ENERGY LEVELS IN ONE DIMENSION

Consider a free electron gas in one dimension taking into account quantum theory and the Pauli's principle. The wave function of electrons confined to a length L by infinite barrier potential is the solution of Schrödinger equation

$H\psi = E\psi$

where $H = \frac{p^2}{2m} = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$ is the Hamiltonian and m is the mass of the electron.

Substitution gives $H\psi_n = \frac{-\hbar^2}{2m}\frac{d^2\psi_n}{dx^2} = E_n\psi_n$.

$\Rightarrow \frac{d^2\psi_n}{dx^2} + k^2\psi_n = 0$, where $k^2 = \frac{2mE_n}{\hbar^2}$.

Let the solution be $\psi_n(x) = Acoskx + Bsinkx$.

The boundary conditions $\psi_n(0) = 0$ and $\psi_n(l) = 0$.

Using $\psi_n(0) = 0$, A=0.

$\Rightarrow \psi_n(x) = Bsinkx$.

Using $\psi_n(l) = 0$, $Bsinkl = 0$. But $B \neq 0$.

$\Rightarrow sinkl = 0$

$kl = n\pi$

$\Rightarrow k = \frac{n\pi}{l}$.

The boundary conditions are satisfied if the wave function is sinusoidal with an integral number n of half wavelength between zero and l.

$l = \frac{n\lambda_n}{2}$.

Thus $k = n\pi.\frac{2}{\lambda_n} = \frac{2\pi}{\lambda_n}$.

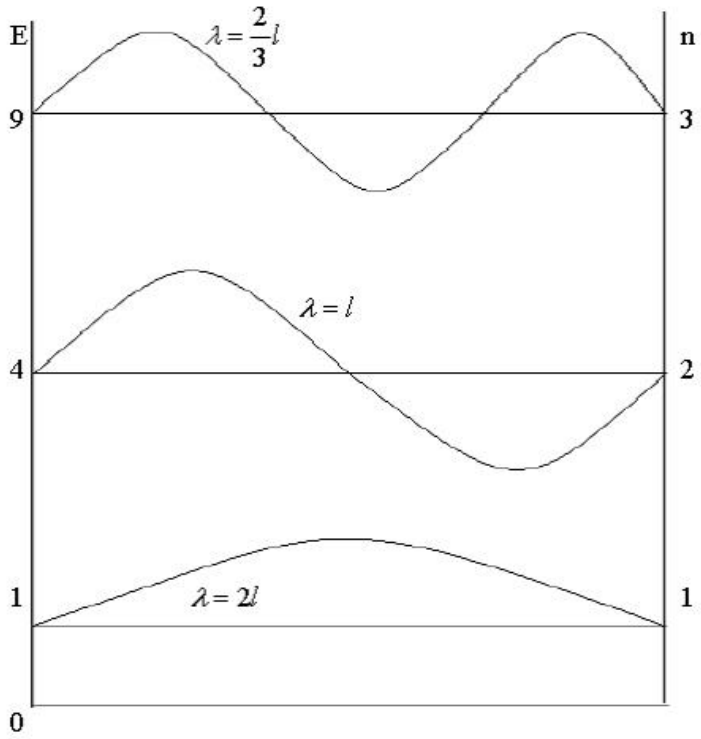
$\psi_n(x) = Bsin(\frac{2\pi}{\lambda_n})x$.

Hence using $k^2 = (\frac{n\pi}{l})^2$.

Equating the two equations for k^2 gives

$\frac{2mE_n}{\hbar^2} = (\frac{n\pi}{l})^2$.

$\Rightarrow E_n = \frac{\hbar^2 n^2 \pi^2}{2ml^2} = \frac{\hbar^2}{2m}(\frac{n\pi}{l})^2$.



Suppose N electrons are to be accomodated on a line. According to the Pauli exclusion principle, no two electrons can have all their quantum numbers identical. However more than one orbital can have the same energy. This is called degeneracy.

Let n_f denote the top most filled energy level where we start filling from the bottom and continue until N electrons are accomodated. It is convenient to assume that N is even.

$\Rightarrow 2n_f = N$.

Using the condition $n_f = \frac{N}{2}$, then $E_f = \frac{\hbar^2}{2m}(\frac{N\pi}{2l})^2$, which is an expression for Fermi energy in one dimension.

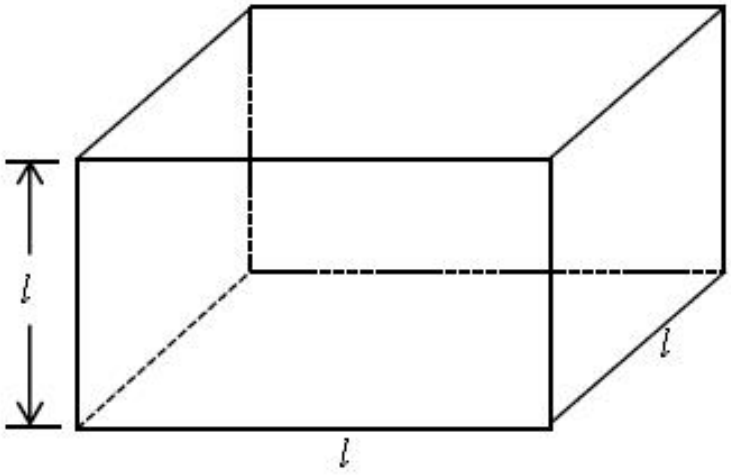
Definition: Fermi energy is the energy of the highest occupied level in the ground state of the N electron system. The ground state is the state of the N electron system at absolute zero.

FREE ELECTRON GAS IN 3-D

The free particle Schrödinger equation in 3-D is

$-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2})\psi_k(\vec{r})=E_k\psi_k(\vec{r})$

Consider a cube of edge l



If the electrons are confined to such a cube

$\psi_n(\vec{r})=Asin(\frac{\pi n_x x}{l})sin(\frac{\pi n_y y}{l})sin(\frac{\pi n_z z}{l})$.

where n_x, n_y, n_z are positive integers. Letting $\psi=X(x)Y(y)Z(z)$,

From $\frac{\partial^2\psi}{\partial x^2}=YZ\frac{\partial^2 X}{\partial x^2}$

$\frac{\partial^2\psi}{\partial y^2}=XZ\frac{\partial^2 Y}{\partial y^2}$

$\frac{\partial^2\psi}{\partial z^2}=XY\frac{\partial^2 Z}{\partial z^2}$

Then $-\frac{\hbar^2}{2m}(YZ\frac{\partial^2 X}{\partial x^2}+XZ\frac{\partial^2 Y}{\partial y^2}+XY\frac{\partial^2 Z}{\partial z^2})=EXYZ$

$-\frac{\hbar^2}{2m}(\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2})=E$

For convenience, the wave function should be periodic and should satisfy the boundary conditions. The wave function is required to be periodic in XYZ with period l.

Thus $\psi(x+l,y,z) = \psi(x,y,z)$

$\psi(x,y+l,z) = \psi(x,y,z)$

$\psi(x,y,z+l) = \psi(x,y,z)$

Wave functions satisfying free particle Schrödinger equation and periodicity condition are of the form of travelling plane wave

$\psi_k(r) = exp(i\vec{k}.\vec{r})$, provided that k satisfy $k_x = 0, \pm\frac{2\pi}{l}, \pm\frac{4\pi}{l}, ...$ and similarly for k_y and k_z.

Any component of $\vec{k}$ of the form $\frac{2n\pi}{l}$ satify the periodicity condition over a length l for n being a positive or negative integer. The components of $\vec{k}$ are the quantum numbers of the problem along with the quantum number m_s for the spin direction. Hence for k_x,

$exp(ik(x+l)) = exp(i2n\pi(\frac{x+l}{l})) = exp(\frac{i2n\pi x}{l})exp(i2\pi n) = exp(\frac{i2n\pi x}{l}) = exp(ikx)$.

This equation confirms that wave functions of individual components are of the forms of travelling wave.

From $E_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2)$, where $k = \frac{2\pi}{\lambda}$.

Linear momentum operator $p = -i\hbar\nabla$.

Then $p\psi_k(r) = -i\hbar\nabla\psi_k(r) = \hbar k\psi_k(r)$.

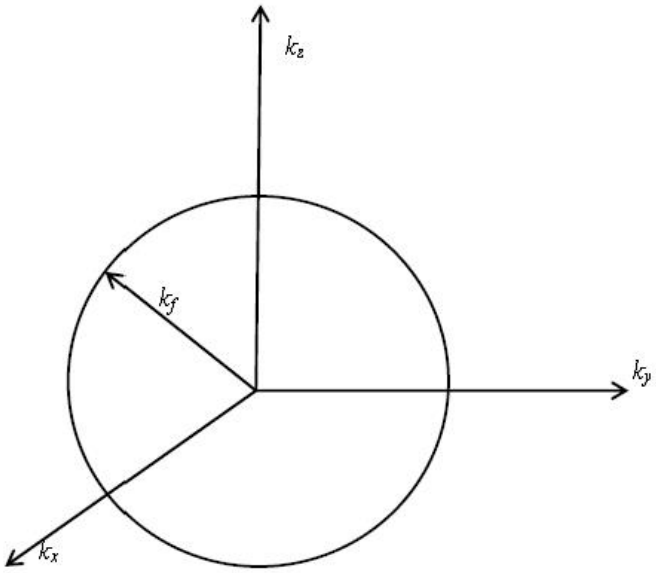
ψ_k is an eigen function of the linear momentum with eigen value $\hbar k$. The particle velocity in orbital k is given by $v = \frac{\hbar k}{m}$.

In the ground state of a system of N free electrons the occupied orbitals may be represented as points inside a sphere in k-space. The energy at the surface of sphere is Fermi energy.

$E_f = \frac{\hbar^2}{2m}k_f^2$.

There is one allowed vector for the volume element $(\frac{2\pi}{l})^3$ of k space. Thus in a sphere of volume $\frac{4\pi k_f^3}{3}$, the total number of orbitals N is

$2.\frac{\frac{4\pi k_f^3}{3}}{(\frac{2\pi}{l})^3} = \frac{Vk_f^3}{3\pi^2} = N$



Hence $k_f = (\frac{3\pi^2 N}{v})^{\frac{1}{3}}$.

But $\frac{N}{V}$=electron concentration.

Hence $E_f = \frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{\frac{2}{3}}$.

The electron velocity at the Fermi surface is $v_f = \frac{\hbar k_f}{m} = (\frac{\hbar}{m}).(\frac{3\pi^2 N}{V})^{\frac{1}{3}}$

$\Rightarrow v_f \propto (\frac{N}{V})^{\frac{1}{3}}$.

The Fermi temperature in Kelvin is given as $T_f = \frac{E_f}{k_B}$, where k_B is Boltzmann constant.

$T_f = \frac{1}{k_B}.\frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{\frac{2}{3}}$

$T_f \propto (\frac{N}{V})^{\frac{2}{3}}$

DENSITY OF STATE

The density of state is the number of orbitals per unit energy range.

From $E_f = \frac{\hbar^2}{2m}(\frac{3\pi^2 N}{V})^{\frac{2}{3}}$

$\Rightarrow N = \frac{V}{3\pi^2}(\frac{2mE}{\hbar^2})^{\frac{3}{2}}$.

Density of state $D(E) = \frac{dN}{dE}$.

$D(E) = \frac{V}{2\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}}E^{\frac{1}{2}}$.

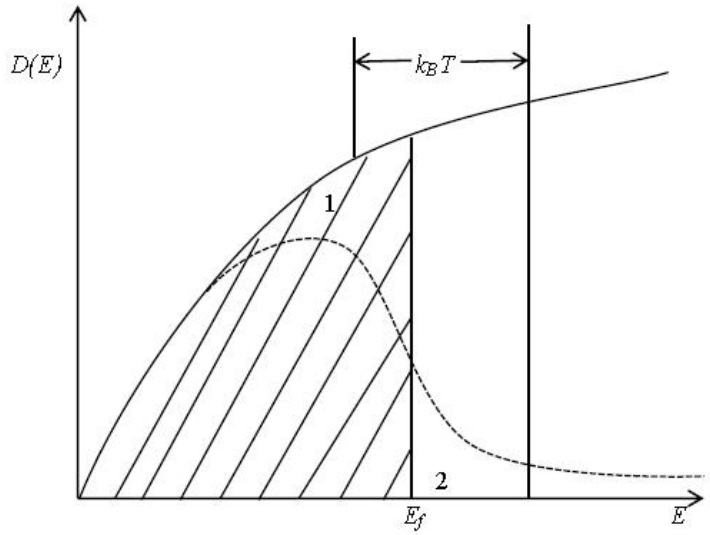
$\Rightarrow N = \frac{V}{3\pi^2}(\frac{2mE}{\hbar^2})^{\frac{3}{2}}$

$\frac{N}{E} = \frac{V}{3\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}}E^{\frac{1}{2}}$

$\frac{3N}{2E} = \frac{V}{2\pi^2}(\frac{2m}{\hbar^2})^{\frac{3}{2}}E^{\frac{1}{2}}$

$\frac{3N}{2E} = D(E)$

A graph of density of orbitals $D(E)$ against energy is of the form shown below:



The shaded area represents filled orbital at absolute zero (Fermi surface). A dashed curve represents density $f(E,T)D(E)$ of filled orbital at a finite temperature such that k_BT is small in comparison with E_f. The average energy is increased when the temperature is increased from 0 to T, for electrons thermally excited from region 1 to region 2.

FERMI DIRAC DISTRIBUTION FUNCTION

As seen earlier when electrons are filling the energy levels, two electrons occupy the lowest energy level, two or more the next level and the process continues until all the electrons in the metal have been accomodated. The distribution of electrons among the levels is best described by the distribution function $f(E)$ which is defined as the probability that the level E is occupied