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Metal free electrons, short review

The free electrons in metal gives rise to a very interesting physical phenomenon in addition to electrical and thermal conductivity as well as magnetism.

Free particles that move without any obstacles and barriers have only kinetic energy in the equation and can be calculated by Schrodinger time-independent equation:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{2mE}{\hbar^2}=0.$$

This is second order differential equation and the solution for the wave function is

$$\psi(x)=Ae^{\prime kx}+Be^{-ikx}$$

Metals are good conductors due to their free electrons which can move unbound between the steady-state protons.

There are two types of solid electron free theory, classical, (Drude-Lorentz) and quantum by Sommerfield.

Metal free electrons are not bounded and can move but confined between the protons within a metal crystal which can be described like particle in infinite potential well.

Infinite potential well: Electron in one dimension box.
(Gurmeet Salhotra 2020).

Assume an electron with mass m confined in one dimension box. The electron can move in a straight line such as x-axis, between x=0 and x=L. The walls are not penetrable.

The potential V is defined as: 0 for 0<x<L and ∞ for x<0 and x>L.

Schrodinger's wave equation for the wave function of the displacing electron along x-axis can be written as:

$$\frac{\partial^2\psi}{\partial x}+\frac{2m}{\hbar^2}(E-v)\psi=0$$

As the potential energy (v) inside the box (Crystal) is 0, the above equation can be written:

$$\frac{\partial^2\psi}{\partial x}+\frac{2mE}{\hbar^2}\psi=0$$

E is the Kinetic energy of the electron.

$$\frac{2mE}{\hbar^2}=K^2$$

Thus, the equation for Kinetic energy can written as: $\frac{\partial^2\psi}{\partial x}+K^2\psi=0$ and the general solution of the equation: $\psi(x)=Asin\,Kx+\mathrm{B}\cos Kx$

A and B are constants that determined by the boundary conditions.

At x=0 and x=L, the wave function ψ=0. If at x=0, ψ = 0, so, 0=0+B, B=0, and ψ = Asin Kx..

At x=L, ψ=0 and AsinKx=0… (A is constant can't be 0). L is the box length.

sin KL= sin nπ, K is wave number and n is energy level.

kL= nπ, K= $\frac{n\pi}{L}$, $K^2 = \frac{n^2\pi^2}{L^2}$

for nth state, ψ = A sin Kx, becomes A sin $\frac{n\pi x}{L}$

Thus, $\frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$ and the electron energy E = $\frac{n^2\pi\hbar^2}{2mL^2}$,

N electrons fill up the energy level from lowest to highest, two at a time (spin up spin down), until the highest energy level is full. The highest level is called the Fermi energy.

Fermi Energy: $E_f - \frac{\hbar^2}{8}\left(\frac{3N}{\Pi v}\right)^{2/3}$

Metallic reflection phenomenon: (http://eng.libertext.org/@/page/342)

Light that encounters a material, radiation can be absorbed or reflected by the surface.

Because the reflectance of light by metals is high their absorption is low since the sum of both have to corresponds to 100% of the incident light.

The absorption of light can occur by the lattice vibration and excitation of electrons to higher energy level.

In addition, high conductivity of the metal, assume to relate to high reflectance in lower frequency according to **Hagens-Ruben** relation.

Absorption:

When light beam of certain wavelength focuses on a metal, the radiation is attenuated by energy loss from lattice vibrations and excitation of electrons from the valence band to conduction band.

When electromagnetic radiation meets the metallic surface, the intensity of the incident light decreases exponentially while it travels through the metal, leading to transmitted light of lower intensity.

The ratio between transmitted intensity and initial intensity is defined as transmittance(T).

$$T = \frac{I}{I_0}$$

Reflection:

Metals have high reflectivity, reflecting almost all wavelength in the visible region of the spectrum.

Reflectance and conductivity:

The Hagens-Ruben equation can relate the metallic reflectance to conductivity.

$$R = 1 - 4\sqrt{\frac{\nu\pi\varepsilon_0}{\sigma}}$$

In the infrared region (low frequency), this equation shows that metals with high reflectance also are good conductors.

Experiments by Hagens-Ruben showed that at low frequency the optical constant of metal similar to the values of Drude's function, but in high frequency deviations of Drude' approach appear. This is because bound electrons of the metal start to respond to the incident of light, and not just valence band electrons response.

Electrical Conductivity:

"Electrical conductivity is defined as the amount of electricity that flows in unit time per unit area of cross-section of the conductor per unit potential gradient" (Gurmeet Salhotra 2020).

The acceleration of an atomic electron by source electric field can be calculated from the equation of motion of an electron of rest mass. The acceleration of the electron induced by the Lorentz force due to the incident electromagnetic field, (Jay Theodore and Cremer Jr, Neutron and X-ray Optics, 2013). $m_0 \frac{d^2x}{\partial t} s + m_0 \frac{\partial xs}{dt} + m_0 W_s^2 x = -e(E_i + V_s \times B_i)$

However, solid free electron theory, suggests free movement of electrons. When electric field E is applied, the electron with its charge is accelerate: $a = \frac{d^2x}{dt^2} = \frac{eE}{m}$

By integrating $\int \frac{d^2x}{\partial t^2} = \frac{eE}{m}\int t\, dx$

$\frac{dx}{dt} = \frac{eE}{m}t + C$ at t = 0, c =0. We get: v =$\frac{eE}{m}t$

If λ is the mean free path of electrons, then relaxation time τ between collisions is $\tau = \frac{\lambda}{v}$

And average velocity between two successive collisions:

$\bar{v} = \frac{1}{\tau}\int_0^\tau \frac{eE}{m} t\, dt = \frac{eE}{\tau m}\int_0^\tau t\, dt$ $\bar{v}$= $\frac{eE\tau}{2m}$

As $\tau = \frac{\lambda}{v}$ $\bar{v}$ = $\frac{eE\lambda}{2vm}$

At collision, the current density J is due to n electrons per unit volume of charge e and drift velocity v, J= nev = ne($\frac{eE\tau}{m}$) = σE

$$\sigma = \frac{J}{E} = \frac{ne^2\tau}{m}$$

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The velocity in a unit electrical field, v/E is the mobility μ of the electron.

$\mu = \frac{v}{E} = \frac{e\tau}{m}$

J= ne μE

σ = ne μ

if q charge is flowing through a conductor with cross-section A at t time, then q=σAEt

or $\frac{q}{t} = \sigma AE = i$

$\sigma = \frac{i}{E}$, for unit are of cross section $\sigma E = J = \frac{i}{A}$

DC field, analysis of Drude model consider uniform electric field and constant so the thermal velocity of electrons is just allowed infinitesimal amount of momentum dP between collisions that occur every τ seconds. An electron on average travelled for time τ since its last collision, so a momentum will accumulate. d<P> = qE τ.

Substituting the relations <p> =m<v>, J=nq<v> result in formulation of Ohm's law.

J= $(\frac{nq^2\tau}{m})$E

Hence, it was concluded that the most significant results of Drude model are the equation of electron motion $\frac{d}{\partial t}\langle p(t)\rangle = q\left(E + \frac{\langle p(t)\rangle}{m} \times B\right) - \frac{\langle p(t)\rangle}{\tau}$

As well as a linear relationship between current density J and electric Field E

J= $(\frac{nq^2\tau}{m})$E.

In my work I use the formulation $n = \frac{\sigma m}{e^2\tau}$ to get electrons density.

Here some reference for Conductivity (S/m) and Resistivity (Ω.m) at room temperature:

Aluminium: 3.77* 1073.77 10^7 S/m, 2.65*10-82.65 10^-8 Ω.m

Silver: 6.30*1076.3 10^7 S/m, 1.59* 10-81.59 10^-8 Ω.m

<u>Plasma Oscillation: (</u>A.H.Harker, Physics and Astronomy)

Since free electrons in metals allowed to move freely in steady state positive charge environment, the situation enhance collective motion of the electrons in a way like a cloud, relative to the positive background.

If a cloud of electrons, n electrons/volume, move at a distance x relative to the positive background, it gives a surface charge density. $\sigma = -enx$ on the positive x side.

This gives an electric field Ɛ = - $\frac{\sigma}{\varepsilon 0}$ which tries to restore the electrons to their previous position by exerting force F=-eƐ = - $-\frac{ne^2}{\varepsilon_0}x$ on an electron.

So at acceleration, m$\ddot{x} = -\frac{ne^2}{\varepsilon_0}x$,

This is a simple harmonic oscillator with angular frequency ${\omega^2}_P$ = $\frac{ne^2}{\varepsilon_0}$

$\omega_P = 1\sqrt{\frac{ne^2}{\varepsilon_0 m}}$ at resonance frequency ω_P *called the plasma* frequency which is a plasma oscillation resonance or plasmon.

In a straight line with angular frequency, below the plasma frequency will be totally reflected. Above the plasma frequency the light waves can penetrate the sample.

Simple Harmonic Oscillator (http://libertext.org/@page/1589), (libertext/physics).

The classic Hamiltonian of simple harmonic oscillation is:

$$H = \frac{P^2}{2m} + \frac{1}{2}Kx^2$$

Assuming that the quantum mechanical Hamiltonian has the same form, the time-independent Schrodinger equation for a particle of mass m and energy E moving in a simple harmonic potential becomes:

$\frac{d^2\psi}{2x^2} = \frac{2n}{\hbar^2}\left(\frac{1}{2}k^2 - E\right)\psi$ let $\omega = \sqrt{k\ /\ m}$ oscillator's classical angular frequency.

Quantum Harmonic Oscillator:

$u_x = \frac{1}{2}m\omega^2x^2$ Potential energy

Time independent Schrodinger equation:

$$-\frac{\hbar}{2}m\frac{\partial^2\psi_{(x)}}{\partial x^2} + \frac{1}{2}m\omega^2x^2\psi_{(x)} = E\psi_{(x)}$$

The solution for the equation is: $E_n = \left(h + \frac{1}{2}\right)\hbar\omega = \frac{2n+1}{2}h\omega$, meaning the electrons can transit between energies only by quantum of energies.

n = 0, 1, 2, 3, …

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