Lecture 14

The Free Electron Gas: Density of States

Today:

1. Spin.

2. Fermionic nature of electrons.

3. Understanding the properties of metals: the free electron model and the role of Pauli's exclusion principle.

4. Counting the states in the Free-Electron model.

Questions you should be able to answer by the end of today's lecture:

1. Electron spin and it's implications for multi-electron wavefunctions.

2. Understand how to count the number of allowed eigenstates using the k-space graphic description.

3. What assumptions are used in the free electron model?

4. How do would you calculate the DOS? What is its significance?

What is Spin?

Spin is a property of a particle and does not change. The spin can be represented with a spin operator: $\hat{\vec{S}} = \left[\hat{S}_x, \hat{S}_y, \hat{S}_z \right]$

The properties of the spin operator are similar to those of angular momentum:

$$\left[\hat{S}_x, \hat{S}_y \right] = i\hbar \hat{S}_z$$

$$\left[\hat{S}_y, \hat{S}_z \right] = i\hbar \hat{S}_x$$

$$\left[\hat{S}_z, \hat{S}_x \right] = i\hbar \hat{S}_y$$

So akin to orbital angular momentum no two components of Spin can be measured simultaneously. However each of the components can be measured simultaneously with the length of the spin-vector:

$$\left[\hat{S}^2, \hat{S}_x \right] = 0$$

$$\left[\hat{S}^2, \hat{S}_y \right] = 0$$

$$\left[\hat{S}^2, \hat{S}_z \right] = 0$$

Similarly to angular momentum we pick z-component of Spin and then we can find the eigenvalues and eigenfunctions of the Spin vector length and the z-projection:

$$\hat{S}^2 \chi_{sm_s} = \hbar^2 s(s+1) \chi_{sm_s}$$

$$\hat{S}_z \chi_{sm_s} = \hbar m_s \chi_{sm_s}$$

s is a characteristic number for any particle and can take values: $s = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, \ldots$

m_s defines the direction of the spin vector and analogous to the magnetic quantum number can be positive or negative: $m_s = -s, -s+1, \ldots 0, \ldots, s-1, s$

For example for an electron: $s = \frac{1}{2}$, $m_s = \pm\frac{1}{2}$

s never changes for a particle and is rarely discussed. We will focus on m_s, which can change and switch sign. m_s is used to label states.

Example 1 Hydrogen atom: To label a particular electron state we need to include m_s:
$u_{n,l,m,m_s}(r,\theta,\varphi)$ To shorten the lengthy labeling the label vector $\alpha = (n,l,m,m_s)$ is used, so the state will be labeled as $u_\alpha(\vec{r})$.

Example 2 Periodic potential: To label a particular electron state we need to include m_s:
$\varphi_{n,k,m_s}(\vec{r})$. Here the label vector $\alpha = (n,k,m_s) \Rightarrow \varphi_{n,k,m_s}(\vec{r}) = \varphi_\alpha(\vec{r})$.

If we have many electrons in the system their eigenfunctions will be labeled as:
$u_{\alpha 1}(\vec{r}_1)$, $u_{\alpha 2}(\vec{r}_2)$,..., $u_{\alpha N}(\vec{r}_N)$ or for shortness: $u_{\alpha 1}(1)$, $u_{\alpha 2}(2)$,..., $u_{\alpha N}(N)$, where 1, 2... N is number of the electron.

But can we really distinguish electrons from each other experimentally? – Generally NO.

Definition:

Two particles are identical if their intrinsic properties are the same and we cannot set up an experiment to distinguish them.

In Quantum Mechanics we cannot distinguish between electron within the same potential.

Example: Collision
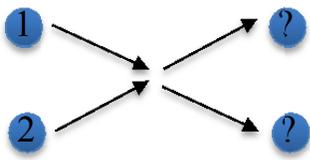
We cannot distinguish which particle started out as *1* and which started as *2* since all their measurable properties are identical.

So how do we construct a multi-particle wavefunction (wavevector) in a system where all particles look identical?

Symmetrization:

Only certain wavefunctions (wavevectors) can be used to describe a physical system, which consists of identical particles. These vectors are either _symmetric_ or _anti-symmetric_ with respect to particle permutation.

Particles that result in **symmetric** wavefunctions are called **Bosons**.
Particles that result in **anti-symmetric** wavefunctions are called **Fermions**.

What does it mean for a function to be _symmetric_ or _anti-symmetric_ with respect to particle permutation?

1. Let's consider an example of a wavefunction $\psi_s(\vec{r}_1, \vec{r}_2) = \psi_s(1,2)$ for two particles described by functions $\varphi_{\alpha i}(\vec{r}_i) = \varphi_{\alpha i}(i)$, where α_i are the state labels:

$$\psi_s(1,2) = \frac{1}{\sqrt{2}}\left(\varphi_{\alpha 1}(1)\varphi_{\alpha 2}(2) + \varphi_{\alpha 2}(1)\varphi_{\alpha 1}(2)\right)$$

So if we now swap 1 and 2, we'll see that the system wavefunction does not change:
$\psi_s(1,2) = \psi_s(2,1)$ **- this function is symmetric with respect to 1 to 2 swap.**

2. Let's consider another wavefunction $\psi_a(\vec{r}_1, \vec{r}_2) = \psi_a(1,2)$ for two particles described by functions $\varphi_{\alpha i}(\vec{r}_i) = \varphi_{\alpha i}(i)$, where α_i are the state labels:

$$\psi_s(1,2) = \frac{1}{\sqrt{2}}\left(\varphi_{\alpha 1}(1)\varphi_{\alpha 2}(2) - \varphi_{\alpha 2}(1)\varphi_{\alpha 1}(2)\right)$$

So if we now swap 1 and 2, we'll see that the system wavefunction changes sign:
$\psi_a(1,2) = -\psi_a(2,1)$ **- this function is anti-symmetric with respect to 1 to 2 swap.**

Note, that if $\alpha_1 = \alpha_2$, then $\psi_a(1,2) = 0$! This means that such system cannot exist!

Two Fermions cannot occupy the same state!

How do electrons get distributed within bands?

How many electrons per band?

What makes metal a metal and semiconductor a semiconductor?

All crystalline materials have energy bands and band gaps. It's the filling of those bands that defines whether the material will be a metal, a semiconductor or an insulator:

Figure removed due to copyright restrictions. Fig. 1: Kittel, Charles. *Introduction to Solid State Physics*. 8th ed. Wiley, 2004, p. 174.

In order to find out how bands get filled with electrons we need to consider two important concepts:

Density of states (D.O.S) – How many states per unit energy can our crystal provide?

Electron Distribution Function – Given the Fermionic nature of electrons how can we distribute them among the available states?

Let's first consider a Density of States function.

Free Electron Gas Density of States.

Let's start with metals, which can be approximated as a free space occupied with non-interacting electrons behaving like a gas – "Free electron Gas".

Gas of N independent free electrons in a volume V:
(Assuming periodic (Born - Von Karman) boundary conditions)

I The system

N electrons in a box of side **L** such that $V = L^3$

II The Hamiltonian

$$\hat{H}\left(\vec{r}_1, \vec{r}_2, ... \vec{r}_N\right) = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 = \sum_{i=1}^{N} \hat{H}_i$$

III Eigenvalues and eigenfunctions:

$$\hat{H}_i u_k\left(x, y, z\right) = E_k u_k\left(x, y, z\right)$$

$$u_k\left(x, y, z\right) = u_k\left(\vec{r}\right) = \frac{1}{V^{1/2}} e^{i\vec{k}\cdot\vec{r}}$$

$$\varepsilon_k = \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2m}$$

Important comment: recall that the functional form of the dispersion relation for the free particle is *parabolic* the discussion is relevant to other cases where the bands have a parabolic shape.

III Boundary condition: Born Von-Karman

$$u_k\left(x+L, y, z\right) = u_k\left(x, y, z\right)$$

$$u_k\left(x, y+L, z\right) = u_k\left(x, y, z\right)$$

$$u_k\left(x, y, z+L\right) = u_k\left(x, y, z\right)$$

The $\vec{k}$ vector in this case is the momentum ($\hbar\vec{k}$) and the energy eigenfunctions are correspondingly are the momentum eigenfunctions: $\hat{\vec{p}}u_k\left(\vec{r}\right) = -i\hbar\vec{\nabla}u_k\left(\vec{r}\right) = \hbar\vec{k}\cdot u_k\left(\vec{r}\right)$

We can also interpret the $\vec{k}$ vector as a wavevector: $\left|\vec{k}\right| = \frac{2\pi}{\lambda}$, where λ is the de-Broglie wavelength.

The application of the periodic boundary condition leads to the condition on $\vec{k}$:

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1$$

These conditions lead to the quantization of $\vec{k}$ vectors and the corresponding energies:

$$k_{x,y,z} = \frac{2\pi n_{x,y,z}}{L}$$

$$\varepsilon_k = \frac{\hbar^2 (2\pi)^2 \left(n_x^2 + n_y^2 + n_z^2 \right)}{2mL^2}$$

The quantization of the k number resulting from the boundary conditions, results in a finite number of states per unit length of $\left| \vec{k} \right|$.

For example in the 1D case the length of the Brillouin zone is: $\dfrac{2\pi}{a}$.

The separation between two **k** points is $\dfrac{2\pi}{L}$ thus the number of states in a band is:

$$N = 2\frac{2\pi/a}{2\pi/L} = 2\frac{L}{a} = 2 \times \text{ \# of unit cells in the crystal}$$

Enumerating the states

(2D $k_x - k_y$ plot introduction to $\vec{k}$ space – just an efficient way to display information)

The number of allowed points is just the volume of the **k**-space divided by the volume occupied per point.
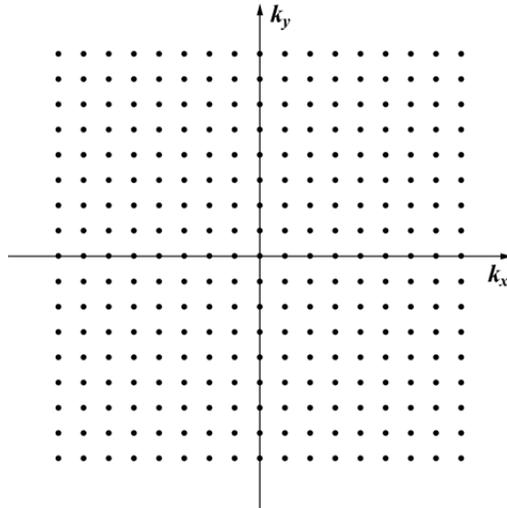
The region of **k**-space of volume Ω will contain **N** allowed **k** points or spatial states:

$$N_{spatial\ states} = \frac{\Omega}{\left(\dfrac{2\pi}{L} \right)^2} = \left(\frac{L}{2\pi} \right)^2 \Omega = DOS \times area$$

The factor $\left(\dfrac{L}{2\pi} \right)^2$ can be interpreted as the density of spatial states in **k**-space.

Density of Levels

A very useful number is the density of states (DOS) function it tells us the number of states that exist between energies ε and $\varepsilon + d\varepsilon$?

How do we calculate the density of states?

First it is important to realize that $\varepsilon(\vec{k}) = \varepsilon$ represents a surface of constant energy in k-space.

Once we know the surface shape we calculate calculate the volume enclosed between ε and $\varepsilon + d\varepsilon$.

For the free electron case, the surface of constant energy is simply a sphere with radius:

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow k = \sqrt{\frac{2mE}{\hbar^2}}$$
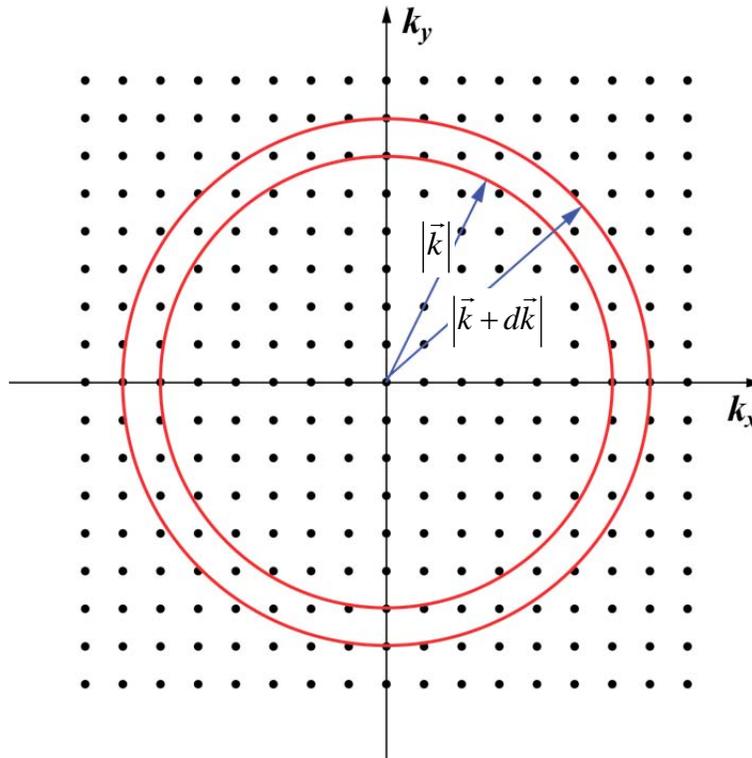
In 3D case we can count how many states fit inside the sphere of the radius k, remembering that each state occupies a volume of $(2\pi/L)^3$ we find:

$$N = 2\frac{4\pi k^3}{3} \cdot \frac{1}{\left(\dfrac{2\pi}{L}\right)^3} = \left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2} \frac{V}{3\pi^2} = N(\varepsilon)$$

The density of states function is then defined as: $\dfrac{dN}{d\varepsilon} = g(\varepsilon) = \dfrac{m}{\hbar^2 \pi^2}\sqrt{\dfrac{2m\varepsilon}{\hbar^2}}$

The number of one-electron levels in the energy range of $\varepsilon \to \varepsilon + d\varepsilon$ per unit volume is: $g(\varepsilon)d\varepsilon$

In general the density of states in a particular band is given by:

$$g_n(\varepsilon) = \frac{1}{4\pi^3} \int_{S_n(\varepsilon)} \frac{dS}{\left| \vec{\nabla}_k \varepsilon(k) \right|}$$

$$g(\varepsilon) = \sum_n g_n(\varepsilon)$$

We are now going to introduce N electrons into the system at T=0 and are going to ask what states are these electrons going to occupy? If there are many electrons they will fill a circle in 2D or a sphere in 3D, the surface of this sphere represents the electrons, which have the maximum energy, and also separates filled from unfilled states and is called the Fermi surface.

3.024 Electronic, Optical and Magnetic Properties of Materials
Spring 2013