

Roll no.

Exam no.

“Education through self help is our motto”
Rayat Shikshan Sanstha
Yashwantrao chavan institute of science,Satara.



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This is to certify that the

- 1.Misal Rahul Dattu.
- 2.Waghmare Mayur Chandrakant.
- 3.Mulik Aniket Hanamant.
- 4.Pawar Karan Jalinder.
- 5.Suryawanshi Sanket Dattajirao.
- 6.Jadhav Abhijit Vishnu.
- 7.Parsi Pravin Vilas.
- 8.Padasare Ganesh Narayan.
- 9.Kadam Ram

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course in physics under star college activity
and this project represent their works in year 2016-17

Teacher in charge

Examiners

**Head of Department
physics**

PREFACE

This project is Primarilly intended for Star collage activity of Shivaji University Kolhapur. This project is tried to make highly innovative. It's our pleasure to present this project to the department. subject metric is presented in lucid and simple language. The project covers all the information related to the metals and its properties. The material is presented in the comprehensive view and sequence of article in project helps to understand the topic of electron theory. Different diagrams are given in the Project to understand the basic principles. we tried our best to study the electron theory and present it in a beautiful manner. The object of these project is to study the most mystirical concepts in Bose-Einstein stastistics.We heartly thankful to the Principal , Head of department and all other teachers for cooperating in these project.

We hope that this project will be found useful for students. We will appreciate any suggestions for improvement of these project.

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Electron

Theory

IN METALS

AIMS

- To study the basic concepts of atoms in the metal.
- To understand the structures and properties of metals. through their electronic structure.
- To apply Bose Einstein statics to metals.
- To study summerfield free electron theory.
- To study the structure of metals.

Introduction:-

What is the electron theory of metals?

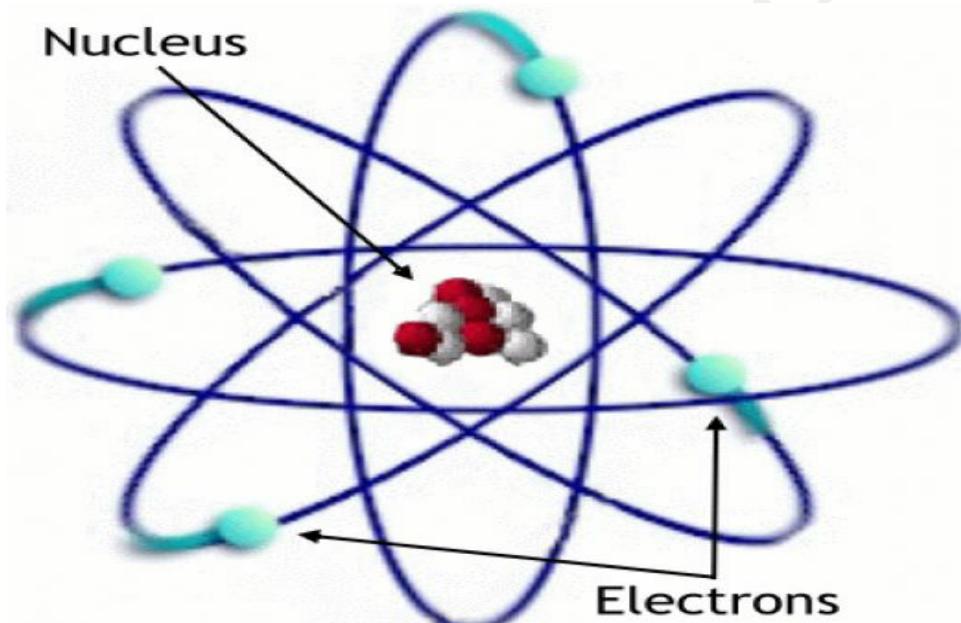
Each element exists as either a solid, or a liquid, or a gas at ambient temperature and pressure. Alloys or compounds can be formed by assembling a mixture of different elements on a common lattice. Typically this is done by melting followed by solidification. Any material is, therefore, composed of a combination of the elements listed in the periodic table. Among them, we are most interested in solids, which are often divided into metals, semiconductors and insulators. Roughly speaking, a metal represents a material which can conduct electricity well, whereas an insulator is a material which cannot convey a measurable electric current. At this stage, a semiconductor may be simply classified as a material possessing an intermediate character in electrical conduction. Most elements in the periodic table exist as metals and exhibit electrical and magnetic properties unique to each of them. Moreover, we are well aware that the properties of alloys differ from those of their constituent elemental metals. Similarly, semiconductors and insulators consisting of a combination of several elements can also be formed. Therefore, we may say that unique functional materials may well be synthesized in metals, semiconductors and insulators if different elements are ingeniously combined. A molar quantity of a solid contains as many as 10^{23} atoms. A solid is formed as a result of bonding among such a huge number of atoms. The entities responsible for the bonding are the electrons. The physical and chemical

properties of a given solid are decided by how the constituent atoms are bonded through the interaction of their electrons among themselves and with the potentials of the ions. This interaction yields the electronic band structure characteristic of each solid: a semiconductor or an insulator is described by a filled band separated from other bands by an energy gap, and a metal by overlapping continuous bands. The resulting electronic structure affects significantly the observed electron transport phenomena. The electron theory of metals in the present book covers properties of electrons responsible for the bonding of solids and electron transport properties manifested in the presence of external fields or a temperature gradient. Studies of the electron theory of metals are also important from the point of view of application-oriented research and play a vital role in the development of new functional materials. Recent progress in semiconducting devices like the IC (Integrated Circuit) or LSI (Large Scale Integrated circuit), as well as developments in magnetic and superconducting materials, certainly owe much to the successful application of the electron theory of metals. As another unique example, we may refer to amorphous metals and semiconductors, which are known as non-periodic solids having no long-range order in their atomic arrangement. Amorphous Si is now widely used as a solar-operated battery for small calculators. It may be worthwhile mentioning what prior fundamental knowledge is required to read this book. The reader is assumed to have taken an elementary course of quantum mechanics. We use in this text terminologies such as the wave function, the uncertainty principle, the Pauli exclusion principle, the perturbation theory etc., without explanation. In addition, the reader is expected to have learned the elementary principles of classical

mechanics and electromagnetic dynamics.

Idea of atom:-

The electron is a subatomic particle, symbol e- or β^- with a negative elementary electric charge. Electrons belong to the first generation of the lepton particle family, and are generally thought to be elementary particles because they have no known components or substructure. The electron has a mass that is approximately 1/1836 that of the proton.

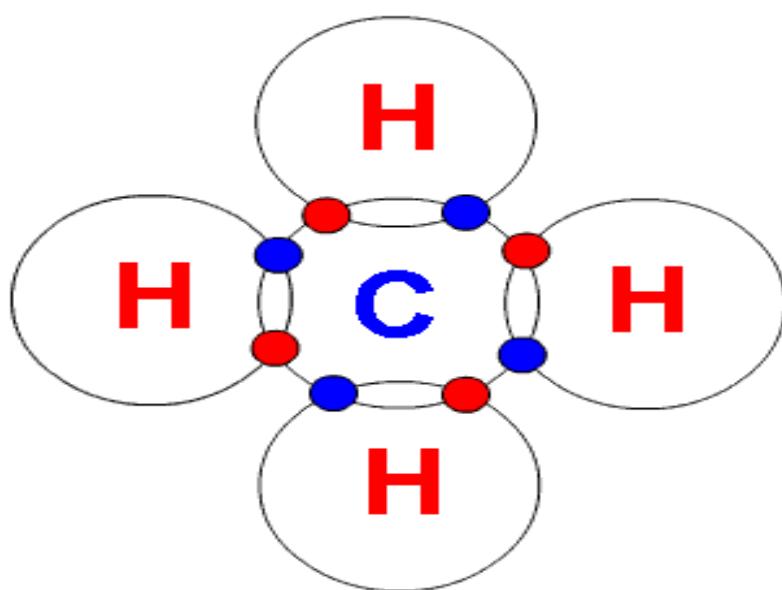


Quantum mechanical properties of the electron include an intrinsic angular momentum (spin) of a half-integer value, expressed in units of the reduced Planck constant, \hbar . As it is a fermion, no two electrons can occupy the same quantum state, in accordance with the Pauli exclusion principle. Like all matter, electrons have properties of both particles and waves: they can collide with other particles and can be diffracted like light. The wave properties of electrons are easier to observe with

experiments than those of other particles like neutrons and protons because electrons have a lower mass and hence a larger De Broglie wavelength for a given energy.

Valence Electron :-

In chemistry, a valence electron is an electron that is associated with an atom, and that can participate in the formation of a chemical bond; in a single covalent bond, both atoms in the bond contribute one valence electron in order to form a shared pair. The presence of valence electrons can determine the element's chemical properties and whether it may bond with other elements: For a main group element, a valence electron can exist only in the outermost electron shell. In a transition metal, a valence electron can also be in an inner shell.



Four covalent bonds. Carbon has four valence electrons and here a valence of four. Each hydrogen atom has one valence electron and is univalent.

An atom with a closed shell of valence electrons (corresponding to an electron configuration s₂p₆) tends to be chemically inert. Atoms with one or two more valence electrons than are needed for a "closed" shell are highly reactive due to following reasons.

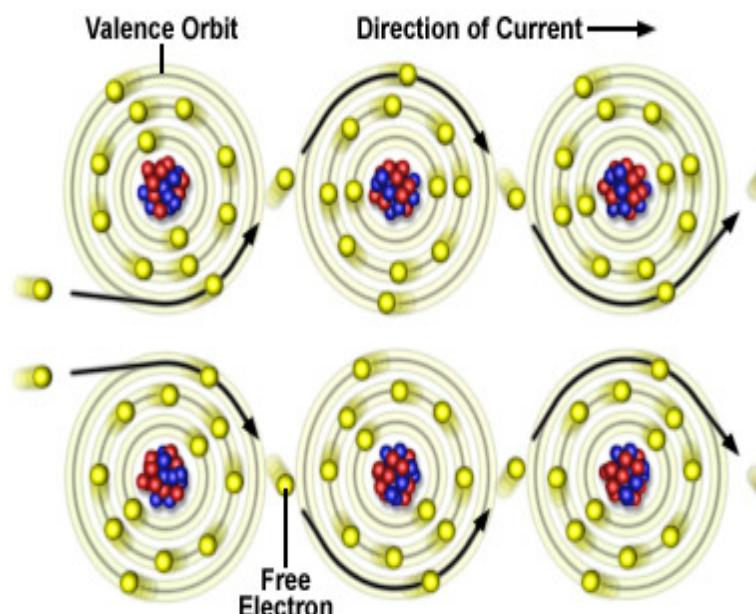
- 1) It requires relatively low energy (compared to the lattice enthalpy) to remove the extra valence electrons to form a positive ion.
- 2) Because of their tendency either to gain the missing valence electrons (thereby forming a negative ion), or to share valence electrons (thereby forming a covalent bond).

Similar to an electron in an inner shell, a valence electron has the ability to absorb or release energy in the form of a photon. An energy gain can trigger an electron to move (jump) to an outer shell; this is known as atomic excitation. Or the electron can even break free from its associated atom's valence shell; this is ionization to form a positive ion. When an electron loses energy (thereby causing a photon to be emitted), then it can move to an inner shell which is not fully occupied. Valence energy levels correspond to the principal quantum numbers ($n = 1, 2, 3, 4, 5 \dots$) or are labeled alphabetically with letters used in the X-ray notation (K, L, M, ...).

The number of valence electrons:-

The number of valence electrons of an element can be determined by the periodic table group (vertical column) in which the element is categorized. With the exception of groups 3–12 transition metals), the digit of the group number identifies how many valence electrons are associated with neutral atom of element listed under that particular column.

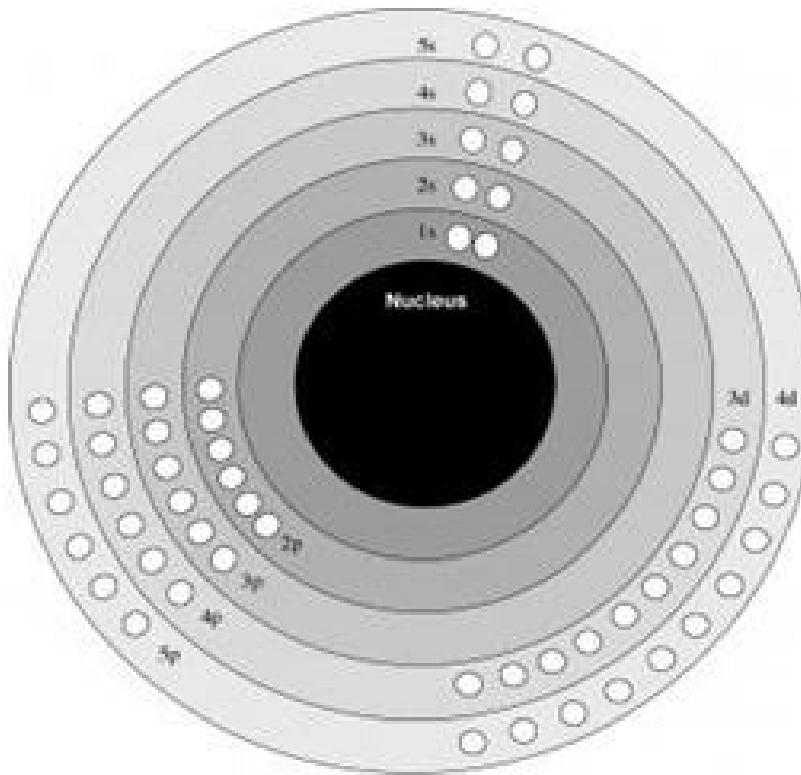
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under that particular column.

Electron configuration:-

The electrons that determine how an atom reacts chemically are those whose average distance from the nucleus is greatest; that is, those with the highest energy.



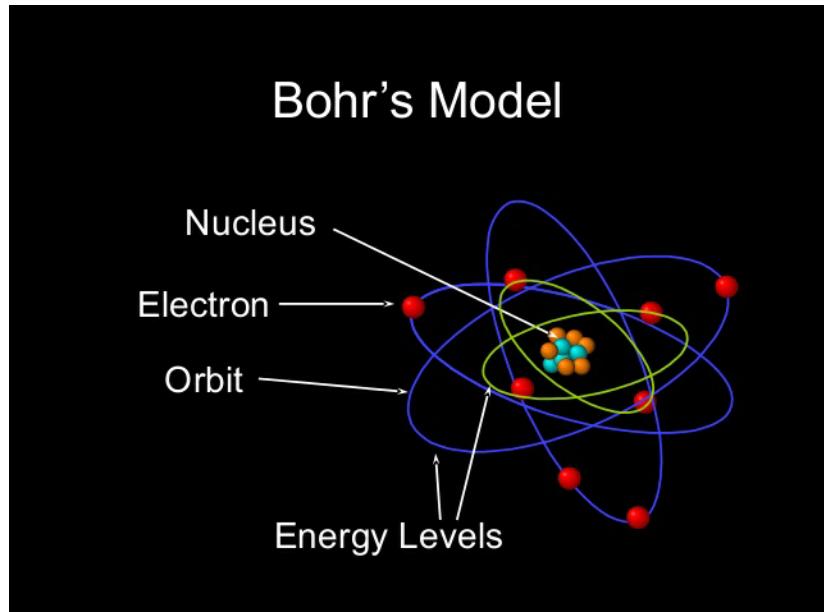
For a main group element, the valence electrons are defined as those electrons residing in the electronic shell of highest principal quantum number n. Thus, the number of valence electrons that it may have depends on the electron configuration in a simple way. For example, the electronic configuration of phosphorus (P) is 1s² 2s² 2p⁶ 3s²

$3p^3$ so that there are 5 valence electrons ($3s^2 3p^3$), corresponding to a maximum valence for P of 5 as in the molecule PF_5 ; this configuration is normally abbreviated to $[Ne] 3s^2 3p^3$, where $[Ne]$ signifies the core electrons whose configuration is identical to that of the noble gas neon. However, transition elements have partially filled $(n - 1)d$ energy levels, that are very close in energy to the ns level. So as opposed to main group elements, a valence electron for a transition metal is defined as an electron that resides outside a noble-gas core. Thus, generally, the d electrons in transition metals behave as valence electrons although they are not in the valence shell. For example, manganese (Mn) has configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$; this is abbreviated to $[Ar] 4s^2 3d^5$, where $[Ar]$ denotes a core configuration identical to that of the noble gas argon. In this atom, a 3d electron has energy similar to that of a 4s electron, and much higher than that of a 3s or 3p electron. In effect, there are possibly seven valence electrons ($4s^2 3d^5$) outside the argon-like core; this is consistent with the chemical fact that manganese can have an oxidation state as high as +7 (in the permanganate ion: MnO_4^-).

4) The farther right in each transition metal series, the lower the energy of an electron in a d subshell and the less such an electron has the properties of a valence electron. Thus, although a nickel atom has, in principle, ten valence electrons ($4s^2 3d^8$), its oxidation state never exceeds four. For zinc, the 3d subshell is complete and behaves similarly to core electrons. Because the number of valence electrons which actually participate in chemical reactions is difficult to predict, the concept of the valence electron is less useful for a transition metal than for a

main group element; the d electron count is an alternative tool for understanding the chemistry of a transition metal.

IDEAS AND ASSUMPTIONS:-



As in the Drude model, valence electrons are assumed to be completely detached from their ions (forming an electron gas). As in an ideal gas, electron-electron interactions are completely neglected. The electrostatic

fields in metals are weak because of the screening effect.

The crystal lattice is not explicitly taken into account. A quantum-mechanical justification is given by Bloch's Theorem: an unbound electron moves in a periodic potential as a free electron in vacuum, except for the electron mass m becoming an effective mass m^* which may deviate considerably from m (one can even use negative effective mass to describe conduction by electron holes). Effective masses can be derived from band structure computations. While the static lattice does not hinder the motion of the electrons, electrons can be scattered by impurities and by phonons; these two interactions determine electrical and thermal conductivity (superconductivity requires a more refined theory than the free electron model).

According to the Pauli exclusion principle, each phase space element $(\Delta k)^3(\Delta x)^3$ can be occupied only by two electrons (one per spin quantum number). This restriction of available electron states is taken into account by Fermi–Dirac statistics (see also Fermi gas). Main predictions of the free-electron model are derived by the Sommerfeld expansion of the Fermi–Dirac occupancy for energies around the Fermi level.

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

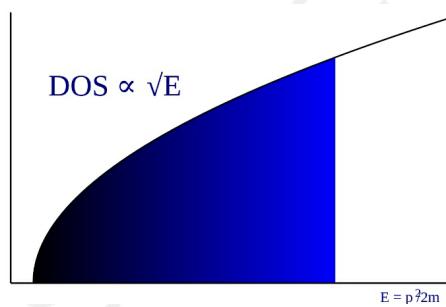
(iii). The Zone theory:

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”.

Sommerfield Free electron model:-

In solid-state physics, the free electron model is a simple model for the behavior of valence electrons in a crystal structure of a metallic solid. It was developed principally by Arnold Sommerfeld who combined the classical Drude model with quantum mechanical Fermi–Dirac statistics and hence it is also known as the Drude–Sommerfeld model.

In three dimensions, the density of states of a gas of fermions is proportional to the square root of the kinetic energy of the particles.



The free electron empty lattice approximation forms the basis of the band structure model known as nearly free electron model. Given its simplicity, it is surprisingly successful in explaining many experimental phenomena, especially

- the Weidman–Franz law which relates electrical conductivity and thermal conductivity;

- the temperature dependence of the heat capacity;
- the shape of the electronic density of states;
- the range of binding energy values;
- electrical conductivities;

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t)$$

- thermal electron emission and field electron

emission from bulk metals.

Bose-Einstein statics:-

Solution of the Schrödinger equation:-

The Schrödinger equation For a free particle the potential is $v(r)=0$, so the Schrödinger equation for the free electron is

This is a type of wave equation that has numerous kinds of solutions. One way of solving the equation is splitting it in a time-dependent oscillator equation and a space-dependent wave

The Schrödinger equation can be split in a time dependent part and a time independent part. Which is derived

Solution of the time dependent equation:-

The peculiar time dependent part of the Schrödinger equation is, unlike the Klein–Gordon equation for pions and most of the other well known wave equations, a first order in time differential equation with a 90° out of phase driving mechanism,

$$i\hbar \frac{\partial}{\partial t} e^{\alpha t} = E e^{\alpha t}.$$

The complex (imaginary) exponent is proportional to the energy

$$\alpha = -\frac{iE}{\hbar}$$

The imaginary exponent can be transformed to an angular frequency

$$E = i\hbar\alpha = \hbar\omega$$

The wave function now has a stationary and an oscillating part

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-i\omega t}$$

while most oscillator equations are second order in time differential equations with 180° out of phase driving mechanisms.

The equation that has to be solved is

The stationary part is of major importance to the physical properties of the electronic structure of matter.

Solution of the time independent equation:-

The wave function of free electrons is in general described as the solution of the time

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

The Laplace operator in Cartesian coordinates is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

independent Schrödinger equation for free electrons

$$\psi(\mathbf{r}) = \phi_x(x)\phi_y(y)\phi_z(z)$$

The wave function can be factorized for the three Cartesian directions

Now the time independent Schrödinger equation can be split in three independent parts for the three different Cartesian direction

0

As a solution an exponential function is substituted in the time independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \phi_x(x) = E_x \phi_x(x)$$

$$\frac{\partial^2}{\partial x^2} \phi_x(x) = \kappa^2 N_x e^{\kappa x} = -\frac{2m}{\hbar^2} E_x N_x e^{\kappa x}$$

gives the exponent

$$\kappa = ik_x = i\sqrt{\frac{2mE_x}{\hbar^2}}$$

which yields the wave equation

$$\psi(\mathbf{r}) = N_x N_y N_z e^{i(k_x x + k_y y + k_z z)} = N_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

and the energy

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2)$$

$$1 = \int_{\Omega_r} |\psi_{\mathbf{k}}(\mathbf{r})|^2 d\mathbf{r} = \int_{\Omega_r} \psi_{\mathbf{k}}^*(\mathbf{r}) \psi_{\mathbf{k}'}(\mathbf{r}) d\mathbf{r} = \int_{\Omega_r} (N_{\mathbf{k}}^* e^{-i\mathbf{k}\cdot\mathbf{r}}) (N_{\mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{r}}) d\mathbf{r} = N_{\mathbf{k}}^2 |\Omega_r|_{vol}$$

and the wave vector magnitude

$$k = \sqrt{k_x^2 + k_y^2 + k_z^2}$$

With the normalization

we arrive at the plane wave solution with a wave function

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_r}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

for free electrons with a **wave vector** \mathbf{k} and a kinetic energy

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

in which V is the volume of space occupied by the electron.

The traveling plane wave solution:-

The product of the time independent stationary wave solution and time dependent oscillator solution

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})e^{-i\omega t}$$

gives the traveling plane wave solution

$$\Psi(\mathbf{r}, t) = \frac{1}{\sqrt{\Omega_r}} e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}$$

which is the final solution for the free electron wave function.

Fermi energy:-

According to the Pauli principle, the electrons in the ground state occupy all the lowest-energy states, up to some Fermi energy . Since the energy is given by

$$E(\mathbf{k}) = \frac{\hbar^2 k^2}{2m},$$

this corresponds to occupying all the states with wave vectors \mathbf{k} , where k_F is so-called Fermi wave vector,

given by

$$k_F = (3\pi^2 N_e/V)^{1/3},$$

where N is the total number of electrons in the system, and V is the total volume. The Fermi energy is then

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N_e}{V} \right)^{2/3}$$

In a nearly-free-electron model of a -valent metal, one can replace N_e with N , where N is the total number of metal ions.

FERMI-DIRAC DISTRIBUTION:-

The free electron model of a metal has survived to the present time because it is fairly close approximation to the actual situation in metals particularly the monovalent elements such as alkali metals. Quantum mechanics requires that all valence or free electrons should be indistinguishable but that the state of each electron be specified by three quantum numbers n_x n_y , n_z together with spin which can have either of two values $\pm \frac{1}{2}$. Moreover, the Pauli's exclusion principle does not permit more than one electron to have the same four quantum numbers. By using quantum statistics, Fermi-Dirac derived the formula to state the probability $F(E)$ that a particular quantum state is having energy(E) occupied by the free electron and is given by

This is called as F.D. distribution formula. Where E_F is Fermi-energy of the metal, k is Boltzmann constant and T is the temperature of metal. The distribution of free electrons in the metal can be studied by F.D. distribution as

- (i) At $T = 0$ and $E \ll E_F$, the exponential term in equation is very small so that $F(E)$ is essentially equal to unity.

The probability that a particle will have energy E

At absolute zero, fermions will fill up all available energy states below a level E_F called the Fermi energy with one (and only one) particle. They are constrained by the Pauli exclusion principle. At higher temperatures, some are elevated to levels above the Fermi level.

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

See the Maxwell-Boltzmann distribution for a general discussion of the exponential term.

For low temperatures, those energy states below the Fermi energy E_F have a probability of essentially 1, and those above the Fermi energy essentially zero.

The quantum difference which arises from the fact that the particles are indistinguishable.

I. e. for $E \ll E_F$, $F(E)=1$

This means that all the states having energy smaller than Fermi-energy are completely occupied.

(ii) At $T=0$ but $E \gg E_F$, the exponential term is very large and $F(E)$ rapidly tends to zero as energy increases

I. e, for $E \gg E_F$, $F(E)=0$

This means that all the states having energy greater than Fermi-energy are virtually empty

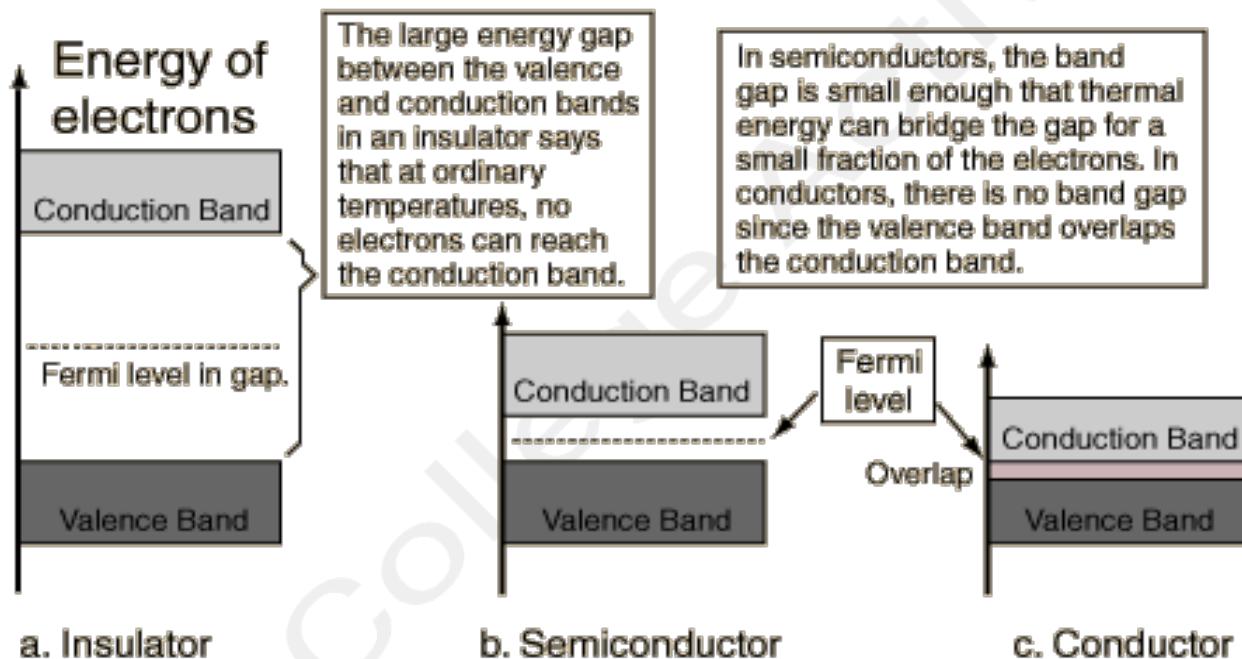
(iii) If $T=0$ i.e. $T \neq 0$ and $E=E_F$, then $F(E)=0.5$

This means that the states are half filled (50%) and half empty (50%) The actual distribution of free electrons is as shown in Fig. and it is evident that the higher energy states are virtually empty.

ORIGIN OF ENERGY BANDS :-

A solid contains an enormous number of atoms together. Each atom when isolated has a discrete set of energy levels 1s, 2s, 2p etc.

If we imagine all N atoms of the solid to be isolated from one another, they would have completely coincide schemes of their energy levels. The energies of electrons within any one isolated atom obeyed following conditions



1) There are specific electronic energy levels around each atom. Electrons cannot occupy spaces between these levels

(i) Electrons fill the lowest energy level first. A specific quantity of energy called a quantum of energy, must be supplied to move an electron to the next higher level.

(ii) According to Pauli's exclusion principle, no two electrons can

occupy the same quantum states. Not more than two electrons may occupy any one energy level. Two electrons may occupy the same energy level because they have opposite magnetic directions

Valence band:-

The energy occupied by the valence electron is called as valence band. It is lower band. This band may be either completely filled or partially filled with electrons but can never be empty. It is completely filled in case of insulators.

Conduction band:-

The electrons which have left the valence band are called as conduction band. They practically leave the atom or only weakly bound the nucleus. The band occupied by these electrons is called as conduction band. This band lies above the valence band. It may be either empty or partially filled with conduction electrons. In conduction band the electrons move freely and conduct electric current through the solid. It is completely empty in case of insulator.

Forbidden energy gap:-

The V.B. and C.B. are separated by energy gap known as forbidden energy gap. The width of forbidden energy gap (E_g) is the characteristic of the solid. Forbidden energy gap is nothing but the energy required to lift an electron from V.B. and put it into C.B. For example, E_g for Ge is 0.72 eV, for Si 1.12 eV.

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 metalsl.

Drawbacks of classical free electron theory:

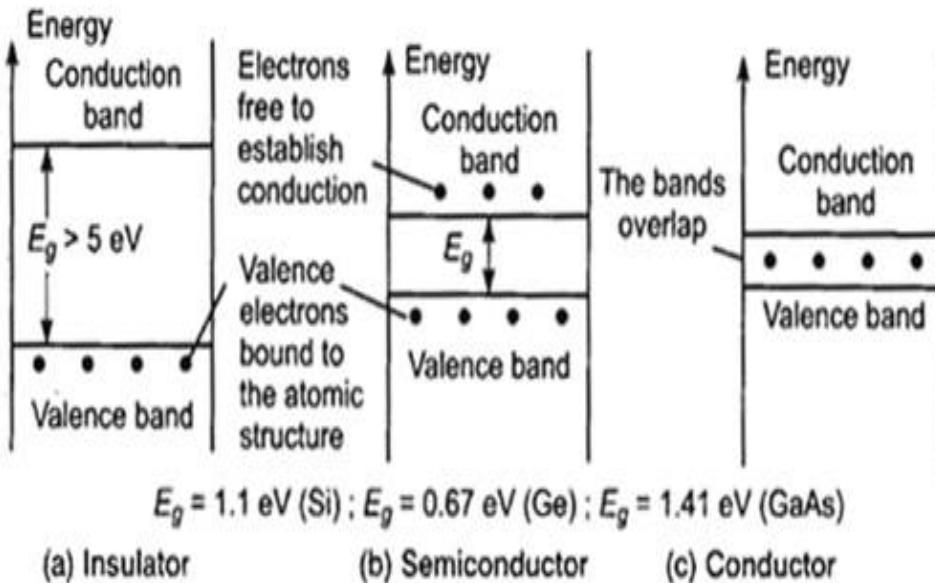
1. The phenomena such a photoelectric effect, Compton effect and the black body radiation couldn't be explained by classical free electron theory.
2. According to the classical free electron theory the value of specific heat of metals is given by $4.5R_u$ is the Universal gas constant whereas the experimental value is nearly equal to $3R_u$. Also according to this theory the value of electronic specific heat is equal to $3/2R_u$ while the actual value is about $0.01R_u$
3. Electrical conductivity of semiconductor or insulators couldn't be explained using this model.
4. 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.
5. Ferromagnetism couldn't be explained by this theory. The theoretical value of paramagnetic susceptibility is greater than

the experimental value.

CLASSIFICATION OF MATERIALS:-

Based on „band theory”, solids can be classified into three categories, namely,

1. insulators,
 2. semiconductors &
 3. conductors.



INSULATORS :-

- Bad conductors of electricity
 - Conduction band is empty and valence band is full, and these bands are separated by a large forbidden energy gap.
 - The best example is Diamond with $E_g=7\text{ev}$.

SEMI CONDUCTORS:-

- Forbidden gap is less
- Conduction band and valence band are partially filled at room temperature.
- Conductivity increases with temperature as more and more electrons cross over the small energy gap.
- Examples Si(1.2ev) & Ge(0.7ev)

CONDUCTORS:-

- Conduction and valence bands are overlapped
- Abundant free electrons already exist in the conduction band at room temperature hence conductivity is high.
- The resistivity increases with temperature as the mobility of already existing electrons will be reduced due to collisions.
- Metals are best examples.

References:

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- www.physicscentral.com
- Teachers advice

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Guide signature:-

Yours faithfully,

Rahul Misal