§5.2 Weak potential approximation.

This is a next level approximation to description the properties the gas of free electrons. Let's use the one dimensional crystal to simplify the calculations. The main goal is to understand how the weak periodic potential affects the physical properties of free electrons.

Generally this task is an eigenvalue problem for Hamilton operator (Schrodinger equation):

$$\hat{H}\varphi = E\varphi \tag{1}$$

Let's for simplification assume that crystal is one dimensional. In one dimensional case:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx}\varphi(x) + U(x)\cdot\varphi(x) = E\cdot\varphi(x) \tag{2}$$

Here U-is a weak periodical function of potential energy but only for one electron. The one-electron approximation is applicable due to the non interactive of electrons. In framework of this approximation free electrons move in the potential created only by nuclei periodically located at the lattice sites. It is important to note that the temperature of the crystal is zero, which means that the nuclei motionless. The weakness of the potential means that its influence can be estimated within the framework of perturbation theory.

The periodical lattice and nuclei location is looks like follows:

Figure 7
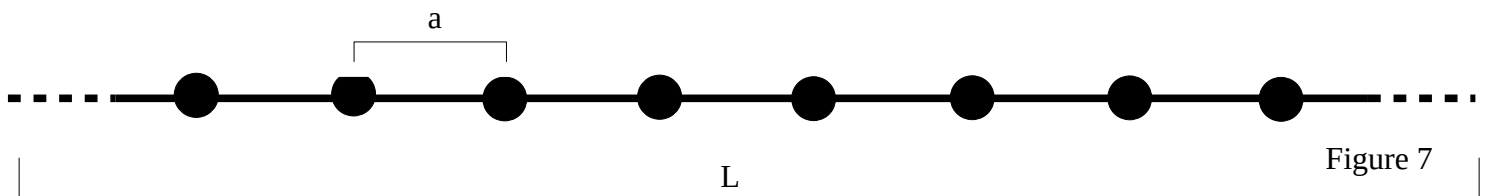
Here a-unit cell length and L-total length of lattice. For the periodical boundary conditions we have relation:

$$L = N\cdot a \quad \text{, here N-total number of unit cells} \tag{3}$$

In this case, the potential energy U (x) satisfies the relation

$$U(x) = U(x + n*a) = U(x + L). \tag{4}$$

The solution of equation (2) I start searching from zero potential approximation (potential satisfy to (5.1/30) but equal to zero). The corresponding solution was already found (5.1/15):

Wave function (Eigenfunction) $\quad \varphi_{k_x}(x) = \frac{1}{\sqrt{L}}e^{ik_x x}$,

Energy (Eigenvalues) $\quad E(k_x) = \frac{\hbar^2 k_x^2}{2m}$ $\qquad\qquad$ (5)

Wave vectors $\quad k_x = \frac{2\pi}{L}n_x, \ n_x \in Z$

We'll use the replacements $n_x = n$ and $k_x = k$. Some remarks about wave vector $\quad k = \frac{2\pi}{L}n = \frac{2\pi}{a}\frac{n}{N}, n\in Z$ and N-total number of equivalent unit cells.

According to Bloch's theorem, the wave functions of electrons in a periodic structure must satisfy an additional condition. Due to the periodicity of the crystal, the calculated value of the physical quantity at the equivalent points of different elementary cells must be the same. The square of the wave function should also have the same property. This means that the wave function in an ideal crystal can be represented as follows:

$$\varphi(\vec{r},\vec{k})=A\cdot u(\vec{r},\vec{k})\cdot e^{i\vec{r}\cdot\vec{k}} \quad \text{but}$$

according to Bloch theorem $\quad |\varphi(\vec{r},\vec{k})^2|=A^2\cdot u(\vec{r},\vec{k})^2=|\varphi(\vec{r}+\vec{R}_n,\vec{k})^2|=u(\vec{k},\vec{r}+\vec{R}_n)^2\quad$ this means that $\quad u(\vec{r},\vec{k})$ must be periodic with the translation vector of the crystal $\quad u(\vec{r},\vec{k})=u(\vec{r}+\vec{R}_n,\vec{k})\quad$. This means that wave function is periodical not only in real lattice with vector of translation $\quad a\cdot n, n\in Z\quad$ but in the reciprocal lattice too with vector of translation $\quad b_g=\dfrac{2\pi}{a}g, g\in Z\quad$. It can be seen from (6) that it makes sense to take into account only nonequivalent values for the wave vectors located in the region of values from $\quad -\dfrac{\pi}{a}\quad$ to $\quad +\dfrac{\pi}{a}\quad$ and the total number of k-vector values inside of this region is N. Due to this property of periodicity the energy must also be periodic in the reciprocal lattice:

$$E(k)=\frac{\hbar^2(k+b_g)^2}{2m}=\frac{\hbar^2\left(k+\dfrac{2\pi}{a}\cdot g\right)^2}{2m}, g\in Z \quad \text{see figures 8 and 9} \tag{6}$$
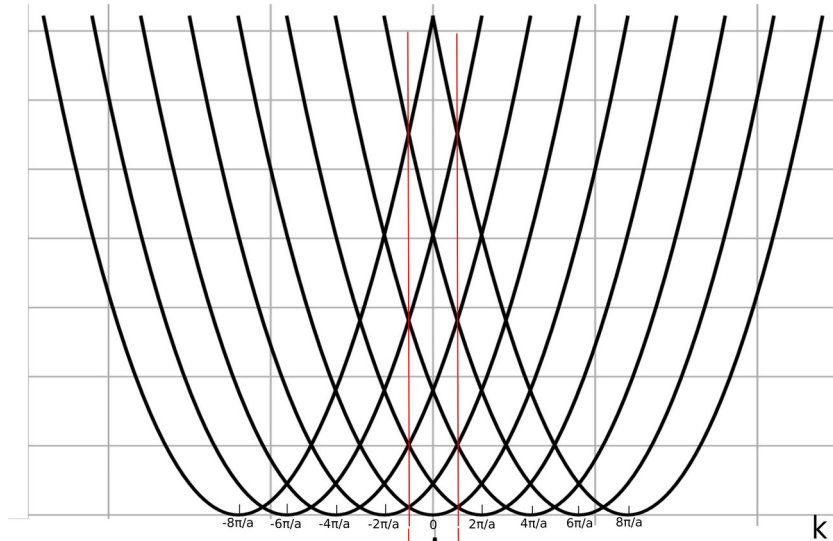

Figure 8

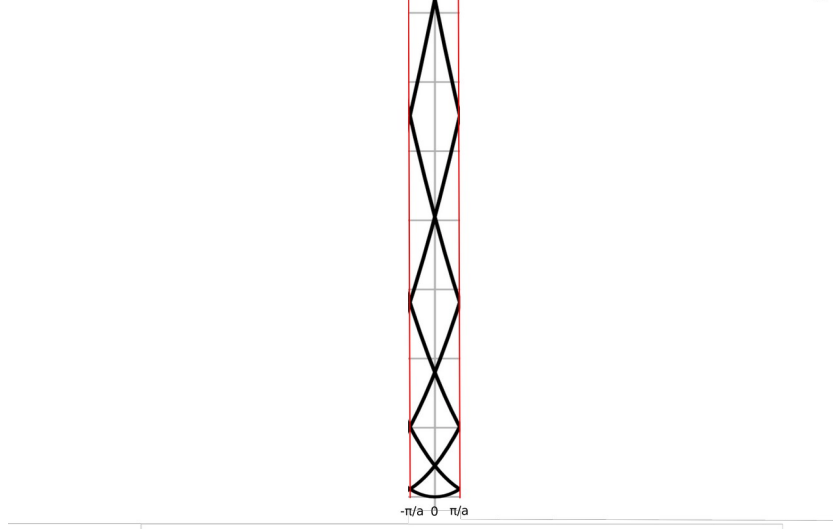Energy bands located outside the [-π/a,+π/a] area can be reflected back into it.
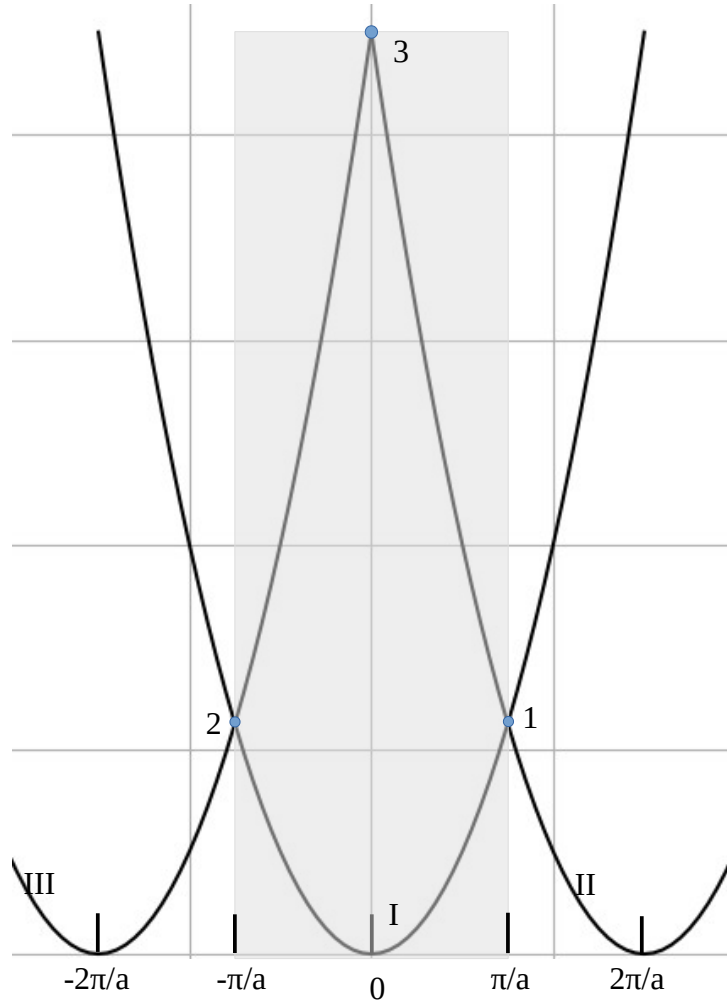

Figure 9

Figure 10

As you see on Figure 9 the energy of free electrons in empty crystal (nuclei are exist but but not create the periodic potential) can be presented as a set of energy bands $E_m(k_x)$, here **m** is number of band (total number of different bands is infinitely large). But our model is oversimplified. In fact, electrons move in a periodic potential created by nuclei.

Let's take into the account the influence of weak periodic potential. It is enough to consider the behavior of the energy at the points of intersection of the energy curves 1,2,3,…(Figure 10) and so on (periodically shifted curves I,II,III,... and so on).

Let's start from points number 1 and 2. This point is doubly degenerate it means that we have two different states with the same energy. Corresponding wave functions:

$$\varphi_1(x)=\frac{1}{\sqrt{L}}e^{i\frac{\pi}{a}x} \text{ and } \varphi_2(x)=\frac{1}{\sqrt{L}}e^{-i\frac{\pi}{a}x} \quad . \tag{7}$$

The Schrodinger equation for perturbed model is looks like so:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx}\varphi(x)+U(x)\cdot\varphi(x)=(E_0+E')\cdot\varphi(x) \tag{8}$$

Here, E_0 is energy for non perturbed model (2) , E' – correction of energy which can be calculated by perturbation theory for degenerate states and U(x) - weak periodical potential creating by nuclei. In our case we can choose a harmonic function as periodic potential with period "a" (to simplify calculations) :

$$U(x) = U_0 \cos\left(\frac{2\pi}{a} x\right) \tag{9}$$

The correction for energy E' we can calculate from the determinant:

$$\begin{vmatrix} V_{11} - E' & V_{12} \\ V_{21} & V_{22} - E' \end{vmatrix} = 0 \tag{10}$$

Here $V_{11}, V_{12}, V_{21}, V_{22}$ are corresponding matrix elements for perturbation potential:

$$V_{11} = N \int_0^a \varphi_1(x) U(x) \varphi_1(x) dx \tag{11}$$

$$V_{12} = N \int_0^a \varphi_1(x) U(x) \varphi_2(x) dx \tag{12}$$

$$V_{21} = N \int_0^a \varphi_2(x) U(x) \varphi_1(x) dx \quad \text{г.} \tag{13}$$

$$V_{22} = N \int_0^a \varphi_2(x) U(x) \varphi_2(x) dx \tag{14}$$

This integrals can be calculated directly by using expression $\int \cos^2(x) dx = \frac{x}{2} + \frac{\sin(2x)}{4}$:

$$V_{11} = V_{22} = N \int_0^a \varphi_1(x) U(x) \varphi_1(x) dx = \frac{N}{L} \int_0^a e^{i\frac{\pi}{a}x} U_0 \cos\left(\frac{2\pi}{a}x\right) e^{-i\frac{\pi}{a}x} dx = \frac{1}{a} U_0 \int_0^a \cos\left(\frac{2\pi}{a}x\right) dx = 0$$

$$V_{12} = V_{21} = N \int_0^a \varphi_1(x) U(x) \varphi_2(x) dx = \frac{N}{L} \int_0^a e^{i\frac{\pi}{a}x} U_0 \cos\left(\frac{2\pi}{a}x\right) e^{i\frac{\pi}{a}x} dx = \frac{1}{a} U_0 \int_0^a \cos\left(\frac{2\pi}{a}x\right) e^{i\frac{2\pi}{a}x} dx = \frac{U_0}{2}$$

After replacement to (11) :

$$(E')^2 = \frac{U_0^2}{4} \text{ and for corrections of energy } E'_{1,2} = \pm \frac{U_0}{2} \tag{15}$$

As you can see, a weak periodic potential eliminates the degeneracy at the boundary and in the center of the Brillouin zone (points 1,2,3... and so on) see Figure 11. One curve goes up and the other goes down, which leads to the appearance of a forbidden zone. The width of the band gap E_g depends on the strength of the periodic potential. The band structure (dependence energy of free electrons moving in weak periodical potential) for first 4 energy zone you can see on Figure 12.

It is clear that for real 3-D crystals electron energy depend on three parameters $E_n(k_x . k_y . k_z)$ - here n-number of energy zone (energy band) and [k_x k_y k_z] projections of wave vector and looks more complicated than in the case of the one-dimensional weak potential model.

On Figure 13 you can see the band structure for Si and Ge in some symmetrical directions for wave vectors. All zones with energy less than 0 eV is filled by electrons (valence zones). Zones with energy over 0 eV not filled are free (conducting zones). Forbidden band located between the upper valence and lower conduction bands.

For Ge the maximum of upper valence zone (HOMO) and minimum of conducting zone (LUMO) is located in center of Brillouin zone (Γ point where $k_x = k_y = k_z = 0$). This means that forbidden zone is direct with the width 0.8 eV. The Fermi level located at zero energy for both crystals.
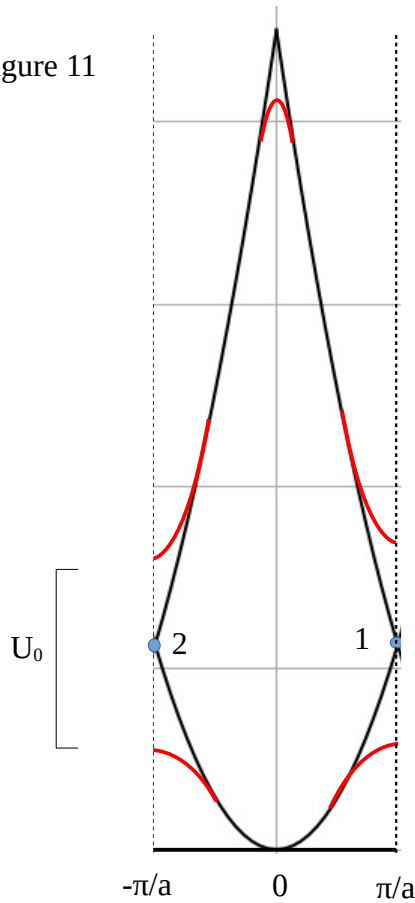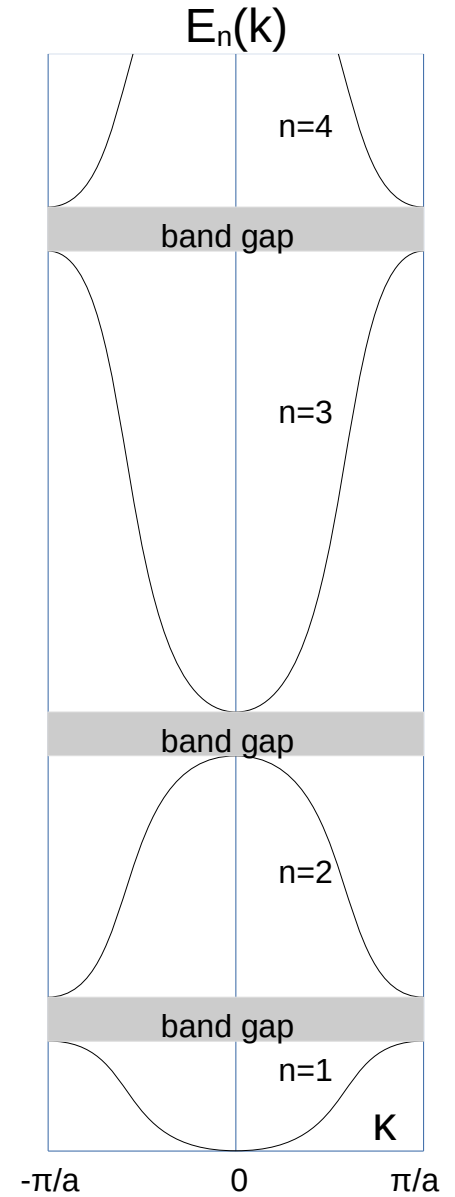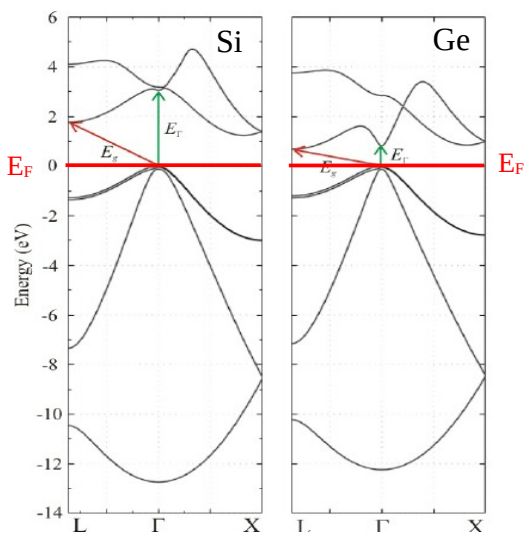
Figure 11

Figure 12

Figure 13

For Si the maximum of upper valence zone (HOMO-Highest Occupied Molecular Orbital) and minimum of conducting zone (LUMO-Lowest Unoccupied Molecular Orbital) is located in different points of Brillouin zone. This means that forbidden zone is non direct with the width 1.1 eV.

In Table you can see the band gap width for different semiconductors and insulators.

Material	Symbol	Eg (eV)	
		T = 0 K	T = 300 K
Silicon	Si	1.17	1.11
Germanium	Ge	0.74	0.66
Indium antimonide	InSb	0.23	0.17
Indium arsenide	InAs	0.43	0.36
Indium phosphide	InP	1.42	1.27
Gallium nitride	GaP	2.32	2.25
Gallium arsenide	GaAs	1.52	1.43
Gallium antimonide	GaSb	0.81	0.68
Cadmium selenide	CdSe	1.84	1.74
Cadmium telluride	CdTe	1.61	1.44
Zinc oxide	ZnO	3.44	3.2
Zinc sulfide	ZnS	3.91	3.6
Sodium Chloride	NaCl	8.97	
Calcium fluoride	CaF	12.1	

The band gap values tend to decrease with increasing temperature. This behavior is associated with a decrease in the overlap of wave functions due to the thermal expansion of matter.
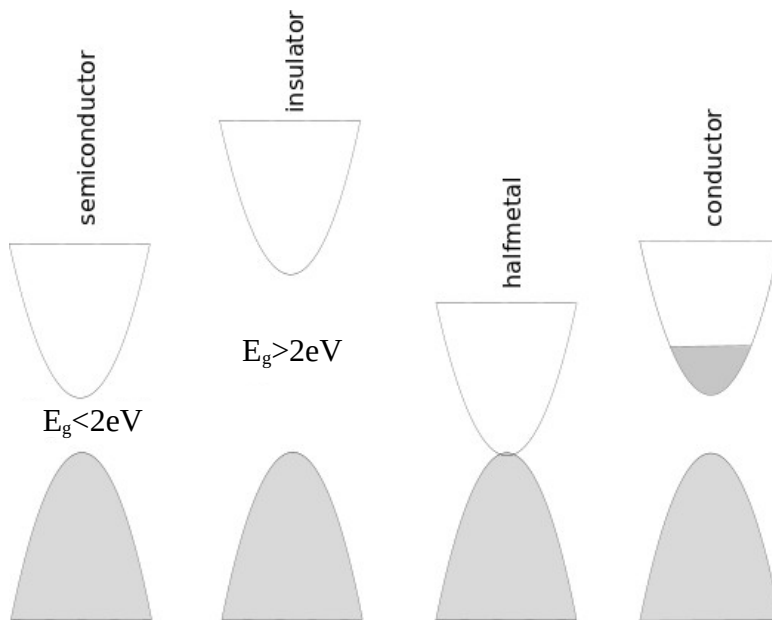
The electrical conductivity of materials depends on the shape of the energy zones and their filling (see Figure 14).

We assume there are two energy zones. For **semiconductors** and **dielectrics**, the lower band is completely filled, and the upper one is not filled at T = 0. Different semiconductors and dielectrics depend on the band gap. It is clear that this division is pretty conditional.

For **metals** (**conductors**) energy zone is partially filled .

In **half-metals**, the valence band for one spin orientation is partially filled while there is a gap in the density of states for the other spin orientation. This results in conducting behavior for only electrons in the first spin orientation. It is clear that half-metals are rather exotic materials.

semiconductor

insulator

halfmetal

conductor

$E_g > 2eV$

$E_g < 2eV$

Figure 14