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LECTURE NOTES

Classical free electron theory - Expression for electrical conductivity - Thermal conductivity, expression - Wiedemann-Franz law - Success and failures - electrons in metals - Particle in a three dimensional box - degenerate states - Fermi- Dirac statistics - Density of energy states - Electron in periodic potential: Bloch thorem - metals and insulators - Energy bands in solids- tight binding approximation - Electron effective mass - concept of hole.

INTRODUCTION

- Low resistivity materials, which conduct heat as well as electricity.
- > Electrical conduction is due to free electrons

BASIC TERMINOLOGIES

Conductors

- \triangleright Metals and their alloys exhibit large electrical conductivity in the order of 10 Ω m.
- > Conducting materials are the materials having high electrical and thermal conductivities.

Bound Electrons

All the valence electrons in an isolated atom are bound to their parent nuclei.

Free Electrons

- ➤ Valence electrons find continuity from atom to atom. He can move easily throughout the solid.
- All such valence electrons of its constituent atoms in a solid are called free electrons.

Difference between Ordinary Gas and Free Electron Gas

The molecules of ordinary gas are neutral. But, the free electron gas is charged. The density of molecules is smaller than the density of free electrons.

Electric Field (E)

The electric field (E) of a conductor having uniform cross section is defined as the potential drop (V) per unit length (1).

$$\begin{split} E &= V/1 \\ Unit &= Vm^{-1} \end{split}$$

Current Density (J)

Current per unit area of cross section of an imaginary plane.

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Direction of flow of current in a current carrying conductor.

If 'I' is the current, and 'A' is the area of cross section

$$J = I / A$$
 Unit $-A m^{-2}$

CONDUCTING MATERIALS

There are three major categories based on the conductivity.

- (i) Zero resistive materials
- (ii) Low resistive materials
- (iii) High resistive materials
- (i) Zero resistive materials
- The super conductors like alloys of aluminium, zinc, gallium, niobium, etc.,
- Electricity almost with zero resistance blow transition temperature.
- These materials are used for saving energy in the power systems, super conducting magnets, memory storage elements etc.,
- (ii) Low resistive materials was in Supering the Employee many
- > The metals like silver, aluminium and alloys have high electrical conductivity.
- ➤ They are used as conductors, electrical conduct etc., in electrical devices and electrical power transmission and distribution, winding wires in motors and transformers.
- (iii) High resistive materials
- > The materials like tungsten, platinum, nichrome etc.,
- > Such a metals and alloys are used in the manufacturing of resistors, heating elements, resistance thermometers.
- > The conducting properties of solid do not depend on the total number of the electrons available.
- > Because only the valance electrons of the atoms take part in the conduction.
- ➤ When these valance electrons detached from the orbit they are called free electrons or conduction electrons.
- In a metal, the number of free electrons available is proportional to its electrical conductivity.
- ➤ Hence, electronic structure of a metal determines its electrical conductivity.

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ELECTRON THEORY OF SOLIDS

- > The structure and properties of solids through their electronic structure.
- This theory is applicable to all solids, both metals and nonmetals.
 - (i). The behavior of conductors, semiconductors, and insulators.
 - (ii). The electrical, thermal and magnetic properties of solids.

So far three electron theories have been proposed.

(i) Classical free electron theory

- Macroscopic theory, proposed by Drude and Lorentz in 1900.
- Free electrons are mainly responsible for electrical conduction in metals.
- This theory obeys laws of classical mechanics.

(ii) Quantum free electron theory

- It is a microscopic theory, proposed by sommerfeld in 1928.
- The electrons in a metals move in a constant potential.
- This theory obeys laws of quantum mechanics.

(iii) Zone theory or band theory of solids

- Bloch proposed this theory in the year 1928.
- The free electrons move in a periodic potential.
- This theory explains electrical conductivity based on the energy bands.

CLASSICAL FREE ELECTRON MODEL

- Free electron theory of metals was proposed by P. Drude in the year 1900.
- To explain electrical conduction in metal. This theory was further extended by sha. Lorentz in the year 1909.

DRUDE LORENTZ THEORY

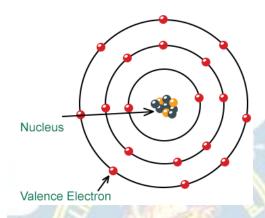
Principle

- A metal consists of a very large number of free electrons.
- These free electrons can move freely throughout the volume of the metal. Responsible for the electrical conduction in the metal.

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Explanation

- Atom consists of a central nucleus with positive charge surrounded by the electrons of negative charge.
- The electros in the inner shells are called core electros.
- And those in the outermost shell are called valence electrons.



POSTULATES OF FREE ELECTRON THEORY

- > Drude assumed that the free electrons in a metal form an electron gas.
- These free electrons move randomly in all possible directions just like the gas molecules in a container.

In the absence of electrical field

- When an electrical field is not applied, the free electrons move everywhere in a random manner.
- ➤ They collide with other free electrons and positive ion core.

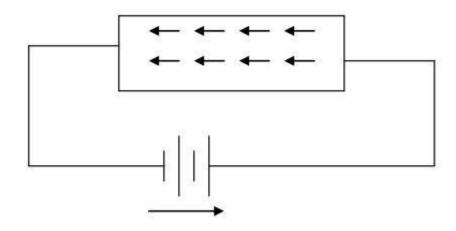


> This collision is known as elastic collision.

In the presence of electric field

- > When the electrical field is applied, the electrons get some amount of energy from the applied electric field.
- ➤ And they begin to move towards the positive potential. (In the opposite direction to the applied electric field).

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Field direction

It's to be a perfect gas, they obey the laws of kinetic theory of gases.

Drift velocity (v_d)

Average velocity acquired by the free electrons in a metal in a particular direction by the application of an electrical field.

Mean free path (λ)

The average distance travelled by a free electron between any two successive collisions an applied electric field.

$$\Lambda = (v_d)_X(\iota_c)$$

> It is the product of drift velocity of free electron and collision time

Collision time

- The average time taken by a free electron between any two successive collisions.
- ➤ It is expressed mathematically as

$$l_{c} = \lambda / v_d$$

Relaxation time

- ➤ The average time taken by a free electron to reach its equilibrium position from its disturbed position due to external electrical field.
- \triangleright It is approximately equal to 10^{-14} second.

DERIVATION OF ELECTRICAL CONDUCTIVITY

Definition

The amount of electrical charge conducted (Q) per unit time across unit area (A) of a solid given by $\sigma = Q/tAE$

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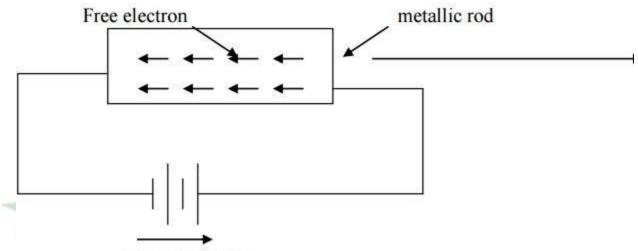
If
$$t = 1$$
 second $E = 1$ volt, $A = 1$ metre $\frac{2}{\sigma}$
 $\sigma = Q$
 $\sigma = Q / tAE = J / E$

Where J is the current density and it is given by Q / tA.

Also $J = \sigma E$ (according to ohm's law)

Expression for electrical conductivity

- Absence of external electric field, the motion of electrons in a metal moves randomly in all directions.
- \triangleright When electric field rod, the electron moves in opposite direction to the applied field with velocity v_d this velocity is known as drift velocity.



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Field direction

Lorentz force acting on the electron F = eE --- (1)

Newton's force second law of

From equations (1) & (2)

$$ma = eE$$
 (or)

$$a = eE / m --(3)$$

The acceleration of electron is given by

Acceleration (a) = Drift velocity (v_d) / Relaxation time (τ)

$$a=v_d\,/\,\tau$$

$$v_d = a \tau$$

Substituting equation (3) in (4)

$$v_d = [e\tau/m] E ---(5)$$

Where ' σ ' is the electrical conductivity of velocity is given as

$$J = ne v_d --(6)$$

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Substituting equation (5) in (7), we have $J = ne [e \tau / m] E$ ---(7)

 $J = [ne^2 \tau / ne. m]$ E, in terms of effective mass m* of an electron,

$$J = [ne^2 \tau / m^*] E$$
 ---(8)

From microscopic form of Ohm's law, the current density 'J' is expressed as,

$$J = \sigma E ---(9)$$

On comparing equations (8) & (9), we have Electrical conductivity

$$\sigma = ne^2 \tau / m^* ---(10)$$

From equation (10), we know that,

- \triangleright With increase of electron concentration 'n' the conductivity ' σ ' increases.
- As m* increases, the motion of electron becomes slow and the electrical conductivity.

THERMAL CONDUCTIVITY

Definition

The amount of heat flowing per unit time through the material having unit area of cross section per unit temperature gradient.

ie).,
$$Q = K dT/dx$$

Thermal conductivity of the material

$$K = Q / dT/dx$$

Q – Amount of heat flowing per unit time through unit cross sectional area

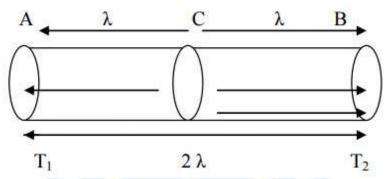
dT/dx -Temperature gradient.

Expression for thermal conductivity

Let us consider a uniform rod AB with temperatures T1 (Hot) at end A and T2 (cold) at end B.

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 \triangleright Heat flows from hot end A to the hold end B. Let us consider cross sectional area C which is at a distance equal to the mean free path (λ) of t in fig.



- The conduction electron per unit value is n and average velocity of these electrons is v.
- During the movement of electrons in the rod, the collision takes place.
- Hence, the electrons near A lose their kinetic energy while electrons near B gain kinetic energy.

At A, average kinetic energy of en electron = 3/2 kT -----(1)

Where k- Boltzmann's constant and T is temperature

At B average kinetic energy of the electron = 3/2 k (T - dT)----(2)

The excess of kinetic energy carried by the electron from A to B

$$= 3/2 kT - 3/2 k (T - dT)$$

$$= 3/2 kT - 3/2 kT + 3/2 k dT ---- (3)$$

Number of electrons crossing per unit area per unit time from A to B

= 1/6 nv.

The excess of energy carried from A to B per unit area in unit time

$$= 1/6 \text{ nv } X 3/2 \text{ kdT}$$

$$= 1/4 \text{ n v k dT}$$
----(4)

Similarly, the deficient of energy carried from B to A per unit area per unit time

$$= -1/4 \text{ n v kdT}$$
----(5)

Hence, the net amount of energy transferred from A to B per unit area per unit time

$$Q = 1/4 \text{ nvkdT} - (-1/4 \text{ nvkdT})$$

$$Q = 1/4 \text{ nvkdT} + 1/4 \text{ nvkdT}$$

$$Q = 1/2 \text{ nvkdT---(6)}$$

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But from the basic definition of thermal conductivity, the amount of heat conducted per unit area per unit time

$$Q=K \quad dT/\lambda$$

$$[Q = KdT/dx ; \quad \lambda=dx]$$
¹/₂ n u k dT = KdT/\lambda
$$K = \frac{1}{2} \text{ nv k } \lambda----(7)$$

We know that for the metals

Relaxation time = collision time
$$\tau = \tau c = \lambda / v$$

$$\tau \, \mathbf{v} = \lambda \qquad ---(8)$$

Substituting equation 8 in the equation 7, we have

$$K = \frac{1}{2} \text{ n v k } \tau \text{ v}$$

 $K = \frac{1}{2} \text{ n v}^2 \text{ k } \tau$ ---(9)

WIDEMANN -FRANZ LAW

Statement

- > The metals, the ratio of thermal conductivity to electrical conductivity is directly proportional to the absolute temperature.
- > This ratio is a constant for all metals at given temperature.

 $K/\sigma \alpha T$ (or) $K/\sigma = LT$

➤ Where L is a proportionality constant. It is known as Lorentz number.

Its value is
$$2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$$

At T = 293 K.

Derivation

Widemann – Frantz law is derived from the expressions of thermal conductivity and electrical conductivity of metal.

We know that.

Electrical conductivity of a metal
$$\sigma = ne^2\tau/m$$
 ------(1)

Thermal conductivity of a metal
$$K = \frac{1}{2} \text{ n } v^2 k \tau$$
-----(2)

Thermal conductivity =
$$\frac{1}{2}$$
 n v² k τ

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Electrical conductivity
$$= ne^2 \tau / m \, K / \sigma$$

$$= \frac{1}{2} \text{ mv}^2 \text{ k} / \text{e}^2$$
 (3)

We know that the kinetic energy of an electron or

$$= \frac{1}{2} \text{ mv}^2 = \frac{3}{2} \text{ kT}$$
 -----(4)

Substituting equation (4) in equation (3),

We have
$$K / \sigma = 3/2 kT X k / e^2$$

$$= 3/2 [k/e]^2 T$$

$$K / \sigma = LT ----(5)$$

where L = 3/2 [k/e] ² is a constant and it is known as Lorentz number

$$K / \sigma = \alpha T - - - (6)$$

Thus it is proved that, the ratio of thermal conductivity to electrical conductivity of a metal is directly proportional to the absolute temperature of the metal.

Conclusion

Wiedamann – Franz law clearly shows that if a metal has high thermal conductivity, it will also have high electrical conductivity.

LORENTZ NUMBER

The ratio of thermal conductivity (K) of of the metal and absolute temperature (T) of the metal is a constant. It is known as Lorentz number and it is given by

$$L = K / \sigma$$

L = K / σ MERITS OF CLASSICAL FREE ELECTRTON THEORY

- 1. It is used to verify Ohm's Law.
- 2. The electrical and Thermal conductivities of metals can be explained by this theory.
- 3. It is used to derive Wiedemann- Franz law.
- 4. It is used to explain the optical properties of metals.

DRAWBACKS OF CLASSICAL FREE ELECTRON THEORY

It is a macroscopic theory

- Classical theory states that all free electrons will absorb energy, but quantum theory states that only few electrons will absorb energy.
- This theory cannot explain the Compton effect, photoelectric effect, paramagnetism, ferromagnetism etc.,

The theoretical and experimental values of specific heat and electronic specific heat are not matched.

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- The Lorentz number by classical theory does not have good agreement
- > with experimental value and it is rectified by quantum theory

QUANTUM THEORY

- The drawbacks of classical theory can be rectified using quantum theory.
- In classical theory the properties of metals such as electrical and thermal conductivities.
- According to classical theory, the particles of gas (electrons) at zero Kelvin will have zero kinetic energy, and hence all the particles are at rest.
- ➤ But according to quantum theory when all particles at rest, all of them should be filled only in the ground state energy level, which is impossible and is controversial to the pauli's exclusion principle.

Thus in order to fill the electrons in a given energy level, we should know the following.

- Energy distribution of electrons
- Number of available energy states
- Number of filled energy states Probability of filling an electron in a given energy state, etc.,

FERMI DIRAC DISTRIBUTION FUNCTION

- ➤ The classical and quantum free electron theories failed to explain many electrical and thermal properties of solids.
- Using Fermi –Dirac statistics.
- Fermi –Dirac statistics deals with the particles having half integral spin.
- The particles like electrons are the examples of half integral spin and hence they are known as Fermi particles or Fermions.

Definition

- ➤ Distributions of electrons among the various energy levels as a function of temperature is known as Fermi distribution function.
- ➤ It is the probability function F(E) of an electron occupying given energy level at absolute temperature. It is given by

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

Where

E – Energy of the level whose occupancy is being considered

EF – Energy of the Fermi level

K –Boltzmann's constant,

T – Absolute temperature

- The probability value of F(E) lies between 0 and 1.
- \triangleright If F(E) = 1, the energy level is occupied by an electron.
- \triangleright If F(E) = 0, the energy level is vacant.
- If $F(E) = \frac{1}{2}$ or 0.5 then there is a 50% chance for the electron occupying in that energy level.

Effect of temperature on Fermi function

The effect of temperature on Fermi function F(E) can be discussed with respect to equation 1.

1. At 0 kelvin

- At 0 kelvin, the electron can be filled only upto a maximum energy level called Fermi energy level (EF0), above EF0 all the energy levels will be empty.
- It can be proved from the following conditions.

(i.e. 100% chance for the electron to be filled within the Fermi energy level)

When E>EF, equation 1 becomes

(i.e. zero% chance for the electron not to be filled within the Fermi energy level)

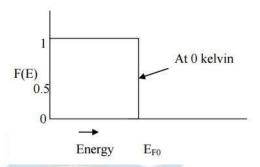
When E = EF, equation 1 becomes

$$F(E) = \frac{1}{1+1} = \frac{1}{2} = 0.5$$

(i.e. 50% chance for the electron to be filled within the Fermi energy level)

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- \triangleright This clearly shows that at 0 kelvin all the energy states below E_F are filled and all those above it are empty.
- > The Fermi function at 0 kelvin can also be represented graphically as shown in fig.



Fermi energy and its importance Fermi energy level

Fermi energy level is the maximum energy level up to which the electron can be filled at 0k.

Importance:

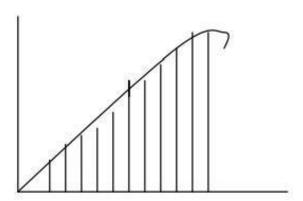
- Thus it act as a reference level which separates the vacant and filled energy states at 0k.
- At 0k, blow Fermi energy level electrons are filled and above Fermi energy level it will be empty.
- ➤ When the temperature is increased, few electrons gains thermal energy and it goes to higher energy levels.

Conclusions:

> In the quantum free electron theory, though the energy levels are discrete,

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

The number of energy levels N(E) that are filled with electrons per unit energy increases parabolic all0y with increase of energy E as shown in fig.



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- Each energy level can provide only two states, namely, one for spin up and other for spin down and hence only two electrons can be exclusion principle.
- At T = 0, if there are N number of atoms, then we have N/2 number of filled energy levels and other higher energy levels will be completely empty.
- \triangleright This $(N/2)^{th}$ energy level is the highest filled energy level is known as Fermi energy level (E_{F0}) .
- The electrons are filled in a given energy no two electrons can have the same set of four quantum numbers.
- At room temperature, the electrons within the range of K_BT below the Fermi energy level will absorb thermal energy = K_BT and goes to higher energy states with energy $E_{F0} + K_BT$.

DENSITY OF STATES

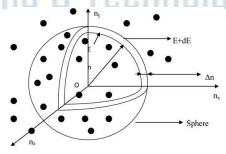
- > The Fermi function F(E) gives only the probability of filling up of electrons on a given energy state.
- The number of available energy states so called density of states.

Definition

Density of states Z(E)dE is defined as the number of available electron states per unit volume in an energy interval (dE).

Explanation

- Find the number of available energy states within a given energy interval.
- Number of available energy levels can be obtained for various combinations of quantum numbers n_x , n_y , and n_z . (i.e) $n^2 = n_x^2 + n_y^2 + n_z^2$ -----(1)
- \triangleright Let us construct three dimensional space of points which represents the quantum numbers n_x , n_y , and n_z as in this space each point represents an energy level.



DERIVATION OF DENSITY OF ENERGY STATES

- To find the number of energy level find number of electrons that can be filled in a given energy level, 1
- \triangleright The sphere is further divided in to many shells of quantum numbers (n_x , n_y and n_z) and therefore represents a particular energy value.

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 \triangleright Let us consider two energy values E and E + dE. The number of energy states between E and E + dE number of energy states between the shells of the radius n and n + Δ n,

The number of energy states within the sphere of radius $n = 4/3 \pi n^3$ -----(4)

- \triangleright Since n_x , n_y , and n_z will have only positive values, we have to take only one octant of the sphere (i.e) 1/8 th of the sphere volume.
- The number of available energy states within the sphere of radius $n = 1/8 [4/3 \pi n^3]$
- Similarly the number of available energy states within the sphere of radius $n + dn = 1/8 \left[\frac{4}{3} \pi (n+dn)^3 \right]$ -----(3)
- \triangleright The number of available energy states between the shells of radius n and n + dn (or) between the energy level

$$2ndn = \frac{8m \ell^2}{h^2} dE$$

$$ndn = \frac{8m \ell^2}{2 h^2} dE$$

Equation 1 can be written as

$$Z(E)dE = \pi / 2(n^2 dn)$$

$$Z(E)dE = \pi / 2 n (n dn)$$

Substituting equation (3) and (4) in the above equation we have

$$Z(E)dE = \pi / 2 \qquad \left[\frac{8m \ \ell^2 E}{h^2} \right] \left[\frac{8m \ \ell^2}{2 \ h^2} dE \right]$$

$$Z(E)dE = \pi / 2 \times 1/2 \left[\frac{8m \ell^2}{h^2} \right]^{1/2} \left[\frac{8m \ell^2}{h^2} \right]$$
 $E^{1/2} dE$

(4)

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$$Z(E)dE = \pi / 4$$
 $\left[\begin{array}{c} 8m \ell^2 \\ h^2 \end{array}\right]^{3/2} E^{1/2} dE$

$$Z(E)dE = \pi / 4$$
 $\begin{bmatrix} 8m \\ h^2 \end{bmatrix}$ $\ell^3 \cdot E^{1/2} dE$

Here ℓ 3 represents the volume of the metal piece. If ℓ 3 = 1, then we can write that

The number of available energy states per unit volume (i.e) Density of states

$$Z(E)dE = \pi / 4$$
 $\left(\frac{8m}{h^2} \right)^{3/2} E^{1/2} dE$ (5)

Since each energy level provides 2 electron states one with spin up and another spin d



Density of states

$$Z(E)dE = 2x \pi/4 \left[\frac{8m}{h^2} \right]^{3/2} E^{1/2} dE$$

$$Z(E)dE = \pi/2 \left[\frac{8m}{h^2} \right]^{3/2} E^{1/2} dE$$
(6)

CALCULATION OF CARRIER CONCENTRATION

Let N(E) dE represents the number of filled energy states between the interval of energy dE . energy state is given by Fermi function F(E).

$$N(E) = Z(E)dE \cdot F(E)$$
----(7)

Substituting equation (6) in equation (7),

we get Number of filled energy states per unit volume

$$N(E) = \pi / 2 [8m / h^2] E^{1/2} dE. F(E)----(8)$$

N(E) is known as carrier distribution function (or) carrier concentration in metals.

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CALCULATION OF FERMI ENERGY

Case (i) At T = 0K

$$E_f = [3Nh^3/\pi(8m)^{3/2}]^{2/3} = h^2/8m[3N/\pi]^{2/3}$$

Case(ii) At T> 0K

$$E_f = [3Nh^3/\pi(8m)^{3/2}]^{2/3} = h^2/8m[3N/\pi]^{2/3}$$

AVERAGE ENERGY OF AN ELECTRON AT OK

Average energy = Total energy / Carrier Concentration

Total Energy =
$$\pi/5h^3(8m)^{3/2}E_{f0}^{5/2}$$

Carrier Concentration = $\pi/3h^3(8m)^{3/2}E_{f0}^{3/2}$

Average energy =
$$\pi/5h^3(8m)^{3/2}E_{f0}^{5/2}$$

 $\pi/3h^3(8m)^{3/2}E_{f0}^{3/2}$

$$E_{avg}$$
= 3/5 E_{fo}