

Lecture 2

In lecture 1 we started discussing the problem of many interacting electrons in a solid. To move ahead we need to recall some useful facts from single-particle quantum mechanics.

Consider free (no external potential) noninteracting electrons.

The SE for a single free electron is:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) = E \psi(\vec{r})$$

The solutions are plane waves,

$$\psi_{\vec{k}}(\vec{r}) \sim e^{i\vec{k} \cdot \vec{r}}$$

Corresponding energy $E_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}$

\vec{k} is a wavevector, $\hbar \vec{k}$ - momentum.

Sometimes will also call \vec{k} momentum.

It is convenient to assume we have a finite sample of volume $V = L^3$ (L - length in each direction) and impose periodic boundary conditions:

$$\psi_{\vec{k}}(x, y, z) = \psi_{\vec{k}}(x+L, y, z) \text{ - same for all other directions.}$$

This means that:

$$e^{i\vec{k}\cdot\vec{r}} = e^{i(k_x x + k_y y + k_z z)} = e^{i(k_x + L)x + i k_y y + i k_z z}$$

For this to be true we must have:

$$e^{i k_x L} = 1 \Rightarrow k_x L = 2\pi n_x$$

$$k_x = \frac{2\pi n_x}{L}, \quad n_x = 0, \pm 1, \pm 2, \dots$$

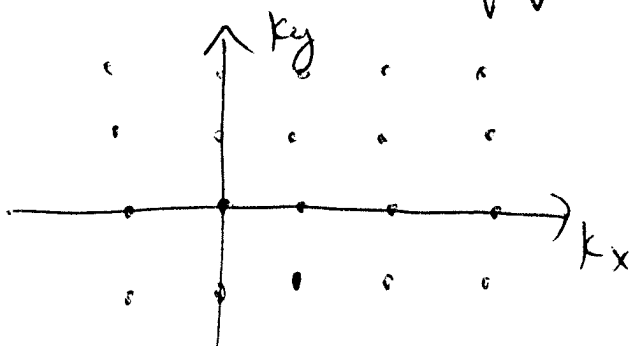
$$k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L}$$

Periodic b.c. in a finite volume lead to quantization of the values of momentum.

It is convenient to normalize the wavefunctions to unity in the sample volume:

$$\int d\vec{r} |\psi_k(\vec{r})|^2 = 1$$

$$\psi_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$



Volume per one allowed ~~state~~ state in momentum space is:

$$\frac{\pi}{L} \times \frac{\pi}{L} \times \frac{\pi}{L} = \frac{(\pi)^3}{V}$$

$$\sum_{\vec{k}} \leftrightarrow \int \frac{d\vec{k}}{(\pi)^3} = V \int \frac{d\vec{k}}{(\pi)^3}$$

$$\frac{1}{V} \sum_{\vec{k}} \leftrightarrow \int \frac{d\vec{k}}{(\pi)^3}$$

Now assume we have N free and still noninteracting electrons. let's ignore electron spin for now. ~~For example, it is possible to have~~

How do we write down the wavefunction of N ~~free~~ free noninteracting electrons!

The simplest guess:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \Psi_{k_1}(\vec{r}_1) \Psi_{k_2}(\vec{r}_2) \dots \Psi_{k_N}(\vec{r}_N)$$

$$|\Psi(\vec{r}_1, \dots, \vec{r}_N)|^2 = |\Psi_{k_1}(\vec{r}_1)|^2 \dots |\Psi_{k_N}(\vec{r}_N)|^2$$

This turns out to be wrong.

Electrons are fermions and all fermions are characterized by the following property:

$$\Psi(\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_N) = -\Psi(\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N)$$

Interchange of any two electrons leads to a sign change of the wavefunction.

It also means that electrons are indistinguishable.

Many-electron wavefunction must be totally antisymmetric must change sign under the interchange of any two coordinates.

Given this requirement, the correct way to write down ~~the~~ the wavefunction of N noninteracting electrons is the Slater determinant:

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(\vec{r}_1) & \dots & \psi_{k_1}(\vec{r}_N) \\ \vdots & & \vdots \\ \psi_{k_N}(\vec{r}_1) & \dots & \psi_{k_N}(\vec{r}_N) \end{vmatrix}$$

For example, $N=2$:

~~$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \psi_{k_1}(\vec{r}_1) & \psi_{k_1}(\vec{r}_2) \\ \psi_{k_2}(\vec{r}_1) & \psi_{k_2}(\vec{r}_2) \end{vmatrix}$~~

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{k_1}(\vec{r}_1) & \psi_{k_1}(\vec{r}_2) \\ \psi_{k_2}(\vec{r}_1) & \psi_{k_2}(\vec{r}_2) \end{vmatrix} =$$

$$= \frac{1}{\sqrt{2}} \left[\psi_{k_1}(\vec{r}_1) \psi_{k_2}(\vec{r}_2) - \psi_{k_1}(\vec{r}_2) \psi_{k_2}(\vec{r}_1) \right]^5$$

~~NOTE~~ Note ~~another~~ a very important property:

$$\text{If } k_1 = k_2 \quad \psi(\vec{r}_1, \vec{r}_2) \equiv 0.$$

More generally, if any two state labels are equal in a Slater determinant, it is identically zero.

This is Pauli principle: a given quantum state can be occupied by at most one electron.

It is a consequence of the antisymmetry of the many-electron wavefunction.

Now we can ask the question: what is the ground state of N free noninteracting electrons in volume V ?

As before, we assume periodic b.c.
The single-electron states are labelled by momentum $\vec{k} = \left(\frac{2\pi n_x}{L}, \frac{2\pi n_y}{L}, \frac{2\pi n_z}{L} \right)$ and spin \uparrow, \downarrow .

Now every momentum state can be occupied by no more than two electrons (one for each spin).

For a given total number of electrons N , momentum states will be filled up to some maximum momentum, which is called k_F - the Fermi momentum.

~~The volume~~ For free noninteracting electrons the eigenenergies are $E_k = \frac{\hbar^2 k^2}{2m}$ - isotropic in momentum space \Rightarrow the states will be filled isotropically, as a sphere.

The volume of filled states in momentum space is

$$\frac{4\pi k_F^3}{3} \quad \text{- volume of a sphere with radius } k_F.$$

The volume per momentum is ~~(the volume)~~ $\frac{(2\pi)^3}{V}$.

Since we have two electrons per each filled momentum state (one for each spin direction), we have:

$$2 \cdot \frac{4\pi k_F^3}{3} \frac{1}{\frac{(2\pi)^3}{V}} = \frac{V}{3\pi^2} k_F^3 = N$$

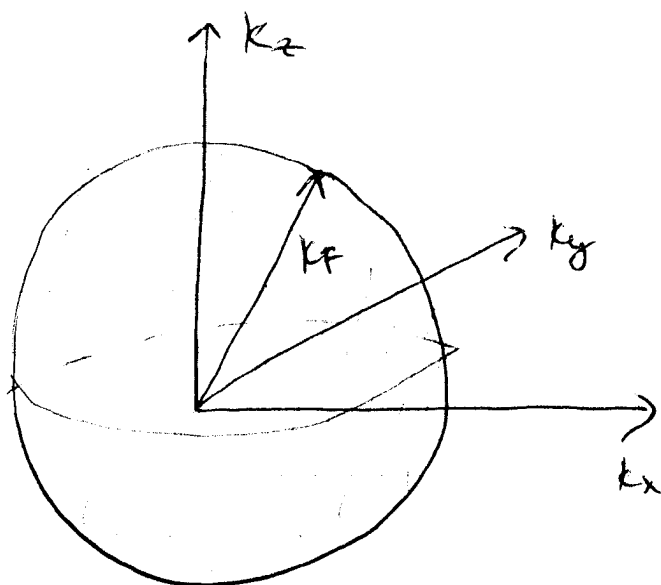
$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3} = (3\pi^2 n)^{1/3}$$

$$n = \frac{N}{V} \quad \text{- electron density.}$$

The corresponding energy:

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad \text{- Fermi energy.}$$

The highest energy of an occupied state.



The surface in momentum space that separates filled from unfilled states is called the Fermi surface (sphere in the case of free electrons).

The volume of the filled states is called Fermi sea.

The ground state of free noninteracting electrons is the Fermi sea.

~~However~~ We will see that even when interactions and crystal potential are included, ~~in many cases~~ in many cases the ground state is still the Fermi sea. Such states are often called Fermi liquids. Most metals are Fermi liquids.

Express k_F and E_F through the parameter r_s .

$$n = \frac{3}{4\pi r_s^3}$$

$$k_F = \left(3\pi^2 n \right)^{1/3} = \left(3\pi^2 \cdot \frac{3}{4\pi r_s^3} \right)^{1/3} = \left(\frac{9\pi}{4} \right)^{1/3} \frac{1}{r_s}$$

$k_F \sim \frac{1}{r_s}$ - recall uncertainty principle $\hbar k r \sim 1$.

Another way to look at this: the only parameter with the dimensions of length in a free electron gas is r_s . Any k_F , which has dimensions of inverse length, must be proportional to $\frac{1}{r_s}$.

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \sim \frac{\hbar^2}{m r_s^2} \sim 1 \text{ eV}.$$