10.95 – Lecture 18 Electronic structure of electrodes

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1. Free electron in d dimensions

From last lecture, we know that the number of states inside a d-dimensional region is just twice (spin up and down) the product of the volume of that region and density of states. Following relationship between electron energy E and wavevector k for free electron:

$$\frac{\hbar^2 k_E{}^2}{2m} = E$$

$$k_E = \sqrt{\frac{2mE}{\hbar^2}}$$

We will easily get N(E), which is the number of states inside a d-dimensional region, as well as g(E), which is number of states with energy between E and E+dE.

Interestingly, there is a strong dependence of N(E) and g(E) on the dimensionality d.

(1) d=3:

From last lecture, we prove that lattice spacing is $\dfrac{2\pi}{L}$, thus,

$$N_{(E)} = (\frac{4}{3}\pi k_E^3)2(\frac{2\pi}{L})^{-3} = (\frac{L^3}{3\pi^2})(\frac{2mE}{\hbar^2})^{3/2}$$

$$g_{(E)} = N'_{(E)} = (\frac{L^3}{2\pi^2})(\frac{2m}{\hbar^2})^{3/2}\sqrt{E} \propto \sqrt{E}$$

We also defined $f_{(E)}$ as the probability of an electron occupying an energy level E, and proved it follows the *Fermi-Dirac distribution*. Thus,

$$N_{(E)} = g_{(E)}f_{(E)}$$

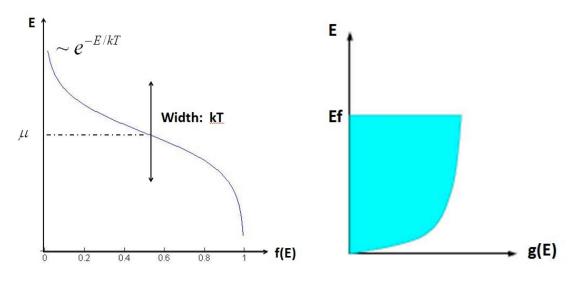$$where\ f_{(E)} = \frac{1}{1+e^{\frac{E-\mu}{kT}}}$$

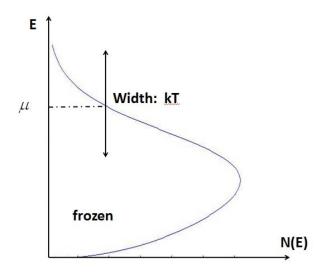Fig1. E vs. f(E) and E vs. g(E) in three dimensional case

Fig2. E vs. N(E) in three dimensional case

In Fig2 we can see that electrons at low energy levels are frozen, while those with energy around or above chemical potential are mobile or free electrons.

In three dimensional case, Fermi surface is a spherical surface:

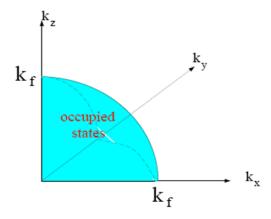$$E_f = \frac{\hbar}{2m}(\frac{3\pi^2 N}{L^3})^{2/3} \propto N^{2/3}$$

Figure 3. Fermi energy surface Ef in three dimensional case. States inside this surface are occupied at 0K.

(2) d=2:

In two dimensional case, the Fermi energy is a circle,

$$N_{(E)} = (\pi k_E^2)2(\frac{2\pi}{L})^{-2} = \frac{L^2 m}{\pi \hbar} E$$

$$g_{(E)} = N'_{(E)} = \frac{L^2 m}{\pi \hbar} = const$$

$$E_f = \frac{\pi \hbar}{L^2 m} N \propto N$$

Now g(E) is a constant, rather than square root dependence on energy E.

(3) d=1:

Similarly, we derive N(E) and g(E) in one dimensional case as follows:

$$N_{(E)} = (2k_E)2(\frac{2\pi}{L})^{-1} = \frac{L}{\pi}\sqrt{\frac{2mE}{\hbar}} \propto \sqrt{E}$$

$$g_{(E)} = N'_{(E)} = \frac{L}{2\pi}\sqrt{\frac{2m}{\hbar}}\frac{1}{\sqrt{E}} \propto \frac{1}{\sqrt{E}}$$

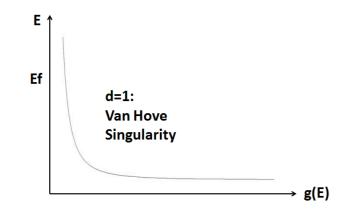Thus, energy diverges in 1d case, and shows *Van Hove Singularity*.

Figure 4. Van Hove Singularity of g(E) in 1 dimensional case

What is more, we can get a general conclusion about the Fermi energy, $E_f \propto N^{2/d}$

From the above comparison, we can see the dimension dependence of free electron gas.

2. Electrons in a crystal:

Considering the crystal structure, we start to include a periodic potential in the solid. $U(\vec{r}) = U(\vec{r} + \vec{R})$ $\vec{R} \in Bravais\ lattice$

Electrons move in this periodic potential, thus Schrodinger equation becomes:

$$[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})]\psi = H_{OP}\psi = E\psi$$

Bloch's theorem states that the wavefunctions of the one electron Hamiltonian

$H_{OP} = -\dfrac{\hbar^2}{2m}\nabla^2 + U(\vec{r})$ can be chosen to have the form of a plane wave times a function with

the periodicity of the lattice.

$$\psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\vec{r}} \cdot u_n(\vec{r})$$

$$where\ u_n(\vec{r}) = u_n(\vec{r} + \vec{R})$$

The subscript n (band index) refers to the nth state associated with the wavevector k.

An alternative form of the Bloch's theorem is:

$$\psi_{n\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k}\vec{R}} \cdot e^{i\vec{k}\vec{r}} \cdot u_n(\vec{r}) \ = \ e^{i\vec{k}\vec{R}} \cdot \psi_{n\vec{k}}(\vec{r})$$

If whole shifted by $\vec{R}$, we should have the same solution, because

$$P_{n\vec{k}}(\vec{r} + \vec{R}) = \left|\psi_{n\vec{k}}(\vec{r} + \vec{R})\right|^2 \ = \left|e^{i\vec{k}\vec{R}}\right|^2 \cdot \left|\psi_{n\vec{k}}(\vec{r})\right|^2 \ = \ P_{n\vec{k}}(\vec{r})$$

This means that there is equal probability of finding a given electron at r or at r+R, implying equal charge density at the two points.

Electronic band structure:

From Bloch's theorem, we can associate a wave-vector k with each energy state Enk of a periodic solid. It is often useful to plot a diagram of the energies Enk as a function of k, which is then referred to as the band structure of the given solid. The band structure for an electron in

free space is described by the parabola $E = \dfrac{\hbar^2 k^2}{2m}$.

The electron band structure is modified in several ways in a periodic solid. In particular, the wavevector k associated with a given state is no longer uniquely defined. If we make shift ψ in k vector here, we can see that

$$\psi_{\vec{k}+\vec{K}}(\vec{r}) = e^{i\vec{k}\vec{r}} \cdot e^{i\vec{K}\vec{r}} \cdot u_n(\vec{r})$$

$$\psi_{\vec{k}+\vec{K}}(\vec{r} + \vec{R}) = e^{i\vec{k}\vec{r}} \cdot e^{i\vec{K}\vec{r}} \cdot e^{i\vec{k}\vec{R}} \cdot e^{i\vec{K}\vec{R}} \cdot u_n(\vec{r})$$

where $\overrightarrow{K} \in reciprocal\ lattice\ vector$. Then energy that goes with it follows $E_n(\vec{k} + \vec{K}) = E_n(\vec{k})$

Thus, ψ and energy E will not change if we replace k by $k' = k + K = k + (2n\pi/R)$.

We start with plotting 1-D free electron band structure in free space ($U(\vec{r}) = 0$). If we plot in repeated zone scheme, we include on the plot all wavevectors k associated with a given energy state. But this contains lots of redundant information. Thus, we choose the wavenumber k for each state such that the magnitude of the wavenumber k is minimized, and plot in a reduced zone scheme only. That is replacing k by $k' = k - (2n\pi/R)$, where n is an integer chosen to limit k' to the interval $[-\pi/R, \pi/R]$. This reduced zone is widely referred to as *the first Brillouin zone*.
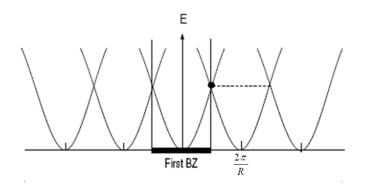

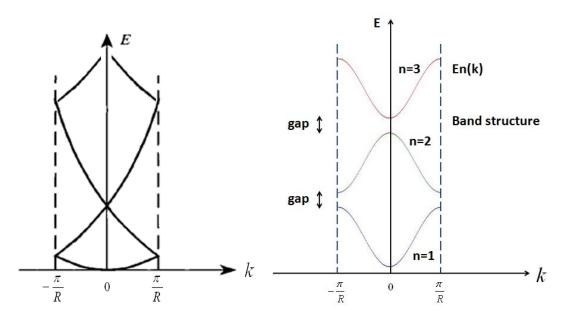Figure 5. One dimensional free electron band structure in repeated zone scheme

Figure 6. One dimensional band structure in the the first Brillouin zone.

(Left: free electron; Right: electron in periodic potential U(r))

When periodic potential $U(\vec{r}) \neq 0$, the band structures in the first Brillouin zone will split into several bands with gaps in between. Width of these gaps is proportional to the periodic potential $U(\vec{r})$. Those energy bands are allowable energy state bands. In the following, we will represent electron band structures using several half circles with gaps in between.

Band structures for metal, insulator and semiconductors:

Any solid has a large number of bands. Now, we define types of solids through their different electron band structures and Fermi energy.

First type is metal. There are two types of electrons in metal, free "conduction" electron which can flow freely and confined "core" electrons which are trapped by the nuclei. As shown below, metals contain a band that is partly empty and partly filled regardless of temperature, and Fermi energy sits in this band. Confined "core" electrons just below Ef will be easily excited to conductionand leads to conductivity of metal. Thus, metals have very high conductivity because g(E) is large near Ef.

Note that Ef is defined at T=0K, and chemical potential is defined at given temperature, thus, they are a little bit different.
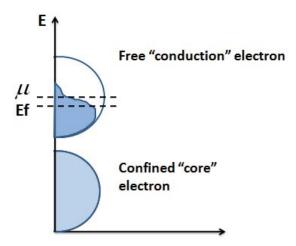

Figure 7. Band structure for metals.

The other two types of solids are insulator and semiconductor. Unlike for a metal, the Fermi level lies in between bands, thus separating them into full and empty bands at zero tempterature. The highest fully occupied band in an insulator or semiconductor is called the *valence band,* since these involve the highest-energy valence electrons of individual atoms, which tend to be bound on the nuclei (unlike a metal where they form extended states). The

lowest unoccupied band is called the *conduction band* because only when electrons are excited to the conduction band can current flow in these materials. Fermi energy sits in the gap between these two energy bands.

For insulators, two bands are far from each other and the energy gap is far greater than kT, and the external exciting energy. Thus, for insulator, there are no available states for valence electrons to jump up to the upper conduction band, and thus, insulator does not show any conductivity, except with very large energy input (e.g. by a large applied voltage).
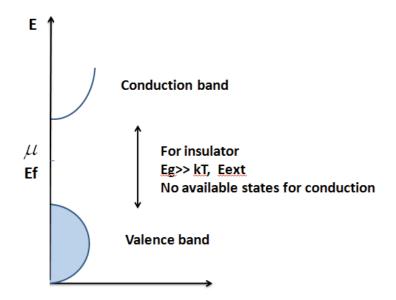

Figure 8. Band structure for insulators.

The difference between semiconductors and insulators is only that the forbidden band gap between the valence band and conduction band is smaller in semiconductor. Although Eg is still larger than kT, but they are of the order of several volts, which might be less than the available external exciting energy. Thus, electrons in the valence band might be excited onto the conduction band, and leave a positive hole in valence band.
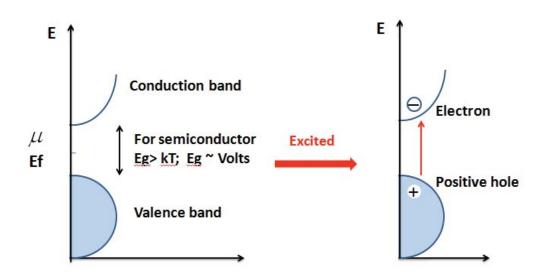
Figure 9. Band structure for semiconductor and the schematic representation of electron excitation.

As we can see, band gap is one of the most useful aspects of the band structure, as it strongly influences the electrical property of the material. Electrons can transfer from one band to the other by means of carrier generation and recombination processes. What is more, defect states can also contribute to conductivity in semiconductor.

Defect states usually sit in the band gap. If it is near the valence band, we call it "acceptor", which can receive excited electrons from the valence band, because the energy difference between acceptor and the conduction band is small. If the defect state is near the conduction band, we call it "donor". Electrons in the donor will be easily excited into the conduction band because the energy difference is very small between donor and conduction band. Thus, defect states created in the band gap by doping can be used to create semiconductor devices.
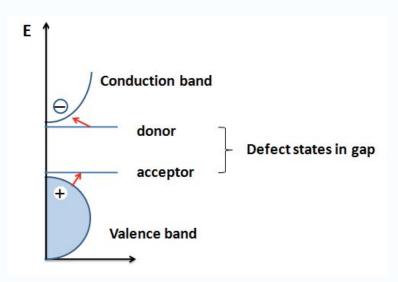

Figure 10. Contribution of defect states in gaps for conductivity of semiconductor.

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