PROPERTIES OF SOLIDS

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STATES OF MATTER

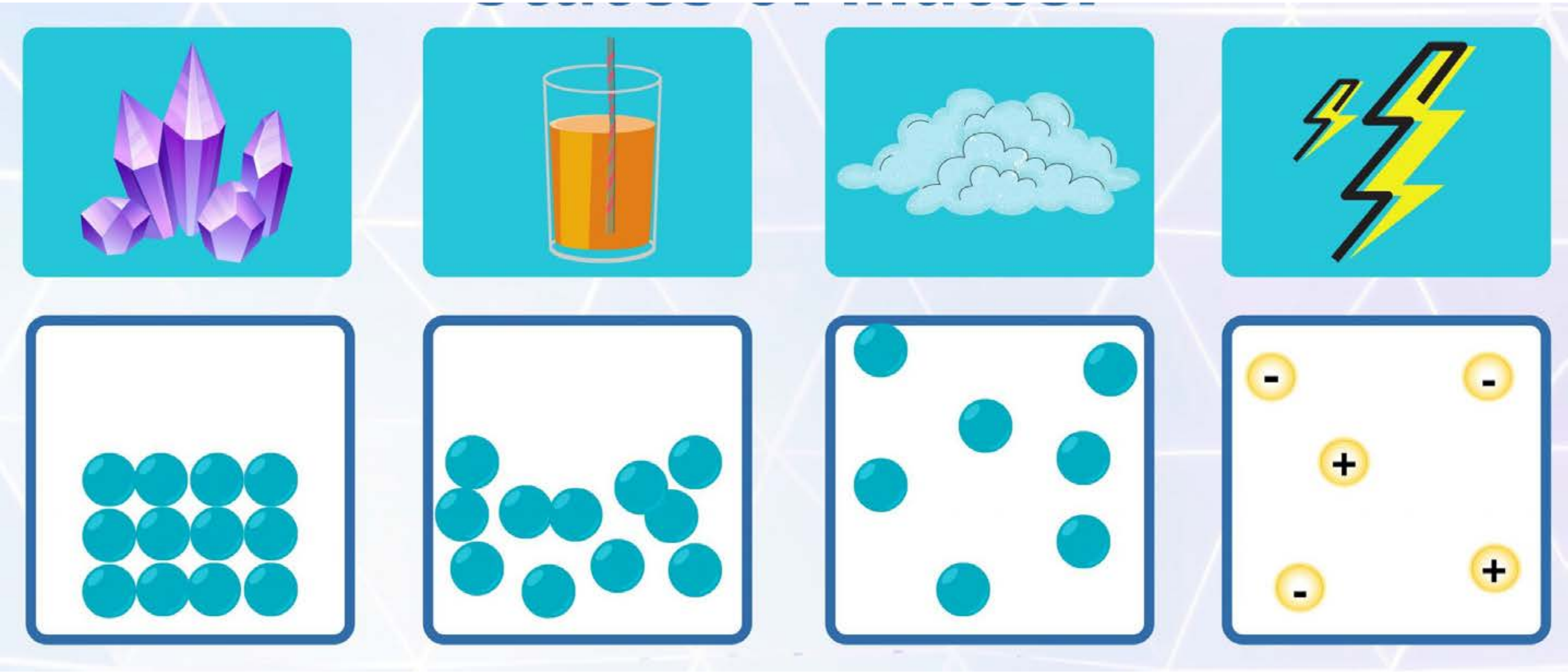
States of Matter

Solid

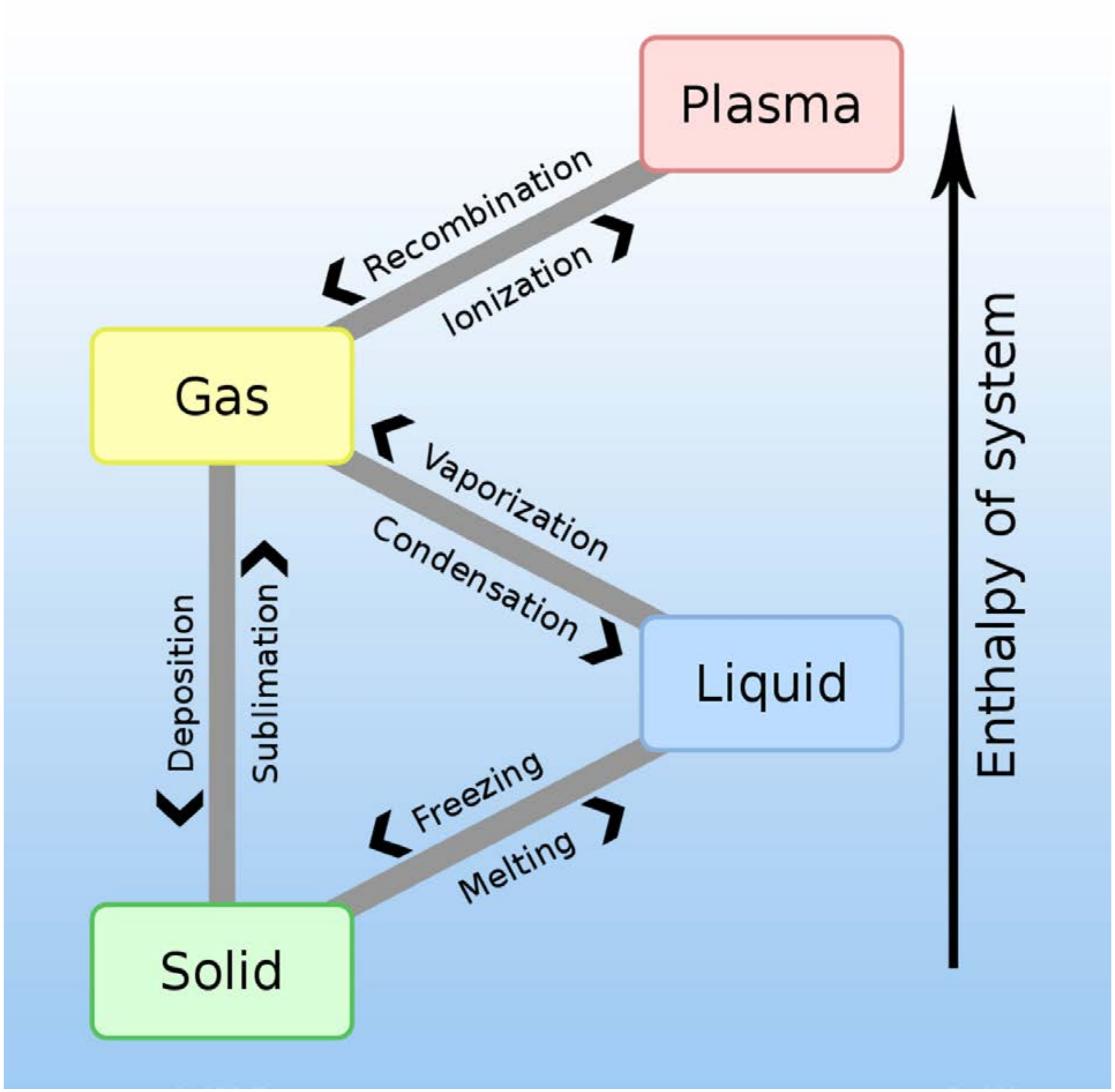
Liquid

Gas

Plasma



STATES OF MATTER



STATES OF MATTER

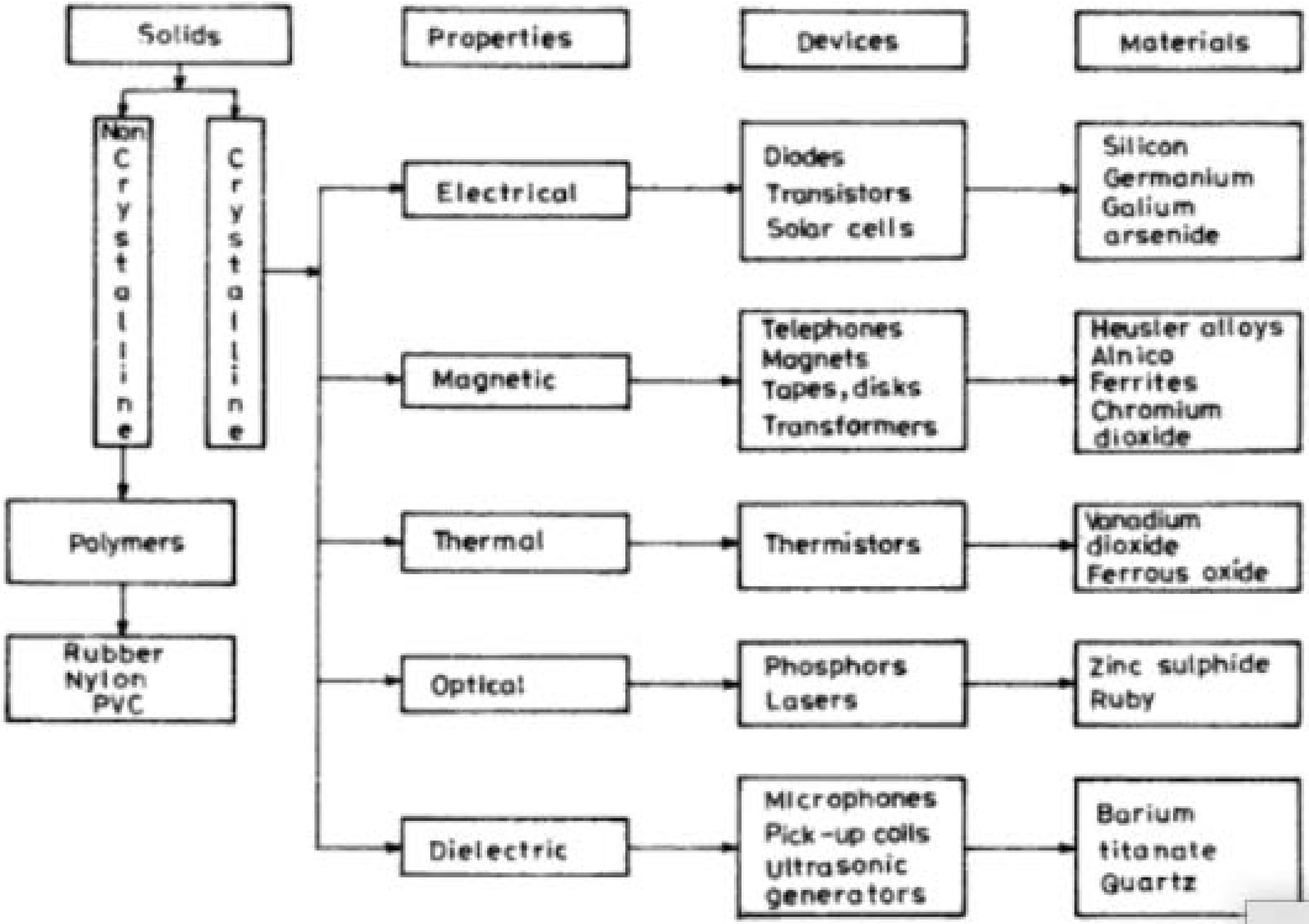


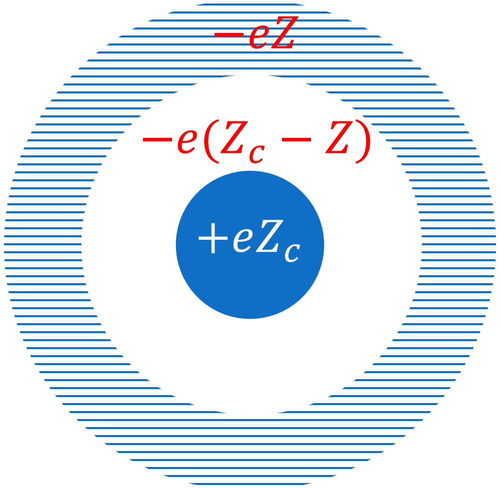
Fig. 1.1 (b) Material properties and devices.

WHAT DO WE KNOW ABOUT METAL?

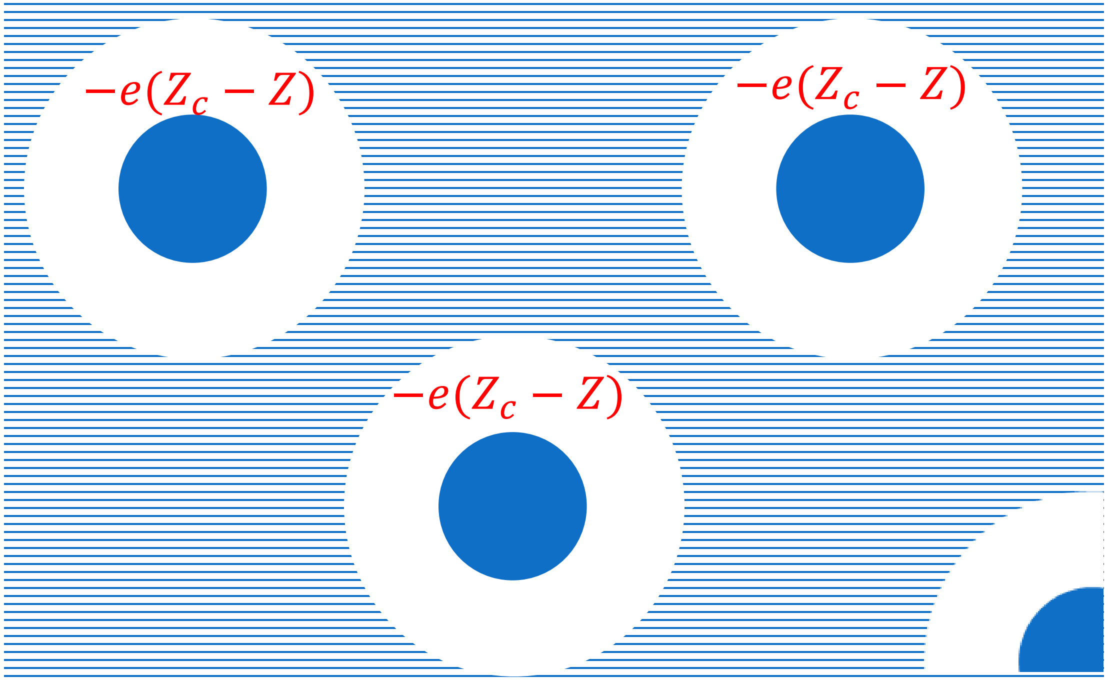
- ✓ The metallic state is favored by element; more than 2/3 are metals.
- ✓ Metal atoms consist of ionic core surrounded by a small number of more loosely bound valence electrons.
- ✓ Metals form crystal structure with relatively large number of neighbor atoms (hcp → 12, fcc → 12, bcc → 8, but ionic & covalent crystals have neighbor atom 4-6). Large coordination number & small valence electron indicate that valence electrons in atoms are occupying space between the ionic cores uniformly.
- ✓ Evenly spreading of valence electrons between the ionic cores suggests that metal atom binds together by undirectional bonds. On the other hand, ionic and covalent solids bind together by directional bonds.
- ✓ A Lot of empty space in metal (Li-Li interatomic distance 3Å, ionic radius is 0.5 Å) implies that there are large volume available for the valence electrons to move around it.
- ✓ Large volume accounts the stability of metal as valence electrons spread out rather confine to small regions and hence reduce zero point energy.

WHAT DO WE KNOW ABOUT METAL?

Single isolated atom



Solid metal



$Z \longrightarrow$ No. of valence electrons

■ Nucleus
□ Core electrons
▤ Valence electrons

Ion { ■ Nucleus
Ion { □ Core electrons
▤ Valence electrons

ELECTRON THEORY OF SOLIDS?

- ✓ The electron theory of solids aims to explain the structures and properties of solids through their electronic structure.
- ✓ The electron theory of solids has been developed in three main stages.
- ✓ **(I) The classical free electron theory:** Drude and Lorentz developed this theory in 1900. According to this theory, the metals containing free electrons obey the laws of classical mechanics.
- ✓ **(II) The Quantum free electron theory**: Sommerfeld developed this theory during 1928. According to this theory, the free electrons obey quantum laws.
- ✓ **(III) The Zone theory**: Bloch stated this theory in 1928. According to this theory, the free electrons move in a periodic field provided by the lattice. This theory is also called “Band theory of solids”.

DRUDE THEORY OF METAL

Assumptions of Drude theory

- In an atom electrons revolve around the nucleus and a metal is composed of such atoms.
- The valence electrons of atoms are free to move about the whole volume of the metals like the molecules of a perfect gas in a container. The collection of valence electrons from all the atoms in a given piece of metal forms electrons gas. It is free to move throughout the volume of the metal
- These free electrons move in random directions and collide with either positive ions fixed to the lattice or other free electrons. All the collisions are elastic i.e., there is no loss of energy.

DRUDE THEORY OF METAL

- ✓ The movements of free electrons obey the laws of the classical kinetic theory of gases.
- ✓ The electron velocities in a metal obey the classical Maxwell - Boltzmann distribution of velocities.
- ✓ The electrons move in a completely uniform potential field due to ions fixed in the lattice.
- ✓ When an electric field is applied to the metal, the free electrons are accelerated in the direction opposite to the direction of applied electric field.

LORENTZ EXTENSION OF DRUDE THEORY FOR METAL

Lorentz modified the oversimplified Drude model and constructed his theory called Drude-Lorentz electron theory on the basis of following points:

- ✓ The assumptions related to move electrons with the same thermal velocity is abandoned.
- ✓ The presence of an electric field or thermal gradient perturbs the classical Maxwell-Boltzmann velocity distribution. Both of these disturbs the equilibrium velocity distribution and distort its symmetry.
- ✓ The Boltzmann transport equation is used to describe the transport of charge and kinetic energy of electrons by a statistical distribution of mobile electrons constituting the electron gas.

LORENTZ EXTENSION OF DRUDE THEORY FOR METAL

Based on these assumptions, Lorentz derived the equation for conductivity of metals

$$\sigma_L = \sqrt{\frac{8}{3\pi}}\frac{ne^2\Lambda}{\sqrt{3mkT}}$$

While Drude derived as

$$\sigma_D = \frac{ne^2\Lambda}{\sqrt{3mkT}}$$

The relation between them is as follows:

$$\sigma_D = \sqrt{\frac{8}{3\pi}}\sigma_L = 1.09\sigma_L$$

SUCCESS OF CLASSICAL FREE ELECTRON THEORY

- ✓ (1). It verifies Ohm's law.
- ✓ (2). It explains the electrical and thermal conductivities of metals.
- ✓ (3). It derives Wiedemann - Franz law. (i.e., the relation between electrical conductivity and thermal conductivity)
- ✓ (4). It explains optical properties of metals.

DRAWBACKS OF CLASSICAL FREE ELECTRON THEORY

- The phenomena such a photoelectric effect, Compton effect and the black body radiation couldn't be explained by classical free electron theory.
- According to the classical free electron theory the value of specific heat of metals is given by 4.5**R**, where R is the Universal gas constant whereas the experimental value is nearly equal to 3**R**. Also according to this theory the value of electronic specific heat is equal to 3/2R while the actual value is about 0.01**R** only.
- Electrical conductivity of semiconductor or insulators couldn't be explained using this model.
- Though $K/\sigma T$ is a constant (Wiedemann – Franz Law) according to the Classical free electron theory, it is not a constant at low temperature.
- Ferromagnetism couldn't be explained by this theory. The theoretical value of paramagnetic susceptibility is greater than the experimental value.

QUANTUM FREE ELECTRON THEORY

In 1928, Arnold Sommerfeld modified classical free electron theory using Plank's Quantum mechanical principles and Pauli Exclusion Principle.

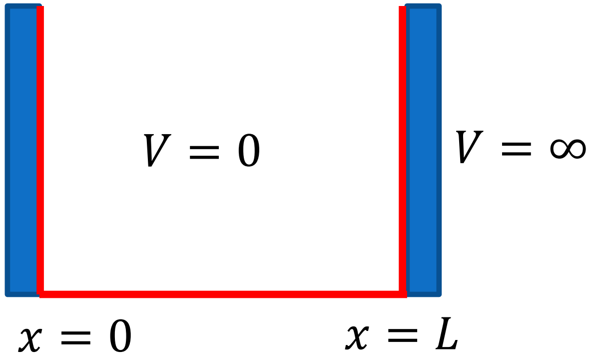
Assumptions:

- ✓ The energy values of conduction electrons are quantized with various allowed energy levels.
- ✓ The distribution of electrons in these allowed energy level takes place as per Pauli exclusion principle.
- ✓ The free electrons travel in a constant potential inside the metal but confined their stay within the metal. (CFE)
- ✓ The attractive force between free electrons and lattice ions; and repulsive force between free electrons themselves are ignored. (CFE)

QUANTUM FREE ELECTRON THEORY

Schrodinger Equation:

$$\frac{\hbar^2}{2m_e}\frac{d^2\psi}{dx^2} = (E - V)\psi \Rightarrow \frac{d^2\psi}{dx^2} = \frac{2m_eE}{\hbar^2}\psi$$



For one-dimensional box:

$$E = \frac{n^2\pi^2\hbar^2}{2m_ea^2} \qquad \psi = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$$

For three-dimensional box:

$$E = \frac{\pi^2\hbar^2}{2m_e}\left(\frac{n_a^2}{a^2} + \frac{n_b^2}{b^2} + \frac{n_c^2}{c^2}\right)$$

$$\psi = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_a\pi}{a}x\right)\sin\left(\frac{n_b\pi}{b}y\right)\sin\left(\frac{n_c\pi}{c}z\right)$$

Electrons travels inside box freely, and hence *V* is zero. Electron is not allowed outside the box, so the *V* is ∞ outside the box.

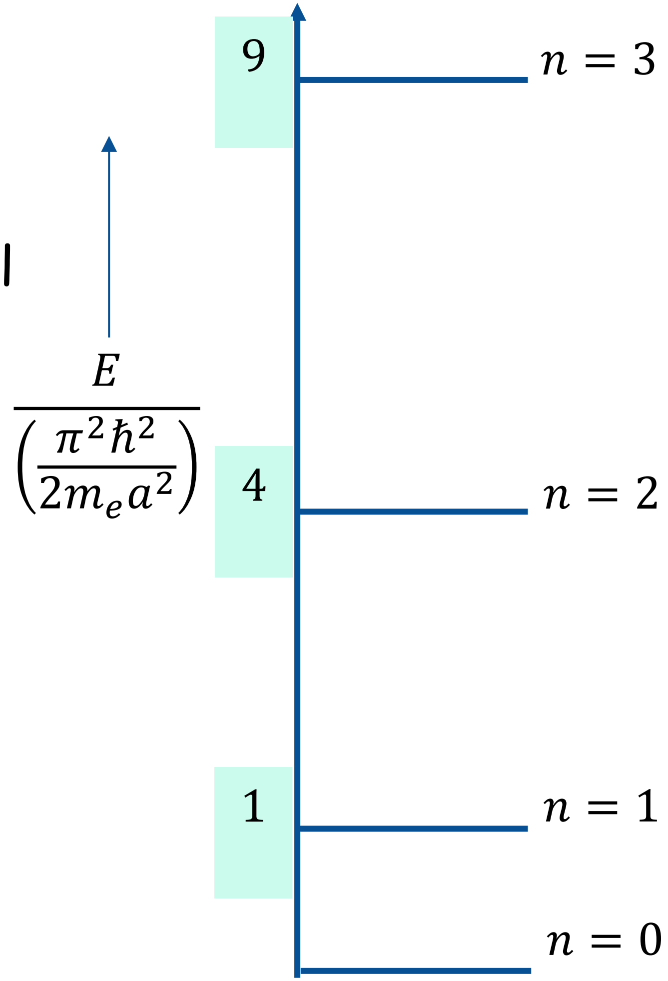
QUANTUM FREE ELECTRON THEORY

Energy levels:

- For one-dimensional solids, each *n* value produces a single energy level.
- However, for 3-D solids there are multiple combination of n_a, n_b, n_c that will give the same energy.

$\frac{n_a}{a}$	$\frac{n_b}{b}$	$\frac{n_c}{c}$	$\frac{n_a^2}{a^2}+\frac{n_b^2}{b^2}+\frac{n_c^2}{c^2}$
6	6	6	108
2	2	10	108
2	10	2	108
10	2	2	108

- With a crystal with ~10^{20} atoms, it becomes difficult to work out all the possible combinations.



QUANTUM FREE ELECTRON THEORY

Wave vectors and k space

- It is defined as the number of energy states per unit volume of metal in an energy interval between *E* and *E+dE*.

$$N(E)dE = \frac{\text{Number of energy states between E and E + dE}}{\text{Volume of the metal}}$$

$$N(E)dE = \frac{D(E)dE}{V} \qquad (1)$$

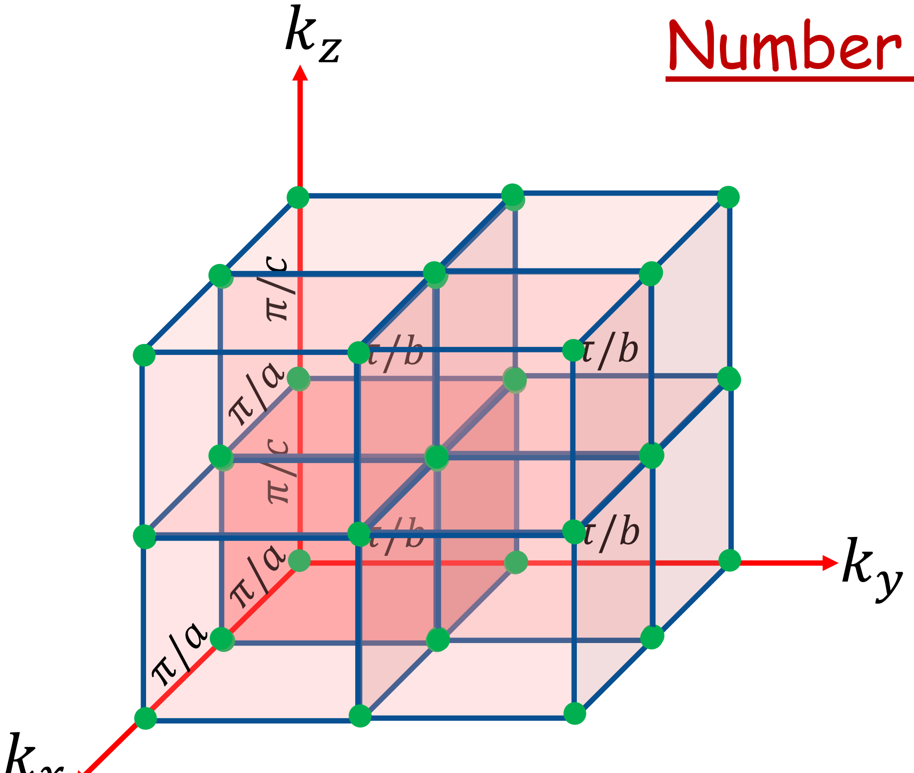
- The energy for 3D solids

$$E = \frac{\pi^2\hbar^2}{2m_e}\left(\frac{n_a^2}{a^2} + \frac{n_b^2}{b^2} + \frac{n_c^2}{c^2}\right) \quad \Longrightarrow E = \frac{\hbar^2}{2m_e}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2 k^2}{2m_e} \qquad (2)$$

Where, $k_x = \frac{\pi n_a}{a}$, $k_y = \frac{\pi n_b}{b}$, $k_z = \frac{\pi n_c}{c}$ and $k^2 = k_x^2 + k_y^2 + k_z^2$

QUANTUM FREE ELECTRON THEORY

Number of States



Combination	No. of states
111	1
112, 121, 211	3
221, 212, 122	3
222	1
Total	8

- Cosider a 3D point grid with intervals of $\frac{\pi}{a}, \frac{\pi}{b}, \frac{\pi}{c}$ along k_x, k_y, k_z respectively.
- Volume $\frac{\pi^3}{abc}$ of single cube represents a state.
- The volume of entire solid with dimensions $\frac{2\pi}{a}, \frac{2\pi}{b}, \frac{2\pi}{c}$ is $\frac{8\pi^3}{abc}$.
- No. of states $= \frac{\text{volume of solids}}{\text{volume of single cube}}$
- No. of states $= \frac{\frac{8\pi^3}{abc}}{\frac{\pi^3}{abc}} = \frac{8\pi^3}{abc} \times \frac{\pi^3}{abc} = 8$

QUANTUM FREE ELECTRON THEORY

Density of States

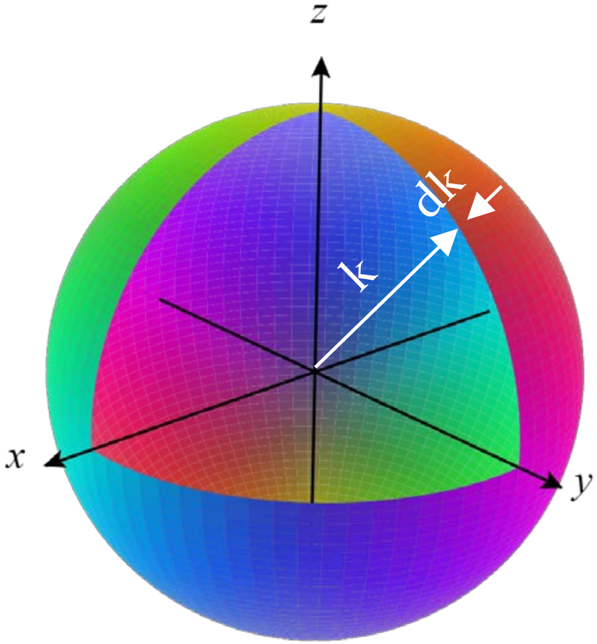
No. of E states within one octant of sphere of radius, *k*

$$= \frac{1}{8} \cdot \frac{4}{3} \pi k^3$$

No. of E states within sphere of radius, *k*+*dk*

$$= \frac{1}{8} \cdot \frac{4}{3} \pi (k + dk)^3$$

No. of E states within thin layer of sphere of radius, dk



$$D(E)dE = \frac{1}{8} \cdot \frac{4}{3} \pi (k + dk)^3 - \frac{1}{8} \cdot \frac{4}{3} \pi k^3$$

$$D(E)dE = \frac{1}{6} \pi (k^3 + 3k^2 dk + 3k dk^2 + dk^3 - k^3)$$

$$D(E)dE = \frac{\pi k^2 dk}{2} \qquad (3)$$

From equ. (2)

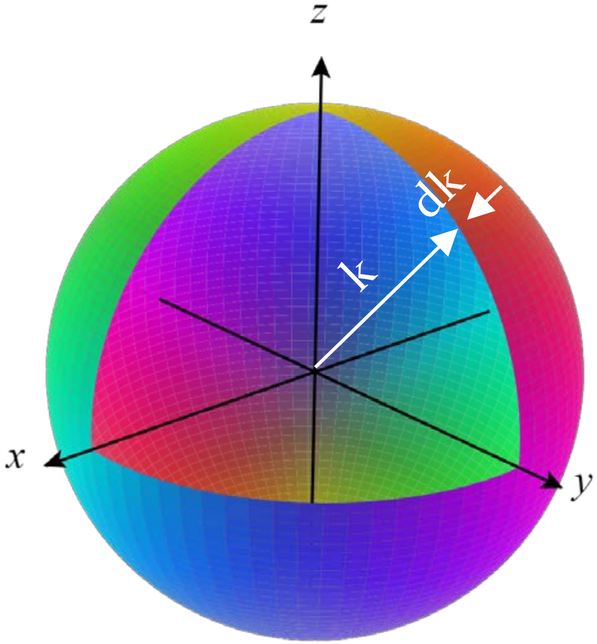
$$dE = \frac{\hbar^2 k dk}{m_e} \qquad k dk = \frac{m_e}{\hbar^2} dE \quad \text{and} \quad k = \sqrt{\frac{2 m_e E}{\hbar^2}}$$

QUANTUM FREE ELECTRON THEORY

Density of States

$$D(E)dE = \frac{\pi}{2} k\, kdk = \frac{\pi}{2}\sqrt{\frac{2m_eE}{\hbar^2}}\frac{m_e}{\hbar^2}dE$$

$$\Rightarrow D(E)dE = \frac{\pi}{2}\sqrt{\frac{2m_eE}{\hbar^2}}\frac{m_e}{\hbar^2}dE = \frac{\sqrt{2}\pi m_e^{\frac{3}{2}}E^{\frac{1}{2}}}{\hbar^3}dE$$



(3)

Applying the value of n and ndn in equ (1)

$$D(E)dE = \frac{\pi}{2} \times \frac{\left(8mL^2E\right)^{1/2}}{(h^2)^{1/2}} \frac{8mL^2}{2h^2} \, dE$$

$$D(E)dE = \frac{\pi}{4} \times \frac{\left(8mL^2\right)^{3/2}}{(h^2)^{3/2}} \mathrm{E}^{1/2} \, dE$$

$$D(E)dE = \frac{\pi}{4\mathrm{h}^3} \times (8m)^{3/2} \, \mathrm{L}^3 \mathrm{E}^{1/2} \, dE$$

$$V = L^3 = 1$$

$$D(E)dE = \frac{\pi}{4\mathrm{h}^3} \times (8m)^{3/2} \, \mathrm{E}^{1/2} \, dE$$

This energy states accommodate two electron based on Pauli's exclusion principle (one is spin up and one is spin down)

$$D(E)dE = 2 \text{ x } \frac{\pi}{4\mathrm{h}^3} \times (8m)^{\frac{3}{2}} \, \mathrm{L}^3 \mathrm{E}^{\frac{1}{2}} \, dE$$

$$D(E)dE = \frac{\pi}{2\mathrm{h}^3} \times (8m)^{\frac{3}{2}} \, \mathrm{L}^3 \mathrm{E}^{\frac{1}{2}} \, dE$$

QUANTUM FREE ELECTRON THEORY

Distribution of Particles over energy

Maxwell-Boltzmann Statistics	$n_i = \frac{g_i}{e^{\frac{E_i - E_F}{kT}}}$	**Distinguishable particle; no restriction on occupation of state**
Fermi-Dirac Statistics	$n_i = \frac{g_i}{e^{\frac{E_i - E_F}{kT}} + 1}$	Indistinguishable; spin multiple of $\frac{1}{2}$; restriction on occupation of states
Bose-Einstein Statistics	$n_i = \frac{g_i}{e^{\frac{E_i - E_F}{kT}} - 1}$	Indistinguishable; spin multiple of integers; no restriction on occupation

QUANTUM FREE ELECTRON THEORY

Distribution of Particles over energy

According to Pauli exclusion principles

One electron can occupy only one quantum state

One energy level accommodate only two electrons corresponding to spin ↑ and spin ↓

Thus filling in energy levels,

- two electrons occupy the lowest level,
- two more in the next level, and
- so forth until all the electrons in metal

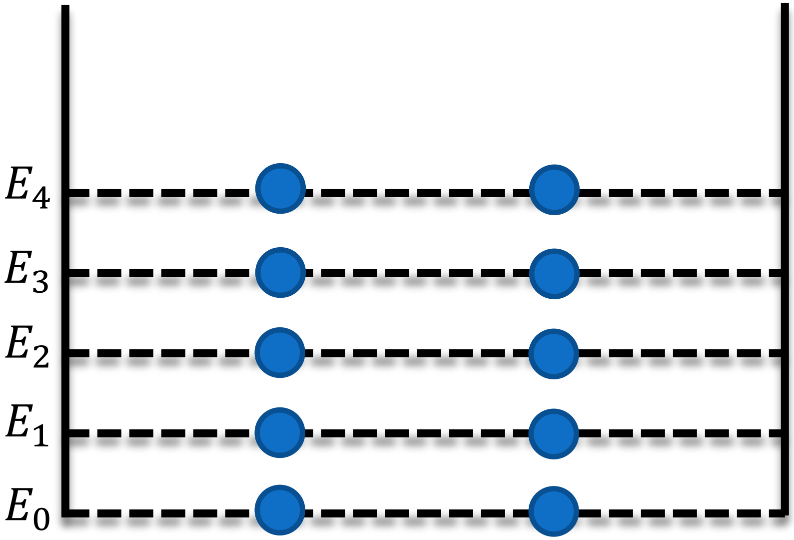


Fig: Filling the energy level in metal

QUANTUM FREE ELECTRON THEORY

Fermi Energy

Fermi-Dirac function:

$$F(E) = \frac{1}{e^{\frac{(E-E_F)}{kT}}+1}$$

Where, $F(E) \rightarrow$ Probability of occupation of a particular quantum state having energy E by an electron.

- $T = 0$ K; $F(E) = 0$ if E>E_F

  $F(E) = 1$ if E<E_F

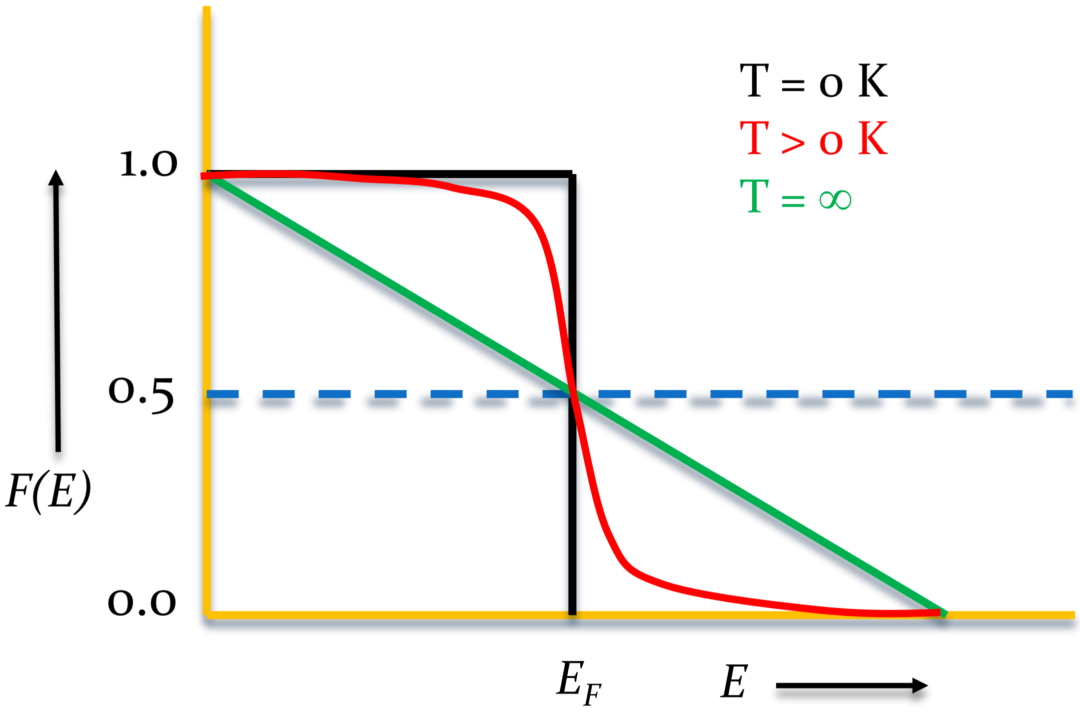
- $T > 0$ K; $F(E) = \frac{1}{2}$ if E=E_F

- If $F(E) = \frac{1}{2}$, then

  $$\frac{1}{2} e^{\frac{(E-E_F)}{kT}} = \frac{1}{2}$$

  $$\Rightarrow e^{\frac{(E-E_F)}{kT}} = 1 = e^0$$

  $$\Rightarrow E = E_F$$



- $E_F \rightarrow$ The energy level at which the probability of occupation is half.

QUANTUM FREE ELECTRON THEORY

Density of States

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$$N(E)dE = \frac{D(E)dE}{V} \qquad (1)$$

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Where, $k_x = \frac{\pi n_a}{x}$, $k_y = \frac{\pi n_b}{y}$, $k_z = \frac{\pi n_c}{z}$ and $k^2 = k_x^2 + k_y^2 + k_z^2$

QUANTUM FREE ELECTRON THEORY

Merits of QFE theory

Successfully explain

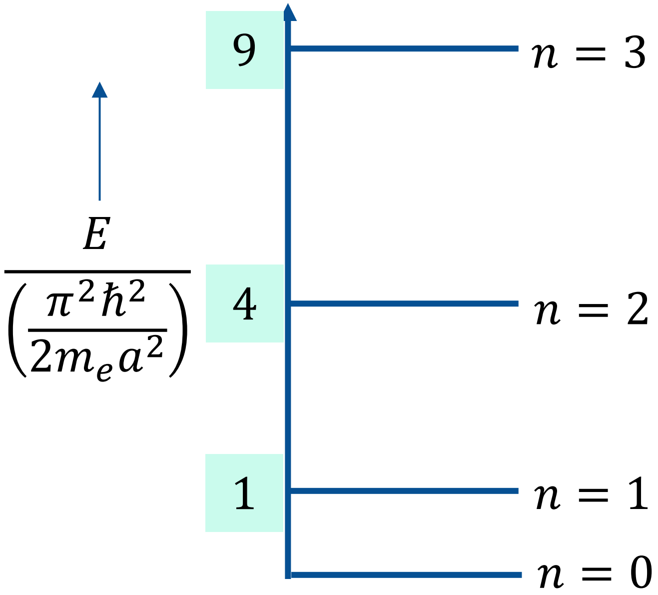
- electrical conductivity of metals
- Specific heat of metal
- Electron concentration in metals
- Only few electrons whose energies lie in the vicinity of E_F contribute to conduction and only such free electrons called conduction electrons

Demerits of QFE theory

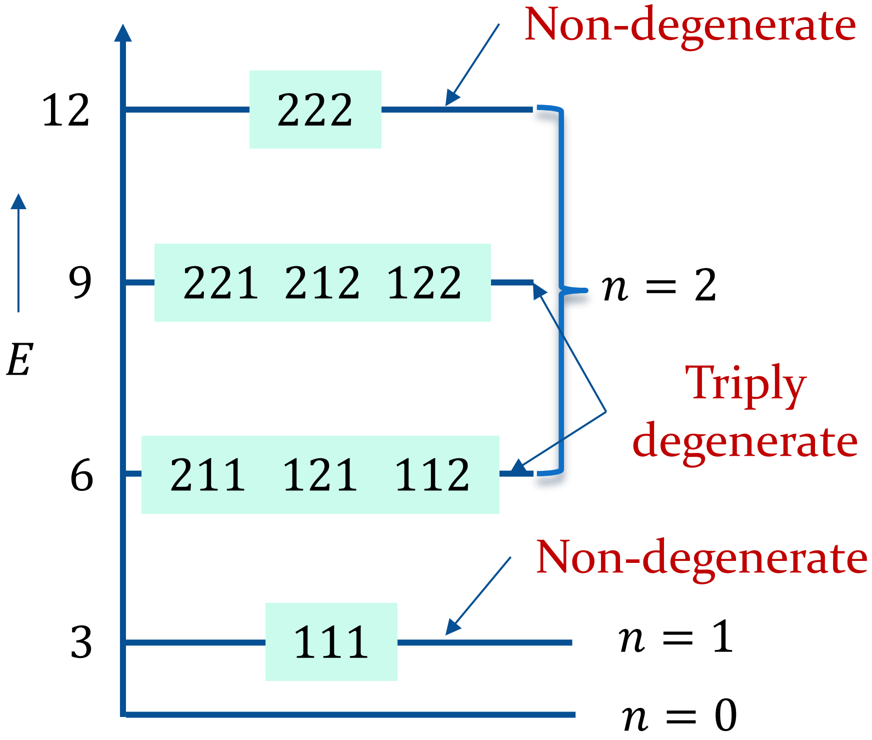
Although semiconductors and insulators contain electrons, QFE theory cannot explain

- electrical conductivity of semiconductors
- electrical conductivity of insulators
- Need development of Band theory solids

QUANTUM FREE ELECTRON THEORY



$\frac{n_a}{a}$	$\frac{n_b}{b}$	$\frac{n_c}{c}$	$\frac{n_a^2}{a^2} + \frac{n_b^2}{b^2} + \frac{n_c^2}{c^2}$
1	1	1	3
2	1	1	6
1	2	1	6
1	1	2	6



If crystal having 10^{23} atoms then

- ✓ How many energy levels are there?
- ✓ How many energy states are there?

Answers are very difficult!!!

BAND THEORY

Origin of band gap

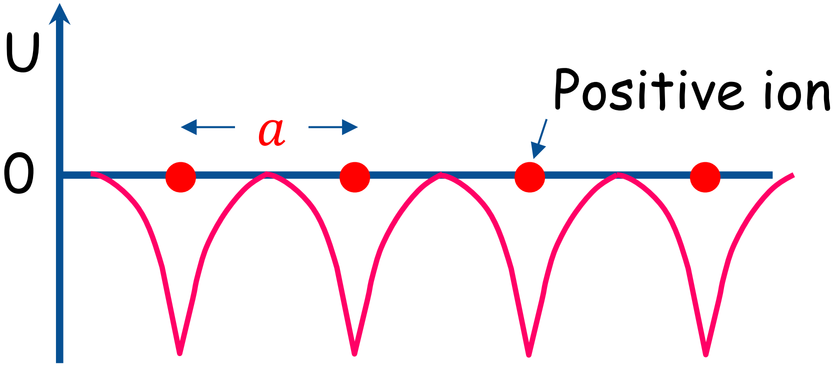
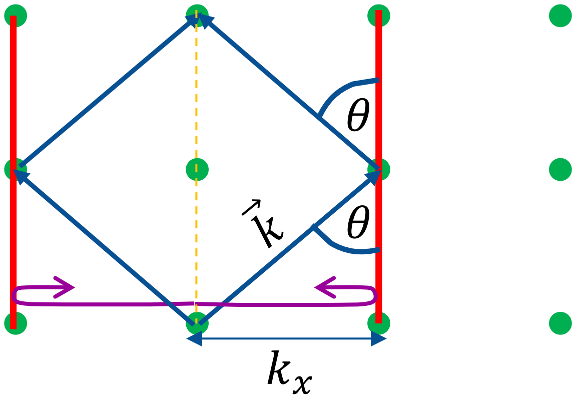


Figure: Variation of potential energy of a conduction electron in a periodic array of positive ions



$$k_x = k\sin\theta = \frac{n\pi}{a\sin\theta}\cdot\sin\theta = \frac{n\pi}{a}$$

- ✓ If the velocity of electron in periodic varying potential is v, then according to de Broglie

$$\lambda = \frac{h}{mv} = \frac{h}{p} = \frac{2\pi\hbar}{\hbar k} = \frac{2\pi}{k}$$

- ✓ If $\lambda \gg a$, then electron moves freely through the crystal. If $\lambda \le a$, then electron diffracts by crystal same as the X-rays which obeys Bragg's law

$$n\lambda = 2a\sin\theta$$

$$n\cdot\frac{2\pi}{k} = 2a\sin\theta$$

$$k = \frac{n\pi}{a\sin\theta}$$

BAND THEORY

Origin of band gap

- ✓ If $k < |\frac{\pi}{a}|$, electron moves freely through the crystal
- ✓ If $k = |\frac{\pi}{a}|$ or $k = \pm\frac{\pi}{a}$, electron is diffracted at $+\frac{\pi}{a}$ and reflected back at $-\frac{\pi}{a}$
- ✓ The wavefunction of electrons in positive x-direction is given by

$$\psi_1 = e^{ikx} = e^{\frac{i\pi x}{a}}$$

- ✓ Whereas in negative x-direction

$$\psi_2 = e^{-ikx} = e^{-\frac{i\pi x}{a}}$$

- ✓ Since electron travels right and left due to Bragg reflection, a resultant wave is a standing wave, which is given by

$$\psi_+ = e^{\frac{i\pi x}{a}} + e^{-\frac{i\pi x}{a}} = 2\cos\frac{\pi x}{a} \qquad \text{and} \quad \psi_+^2 \propto \cos^2\frac{\pi x}{a}$$

$$\psi_- = e^{\frac{i\pi x}{a}} - e^{-\frac{i\pi x}{a}} = 2\,i\sin\frac{\pi x}{a} \qquad \text{and} \quad \psi_-^2 \propto \sin^2\frac{\pi x}{a}$$

BAND THEORY

Origin of band gap

Probability density (ρ)

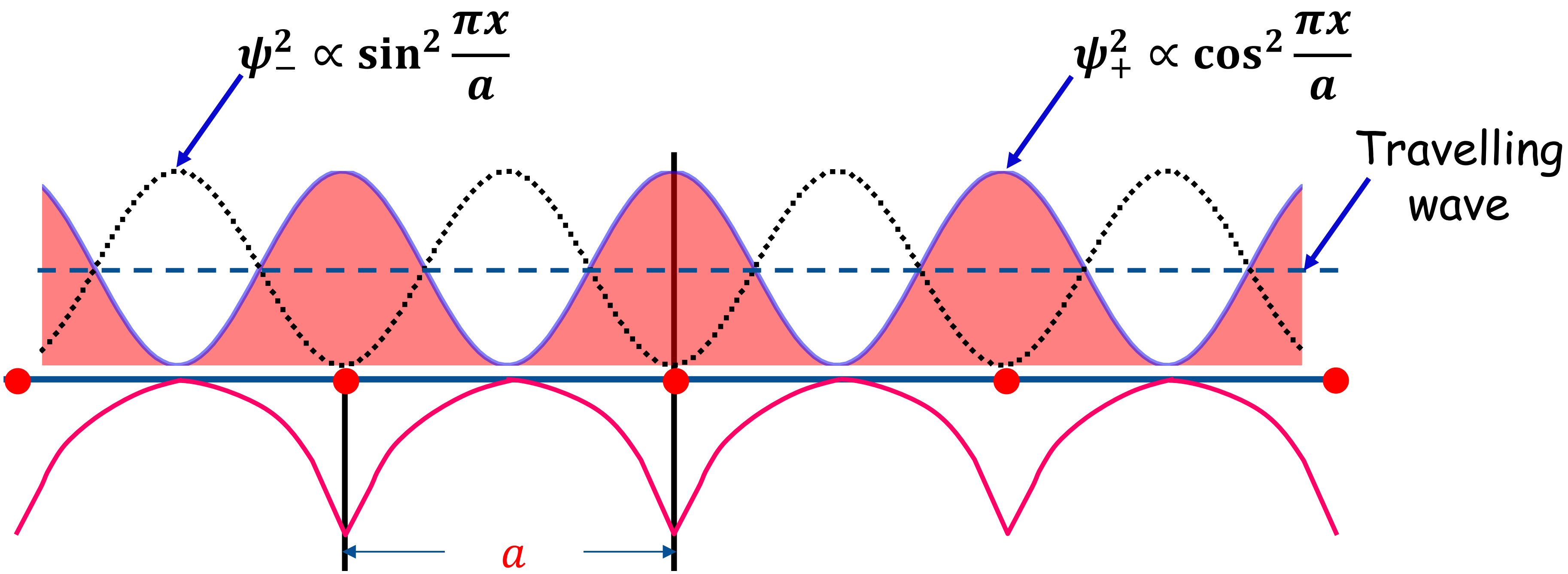


Figure: Distribution of probability density, ρ in the lattice for ψ_{+}^{2} and ψ_{-}^{2}, and for a travelling wave

BAND THEORY

Kroning-Penney Model

- ✓ This model describe the behaviors of electrons in periodic potential
- ✓ The potential energy of electron is represented by rectangular wells of period $a + b$ as shown in **Figure**.
- ✓ For $0 < x < a, V = 0$
- ✓ For $-b < x < 0, V = V_0$

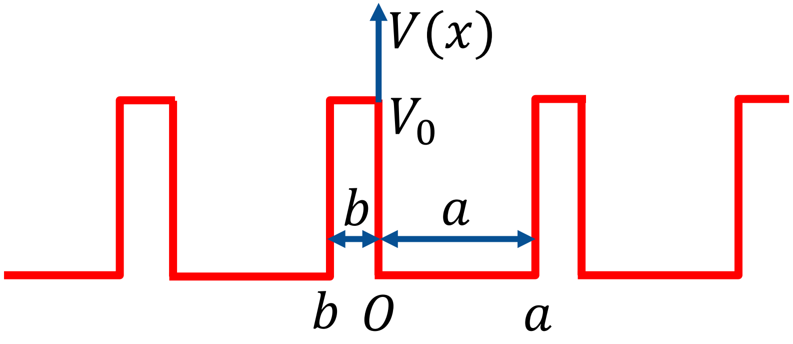


Figure: One-dimensional Kroning-Penney potential

- ✓ The Schrodinger equation in the two regions:

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0 \ \text{ for } 0 < x < a$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0 \ \text{ for } 0 < x < a$$

- ✓ If it is assumed that $E < V_0$ and let $\alpha^2 = \frac{2mE}{\hbar^2}$ and $\beta^2 = \frac{2m}{\hbar^2}(V_0 - E)$

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \quad \text{and} \quad \frac{d^2\psi}{dx^2} - \beta^2\psi = 0$$

BAND THEORY

Kroning-Penney Model

- ✓ According to Bloch theorem, the solution of SE in periodic potential is given by

$$\psi = e^{ikx}u(x)$$

where $u(x)$ has the period of the crystal lattice with

$u(x) = u(x + a)$.

- ✓ Differentiating the Bloch function twice with respect to x and substituting for $\frac{d^2\psi}{dx^2}$ give,

$$\frac{d^2u_1}{dx^2} + 2ik\frac{du_1}{dx} + (\alpha^2 - k^2)u_1 = 0 \tag{1}$$

$$\frac{d^2u_2}{dx^2} + 2ik\frac{du_2}{dx} + (\beta^2 + k^2)u_2 = 0 \tag{2}$$

BAND THEORY

Kroning-Penney Model

- ✓ Solution of eq. (1) and (2) are given by

$$u_1 = Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)} \quad \text{for } 0 < x < a \qquad (3)$$

$$u_2 = Ce^{i(\beta-k)x} + De^{-i(\beta+k)} \quad \text{for } -b < x < 0 \qquad (4)$$

where A, B, C, D are constants which must be determined from the boundary conditions of continuous wavefunctions:

$$u_1(0) = u_2(0), \qquad \left(\frac{du_1}{dx}\right)_{x=0} = \left(\frac{du_2}{dx}\right)_{x=0} \qquad (5)$$

$$u_1(a) = u_2(-b), \qquad \left(\frac{du_1}{dx}\right)_{x=a} = \left(\frac{du_2}{dx}\right)_{x=-b} \qquad (6)$$

The first two conditions are for continuous wavefunction while latter two for continuous derivatives in the two regions.

BAND THEORY

Kroning-Penney Model

- ✓ Applying conditions (5) and (6) in eq. (3) and (4) with simplification gives

$$\frac{\beta^2-\alpha^2}{2\alpha\beta}\sinh\beta b\cdot\sin\alpha a+\cosh\beta b\cdot\cos\alpha a=\cos k(a+b) \qquad (7)$$

- ✓ Eq. (7) can be simplified by assuming that $b \to 0,\ V_0 \to \infty$, but product bV_0 remain finite. Under this condition,

$$\sinh\beta b \to \beta b, \qquad \cosh\beta b \to 1, \qquad (\beta^2-\alpha^2)\to\beta^2 \quad \text{and}$$

Eq. (7) reduces to

$$\frac{\beta^2 b}{2\alpha}\sin\alpha a+\cos\alpha a=\cos ka$$

$$P\left(\frac{\sin\alpha a}{\alpha a}\right)+\cos\alpha a=\cos ka \qquad (8)$$

where $P=\frac{\beta^2 ab}{2}=\frac{mV_0ab}{\hbar^2}=bV_0\times\frac{ma}{\hbar^2}=(\text{Area of potential barrier})\times\frac{ma}{\hbar^2}$

BAND THEORY

Kroning-Penney Model

- P is a measure of the area bV_0 of the potential barrier. Increasing P has the physical meaning of binding a given electron more strongly to a particular potential well.

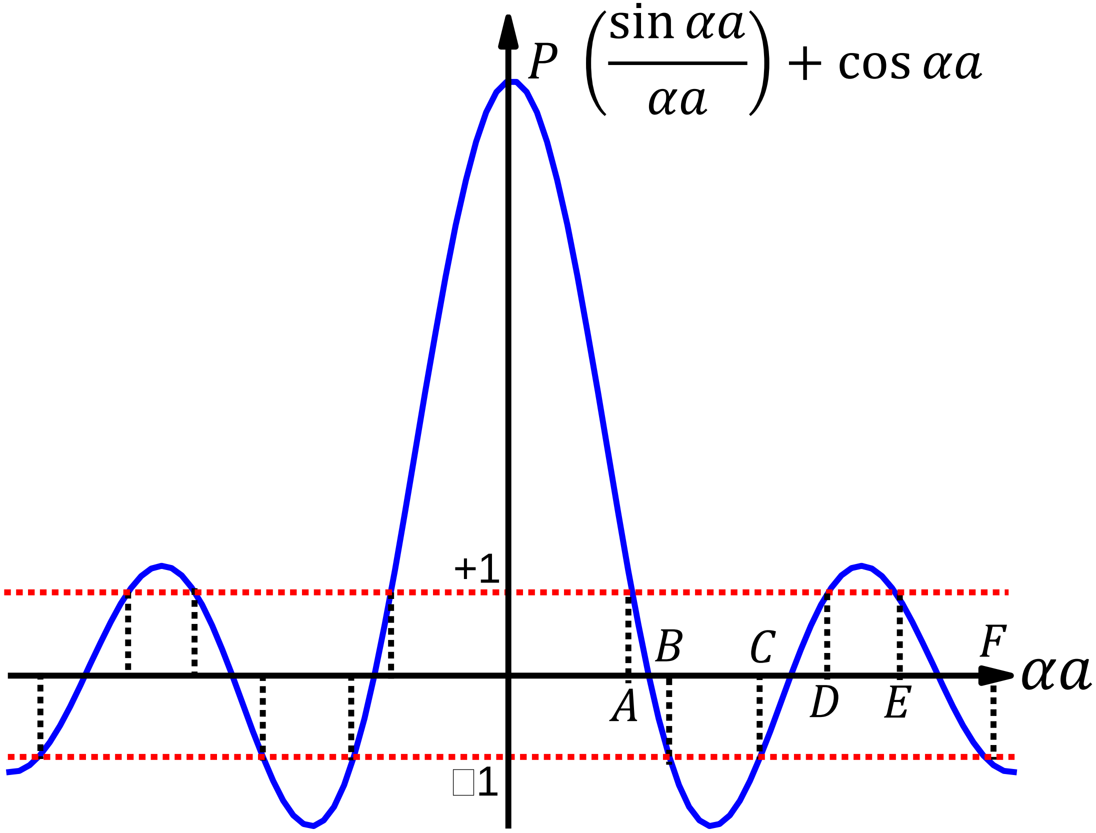


Figure 01: Variation of LHS against αa

- RHS of eq. (8) lies in $-1 \leq \cos ka \leq 1$
- LHS of eq. (8) can be solved graphically against αa for arbitrary value of P, say 2π.
- Eq. (8) is satisfied only for those values of αa for which RHS lies between $+1$ and -1.

BAND THEORY

Kroning-Penney Model

✓ From **Figure 01**, the following conclusions can be drawn:

a) The energy spectrum of electrons in a crystal consists of a number of allowed energy bands, such as AB, $CD, \cdots$ for $\cos \alpha a$ lies between ± 1, separated by forbidden regions, viz., BC, $DE, \cdots$

b) The values of 1st term on LHS of eq. (8) for a given value of P decrease as αa increases. LHS of eq. (8) approaches to a cosine curve. The width of allowed bands increases with increasing values of αa.

c) Effect of P on energy spectrum: if $P = 0$, then LHS of eq. (8) becomes $\cos \alpha a$ and forbidden band disappears. It gives continuous energy spectrum of a free electron.

For $P = 0$, eq. (8) becomes

$$\cos \alpha a = \cos ka \quad \Rightarrow \alpha^2 = k^2 \quad \Rightarrow \frac{2mE}{\hbar^2} = k^2 \quad \Rightarrow E = \frac{k^2 \hbar^2}{2m}$$

BAND THEORY

Kroning-Penney Model

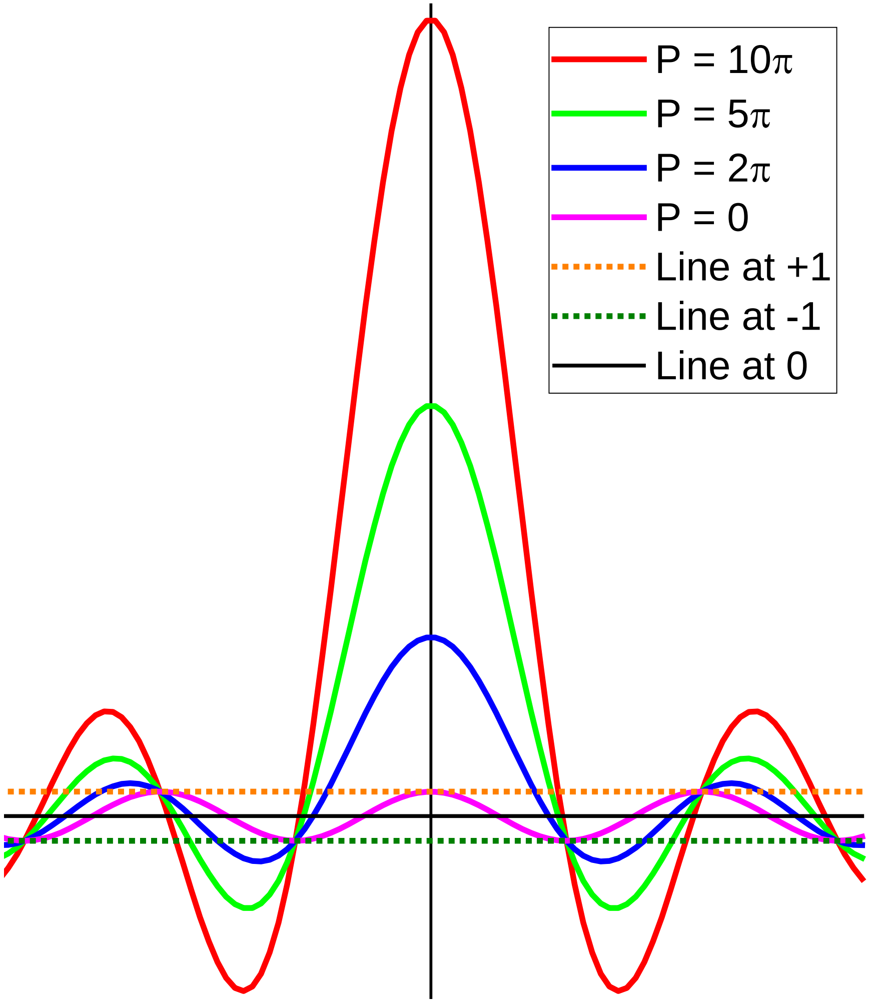


Figure 02: Effect of P on LHS against αa

For $P \to \infty$, $b \to \infty$, but constant period, $a + b$ leads $a \to 0$, also $\alpha a \to 0$ and hence we obtain

$$\sin \alpha a = 0 = \sin \mathrm{n}\pi$$

$$\text{where } n = \pm 1, \pm 2, \cdots$$

$$\alpha a = n\pi \quad \Rightarrow \alpha^2 = \frac{n^2\pi^2}{a^2}$$

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

It is similar to energy levels of particles in a constant potential box of atomic dimension.

BAND THEORY

Kroning-Penney Model

d) From eq. (8) and **Figure 01**, it follows that the energy discontinuity occur when

$$ka = n\pi$$

$$k = \frac{n\pi}{a} \quad where\, n = \pm 1, \pm 2, \cdots$$

✓ These values of k define the boundaries of the Brillouin zones. The range of the allowed values of k between $-\frac{\pi}{a}$ to $\frac{\pi}{a}$ define the first Brillouin zone. The second zone consists of two parts: from $-\frac{2\pi}{a}$ to $-\frac{\pi}{a}$ and $\frac{\pi}{a}$ to $\frac{2\pi}{a}$. The third zone extends from $-\frac{3\pi}{a}$ to $-\frac{2\pi}{a}$ and $\frac{2\pi}{a}$ to $\frac{3\pi}{a}$.