UNIT-III Principles of quantum mechanics

De-Broglie Hypothesis –Matter waves: An electromagnetic wave behaves like particles, particles like electrons behave like waves called matter waves, also called de-Broglie matter waves. The wave length of matter waves is derived on the analogy of radiation. Based on Planck's theory of radiation, the energy of a photon is given by

$$E = h\vartheta = \frac{hc}{\lambda}....(1)$$

C = Velocity of light

 λ = Wavelength of the photon

h = Planck's constant

According to Einstein"s mass energy relation

$$E = mc^2$$
.....(2)

m= mass of the photon

Equating equations (1) and (2)

$$\underline{hc} = mc^2.....(3)$$

$$\lambda = \frac{hc}{mc^2} = \frac{h}{mc} = \frac{h}{R} \quad(4)$$

P = momentum of photon

de-Broglie proposed the concept of matter waves, according to which a material particle of mass"m", moving with a velocity should have an associated wavelength, called de-Broglie wavelength.

$$\lambda = \frac{h}{mv} = \frac{h}{P}$$
 ----- (5) is called de-Broglie's wave equation.

Properties of matter waves:

- 1. Wavelength is associated with moving particle and independent of charge of the particle
- **2.** Greater the mass, velocity of the particle, lesser will be the wavelength.
- 3. When $\mathbf{v} = \mathbf{0}$, $\lambda = \infty$. i.ewave becomes indeterminate and $\mathbf{v} = \infty$, $\lambda = \mathbf{0}$. This shows that matter waves are generated by the motion of particles.
- 4. Matter waves are not electromagnetic waves. They are independent of charge.
- 5. The velocity of matter wave depends on the velocity of matter particle.

- 6. Velocity of matter wave is greater than the velocity of light.
- 7. A particle in motion ,the matter wave has two different velocities. One regarding to the mechanical motion of the particle represented by v and second related to the propogation of the wave represented by ω .

We know that
$$E = h\vartheta$$
 and $E = mc^2$

$$\vartheta = \frac{mc^2}{h}$$
The wave velocity $\omega = \vartheta \times \lambda$

$$= \frac{mc^2}{h} \times \frac{h}{mv} = \frac{c^2}{v}$$

As particle velocity v cannot exceed c, hence ω is greater than velocity of light.

7.de-Broglie wavelength associated with an electron:

If a velocity 'v' is given to an electron by accelerating it through a potential difference'V'then the work done on the electron is 'eV' and the work done is converted into the kinetic energy of an electron.

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

As particle velocity v cannot exceed c, hence ω is greater than velocity of light.

8.de-Broglie wavelength associated with an electron:

If a velocity 'v' is given to an electron by accelerating it through a potential difference'V'then the work done on the electron is 'eV' and the work done is converted into the kinetic energy of an electron.

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

$$eV = \frac{1}{2} \frac{p2}{m}$$

$$p2 = 2meV$$

$$p = \sqrt{2meV}$$

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

by substituting the values of $h = 6.625 \times 10^{-34} J sec$

m = mass of electron = $9.1 \times 10^{-31} Kg$ and

e= charge of electron= 1.6×10^{-19} C

$$\lambda = \frac{12.27}{\sqrt{V}} A^0$$

where V= in volt and λ = in A^0

9. de Broglie wavelength in terms of Kinetic energy

Consider a particle of mass m moving with velocity v. Then Kinetic energy of the particle

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

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

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

Heisenberg's uncertainty principle:

- 1. According to Classical mechanics, a moving particle at any instant has fixed position in space and definite momentum which can be determined simultaneously with any desired accuracy. This assumption is true for objects of appreciable size, but fails in particles of atomic dimensions.
- 2. Since a moving atomic particle has to be regarded as a de-Broglie wave group, there is a limit to measure particle properties.
- 3. According to Born probability interpretation, the particle may be found anywhere within the wave group moving with group velocity.
- 4. If the group is considered to be narrow, it is easier to locate its position, but the uncertainty in calculating its velocity and momentum increases.

5. If the group is wide, its momentum is estimated easily, but there is great uncertainty about the exact location of the particle.

Heisenberg a German scientist in 1927, gave uncertainty principle which states that

"The determination of exact position and momentum of a moving particle simultaneously is impossible' '.

In general, if ox represents the error in measurement of position of particle along xaxis, and op represents error in measurement of momentum, then

$$\Delta x \Delta p = h$$

Or limitation to find the position and momentum of a particle is

$$(\Delta x)(\Delta p) \ge \frac{h}{4\pi}$$

i.e Heisenberg uncertainty principle states that both the position and momentum Can't be measured simultaneously with perfect accuracy.

Schrodinger time independent wave equation

According to de Broglie theory, a particle of mass m is always associated with a wave whose wavelength is given by $\lambda = \frac{h}{mv}$. If the particle has wave properties, it is expected that there should be some sort of wave equation which describes the behaviour of the particle. Consider a system of stationary waves associated with a particle. Ψ is the wave function of the particle along x,y and z axes at any time t.It is assumed that ψ is finite, single valued and periodic function. Based on the Cartesian co-ordinates, one can write the differential wave equation of a progressive wave velocity v as

The value of $\frac{d^2\psi}{dt^2}$ can be obtained by differentiating

$$\Psi = \Psi_0 \, e^{-i\omega t}$$

$$\frac{d^2\psi}{dt^2} = -\omega^2\psi \dots (2)$$

But
$$\omega = 2\pi u = \frac{2v}{\lambda}$$
(3)

$$\frac{d^2\psi}{dt^2} = -(2\pi v/\lambda)^2....(4)$$

Substitute equation (4) in (1)

$$-(2\pi v/\lambda)^2 = v^2\nabla^2 \psi$$

$$\nabla^{2} \psi = -\frac{2m}{\hbar^{2}} [E - V] \psi$$

$$\nabla^{2} \psi + \frac{2m}{\hbar^{2}} [E - V] \psi = 0....(5)$$

Equation (5) is known as Schrodinger time independent wave equation.

For a free particle V = 0,

then the Schrodinger time independent wave equation becomes

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E] \psi = 0$$

Schrödinger Time -dependent wave Equation

Based on the Cartesian co-ordinates, one can write the differential wave equation of a progressive wave velocity v as

$$\frac{d^2\psi}{dx^2} = \frac{1}{v^2} \frac{d^2\psi}{dt^2}$$

The value of $\frac{d\psi}{dt}$ can be obtained by differentiating

$$\psi = \psi_0 \ e^{-i\omega t}$$

$$\frac{d\psi}{dt} = -(i\omega) \, \psi_0 \, e^{-i\omega t}$$

$$\frac{d\psi}{dt} = -(i\omega)\psi$$

But $\omega = 2\pi v$

$$\frac{d\psi}{dt} = -(i\omega)\psi$$

$$\frac{d\psi}{dt} = -(i2\pi\nu)\psi \quad \dots (1)$$

We know that

$$E = hv$$

$$v = \frac{E}{h} \quad \dots \tag{2}$$

From eqn's (1) & (2), we get

Schrodinger time independent wave equation is

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V] \psi = 0$$
(4)

Substitute eqn(3) in (4), we get

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (i\hbar) \frac{d\psi}{dt} - \frac{2m}{\hbar^2} V \psi = 0$$

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (i\hbar) \frac{d\psi}{dt} - \frac{2m}{\hbar^2} V \psi = 0$$

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (i\hbar) \frac{d\psi}{dt} = \frac{2m}{\hbar^2} V \psi$$

Multiply on both sides with $\frac{\hbar^2}{2m}$, we will get

$$\frac{\hbar^2}{2m}\nabla^2 \psi + (i\hbar)\frac{d\psi}{dt} = V\psi$$

$$\frac{\hbar^2}{2m}\nabla^2 \psi - V\psi = (i\hbar)\frac{d\psi}{dt}$$

$$\left(\frac{\hbar^2}{2m}\nabla^2 - V\right)\psi = (-i\hbar)\frac{d\psi}{dt}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = (i\hbar)\frac{d\psi}{dt} \qquad (5)$$

$$H\psi = E\psi \qquad (6)$$

Where H is Hamiltonian Operator and E is Energy Operator

$$H = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)$$

Eqn .(5) is known is Schrodinger time dependent wave equation.

Particle in a box

Let us consider one dimensional potential box of width 'L'. In solids the carriers of electric current are electrons. Since the free electrons can move inside the crystal only, it is assumed that they travel inside the crystal in constant potential. Since they are prevented from leaving the crystal treating the potential outside the crystal as infinity, boundary condition is applied and electrons are confined inside the crystal.

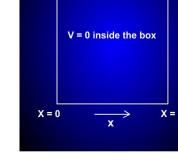
For simplicity, we take V(x) = 0 within the potential box and

 $V(x) = \alpha$ out side the box.i.e boundary conditions are

$$V(x) = 0 \quad 0 < x < L$$

$$V(x) = \infty$$
 $x \le 0$ and $x \ge L$

According to schoridinger time independent wave equation for the particle in a potential box is



V = infinite

V = infinite

$$\frac{d^2\psi(x)}{dx^2} + \frac{2m^2}{\hbar^2} E\psi(x) = 0$$

$$\frac{d^2\psi(x)}{dx^2} + K^2(x) = 0 \quad(1)$$

$$K^2 = \frac{2nE}{\hbar^2}$$
(2)

A possible solution to equation (1) is

$$\psi(x) = Asinkx + Bcoskx$$

where A and B are constants.

Since the particle cannot penetrate an infinitely high potential barrier,

For
$$\psi(x) = 0$$
 at $x = 0$, B must be zero

For $\psi(x) = 0$ at x = L, KL must be an integral multiple of π

$$\psi(x) = Asinkx$$

where

$$K = \frac{n\pi}{L}$$
 (n=1,2,3,...)...(3)

equation (3) is substitute in equation (2), we get

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

$$E = \frac{n^2h^2}{8mL^2}$$

Thus each value of n the possible energy of the particle is given by above equation.

Now the wave function becomes

$$\psi(x) = A \sin\left(\frac{n\pi x}{L}\right)$$

The constant A in wave function can be obtained by applying the normalized condition

$$1 = \int_{-\infty}^{\infty} |\psi_{\pi}|^2 dx = \int_{0}^{L} A^2 \sin^2 \frac{n\pi}{L} x dx = A^2 \int_{0}^{L} (1/2)(1 - \cos \frac{2n\pi}{L} x) dx$$

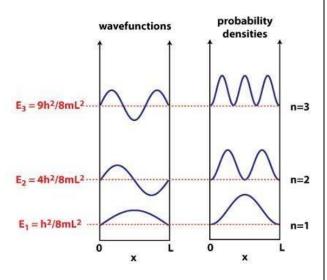
$$= A^2 \left[\frac{L}{2} - \frac{L}{2n\pi} \sin(2n\pi x + L) \right]_{0}^{L} = A^2 L/2,$$

$$\Rightarrow A = \sqrt{2 + L},$$

$$\psi_{\pi} = \sqrt{2 + L} \sin(n\pi x + L)$$

Results:

- 1. When n=1, it is ground state. The probability density is largest in the middle while it decreases towards the boundaries. It means that the electron will be found in the middle of the box for most of the time.
- 2. When n=2, it is first excited state. The electron will be found either in left-hand half or in the right hand half but never in the middle of the box. Thus all the positions in the box are not equally probable for the electron.



Significance of wave function:

The wave function ψ is a mathematical function of a system in quantum mechanical system which describes the complete information about the state of a system at position x and time t.By knowing the value of ψ , It is easy to find the position of a particle in a given space.

- According to Schrodinger, if ψ is the amplitude at any point in space, the probability of finding the particle is proportional to ψ^2 . Hence ψ^2 is a measure of particle density.
- According to Max Born, the probability (P) of finding the particle in the state ψ and the space of volume DV = dx. dy. dz is given by

$$\psi \psi^* dx. dy. dz = \psi^2 dV = P$$

• The total probability of finding a particle somewhere in space is unity, i.e,the particle is certainly to be found somewhere in space. Therefore,

$$\iiint \psi^2 dV = 1$$

• This is the condition is called Normalized condition.

Ψ must have the following properties:

- Ψ must be finite everywhere
- ψ must be single value
- ψ must be continuous and it should be normalized.

CLASSICAL FREE ELECTRON THEORY OF METALS

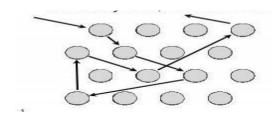
Introduction

Very high electrical and thermal conductivity are the outstanding properties of metals. The positive ion cores and the valence electrons are the charge carriers in metals and hence, good conductivity means the presence of a mobile charge carrier. The observed high conductivity due to conduction by the drift ion cores is difficult to understand. If this happens, then conductivity must increase with increase in temperature. Hence, it may be concluded that mobile charges in metals are valence electrons. The classical free electron theory reveals that the free electrons are fully responsible for electrical conduction.

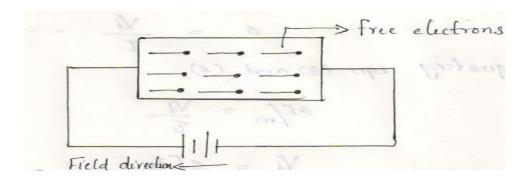
<u>Classical free electron (or) Drude – Lorentz theory of metals</u>

Postulates

- 1. In an atom the electrons revolve around the nucleus and a metal is composed of such atoms.
- 2. The valence electrons of atoms are free to move about the whole volume of the metals like the molecules of a perfect gas in a container.
- 3. These free electrons collide with other free electrons or positive ion cores or the walls of the container. Collisions of this type are known as elastic collisions i.e there is no loss of energy.



4. When an electric field is applied to the metal, the free electrons are accelerated in the direction opposite to the direction of applied electric field. The free electrons available in the metal gain some amount of energy and are directed to move towards a higher potential. These electrons acquire a constant velocity known as drift velocity (v_d) .



ADVANTAGES AND DRAWBACKS

Even though the classical condition and thermal condition of metals, it has many practical applications. The advantages and disadvantages of the classical free electron theory are as follows.

Advantages

- 1. It explains the electrical conductivity and thermal conductivity of metals.
- 2. It explains the wiedemann-Franz law.
- 3. It verifies Ohm's law.
- 4. It is used to explain the optical properties of metals.

DRAWBACKS

- 1. It fails to explain the electric specific heat and the specific heat capacity of metals.
- 2. It fails to explain superconducting properties of metals.
- 3. It fails to explain new phenomena like photo-electric effect, Compton effect, black-body radiation, etc.
- 4. It fails to explain electrical conductivity of semiconductors or insulators.
- 5. The classical free electron model predicts the incorrect temperature dependence of σ . According to the classical free electron theory, $\sigma = ne^2 \tau_r / m$.
- 6. It fails to give a correct mathematical expression for thermal conductivity.
- 7. Ferromagnetism could not be explained by this theory.
- 8. Susceptibility has greater theoretical value than the experimental value

QUANTUM FREE ELECTRON THEORY:

Somerfield applied quantum mechanics to explain conductivity phenomenon in metals. He has improved the Drude- Lorentz theory by quantizing the free electron energy and retaining the classical concept of force motion of electrons at random.

ASSUMPTIONS

- The electrons are free to move with in the metal like gaseous molecules. They are confined to the metal due to surface potential.
- The velocities of electrons obey Fermi-Dirac distribution because electrons are spin half particles.
- The electrons would go into different energy levels and obey Pauli's exclusion principle.

- The motion of the electron is associated with a wave called matter wave, according to the deBroglie hypothesis.
- 5. The electrons can not have all energies but will have discrete energies according to the equation $E_{n=} \frac{n^2 h^2}{8ma^2}$ where a is the dimension of the metals.

Derive an expression for electrical conductivity by using quantum free electron theory

According to Quantum theory

$$p = mv = hK - - - (1)$$
Where $h = \frac{h}{2\pi}$, $K = \frac{2\pi}{\lambda}$

Differentiating equation (1) w.r.t to t

$$a = \frac{dv}{dt} = \frac{h}{m} \frac{dK}{dt}$$

At equilibrium the lorentz force F = -eE acting on the electron is equal and opposite to the product of mass and acceleration of the electron

$$\begin{array}{c}
eE = ma \\
h \ dK
\end{array}$$

$$\Rightarrow m \frac{-}{m} \frac{-}{dt} = eE$$

$$\Rightarrow dK = \frac{eE}{h}dt ---(2)$$

Integrating (2) between the limits 0 and t

$$\int_{1}^{t} dK = \int_{1}^{t} \frac{eE}{h} dt$$

$$K(t) - K(0) = \frac{eE}{h} t$$

$$\Delta K = \frac{eE}{h} t_c$$
 where t_c =men collision time.

But
$$J = ne\Delta v$$
 and $\Delta v = h \frac{\Delta K}{m}$

$$\Delta v = h \frac{\Delta K}{m} = \frac{h}{m} \frac{eE}{h} t = \frac{eEt}{m}$$

$$\therefore J = \frac{ne^2Et}{m^*}$$

From microscopic form of Ohm's law

$$J = \sigma E$$

$$\therefore \sigma = \frac{ne^2t}{m^*}$$
 This is the expression for the electrical conductivity.

FERMI-DIRAC STATISTICS

The distribution of energy states in a semiconductor is explained by Fermi-Dirac statistics since it deals with the particles having half integral spins like electrons. Consider that the assembly of electrons as electron gas which behaves like a system of Fermi particles or Fermions. The Fermions obey Fermi-Dirac statistics, i.e., Pauli's exclusion principle.

Therefore, the probability function of (E) of an electron occupying an energy level E is given by

$$f(E) = \frac{1}{1 + exp[(E - E_F)/KT]}$$
 ----(1)

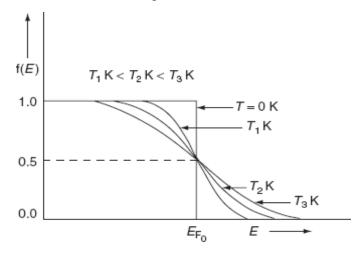
Where E_F is Fermi energy,

K is Boltzmann constant and T is absolute temperature.

In Eq.(1), the probability function f(E) lies between 0 and 1. Hence, there are three possible probabilities namely,

- f(E) = 1 100% probability to occupy the energy level by electrons.
- f(E) = 0 No probability to occupy the energy level by electrons and hence, it is empty.
- f(E) = 0.5 50% probability of finding the electron in the energy level.

The temperature dependence of Fermi distribution function and its effects on the occupancy of energy level by electrons is shown in Fig.



Case-1

Probability of occupation at T=0K and $E < E_F$

Substituting the above condition in Eq.(1), we get

$$f(E) = \frac{1}{1 + e^{-\infty}} = \frac{1}{1} = 1$$
$$f(E) = 1 - \dots (2)$$

Therefore,

Eq. (2), clearly indicates that at T=0K, the energy level below the Fermi energy level E_F is fully occupied by electrons. Therefore, there is a 100% probability that the electrons to occupy energy level below Fermi energy.

Case-2

Probability of occupation at T=0K and $E > E_F$

Substituting the above condition in Eq.(1), we get
$$f(E) = \frac{1}{1 + e^{-\infty}} = \frac{1}{1 + \infty} = \frac{1}{\infty} = 0$$

Therefore,

$$f(E) = 0$$
 -----(3)

Eq. (3), clearly indicates that at T=0K, the energy levels above the Fermi energy level E_F is unoccupied, i.e., vacant. Therefore, there is a 0% probability for the electrons to occupy the energy level above the Fermi energy level.

Fermi energy level is the highest energy level occupied by an electron in a conductor at 0K is the Fermi energy level.

Case-3

Probability of occupation at T > 0K and $E=E_F$

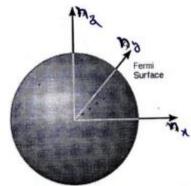
Substituting the above condition in Eq.(1), we get
$$f(E) = \frac{1}{1 + e^0} = \frac{1}{1 + 1} = \frac{1}{2} = 0.5$$

Therefore,

$$f(E) = 0.5$$
 ----(4)

Eq. (4), clearly indicates that at T=0K, there is a 50% probability for the electrons to occupy Fermi energy level. Therefore, the Fermi energy level is defined as the energy level at any temperature, the probability of electron is 50% or ½. Similarly, it is also defined as E_F, the average energy occupied by the electrons which participate in conduction process in a conductor at temperature above 0K.

DENSITY OF STATES



The number of states with energy less than E_f is equal to the number of states that lie within a sphere of radius $|n_f|$ in a region of K-space where n_x , n_y and n_z are positive.

$$\therefore N = 2 \times \frac{1}{8} \times \frac{4}{3} \pi n_f^3$$

$$\therefore N = 2 \times \frac{1}{8} \times \frac{4}{3} \pi n_f^3 = \frac{3N}{\pi} \Rightarrow \boxed{n_f = (\frac{3N}{\pi})^3}$$

So the Fermi energy

$$E_{f} = \frac{h^{2}\pi^{2}n_{f}^{2}}{2ma^{2}} = \frac{h^{2}\pi^{2}}{2ma^{2}} \left(\frac{3N}{\pi}\right)^{\frac{2}{3}}$$

$$E_{f} = \frac{h^{2}\pi^{2}}{2m} \frac{(3N)^{\frac{2}{3}}}{a^{2}} = \frac{h^{2}\pi^{2}}{2m} \frac{(3N)^{\frac{2}{3}}}{(a^{3})^{\frac{2}{3}}} = \frac{h^{2}}{2m} \left(\frac{3N\pi^{2}}{a^{3}}\right)^{\frac{2}{3}} = \frac{h^{2}}{2m} \left(\frac{3N\pi^{2}}{a^{3}}\right)^{\frac{2}{3}} = \frac{h^{2}}{2m} \left(\frac{3N\pi^{2}}{a^{3}}\right)^{\frac{2}{3}}$$

$$\therefore N^{\frac{2}{3}} = \frac{2m}{h^{2}} \left(\frac{V}{3\pi^{2}}\right)^{\frac{2}{3}} E_{f}$$

$$\Rightarrow N = \left(\frac{2m}{h^{2}}\right)^{\frac{2}{3}} \left(\frac{V}{3\pi^{2}}\right)^{\frac{2}{3}} E_{f}$$

Therefore density of states:
$$D(E) = \frac{dN}{dE} = \frac{3}{2} (\frac{2m}{h^2})^{\frac{3}{2}} (\frac{V}{3\pi^2}) E_f^{\frac{1}{2}}$$

$$D(E) = \frac{V}{2\pi^2} (\frac{2m}{h^2})^{\frac{3}{2}} E_f^{\frac{1}{4}}$$

Therefore the total number of energy states per unit volume per unit energy range

$$Z(E) = \frac{D(E)}{V} = \frac{1}{\frac{2\pi^{2}}{4\pi}} \left(\frac{2m}{h^{2}}\right)^{\frac{3}{2}} E_{f}^{\frac{1}{2}} = \frac{1}{2\pi^{2}} \frac{(2m)^{\frac{3}{2}}}{h^{3}} 8\pi^{3} E_{f}^{\frac{1}{2}}$$

$$Z(E) = \frac{1}{h^{3}} (2m)^{2} E_{f}^{\frac{1}{2}}$$

Therefore the number of energy states in the energy interval E and E + dE are

$$Z(E)dE = \frac{4\pi}{h^3} (2m)^{\frac{3}{2}} E_f^{\frac{1}{2}} dE$$

FERMI ENERGY:

The Fermi energy is a concept in quantum mechanics referring to the energy of the highest occupied quantum state in a system of Fermions at absolute zero temperature.

For the one dimensional infinite square well the energy of the particle is given by

$$E = \frac{n^2 h^2}{8ma^2}$$

Suppose now instead of one particle in this box we haven particles in the box and that particles are fermions with spin ½ then only two particles can have the same energy.i.e. Two particles have the same energy of

$$E_1 = \frac{h^2}{8ma^2}$$

Two particles having energy

$$E_2 = \frac{4h^2}{8ma^2}$$

:All the energy levels up to n=N/2 are occupied and all the higher levels are empty.

$$E_f = E_{N/2} = \frac{(N/2)^2 h^2}{8ma^2} = \frac{N^2 h^2}{32ma^2}$$

$$E_f = \frac{N^2 h^2}{32ma^2}$$