Solution of homework # 12

Exercise 1 – Tight-binding method for single atomic s-level

1. In a simple cubic Bravais lattice there are six nearest neighbours $\boldsymbol{R}$ that are located, with respect to the origin, at $(\pm a, 0, 0)$, $(0, \pm a, 0)$ and $(0, 0, \pm a)$ (Fig.1). Because $\gamma(\boldsymbol{R}) = \gamma$ we get:

$$
\begin{aligned}
E(k_x, k_y, k_z) &= E_s - \beta - \gamma \sum_{\text{n.n.}} \cos(\boldsymbol{k} \cdot \boldsymbol{R}) \\
&= E_s - \beta - 2\gamma[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)], \qquad (1)
\end{aligned}
$$

where the factor 2 derives from the fact that cosine is an even function.

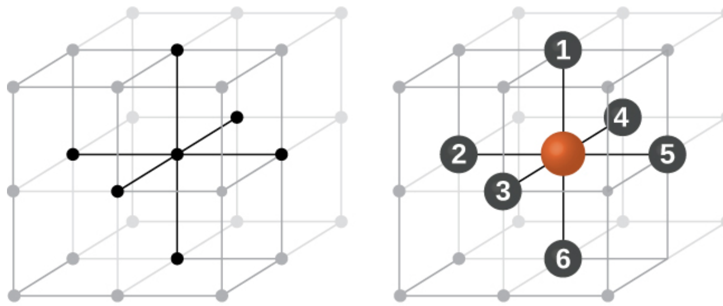

Figure 1: Nearest neighbours in simple cubic lattice.

2. First of all, let us calculate the gradient of the band dispersion written above:

$$
\frac{1}{\hbar} \frac{\partial E(k_x, k_y, k_z)}{\partial \boldsymbol{k}} = \frac{2\gamma a}{\hbar} \big(\sin(k_x a), \sin(k_y a), \sin(k_z a) \big) \qquad (2)
$$

Therefore we have to find for which wavevectors the condition $\sin(k_x a) = \sin(k_y a) = \sin(k_z a) = 0$ is satisfied. We easily find that this condition happens at $k_i = \pm \frac{n\pi}{a}$ $(i = x, y, z)$ with n being an integer. So any $\boldsymbol{k}^* = (k_x, k_y, k_z)$ from points $(0, 0, 0)$, $(\pm\pi/a, \pm\pi/a, \pm\pi/a)$, $(\pm\pi/a, 0, 0)$,$(0, \pm\pi/a, 0)$,$(0, 0, \pm\pi/a)$, $(0, \pm\pi/a, \pm\pi/a)$,$(\pm\pi/a, 0, \pm\pi/a)$, $(\pm\pi/a, \pm\pi/a, 0)$ can give zero velocity. Note that these points are the high symmetry points in the reciprocal lattice of simple cubic (Fig.2).

3. Let us calculate the effective mass at $\Gamma = (0, 0, 0)$ along k_x, k_y and k_z:

$$
\begin{aligned}
\frac{1}{m_x^\star} &= \frac{1}{\hbar^2} \frac{\partial^2 E(k_x, k_y, k_z)}{\partial k_x^2}\Big|_{\boldsymbol{k}=\Gamma} = \frac{2\gamma a}{\hbar^2} \frac{\partial \sin(k_x a)}{\partial k_x}\Big|_{k_x=0} = \frac{2\gamma a^2}{\hbar^2} \cos(k_x a)\big|_{k_x=0} = \frac{2\gamma a^2}{\hbar^2} \\
\frac{1}{m_y^\star} &= \frac{1}{\hbar^2} \frac{\partial^2 E(k_x, k_y, k_z)}{\partial k_y^2}\Big|_{\boldsymbol{k}=\Gamma} = \frac{2\gamma a}{\hbar^2} \frac{\partial \sin(k_y a)}{\partial k_y}\Big|_{k_y=0} = \frac{2\gamma a^2}{\hbar^2} \cos(k_y a)\big|_{k_y=0} = \frac{2\gamma a^2}{\hbar^2} \\
\frac{1}{m_z^\star} &= \frac{1}{\hbar^2} \frac{\partial^2 E(k_x, k_y, k_z)}{\partial k_z^2}\Big|_{\boldsymbol{k}=\Gamma} = \frac{2\gamma a}{\hbar^2} \frac{\partial \sin(k_z a)}{\partial k_z}\Big|_{k_z=0} = \frac{2\gamma a^2}{\hbar^2} \cos(k_z a)\big|_{k_z=0} = \frac{2\gamma a^2}{\hbar^2}
\end{aligned}
$$

As we could have guessed from the cubic symmetry of the lattice the effective mass is isotropic, that is $m_x^* = m_y^* = m_z^*$. So we have found that $\boxed{m_i^* = \hbar^2/2\gamma a^2}$ for $i = x, y, z$.

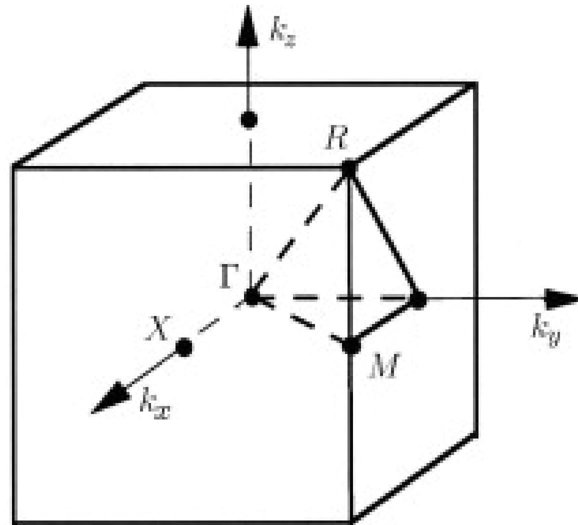

Figure 2: High symmetry points in the reciprocal lattice of simple cubic lattice.

In order to have $m_i^* < m_e$ ($m_e = 9.11 \times 10^{-31}$ Kg is the free electron mass) we need to have that $\gamma > \hbar^2/2m_e a^2$. By setting $a = 2$ Å, we then obtain that the minimum value of γ such that $m_i^* < m_e$ is

$$\gamma_{\text{min}} = \frac{\hbar^2}{2m_e a^2} = \frac{1.055 \times 10^{-34} \text{ J} \cdot \text{s} \cdot 6.582 \times 10^{-16} \text{ eV} \cdot \text{s}}{2 \cdot 9.11 \times 10^{-31} \text{ Kg} \cdot 4 \times 10^{-20} \text{ m}^2} \simeq 0.95 \text{ eV} \tag{3}$$

Knowing that the dimension of Joule is ML^2T^{-2}.

4. Because $k_y = k_z = 0$ we need to plot the function:

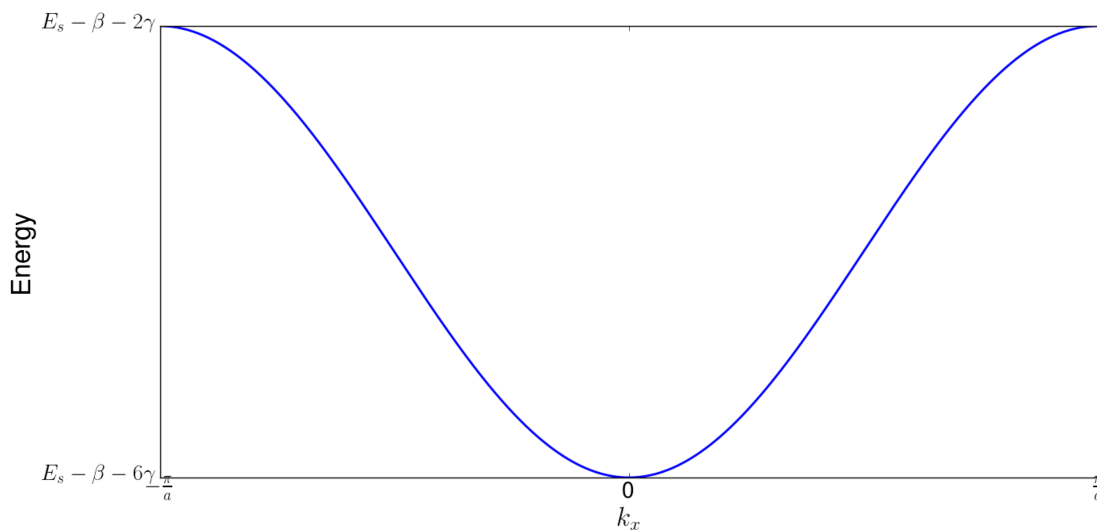

Figure 3: Energy dispersion of the tight-binding band along the direction in the Brillouin zone specified by eq. 4. The point at the center is $\Gamma = (0, 0, 0)$ while the point at the border is called $X = (\pi/a, 0, 0)$.

$$E(k_x, 0, 0) = E_s - \beta - 4\gamma - 2\gamma\cos(k_x a) \qquad -\frac{\pi}{a} < k_x < \frac{\pi}{a} \tag{4}$$

$E(\Gamma) = E_s - \beta - 6\gamma$ and $E(X) = E_s - \beta - 2\gamma$. So the bandwidth along this direction of the Brillouin zone is $E(X) - E(\Gamma) = 4\gamma$.
It is a general feature of the tight-binding model that the bandwidth is proportional to the overlap integral γ. And we notice that the smaller the overlap, the narrower the band.

Exercise 2 - Intrinsic semiconductors

1. For an intrinsic semiconductor each electron in the conduction band results from the thermal excitation of an electron from the valence band and thus leaves a hole behind. As a consequence the density of electrons and holes has to be the same:

$$n_c(T,\mu) = p_v(T,\mu) \ . \tag{5}$$

2. Substituting the expressions for n_c and p_v we find

$$\begin{aligned}
\frac{1}{4}\left(\frac{2m_c k_B T}{\pi\hbar^2}\right)^{3/2} e^{-\frac{\varepsilon_c-\mu_i}{k_B T}} &= \frac{1}{4}\left(\frac{2m_v k_B T}{\pi\hbar^2}\right)^{3/2} e^{-\frac{\mu_i-\varepsilon_v}{k_B T}} \\
m_c^{3/2} e^{-\frac{\varepsilon_c-\mu_i}{k_B T}} &= m_v^{3/2} e^{-\frac{\mu_i-\varepsilon_v}{k_B T}} \\
e^{\frac{2\mu_i}{k_B T}} &= \left(\frac{m_v}{m_c}\right)^{3/2} e^{\frac{\varepsilon_c+\varepsilon_v}{k_B T}} \\
\mu_i(T) &= \frac{\varepsilon_c+\varepsilon_v}{2} + \frac{3}{4}k_B T \log\left(\frac{m_v}{m_c}\right) = \varepsilon_v + \frac{E_g}{2} + \frac{3}{4}k_B T \log\left(\frac{m_v}{m_c}\right)
\end{aligned} \tag{6}$$

where $E_g = \varepsilon_c - \varepsilon_v$ is the energy gap. In the expression above, the subscript i stands for *intrinsic*, i.e. this is the chemical potential in the intrinsic case.

3. At $T = 0$ the intrinsic chemical potential is $\mu_i(T=0) = (\varepsilon_v + \varepsilon_c)/2$ and so it is exactly in the middle of the gap. At any temperature the shift in chemical potential with respect to its zero-temperature value is given by $\Delta\mu = \frac{3}{4}k_B T \log(\frac{m_v}{m_c})$. Its sign thus depends on the ratio between the valence and conduction effective masses. In the case of GaAs $m_v/m_c \simeq 8.1 > 1$, so that $\Delta\mu$ is positive. In particular at $T = 300$ K we have $\Delta\mu \simeq 0.041$ eV. This value is much smaller than the gap of GaAs. This means that μ_i remains close to the middle of the gap and thus far from the conduction and valence band edges.

4. The intrinsic carrier density of electrons and holes for an intrinsic semiconductor is given by:

$$n_i = 2.5\left(\frac{m_c}{m}\right)^{\frac{3}{4}}\left(\frac{m_v}{m}\right)^{\frac{3}{4}}\left(\frac{T}{300\,\mathrm{K}}\right)^{\frac{3}{2}} e^{-\frac{E_g}{2k_\mathrm{B}T}} \cdot 10^{19}\ \mathrm{cm}^{-3} \tag{7}$$

For silicon at room temperature we find that the intrinsic carrier density is

$$n_i \simeq \sqrt{6}\cdot 2.5\cdot(0.3)^{\frac{3}{4}}\cdot(0.55)^{\frac{3}{4}}\cdot e^{-\frac{1.12}{0.05}}\cdot 10^{19}\ \mathrm{cm}^{-3} \simeq 2.96\cdot 10^{9}\ \mathrm{cm}^{-3}. \tag{8}$$

where the factor $\sqrt{6}$ in front comes from the fact that in silicon there are six equivalent conduction band minima and the carrier density is proportional to the square root of the density of available states (see lecture notes).