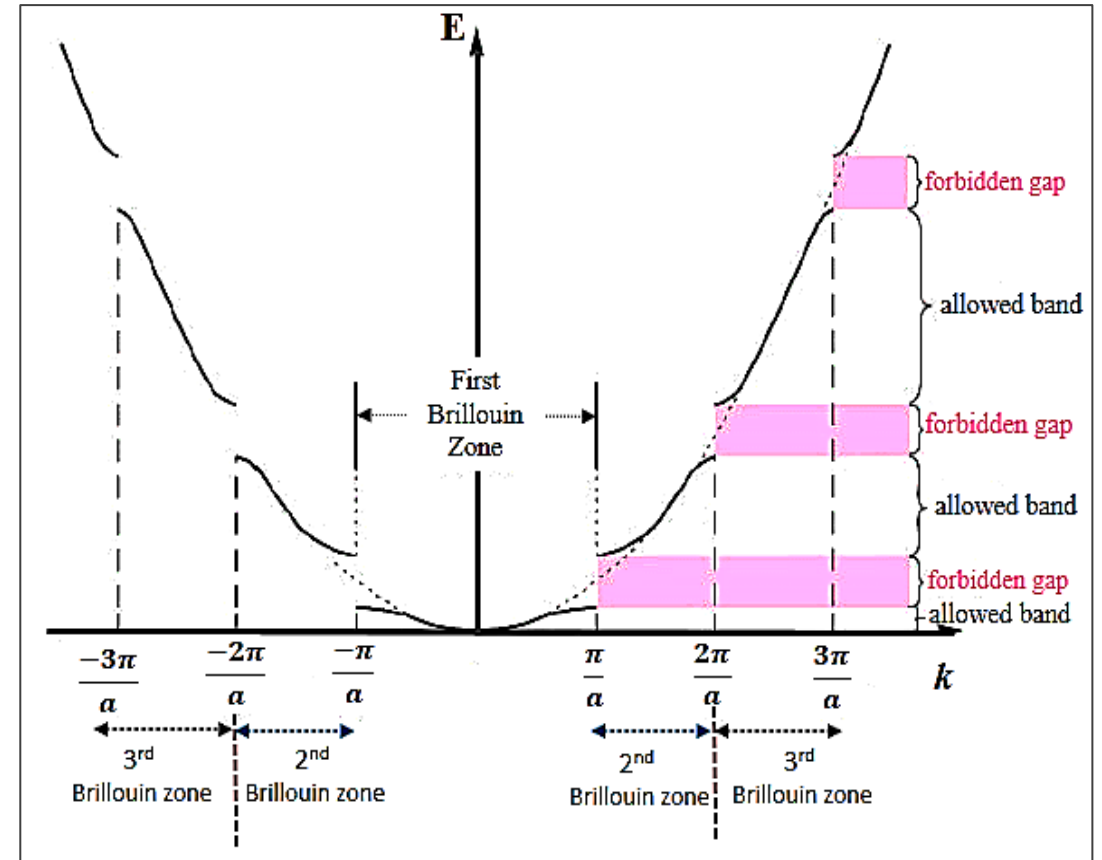
Effective Mass

- It has been observed that the experimentally measured values of mass of an electron in a solid is different (either smaller or larger) from that of the free mass of electron. This experimentally determined electron mass. is called the effective mass m*.
- The cause of this deviation is due to the interaction between the drifting electrons and the atoms in a solid.
- Effective mass is inversely proportional to the curvature of an allowed energy band.
- It implies that effective mass depends on the location of an electron in the allowed energy band.

$$m* = \frac{\hbar^2}{d^2 E / dk^2}$$

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Positive and negative effective mass

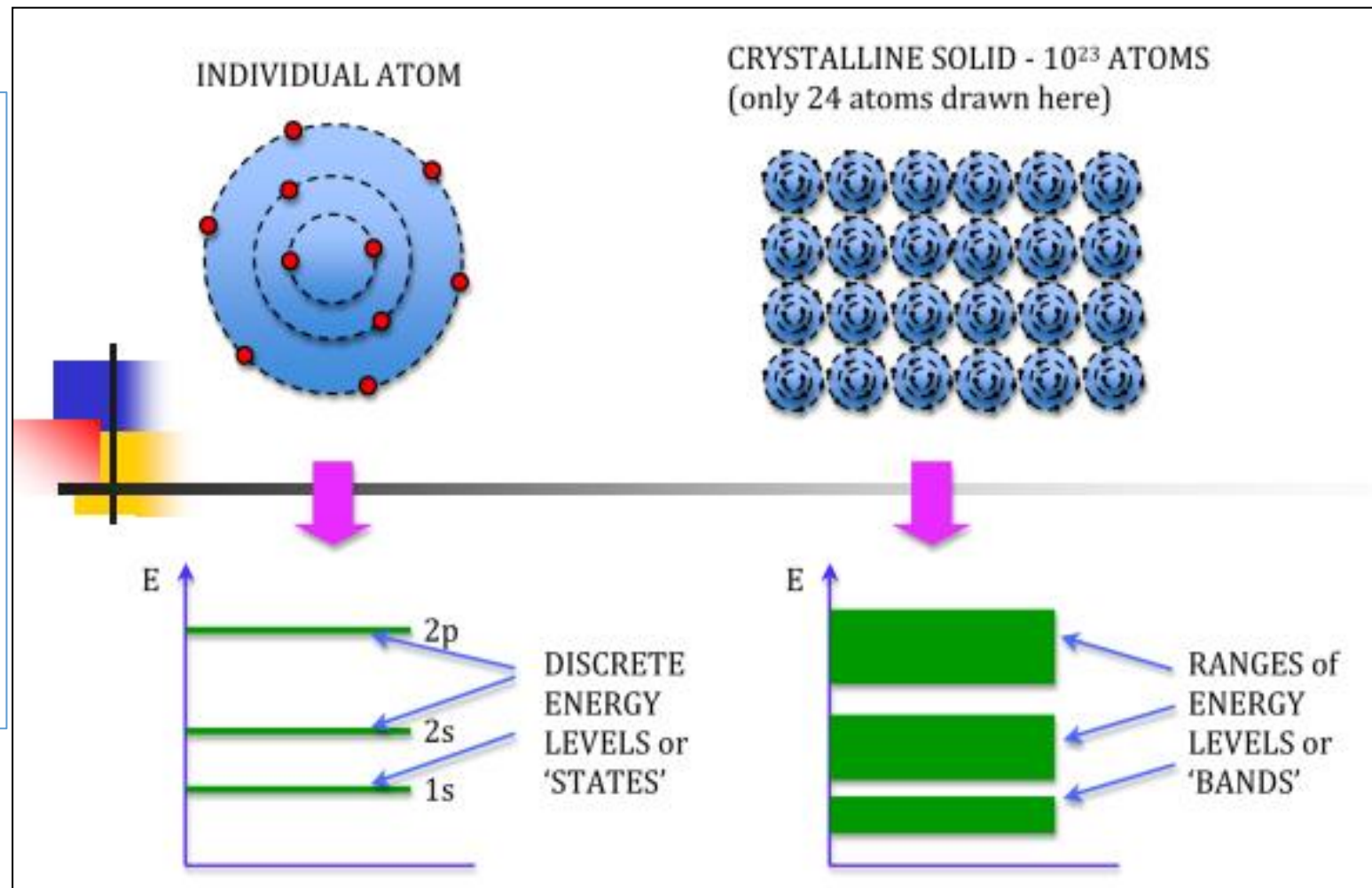Direct-band gap s/c's (e.g. GaAs, InP, AlGaAs)

CB

E

e⁻

k

+

VB
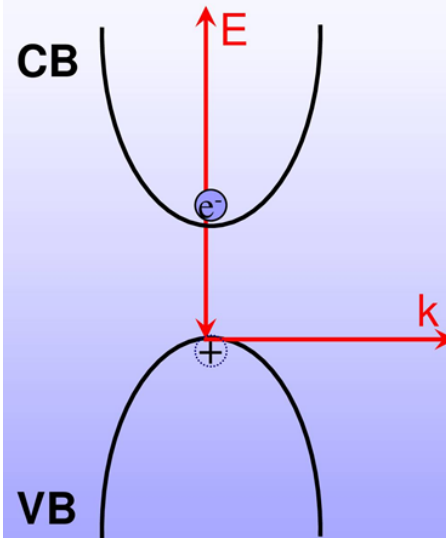
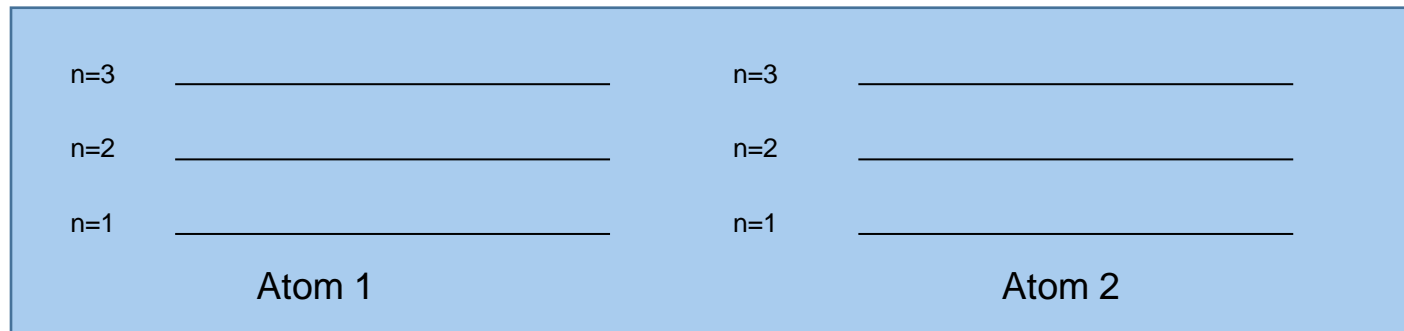$$m^* = \frac{\hbar^2}{d^2E/dk^2}$$

- The sign of the effective mass is determined directly from the sign of the curvature of the E-k curve.

- The curvature of a graph at a minimum point is a positive quantity and the curvature of a graph at a maximum point is a negative quantity.

- Particles(electrons) sitting near the minimum have a *positive effective mass*.

- Particles(holes) sitting near the valence band maximum have a *negative effective mass*.

- A negative effective mass implies that a particle will go *'the wrong way'* when an extrernal force is applied.
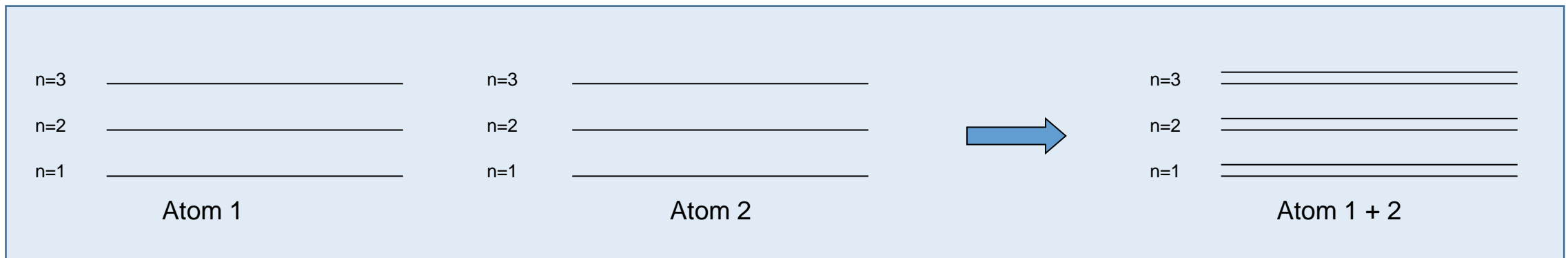
Energy Band Structure of a Solid

- Atoms have been seen to have discrete energy levels.

- When a huge number of atoms are combined to form a solid however, these discrete energy levels are replaced by discrete ranges of energy, or energy bands, within which there are so many individual allowed energy values that within the bands the distribution can be considered to be continuous.
- This idea is seen in the figure shown.

INDIVIDUAL ATOM

CRYSTALLINE SOLID - 10^{23} ATOMS
(only 24 atoms drawn here)

E

2p
2s
1s

DISCRETE ENERGY LEVELS or 'STATES'

E

RANGES of ENERGY LEVELS or 'BANDS'

- A solid is formed by bringing together isolated single atoms.
- Consider the combination of two atoms. If the atoms are far apart there is no interaction between them and the energy levels are the same for each atom. The numbers of levels at a particular energy is simply doubled

n=3 ———————————————————   n=3 ———————————————————

n=2 ———————————————————   n=2 ———————————————————

n=1 ———————————————————   n=1 ———————————————————

Atom 1   Atom 2

- If the atoms are close together the electron wave functions will overlap and the energy levels are shifted with respect to each other.

n=3 ———————————————   n=3 ———————————————   n=3 ═══════════════════

n=2 ———————————————   n=2 ———————————————   ➡   n=2 ═══════════════════

n=1 ———————————————   n=1 ———————————————   n=1 ═══════════════════

Atom 1   Atom 2   Atom 1 + 2

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In an isolated atom, the electrons are tightly bound and have discrete, sharp energy levels.

When two identical atoms are brought closer the outermost orbits of these atoms overlap and interact. When the wave functions of the electrons of the different atoms begin to overlap considerably, the energy levels corresponding to those wave functions split into two as in above Fig. (b).

If more atoms are brought together more levels are formed and for a solid of **N** atoms, each of the energy levels of an atom splits into **N** levels of energy. The levels are so close together that they form an almost continuous band. The width of this band depends on the degree of overlap of electrons of adjacent atoms and is largest for the outermost atomic electrons.

Energy levels for single atom, 2 atoms and N number of atoms (i.e bulk material)
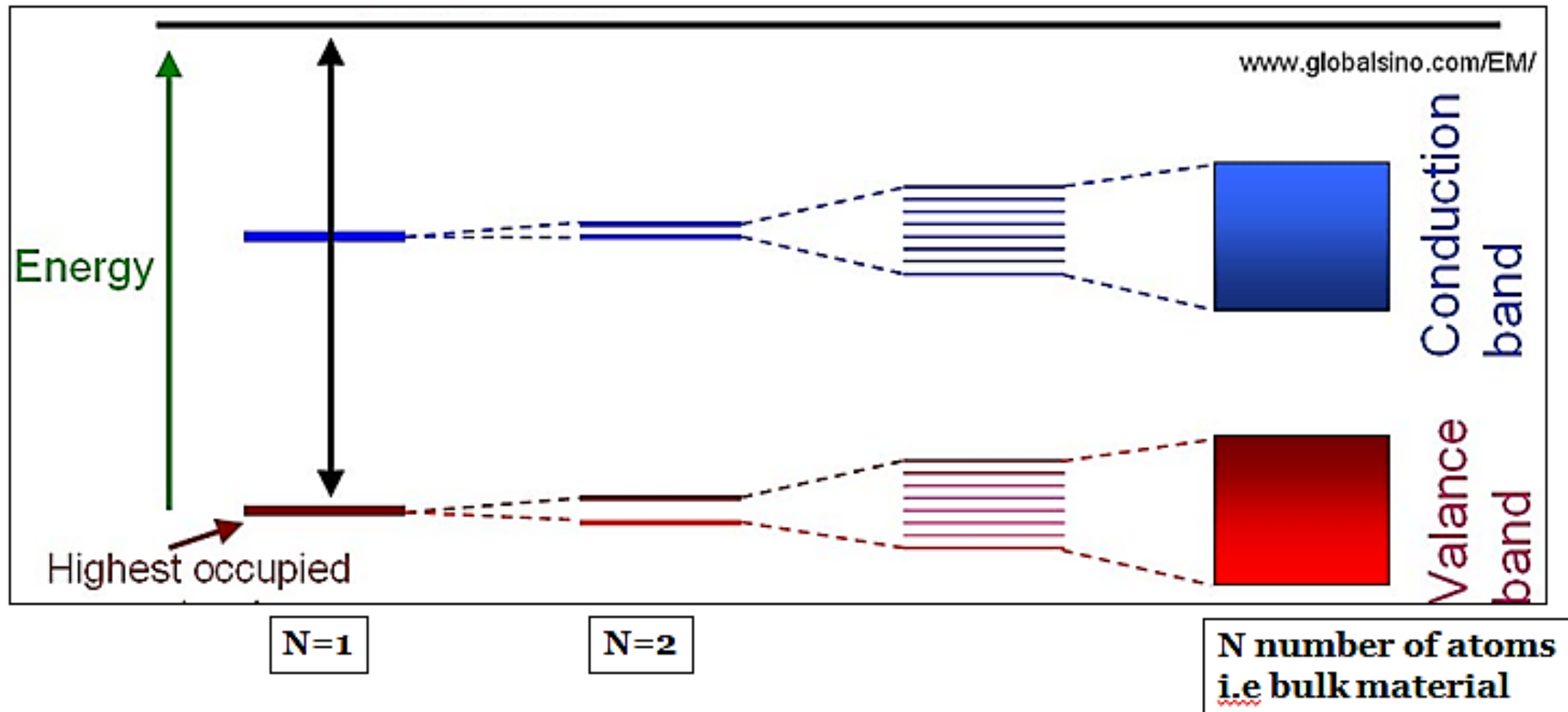
Energy band diagram for a Si crystal as a function of interatomic distance

- A crystal consists of an enormous no. of atoms arranged in a regular periodic structure.

- The extent of energy level splitting in the solid depends on the nearness of the atoms in it.

- In general N interacting atoms cause an energy level to split into $(2\ell +1)N$ levels.

- Thus, s-level ($\ell =0$) splits into N levels whereas p level ($\ell =1$) splits into 3N levels.

- Hence, the maximum electron capacity of an s band is 2N electrons whereas capacity of p band is 6N electrons.

Energy levels splitting in Si as a function of interatomic distance

Energy levels splitting in Si as a function of interatomic distance
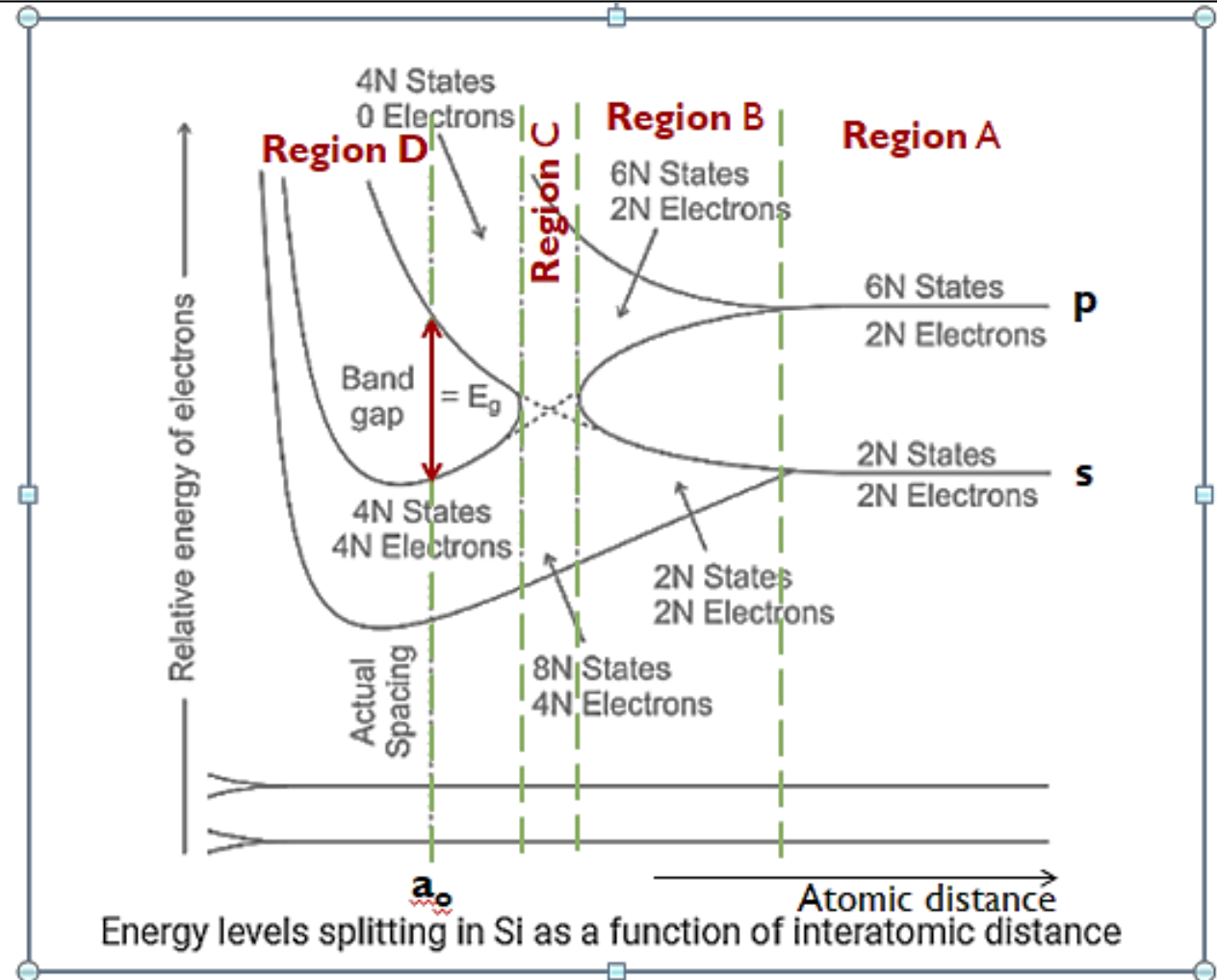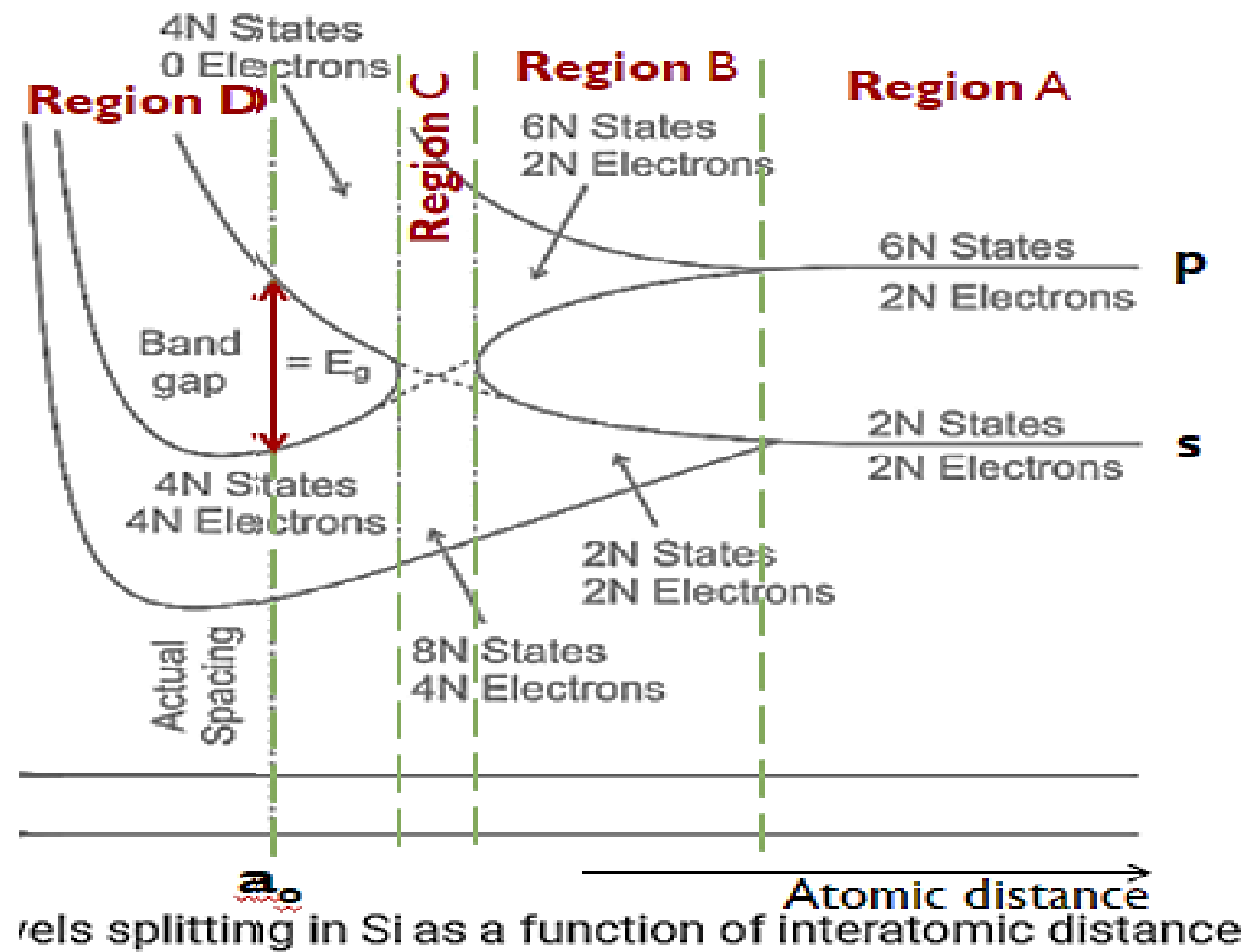
As seen in the diagram below, the graph is divided into 4 regions – Region A, B, C and D

In the region A, the interatomic distance is large between atoms and in region D, the interatomic distance is small.

➤ **Region A**

This is the case of well separated or isolated atoms since the interatomic spacing is large, so their energy levels are discrete as shown in region A.

➤ **Region B**

• Suppose the atoms start coming nearer to each other to form a solid.

• The energies of the electrons in the outermost orbit may increase or decrease, due to the interaction between electrons of different atoms

• The 6N states for $\ell=1$, which originally had identical energies in the isolated atoms, spread out and form an energy band as shown in the region B

• Similarly, the 2N states for $\ell = 0$ split into a second band separated from the first one.

➤ **Region C**

• At still smaller spacing, however, there comes a region in which the bands merge with each other

• In this region, no energy gap exists where the upper and the lower energy states gets mixed
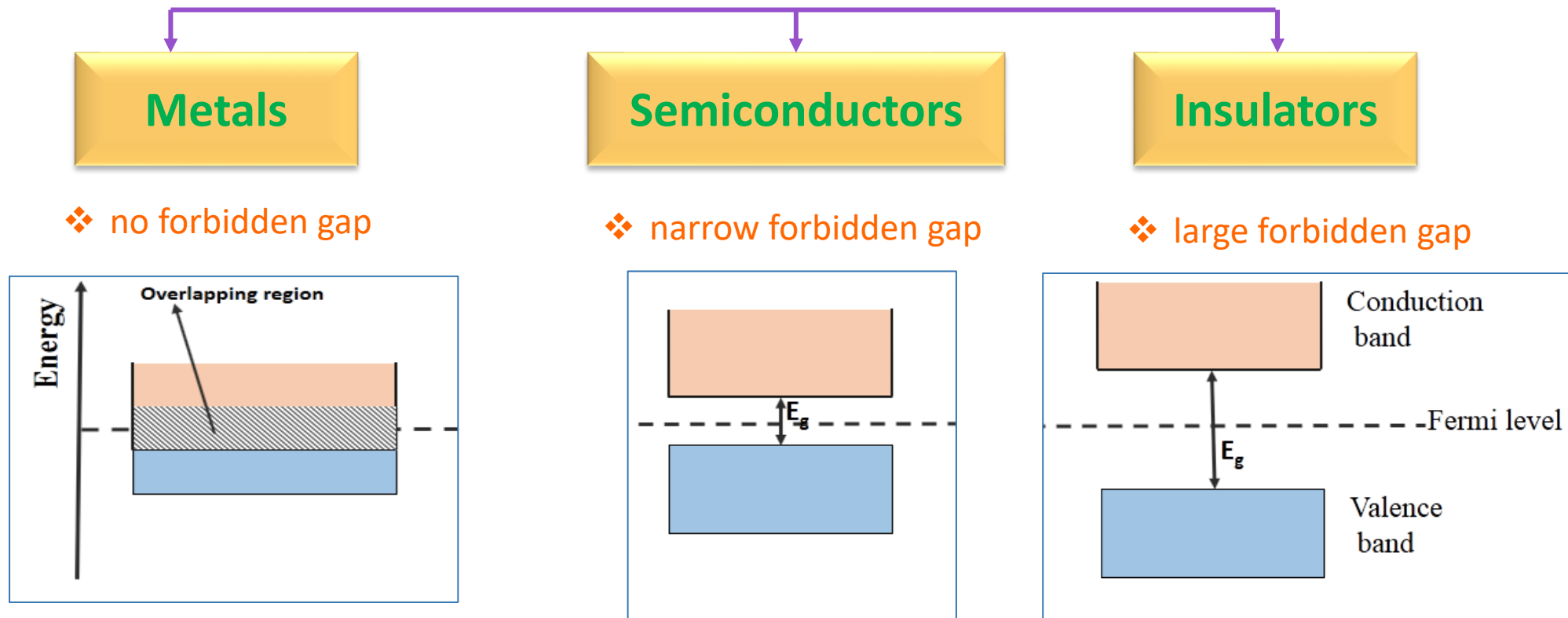
➤ **Region D**

• If the distance between the atom further decreases, the energy bands again split apart and are separated by an energy gap E_g

• The total number of available energy states 8N has been re-apportioned between the two bands (4N states each in the lower and upper energy bands)

• Here there are exactly as many states in the lower band (4N) as there are available valence electrons from the atoms (4N)

• This lower band called the valence band is completely filled while the upper band is completely empty. The upper band is called the conduction band

Electronic configuration of Si is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^2$. (Atomic No. is 14)
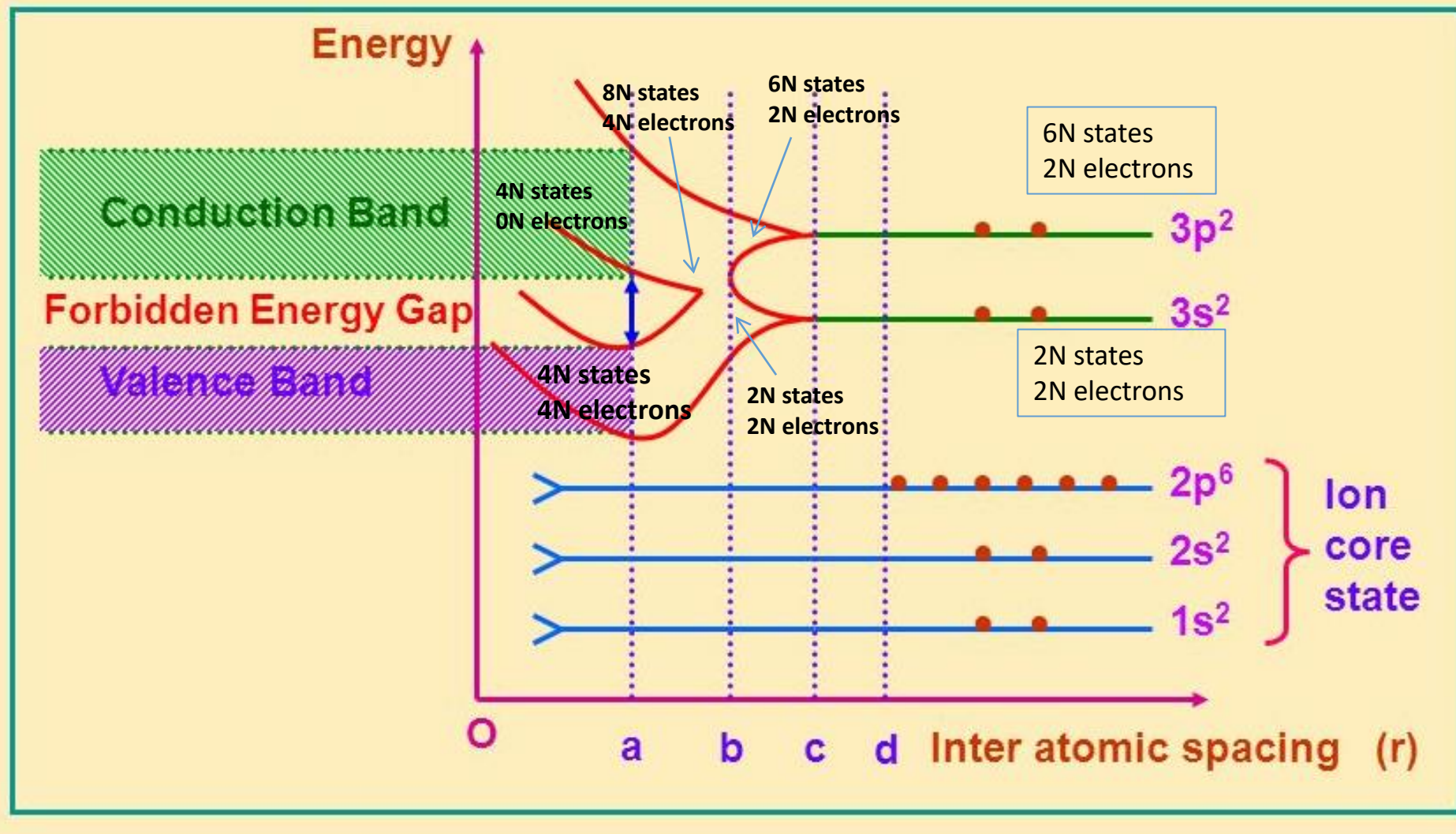
Classification Of Solids Based On Energy Bands As Metals, Semiconductors And Insulators

Energy Band Gap

Metals	Semiconductors	Insulators

❖ no forbidden gap   ❖ narrow forbidden gap   ❖ large forbidden gap
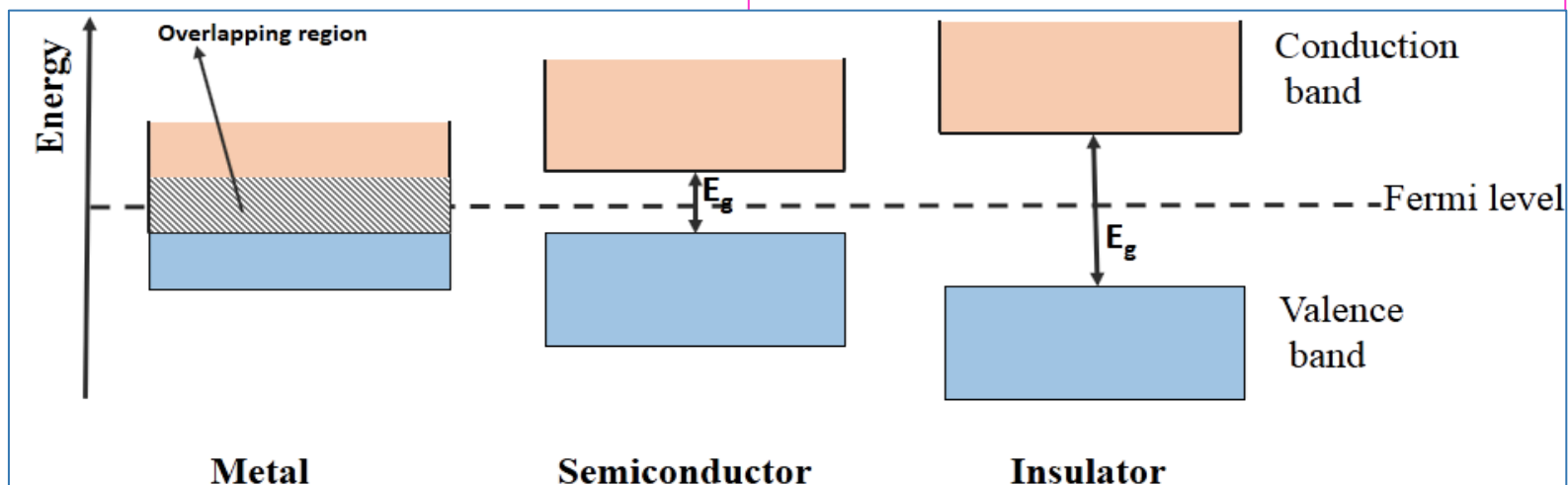

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Conductors:

- In the metals like copper, aluminum there is no forbidden gap between valence band and conduction band.
- The two bands overlap.
- Hence even at room temperature, a large number of electrons are available for conduction.
- So without any additional energy, such metals contain a large number of free electrons and hence called good conductors.

Insulators:

- In case of insulators, there exists a large forbidden gap in between the conduction band and the valence band.
- Practically it is impossible for an electron to jump from the valence band to the conduction band.
- Hence, such materials cannot conduct and called insulators.
- They have completely filled valence band and completely empty conduction band. e.g. glass, wood, mica, paper etc.

Semiconductors

- These materials have a very narrow forbidden gap.
- In semiconductors, the band gap is very small (0.7 eV for germanium and 1.1 eV for silicon).
- The energy provided by the heat at room temperature is sufficient to lift the electrons from the valence band to the conduction band.
- At 0 K, there are no electrons in the conduction band and the valence band is completely filled.
- As the temperature increases, electrons from the valence band jump into conduction band.

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That's all!!!

Thank You!!!!