Quantum Physics: Lecture # Lec 9- 10

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Classical equation : $p^2 / 2m + V = E$

✓ **General expression for matter wave ψ (x,t)**

$$\psi(x,t) = Ae^{-\frac{i}{\hbar}(Et - px)}$$

✓ **Time independent Schrödinger equation**

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

✓ **Time dependent Schrödinger equation**

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

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What we have learnt- an example

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158

$$\psi(x,t) = Ae^{-\frac{i}{\hbar}(Et-px)} = \psi(x)\varphi(t)$$

The stationary states of a system are given by φ_i and the corresponding energies by E_i. At time t= 0, the wave function is $\Psi(0) = \frac{1}{\sqrt{6}}\varphi_1 + \frac{1}{\sqrt{3}}\varphi_2 + \frac{1}{\sqrt{2}}\varphi_3$. What will be the wave function at time t?

Solution: The wave function at time t is,

$$|\psi(t)\rangle = \frac{1}{\sqrt{6}}e^{-\frac{i}{\hbar}E_1 t}|\varphi_1\rangle + \frac{1}{\sqrt{3}}e^{-\frac{i}{\hbar}E_2 t}|\varphi_2\rangle + \sqrt{\frac{1}{2}}e^{-\frac{i}{\hbar}E_3 t}|\varphi_3\rangle.$$

Consider a system whose state is given in terms of an orthonormal set of three vectors: $|\phi_1\rangle$, $|\phi_2\rangle$, $|\phi_3\rangle$ as

$$|\psi\rangle = \frac{\sqrt{3}}{3}|\phi_1\rangle + \frac{2}{3}|\phi_2\rangle + \frac{\sqrt{2}}{3}|\phi_3\rangle.$$

(a) Verify that $|\psi\rangle$ is normalized. Then, calculate the probability of finding the system in any one of the states $|\phi_1\rangle$, $|\phi_2\rangle$, and $|\phi_3\rangle$. Verify that the total probability is equal to one.

(b) Consider now an ensemble of 810 identical systems, each one of them in the state $|\psi\rangle$. If measurements are done on all of them, how many systems will be found in each of the states $|\phi_1\rangle$, $|\phi_2\rangle$, and $|\phi_3\rangle$?

Bra ($|\,\rangle$) and ket ($\langle\,|$) notation

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Solution

(a) Using the orthonormality condition $\langle \phi_j | \phi_k \rangle = \delta_{jk}$ where $j, k = 1, 2, 3$, we can verify that $|\psi\rangle$ is normalized:

$$\langle \psi | \psi \rangle = \frac{1}{3}\langle \phi_1 | \phi_1 \rangle + \frac{4}{9}\langle \phi_2 | \phi_2 \rangle + \frac{2}{9}\langle \phi_3 | \phi_3 \rangle = \frac{1}{3} + \frac{4}{9} + \frac{2}{9} = 1. \qquad (3.11)$$

Since $|\psi\rangle$ is normalized, the probability of finding the system in $|\phi_1\rangle$ is given by

$$P_1 = |\langle \phi_1 | \psi \rangle|^2 = \left| \frac{\sqrt{3}}{3}\langle \phi_1 | \phi_1 \rangle + \frac{2}{3}\langle \phi_1 | \phi_2 \rangle + \frac{\sqrt{2}}{3}\langle \phi_1 | \phi_3 \rangle \right|^2 = \frac{1}{3}, \qquad (3.12)$$

since $\langle \phi_1 | \phi_1 \rangle = 1$ and $\langle \phi_1 | \phi_2 \rangle = \langle \phi_1 | \phi_3 \rangle = 0$.

Similarly, from the relations $\langle \phi_2 | \phi_2 \rangle = 1$ and $\langle \phi_2 | \phi_1 \rangle = \langle \phi_2 | \phi_3 \rangle = 0$, we obtain the probability of finding the system in $|\phi_2\rangle$:

$$P_2 = |\langle \phi_2 | \psi \rangle|^2 = \left| \frac{2}{3}\langle \phi_2 | \phi_2 \rangle \right|^2 = \frac{4}{9}. \qquad (3.13)$$

As for $\langle \phi_3 | \phi_3 \rangle = 1$ and $\langle \phi_3 | \phi_1 \rangle = \langle \phi_3 | \phi_2 \rangle = 0$, they lead to the probability of finding the system in $|\phi_3\rangle$:

$$P_3 = |\langle \phi_3 | \psi \rangle|^2 = \left| \frac{\sqrt{2}}{3}\langle \phi_3 | \phi_3 \rangle \right|^2 = \frac{2}{9}. \qquad (3.14)$$

As expected, the total probability is equal to one:

$$P = P_1 + P_2 + P_3 = \frac{1}{3} + \frac{4}{9} + \frac{2}{9} = 1. \qquad (3.15)$$

(b) The number of systems that will be found in the state $|\phi_1\rangle$ is

$$N_1 = 810 \times P_1 = \frac{810}{3} = 270. \qquad (3.16)$$

Likewise, the number of systems that will be found in states $|\phi_2\rangle$ and $|\phi_3\rangle$ are given, respectively, by

$$N_2 = 810 \times P_2 = \frac{810 \times 4}{9} = 360, \qquad N_3 = 810 \times P_3 = \frac{810 \times 2}{9} = 180. \qquad (3.17)$$

▸ State the main basis of Quantum free electron(Sommerfeld's theory) (Recap)

▸ Quantum theory (recap)

▸ Fermi Dirac Statistics

▸ Problems

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Quantum free electron theory

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162

o **Quantum free electron theory for the assembly of free electrons in a metal was first proposed by Sommerfeld in 1928**

o **He retained vital features of classical free electron theory (Specially uniform potential field)**

o **He included (i) Pauli Exclusion principle and (ii) Fermi- Dirac statistics to formulate his theory**

✓ **Electron travels under constant potential and confine to the boundaries of metal.**

✓ **All attractive and repulsive forces are neglected**

✓ **Energies of free electron are quantized**

✓ **Electron follow Pauli's exclusion principle**

✓ **Electron follows Fermi Dirac statics**

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Quantum free electron theory
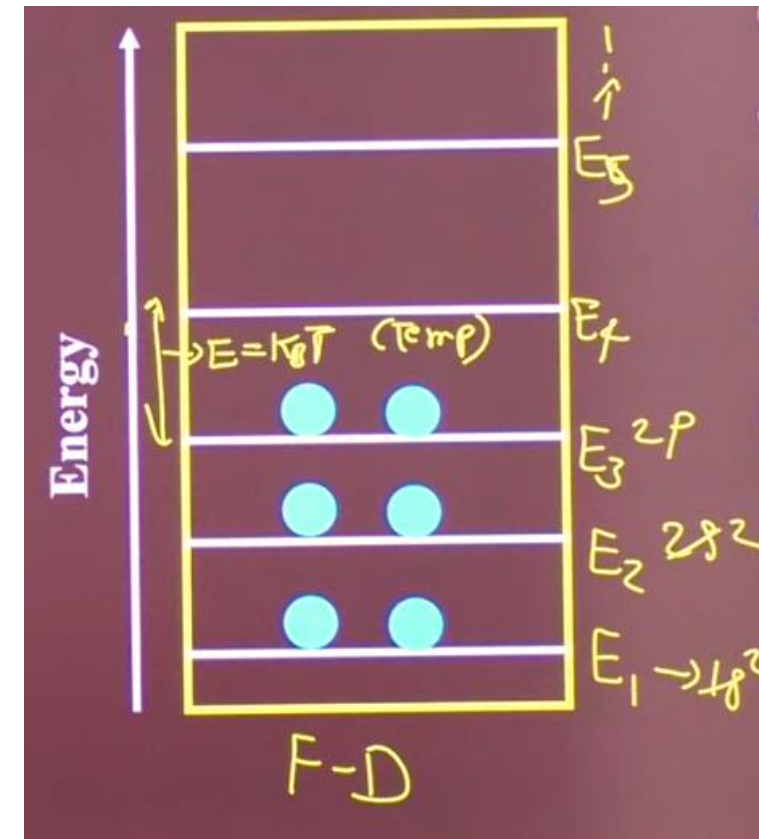
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163
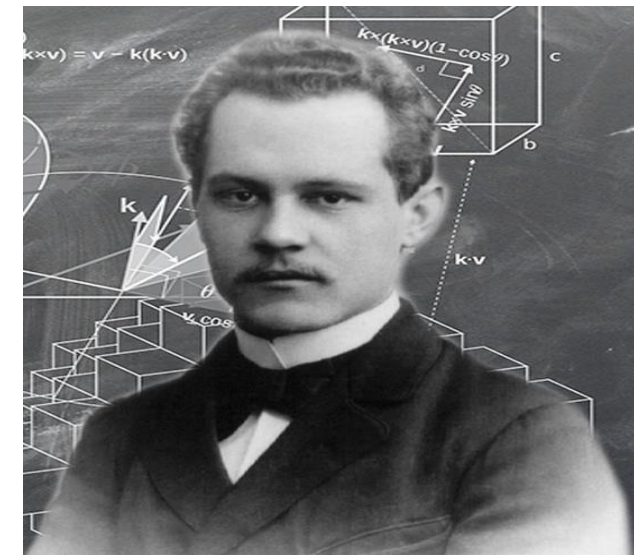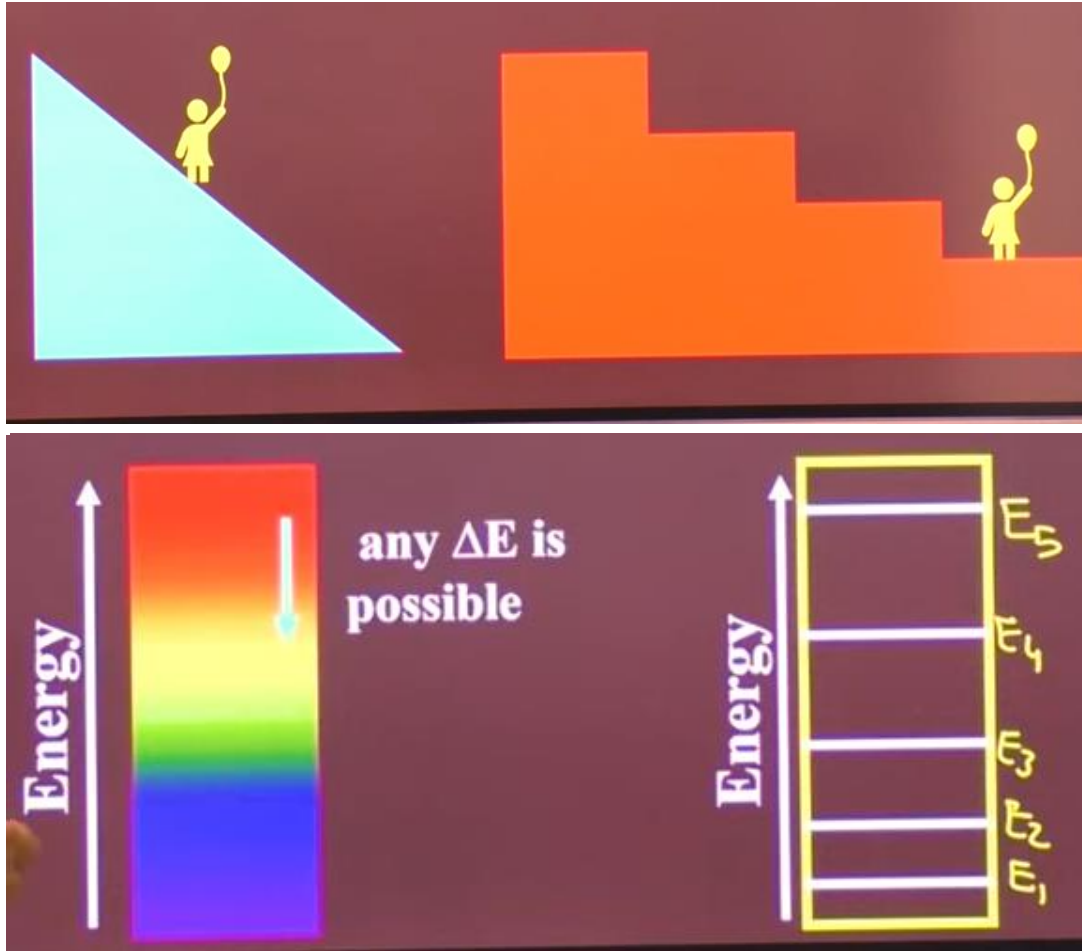
✓ **Energies of free electron are quantized**   ✓ **Electron follow Pauli's exclusion principle**
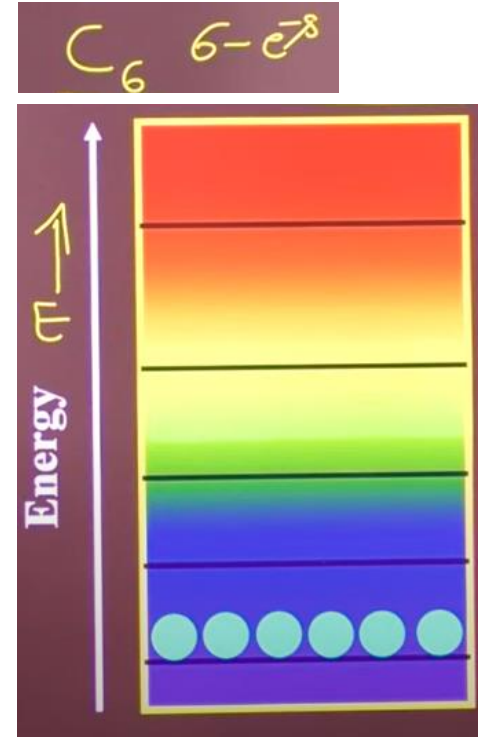
Maxwell-Boltzmann Statistics :

✓ **Only those electrons which are in the range of E= k_BT (T= temp)---**
✓ **thermal energy can excite---**
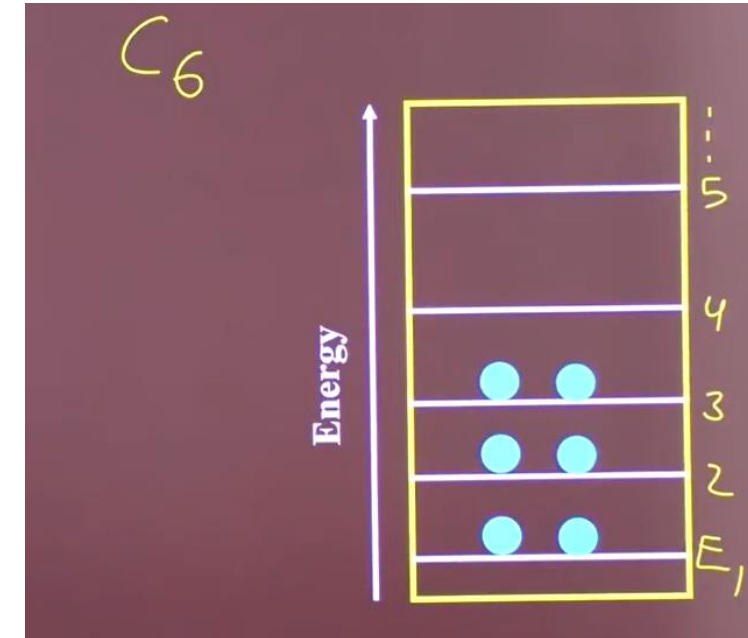✓ **only a fraction of electrons can contribute to conductivity**

o **In quantum mechanics electrons follows Fermi- Dirac statistics**

o **Therefore, electrons are known as Fermions**

o **From Pauli's exclusion principle we have seen this distribution earlier**

o **What Fermi- Dirac distribution tells us**

  ✓ **The probability of finding the particle in a certain energy level**

o **There exists so many energy levels--- How to find the presence of one electron in any particular level**

  ✓ **Given by F-D function**

o **According to F-D statistics, the probability of electron occupying an energy level E is given by**

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

E_F is the Fermi energy, k_B is the Boltzmann constant

- Deals with particles which has half integral spin
- Also known as Fermions
- *Eg.* : Electrons, Protons, Neutrons, Quarks, Neutrinos etc.,

o **@ T= 0 K, top most filled energy level is called as Fermi Energy level.**

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Fermi Dirac Statistics

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Fermi - level, Fermi - energy and Fermi - factor

As we know that for a metal containing N atoms, there will be N number of energy levels in each band. According to Pauli's exclusion principle, each energy level can accommodate a maximum of two electrons, one with spin up (+½) and the other with spin down (-½). At absolute zero temperature, two electrons with opposite spins will occupy the lowest available energy level. The next two electrons with opposite spins will occupy the next energy level and so on. Thus, the top most energy level occupied by electrons at absolute zero temperature is called **Fermi-energy level**. The energy corresponding to that energy level is called **Fermi-energy**.

@ 0 K
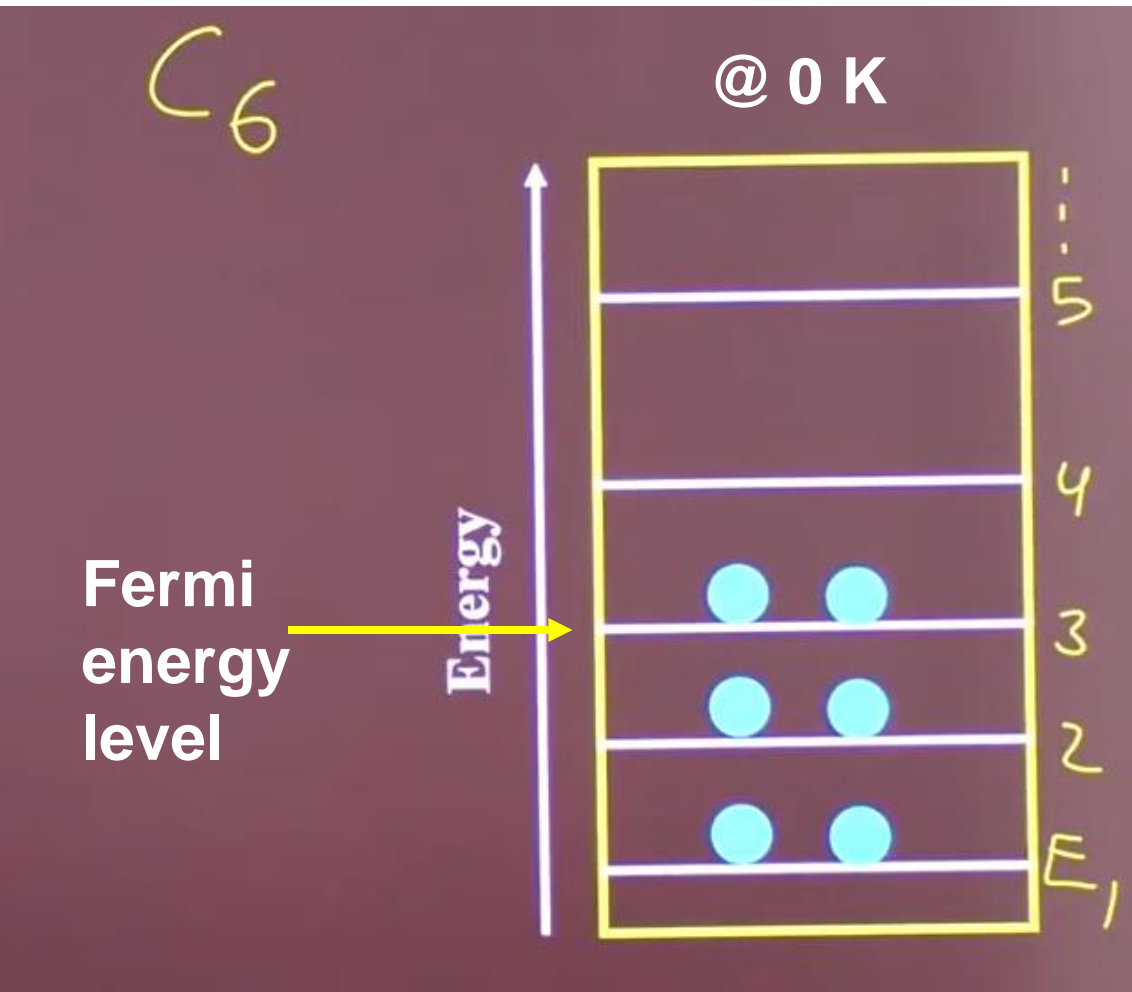
Fermi energy level

The probability of energy above which is 0
----- Fermi level @ T= 0 K

The probability of energy below which is 1
----- Fermi level @ T= 0 K

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The energy of the highest occupied level at zero degree absolute is called Fermi energy, and the energy level is referred to as the Fermi level. The Fermi energy is denoted as E_F.

All energy levels below Fermi level are completely filled and above which all energy levels are completely empty.
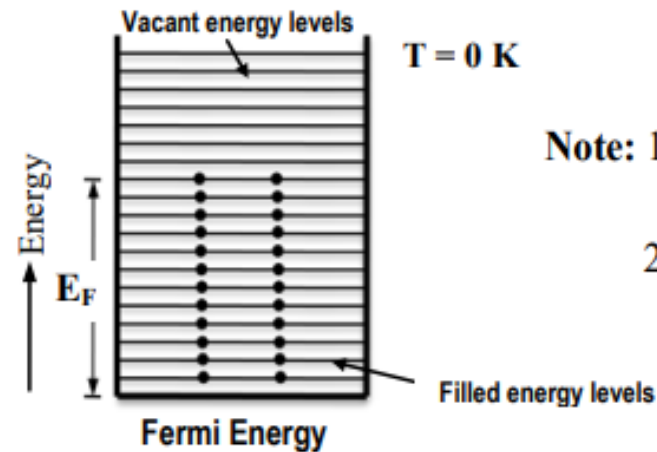
Note: 1. The Fermi-Dirac distribution function $f(E)$ is used to calculate the probability of an electron occupying a certain energy level.

2. The distribution of electrons among the different energy levels as a function of temperature is known as Fermi-Dirac distribution function.

At temperatures above absolute zero, the electrons get thermally excited and move up to higher energy levels. As a result there will be many vacant energy levels below as well as above Fermi energy level. Under thermal equilibrium, the distribution of electrons among various energy levels is given by statistical function $f(E)$. The function $f(E)$ is called **Fermi-factor** and this gives the probability of occupation of a given energy level under thermal equilibrium. The expression for $f(E)$ is given by

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

Where $f(E)$ is called Fermi-Dirac distribution function or Fermi factor, E_F is the Fermi energy, k is the Boltzmann constant and T is the temperature of metal under thermal equilibrium.

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Variation of Fermi factor with Energy and Temperature

Let us consider the different cases by considering the Fermi factor equation

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

Case (i) :- $f(E)$ for $E < E_F$ at $T = 0$ K;

When $E < E_F$ & $T = 0$ K, from the probability function $f(E)$ we have

$$f(E) = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$$

i.e., $f(E) = 1$ for $E < E_F$ at $T = 0$ K.

This implies that at absolute zero temperature, all the energy levels below E_F are 100% occupied which is true from the definition of Fermi energy.

Case (ii) :- $f(E)$ **for** $E > E_F$ **at** $T = 0$ **K;**

When $E > E_F$ & $T = 0$ K, then $f(E)$ becomes

$$f(E) = \frac{1}{e^{\infty} + 1} = \frac{1}{\infty + 1} = \frac{1}{\infty} = 0$$

i.e., $f(E) = 0$ for $E > E_F$ at $T = 0$ K.

This implies that at absolute zero temperature, all the energy levels above E_F are unoccupied (completely empty) which is true from the definition of Fermi energy.

Case (iii) :- $f(E)$ **for** $E = E_F$ **at** $T = 0$ **K;**

When $E = E_F$ & $T = 0$ K, then $f(E)$ becomes

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

$$f(E) = \frac{1}{e^{0/0} + 1} = \text{Indeterminate}$$

i.e., $f(E) = \infty$ for $E = E_F$ at $T = 0$ K.

Hence, the occupation of Fermi level at $T = 0$ K has an undetermined value ranging between zero and unity (0 & 1). The Fermi-Dirac distribution function is discontinuous at $E = E_F$ for $T = 0$ K.

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<u>**Case (iv)**</u> **:- $f(E)$ for $E = E_F$ at $T > 0$ K;**

When $E = E_F$ & $T > 0$ K, then $f(E)$ becomes

$$f(E) = \frac{1}{e^0 + 1} = \frac{1}{1+1} = \frac{1}{2}$$

i.e., $f(E) = ½$ for $E = E_F$ at $T > 0$ K.
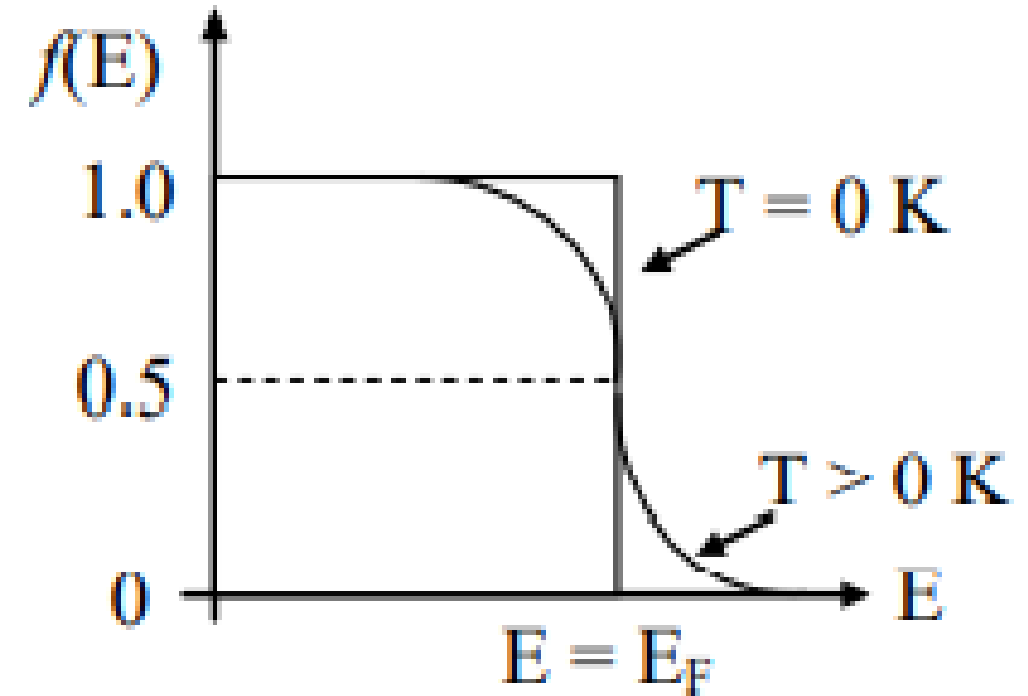
Variation of $f(E)$ with E

If $E \ll E_F$, the probability starts decreasing from 1 and reaches 0.5 (½) at $E = E_F$ and for $E > E_F$, it further falls off as shown in figure. In conclusion, the Fermi energy is the most probable or average energy of the electrons in a solid.

Importance of Fermi Energy

➢ Fermi energy level is used to separate the vacant and filled states at 0 K.

➢ It is used to know the status of the electrons.

➢ Electrons are completely filled below the Fermi energy level and completely empty above the Fermi level at 0 K.

➢ Above 0 K some electrons absorb thermal energy and they jumps to the higher energy levels.
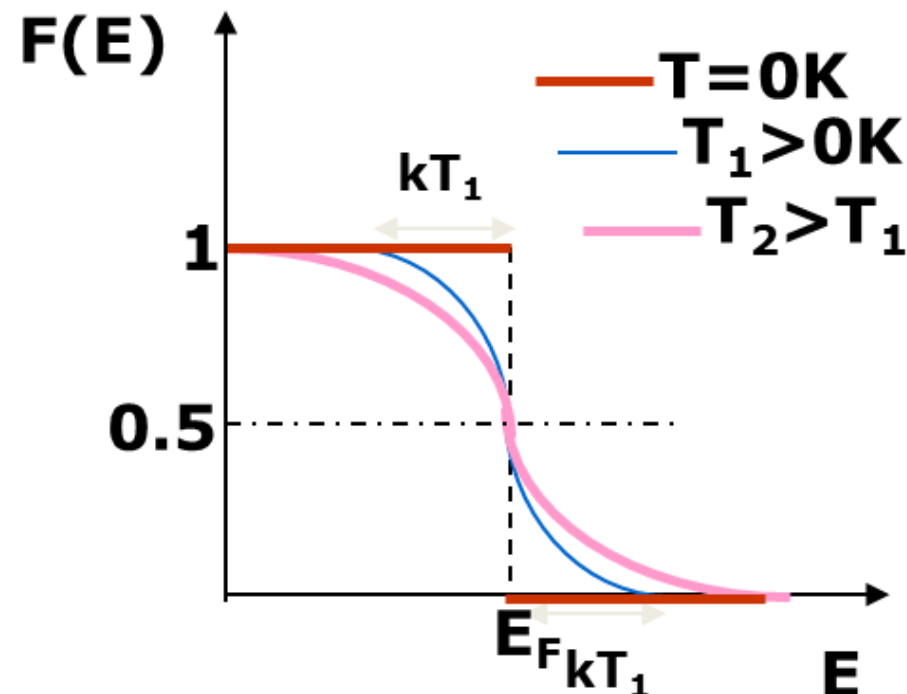
The Fermi-Dirac Distribution Function (1926)

▸ Applicable to fermions, i.e identical particles that obey Pauli's exclusion principle

▸ Represents probability that a particular quantum state of energy E is occupied by an electron and has been derived by Fermi and Dirac to be

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

Where E_F is a constant reference energy level called the Fermi level

What is E_F?

Let us take the case of $E > E_F$ and T=0K, then

$$F(E) = \frac{1}{1 + e^{(E-E_F/0)}} = \frac{1}{1 + e^{\infty}} = 0$$

i.e for all $E > E_F$ at T=0K, F(E)=0 or probability of occupation by an electron for all energy levels higher that Fermi level is zero.

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Fermi Dirac Distribution contd,,,,

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$$F(E) = \frac{1}{1+ e^{(E-E_F/0)}} = \frac{1}{1+ e^{-\infty}} = 1$$

i.e for all $E<E_F$ at T=0K, F(E)=1 or probability of occupation by an electron for all energy levels lower that Fermi level is one.
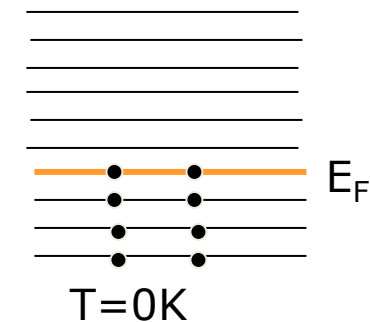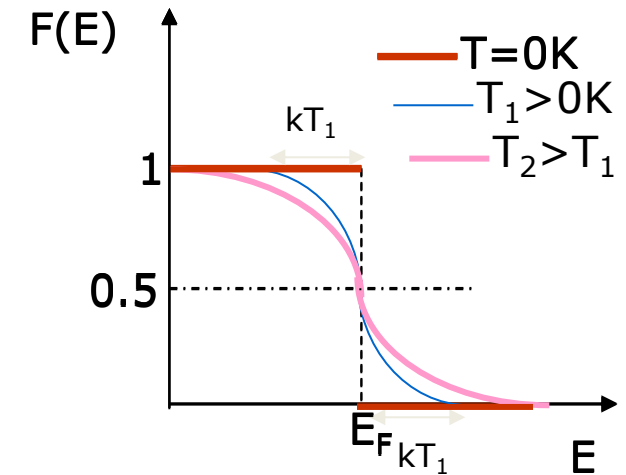
But , if $E=E_F$ at T=0, F(E) is indeterminate

When T>0K, and $E=E_F$,

$$F(E) = \frac{1}{1+ e^{(0/kT)}} = \frac{1}{1+ 1} = 1/2$$

i.e for all T>0K, Fermi level represents the energy level at which the probability of occupation by an electron is 0.5 or 50%.

i.e for all T>0K, electrons from levels kT below the Fermi level can acquire energy kT and move to higher levels thereby giving non-zero probability of occupation above E_F upto E_F+kT and lowers the probability of occupation of levels upto E_F-kT

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Sample problems on Fermi Distribution

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                    4
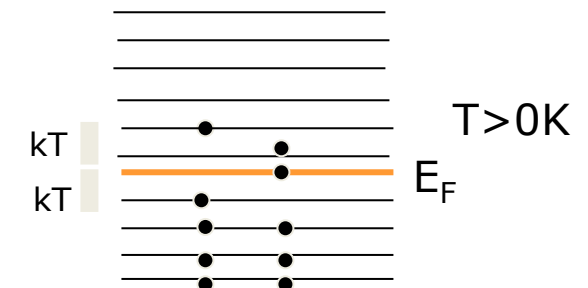
1. Use the Fermi function to obtain the value of F(E) for $(E-E_F)$ =0.01eV at 200K.

Ans:0.36

Given

$(E-E_F)$ =0.01eV= $0.01 \times 1.6 \times 10^{-19}$ J = 0.016×10^{-19} J ,   T=200K,   k=1.38×10^{-23} J/K

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

$$F(E) = \frac{1}{1+ e^{\left(\frac{0.016 \, x \, 10^{-19}}{1.38 \, x \, 10^{-23} \, x \, 200}\right)}} = \frac{1}{1+ e^{0.579}} = \frac{1}{2.785} = 0.36$$

E

T=200K

E_F
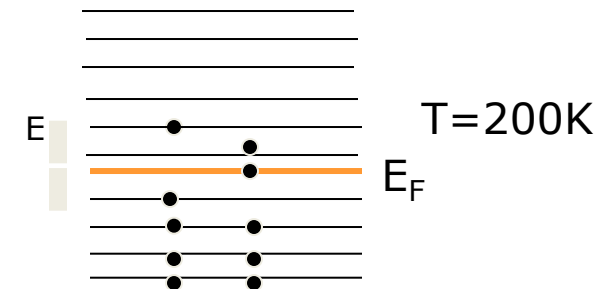
2. Using the Fermi function, evaluate the temperature at which there is 1% probability that an electron in a solid will have an energy 0.5eV above E_F of 5eV. **Ans: 1262K**

Given

$(E-E_F)$ =0.5eV=0.5x1.6x10^{-19}=0.8x10^{-19}, F(E)=.01 k=1.38x10^{-23} J/K, T=?

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

ΔE = 0.5eV

E ——— 5.5 eV

E_F ——— 5 eV

$$0.01 = \frac{1}{1 + e^{((E-E_F)/kT)}}$$

$0.01 (1+ e^{((E-E_F)/kT)}) = 1$

$0.01 \, e^{((E-E_F)/kT)}) = (1- 0.01)= 0.99$

$e^{((E-E_F)/kT)}) = 99$

$(E - E_F)/kT$ = ln (99)=4.595

$T= \dfrac{E-E_F}{k ln(99)} = \dfrac{0.8 \, x \, 10^{-19}}{1.38 \, x \, 10^{-23} \, x \, 4.595} = 1261.57 \text{ K} \approx 1262 \text{ K}$

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Quantum "free" electron theory

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17
6

Postulates of "Quantum free electron theory"

Quantum free electron theory – Wave nature of electrons and quantization of energy levels were taken into consideration

(i) Energy levels are discrete and not continuous

ii. The electrons obey Pauli's exclusion principle

iii. They obey Fermi-Dirac statistics- Only 2 electrons that can occupy one energy level (each of opposite spin)

   Therefore all the electrons in a metal do not take part in the conduction process, only a subset of them, close to the highest filled band at 0K take part in conduction

(iv) The free electrons move in a uniform potential
(v) **"free" and independent electron approximations.** (as was the case in classical Drude model)

Could not still explain superconductivity, bands in solids and hence classification into metals, semiconductors and insulators

Ordinary thermal and electrical energies are only a fraction of E_F
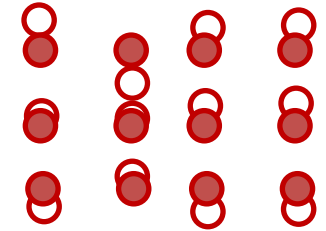
E_F

T=0K
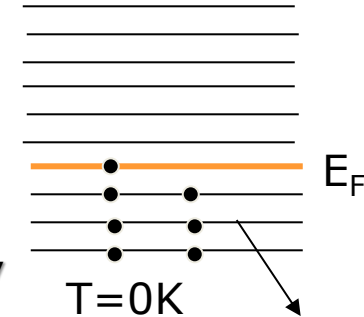
Electrons in lower level can interact with anything only if it can be raised to Fermi level. As there are no empty levels with kT energy gap

(i) Energy levels are discrete and not continuous

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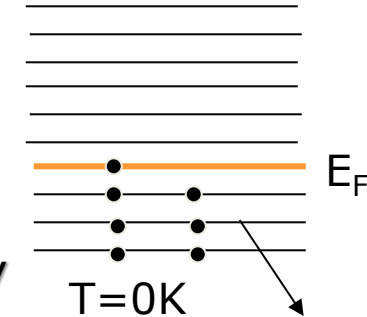
(iv) Electrons move in a periodic potential

(v) In the full fledged quantum theory scattering of electrons are attributed to electron-phonon scattering (lattice deformations due to impurity /dislocation of lattice vibrations-could explain resistivity vs temperature curve. The mass of the electron is replaced by effective mass which depicts the effect of acceleration or deceleration the electron may experience.

(vi) Electron-electron interactions exists (eg: Superconductivity –dominant electron-electron interaction at lower temperatures leading to Bose-Einstein condensation ()-electron distribution changes from Fermi-Dirac to Bose-Einstein statistics

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Quantum "free" electron theory

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178

Postulates of "Quantum free electron theory"

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Therefore all the electrons in a metal do not take part in the conduction process, only a subset of them, close to the highest filled band at 0K take part in conduction

(iv) The free electrons move in a uniform potential
(v) **"free" and independent electron approximations.** (as was the case in classical Drude model)
(vi) n replaced by n_{eff},

Could not still explain superconductivity, bands in solids and hence classification into metals, semiconductors and insulators

Ordinary thermal and electrical energies are only a fraction of E_F

E_F

T=0K

Electrons in lower level can interact with anything only if it can be raised to Fermi level. As there are no empty levels with kT energy gap

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Fermi Levels & Carrier density

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179

Therefore a Fermi level can be defined as

The highest energy level occupied by an electron in a solid at 0K and it also represents , for all temperatures above 0K, the energy level at which the probability of occupation by an electron is 0.5

Number density of electrons in a solid in an interval of energy dE about E is therefore
   = density of allowed states with energy in the interval dE about E x probability that it is occupied by an electron

= g(E) F(E) dE

General expression for number density of electrons in a solid in an interval of energy E_1 to E_2 is density of allowed states with energy in the interval dE about E [g(E)] x probability that it is occupied by an electron [F(E)]

$$= \int_{E_1}^{E_2} g(E)F(E)dE$$

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Quantum theory- distribution of electrons

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✓ **Concentration of electron in any metal, say for example Cu is 10^{28}/ m³, i.e., 10^{22}/cm³**

✓ **Now at thermal equilibrium we have to distribute all these electrons as Pauli's exclusion principle**

✓ **We have to take care of Fermi energy concept**

✓ **Now when we give heat energy only those electrons near to Fermi levels will take energy first and go to high energy, thereby participating in conduction process**

✓ **For the distribution of electrons, Sommerfeld first assume metal as form of 3D box.**
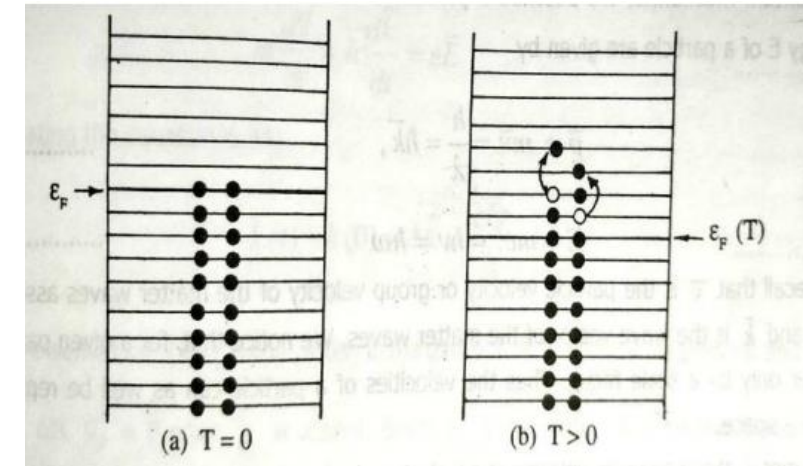
Particle in a 3D box
- We will skip 2D boxes for now
  - Not much different than 3D and we use 3D as a model more often
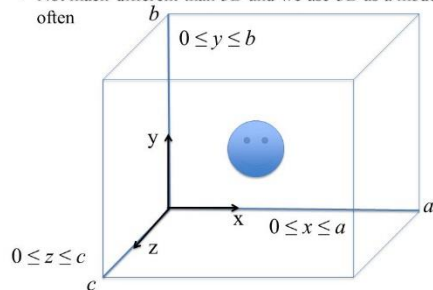
✓ **Remember, particle in 3D box concept**

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1

Particle in a box concept and distribution of electrons

Metal piece

1 cm^3
$10^{22}/ \text{ cm}^3$

✓ **We can calculate the ground state= E_{111}~ 10^{-14} eV**

✓ **Spacing between consequent energy levels= ΔE~ 10^{-14} eV**

✓ **The energy levels are discrete, but the difference is too small**

✓ **Almost continuous----- quasi continuous**

✓ **We are now trying to distribute these 10^{22} electrons in these quasi continuous levels**

✓ **Then we will find how many electrons actually takes $k_B T$ (thermal energy) and participate in conduction process**

✓ **As all these energy levels are closely spaced, it is very difficult to find out in each energy level how many electrons are occupied**

✓ **Whether it is occupied or not**

✓ **In this situation we need to introduce another concept---**

Density of state

At the end of this session, you should be able to

▸ Derive expression for density of states

▸ Average energy of electron at 0K (application).

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Density of states

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18
3

The energy levels of electrons in case of single atom are sharp as we know in case of hydrogen atom. In case of solids, the energy levels of electrons will spread out over a range called energy band due to the presence of large number of atoms. Each energy band consists of a number of states at each energy level that are available to be occupied by the electrons; the concept of density states of a system is introduced. The density of states g(E) is defined as the number of energy states available per unit volume per unit energy centered at E.

The number of states per unit volume between the energy levels E and E+dE is denoted by g(E)dE.

$$\therefore \ g(E)dE = \frac{No. \ of \ energy \ states \ available \ between \ E \ and \ E+dE \ in \ a \ metal}{Volume \ of \ that \ metal}$$

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Let's count apples

We can count easily like

1   2   3   4

Instead of lines of apples, let's take volume of apples

a

L

a
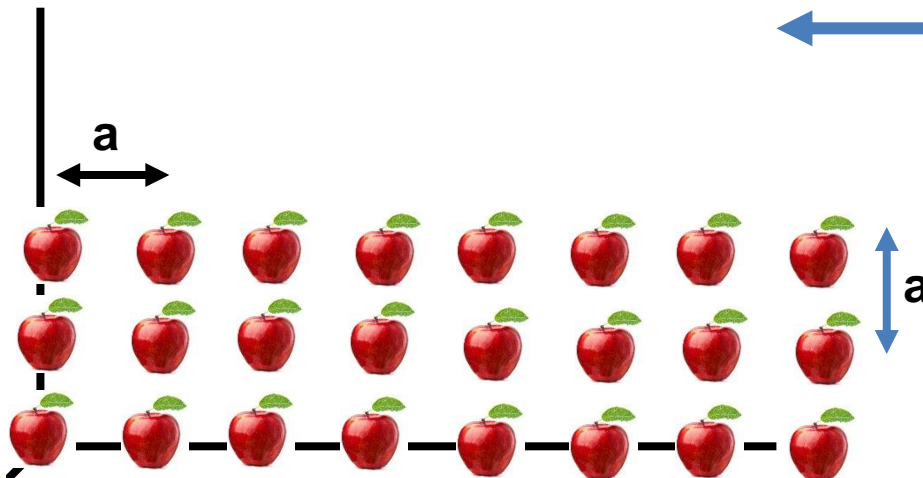
**Now if we count the total number of apples in certain volume--**

What is much more convenient to do this is

Take the total volume V and divide it by the volume density of apples, i.e.

V/ in unit volume the number of apples

We can count the number of apples per unit volume

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18
5

Since, each apple is separated by a distance a, we can draw a cube around one of these apples of side length a and can find the volume density of a single apple is 1 apple per a^3 volume

a

a
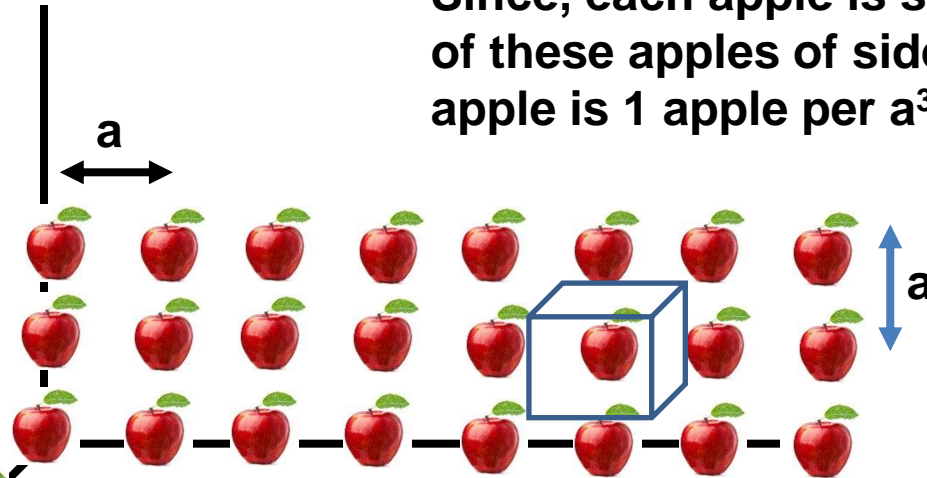
Then we can get,

a^3 volume contains 1 apple

V volume contains V/a^3 apples

Now let's consider a specimen of metal

For simplicity, we consider it to have the shape of a cube with side L

Assume that the free electrons travel absolutely freely within the volume of specimen

Similar like electron in 3D box potential

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6

✓ **It is easy to see that all points on the surface of a sphere of radius n will correspond to same energy**

✓ **All points within the sphere represent quantum states with energies smaller than E**

✓ **Number of energy states within the sphere of radius n= volume of the sphere/ volume density**

✓ **Number of energy states within the sphere of radius n= $\frac{4}{3}\pi n^3 / 1$**

✓ **In the quantum number space, in unit volume there is only one electron**
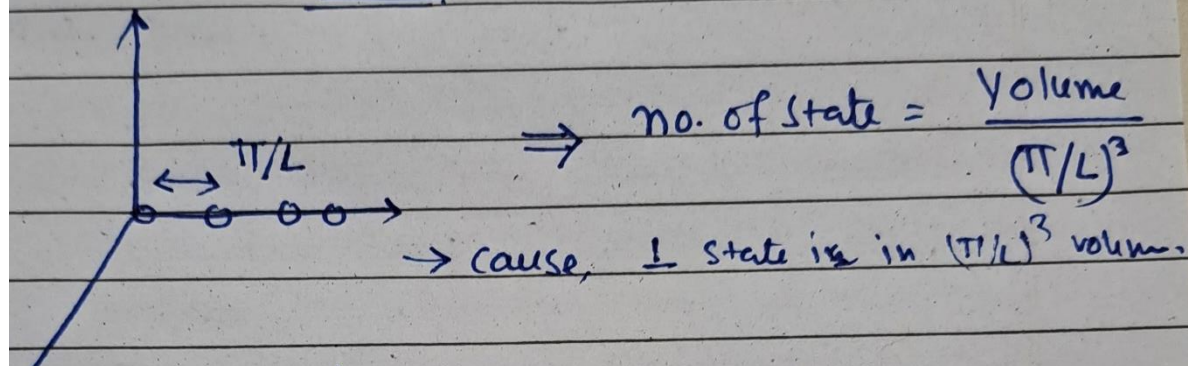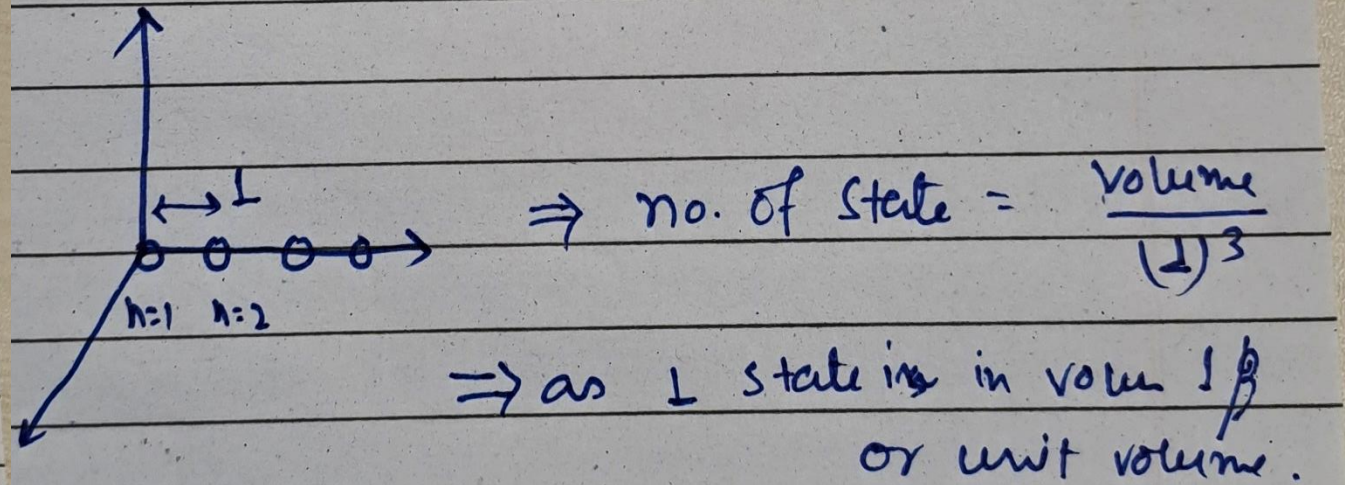
V volume contains V/a³ apples

$$n^2 = n_x{}^2 + n_y{}^2 + n_z{}^2 = \frac{E_n 8mL^2}{h^2}$$

This equation tells us that the energy of an electron can be determined by the sum of the squares of the quantum numbers n_x, n_y, and n_z.

Earlier we have seen that we can get same value of energy for different combinations of these three quantum numbers.

Corresponding to each set we can find a specific energy state E.

We can therefore represent a quantum state by a point in its quantum number space.

▶ **Let us represent each *n* value in a 3D space whose axes are defined by n_x, n_y and n_z . (Remember multiplying n by a constant π/L gives k and this space is therefore called the momentum space.) In this space, all the points that have the same n value, will lie on the surface of a spherical shell.**

$$\boxed{E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2 h^2}{8mL^2} \quad as \quad k = \frac{n\pi}{L}}$$

▶ **But same *n* value indicates same energy E. Thus, a spherical shell of radius *n* in momentum space represents an equipotential surface of energy E.**

✓ **So, the number of energy states within the sphere of radius n= volume of the sphere=$\frac{4}{3}\pi n^3$**

✓ **Since the quantum numbers can have only positive integer values, the n values can only be defined in the positive octant of the sphere**

n_x, n_y & n_z as the three mutually perpendicular axes. Since n_x, n_y & n_z can take only positive integers, the above equation represents $\frac{1}{8}^{th}$ of the sphere called Octant as shown in figures.
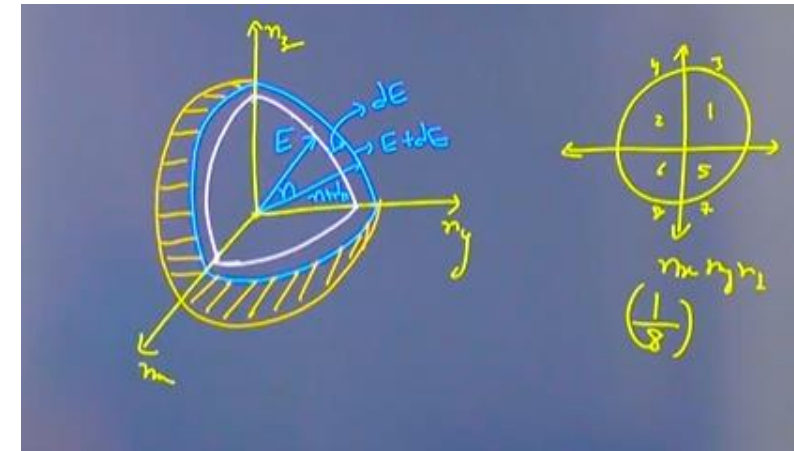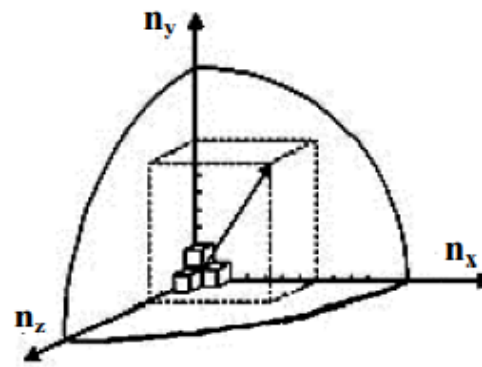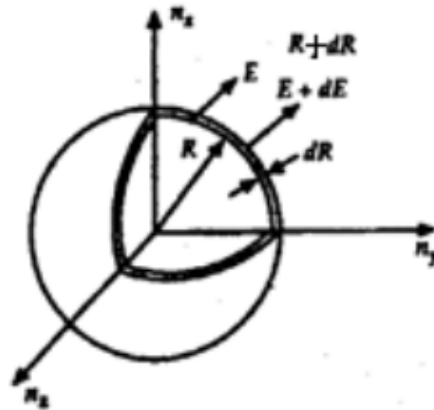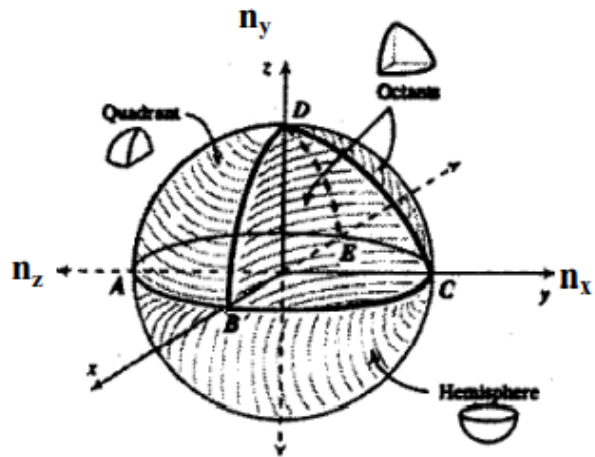

✓ **Therefore, the number of quantum states with energy equal to or smaller than E is proportional to the first octant of the sphere.**

✓ **Number of energy states within one octant of the sphere of radius n= volume of the sphere= $\frac{1}{8}\times\frac{4}{3}\pi n^3$**

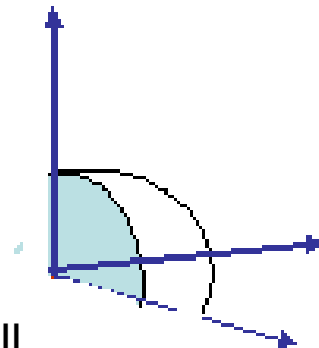**THIS SLIDE IS FOR YOUR UNDERSTANDING ONLY NOT TO BE WRITTEN FOR EXAMS!**
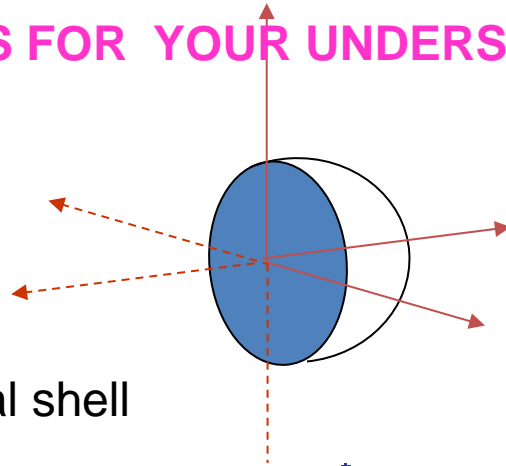
Blue/Red continuous arrows indicate +ve axes of sphere
Red dotted lines indicate –ve axes
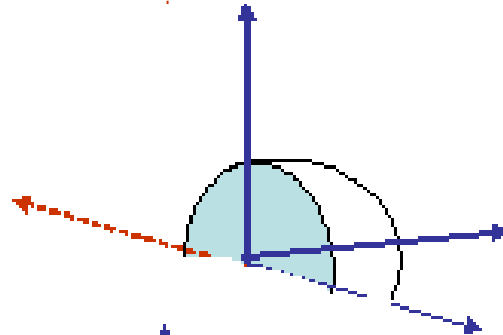
½ a spherical shell

Therefore no. density of allowed states in the interval n & n+dn = Vol of shell in the +ve quadrant
=1/8th the volume of the spherical shell.

$$\frac{1}{2} \cdot \frac{1}{4} = \frac{1}{8}$$

of the spherical shell
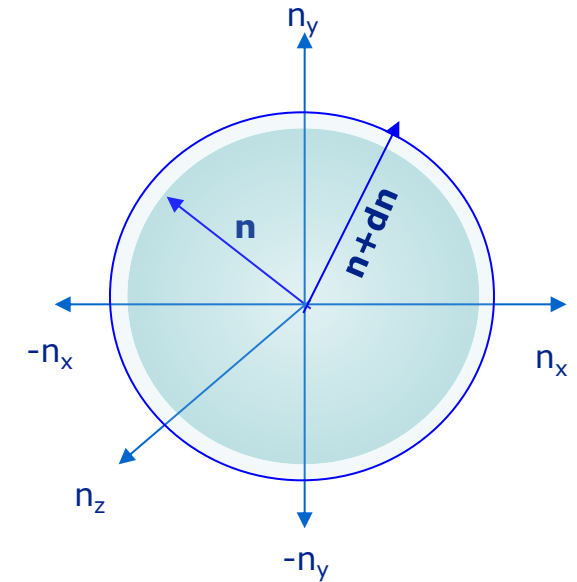
▸ No. of levels between E & E+dE = $4\pi n^2 dn/8 = \pi n^2 dn/2$

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190

✓ **Similarly, the number of energy states within one octant of the sphere of radius (n+dn) corresponding to the energy (E+dE) = volume of the sphere with radius (n+dn)= $\frac{1}{8} \times \frac{4}{3}\pi(n+dn)^3$**

✓ **The number of energy states having energy values between E and (E+dE) =N(E)dE= $[\{\frac{1}{8} \times \frac{4}{3}\pi(n+dn)^3\}-\{\frac{1}{8} \times \frac{4}{3}\pi n^3\}] \sim \frac{\pi}{6}3n^2 dn = \frac{\pi}{2}n^2 dn$**

✓ **Now we know that**

$$E = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{n^2 h^2}{8mL^2}$$

$$\therefore \quad n^2 = \frac{8mL^2}{h^2}E \qquad (28.46)$$

$$n = \left[\frac{8mL^2}{h^2}\right]^{1/2} E^{1/2}$$

or

Differentiating the equation (28.46), we get

$$n\,dn = \frac{4mL^2}{h^2}dE$$

$$\therefore \quad N(E)dE = \frac{\pi}{2}n^2\,dn = \frac{\pi}{2}n(n\,dn)$$

$$= \frac{\pi}{2}\left[\frac{8mL^2}{h^2}\right]^{1/2}E^{1/2} \times \frac{4mL^2}{h^2}dE$$

$$= \frac{\pi}{4}\left[\frac{8mL^2}{h^2}\right]^{3/2}E^{1/2}dE \qquad (28.47)$$

There are two spin states $m_s = \pm\frac{1}{2}$ for an electron. According to Pauli Exclusion Principle, two electrons of opposite spin can occupy each state. Hence, the number of energy states available for electron occupancy is double the above value (28.47) and equals to

$$N(E)dE = \frac{\pi}{2}\left[\frac{8mL^2}{h^2}\right]^{3/2}E^{1/2}dE$$

or

$$N(E)dE = \frac{4\pi}{h^3}(2m)^{3/2}L^3 E^{1/2}dE \qquad (28.48)$$

Density of Energy States
The *density of states* is given by the number of available electron states per unit volume per unit energy range at a certain energy level, E.

$$\therefore \quad Z(E)dE = \frac{N(E)dE}{L^3} = \frac{4\pi}{h^3}(2m)^{3/2}E^{1/2}dE \qquad (28.49)$$

$Z(E)$ is called the **density of states function**. It may noted that $Z(E)$ is independent of the dimensions (L) of the potential box and hence is applicable for any case. We define $Z(E)$ as the number of available states per unit energy interval centered around E.

28.16.1 Energy Distribution of El...
Density of...

▸ No. of levels between E & E+dE in unit volume of material

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

▸ No. density of states between E & E+dE taking into account 2 possible spin states

$$= 2.\left(\frac{2\pi}{h^3} (2m)^{3/2} \sqrt{E} \, dE \right) = \frac{4\pi}{h^3} (2m)^{3/2} \sqrt{E} \, dE$$

▸ Density of states represents all the states per unit volume of material that can be occupied by charge carriers and is given by

$$Z(E) \, dE = \frac{4\pi}{h^3} (2m^*)^{3/2} \sqrt{E} \, dE$$

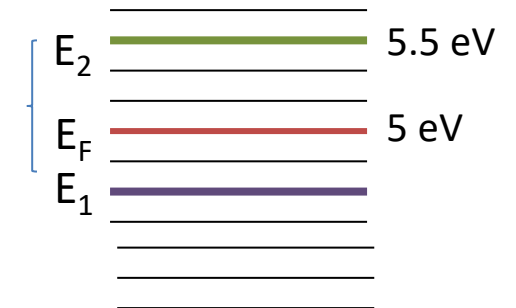m* represents effective mass of electron. It captures the change in velocity of e- in the vicinity of the ion cores

▸ However no. of charge carriers per unit volume will depend on the probability that the charge acquires sufficient energy to occupy these states and is given by Fermi Dirac distribution function F(E).

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Fermi Levels & Carrier density

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19
3

Number density of electrons in a solid in an interval of energy dE about E is therefore
= density of allowed states with energy in the interval dE about E x probability that it is occupied by an electron

$$= Z(E) \, F(E) \, dE$$

General expression for number density of electrons in a solid in an interval of energy E_1 to E_2 is density of allowed states with energy in the interval dE about E [g(E)] x probability that it is occupied by an electron [F(E)]

$$= \int_{E_1}^{E_2} Z(E)F(E)dE$$

E_2 ————— 5.5 eV

E_F ————— 5 eV

E_1 —————

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194

Number density of electrons in a solid in an interval of energy dE about E is therefore
= (density of allowed states with energy in the interval dE about E) x

(probability that it is occupied by an electron)

= g(E) F(E) dE   where

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

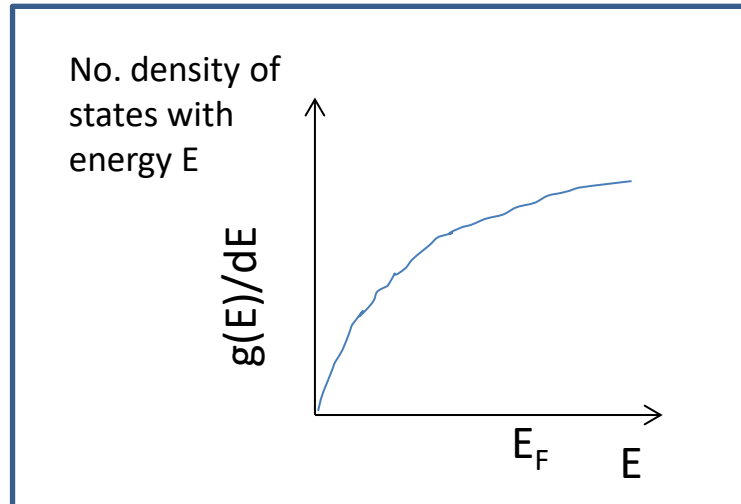$$Z(E)\, dE = \frac{4\pi}{h^3}\, (2m^*)^{3/2}\, \sqrt{E}\, dE$$

General expression for number density of electrons in a solid in an interval of energy E_1 to E_2 is therefore

$$= \int_{E_1}^{E_2} Z(E)F(E)dE$$
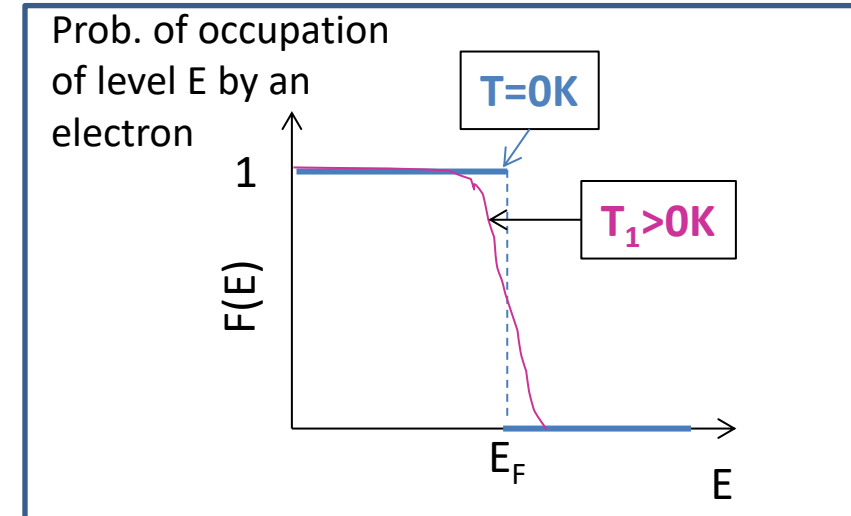
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No. density of states with energy $E = g(E)dE$ is $\propto E^{1/2}$

Graphical representation
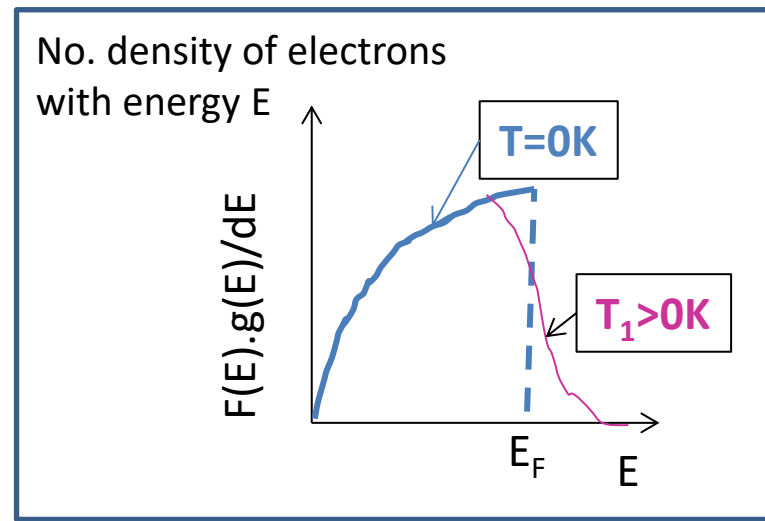
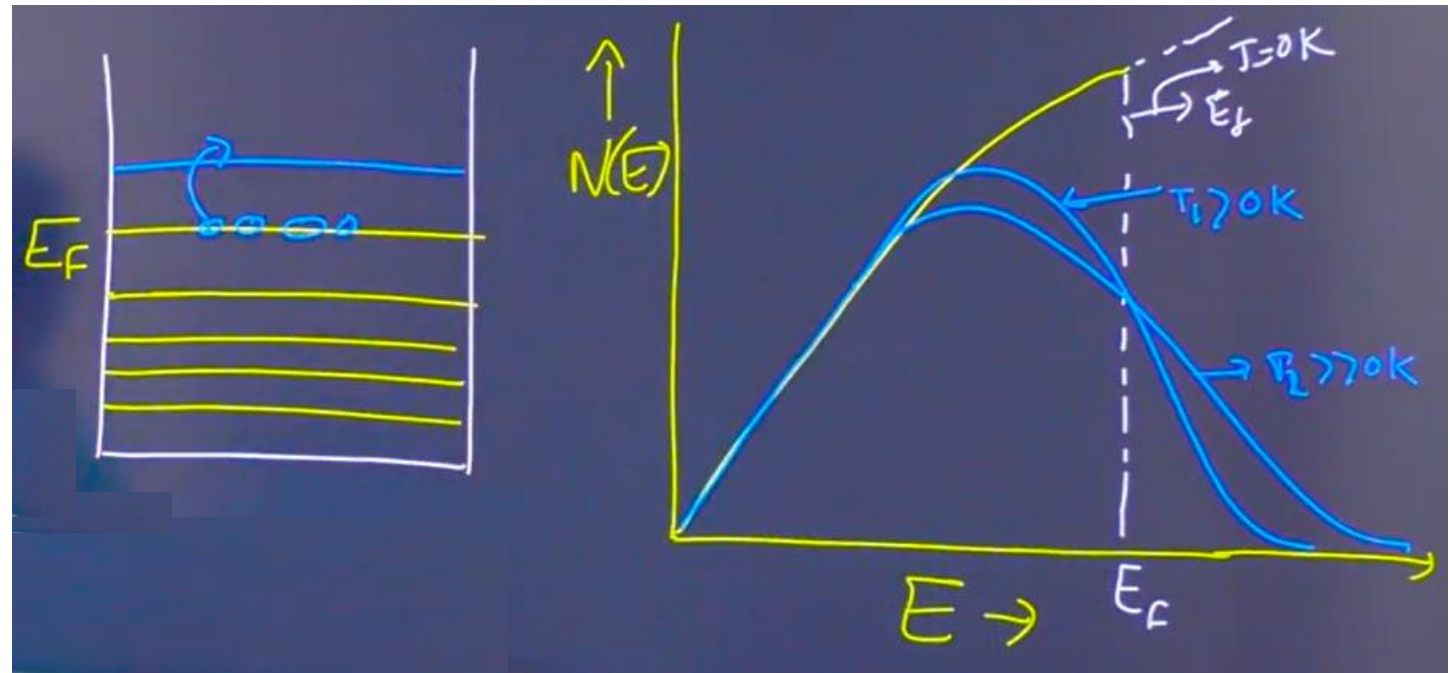No. density of electrons with energy $E = g(E)dE \times F(E)$

$$\boxed{Z'(E)\,dE = \frac{\pi}{2}\left(\frac{8m}{h^2}\right)^{3/2} E^{1/2}\,dE}$$

Density of energy states which are lying b/w E & $E + dE$

$Z(E)$

dE

E

E_F

$N(E)$

$E \rightarrow$

E_F

$T = 0K$

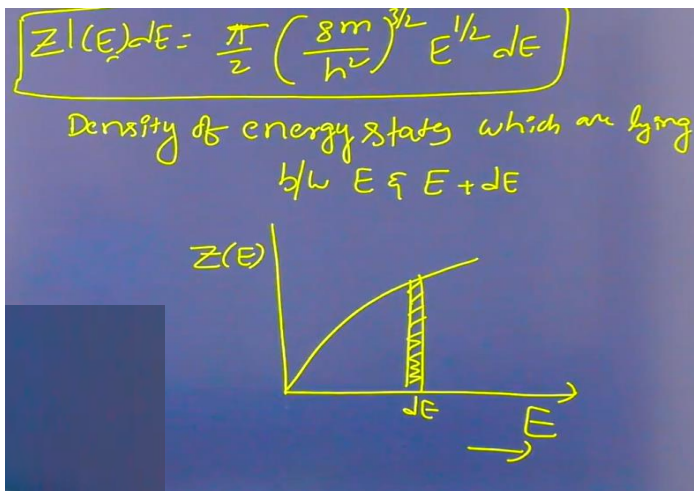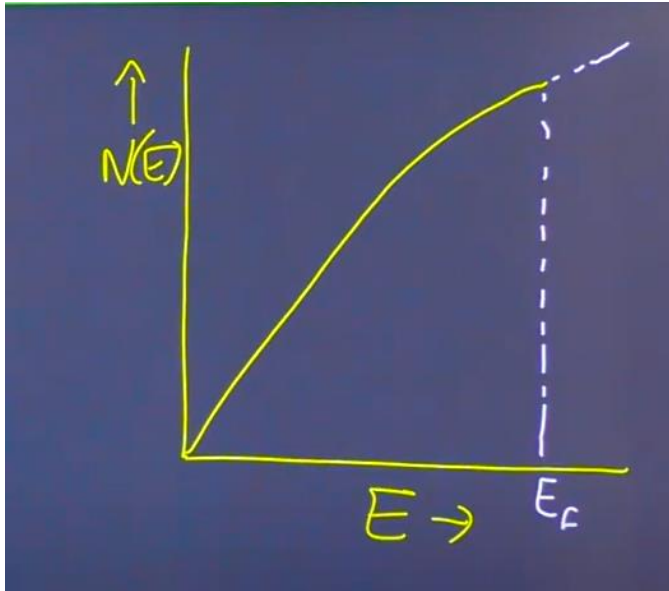E_f

$T_1 > 0K$

$T_2 >> 0K$

$N(E)$

$E \rightarrow$

E_F

Find electron density for metals at 0K.

For metals at 0K , all the levels up to energy level E_F is occupied .
Therefore the number density of electrons available at 0K are those present in energy levels ranging from 0 to E_F.

Hence expression for number density of electrons in a metal at 0K, n_c is

$$n_c = \int_0^{E_F} Z(E)\, F(E)\, dE = (4\pi/h^3)(2m^*_e)^{3/2} \int_0^{E_F} E^{1/2} \cdot 1 \, dE \quad \text{since } F(E) = 1 \text{ upto } E_F$$

$$= (4\pi/h^3)(2m^*_e)^{3/2} \left[E^{3/2} / (3/2) \right] \quad = \gamma \left(\frac{2}{3} E_{F0K}^{3/2} \right) \quad \text{where } \gamma = (4\pi/h^3)(2m_e)^{3/2}$$

$$= (8\pi/3)(2m^*_e/h^2)^{3/2} \; E_F^{3/2}$$

OR Expression for Fermi Energy at 0K for metal is $\quad E_{F(0K)} = (h^2/2m^*_e)(3n_c/8\pi)^{2/3}$

For temperatures above 0K the full expression for F(E) has to be put in during integration . $E_F(T)$ that will be obtained in such as case is given in summary for completion sake. As $k_B T$ is $<< E_{FOK}$, $E_F(T) \approx E_{FO}$ at low temperatures

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Problem

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19
8

Find average energy of electrons in metals at 0K.

Energy of electrons/vol in a material in any level E
= no. of electrons/vol in the energy state E multiplied by the energy of the state
= [g(E). F(E)] E

$$\int_{0}^{E_F} g(E)E\ F(E)\ dE \quad = \quad (4\pi/h^3)(2m_e)^{3/2}\int_{0}^{E_F} E^{1/2}\ .E.1\ dE \quad \text{since F(E) =1 upto } E_F$$

$$= \gamma \left(\frac{2}{5} E_{F0K}^{5/2} \right) \qquad \text{Where } \gamma = \ (4\pi/h^3)(2m_e)^{3/2}$$

Average Energy of electrons/vol in a metal at OK =   (total energy of all electrons/vol in states upto E_F)
(total no of electrons per unit vol)

$$= \frac{\gamma\left(\dfrac{2}{5} E_{F0K}^{5/2} \right)}{\gamma\left(\dfrac{2}{3} E_{F0K}^{3/2} \right)} = \left(\frac{3}{5} E_{F0K} \right)$$

▸ The number density of electrons available for conduction and its variation with temperature is the product of the total no. density of allowed states in the conduction band and the probability that it is occupied.

▸ Density of states in the energy interval dE about E, represents all the states per unit volume of material having energy within dE around E that can be occupied by electrons and is given by

$$g(E)\,dE = \frac{4\pi}{h^3}\left(2m^*\right)^{3/2}\sqrt{E}\,dE$$

$$\left(\frac{4\pi}{h^3}\right)(2m_e)^{3/2} = 1.0619 \times 10^{56}$$

▸ General expression for number density of electrons in a solid in an interval of   energy E_1 to E_2 is therefore

$$= \int_{E_1}^{E_2} g(E)F(E)dE$$

Electron density for metals at 0K., n_c = $(8\pi/3)(2m_e/h^2)^{3/2}$ $E_F^{3/2}$

Fermi energy at 0K, $E_{F(0K)}$ = $(h^2/2m_e)(3n_c/8\pi)^{2/3}$

Fermi energy at any temperature T above 0K,

$$E_F(T) = E_{FO}\left[1 - \frac{\pi^2}{12}\left(\frac{k_BT}{E_{FO}}\right)^2\right]$$

k_BT is $<<$ E_{FOK} so $E_F(T) \approx E_{FO}$

Average energy of electrons in metals at 0K. $= \frac{3}{5}E_{F(0K)}$