Department of physics, NTNU
TFY4340 Mesoscopic Physics
Spring 2010

Solution to Exercise 2

Question 1

Apart from an adjustable constant, the nearest–neighbour (nn) tight–binding (TB) band structure for the 2D triangular lattice is

$$E(k_x, k_y) = \gamma \sum_{j=1}^{3} \left(e^{i\boldsymbol{k}\cdot\boldsymbol{R}_j} + e^{-i\boldsymbol{k}\cdot\boldsymbol{R}_j} \right),$$

with nn lattice vectors

$$\begin{aligned}
\boldsymbol{R}_1 &= a\hat{x} \\
\boldsymbol{R}_2 &= \frac{a}{2}\hat{x} + \frac{\sqrt{3}a}{2}\hat{y} \\
\boldsymbol{R}_3 &= \frac{a}{2}\hat{x} - \frac{\sqrt{3}a}{2}\hat{y}
\end{aligned}$$

Thus, ensuring that $E(0) = 0$,

$$\begin{aligned}
E(k_x, k_y) &= -6\gamma + 2\gamma \left(\cos k_x a + \cos \frac{k_x a + \sqrt{3}k_y a}{2} + \cos \frac{k_x a - \sqrt{3}k_y a}{2} \right) \\
&= -6\gamma + 2\gamma \left(\cos k_x a + 2\cos \frac{k_x}{2} \cos \frac{\sqrt{3}k_y a}{2} \right) \\
&= -8\gamma + 4\gamma \cos \frac{k_x a}{2} \left(\cos \frac{k_x a}{2} + \cos \frac{\sqrt{3}k_y a}{2} \right)
\end{aligned}$$

Here, we have used the trigonometric identities $\cos(a+b) + \cos(a-b) = 2\cos a \cos b$ and $\cos 2a = 2\cos^2 a - 1$.

With $\boldsymbol{b}_i \cdot \boldsymbol{a}_j = 2\pi\delta_{ij}$, one finds reciprocal lattice vectors

$$\begin{aligned}
\boldsymbol{b}_1 &= \frac{2\pi}{a}\left(\hat{x} - \frac{1}{\sqrt{3}}\hat{y} \right) \\
\boldsymbol{b}_2 &= \frac{2\pi}{a}\frac{2}{\sqrt{3}}\hat{y}
\end{aligned}$$

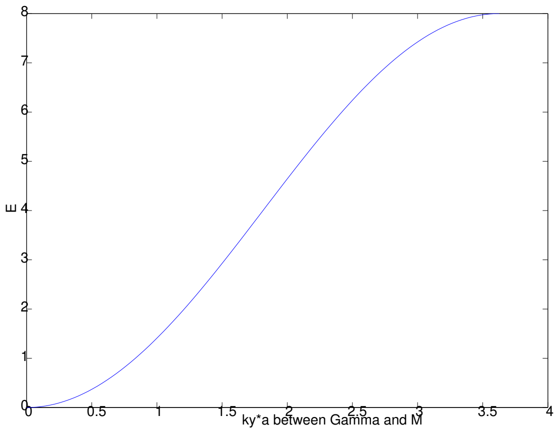
so the reciprocal lattice is also triangular, with "nearest–neighbour distance" $b = b_1 = b_2 = 4\pi/\sqrt{3}a$. The six M–points are located at the midpoints of the edges of the hexagonal 1BZ, one of them is:

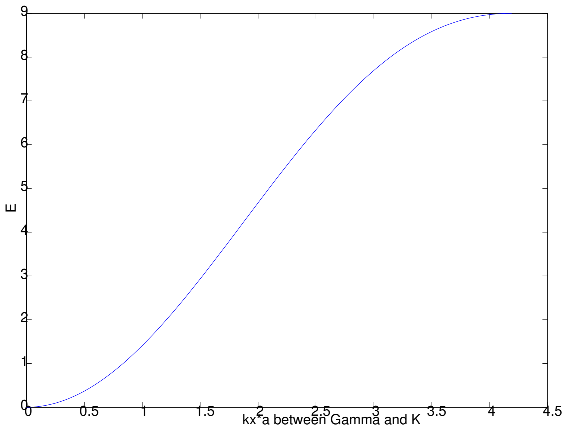
$$\boldsymbol{k}_M = \frac{1}{2}\boldsymbol{b}_2 = \frac{2\pi}{\sqrt{3}a}\hat{y}.$$

The six K–points are located at the corners of the 1BZ, one of them is:

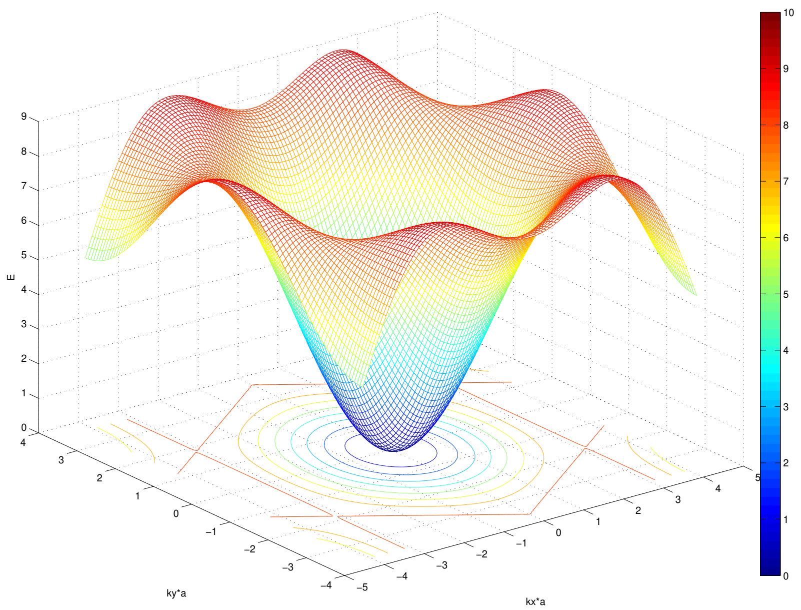
$$\boldsymbol{k}_K = \frac{4\pi}{3a}\hat{x}.$$

Using Matlab, we obtain the following dispersion relation between the Γ–point ($k = 0$) and the M–point, and from Γ to K:





In both figures, the energy E is given in units of $-\gamma = |\gamma|$, as function of the dimensionless quantities $k_y a$ and $k_x a$. The latter figure suggests that the band width equals $9|\gamma|$, with $E_{\text{min}} = 0$ in the Γ–point $k = 0$ and $E_{\text{max}} = -9\gamma$ in the K–points. A 3D plot of the dispersion relation over the 1BZ (actually, over the rectangular area in $\boldsymbol{k}$ space defined by $\pm\boldsymbol{k}_K$ and $\pm\boldsymbol{k}_M$ given above, since I did not take the time to figure out how to limit the plot region to the hexagonal 1BZ) supports this suggestion:



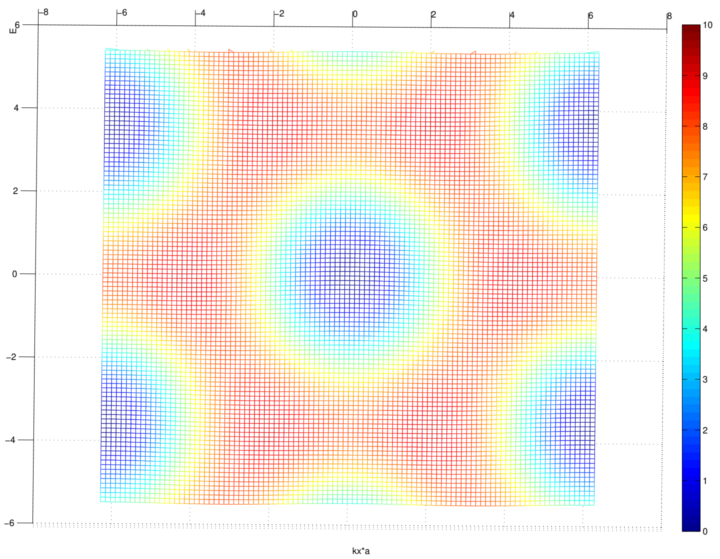
A formal way to find the band width amounts to locating the various stationary points of $E(\boldsymbol{k})$, i.e., to find where $\nabla_k E = 0$, and insert these $\boldsymbol{k}$ values into $E(\boldsymbol{k})$. For the 2D gradient of E to vanish, we must require both $\partial E/\partial k_x = 0$ and $\partial E/\partial k_y = 0$ simultaneously. Let $\alpha = k_x a$ and $\beta = k_y a$. Then

$$
\begin{aligned}
\frac{\partial E}{\partial \alpha} &= -\sin\frac{\alpha}{2}\left(\cos\frac{\alpha}{2} + \frac{1}{2}\cos\frac{\sqrt{3}\beta}{2}\right) = 0 \\
\frac{\partial E}{\partial \beta} &= -\frac{\sqrt{3}}{2}\cos\frac{\alpha}{2}\sin\frac{\sqrt{3}\beta}{2} = 0
\end{aligned}
$$

Here, we have several solutions:

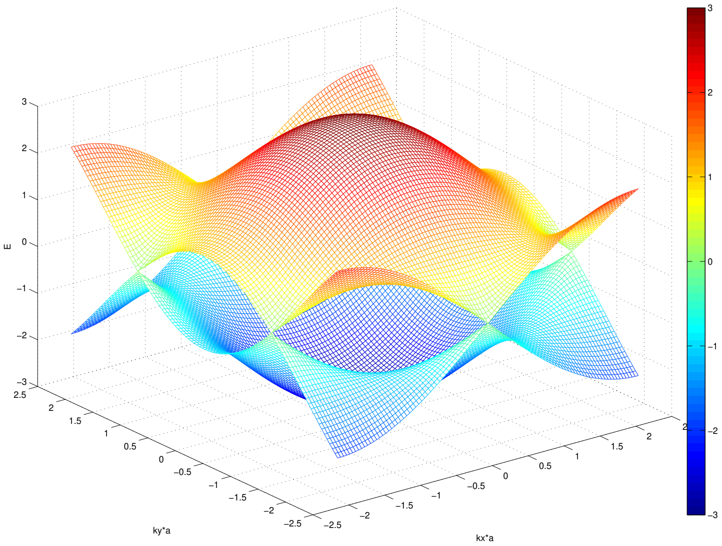
- $\sin(\alpha/2) = 0$ and $\sin(\sqrt{3}\beta/2) = 0$ yields the energy minimum $E_{\min} = 0$ at the Γ–point $k_x = k_y = 0$, as well as saddle points $E_M = -8\gamma$ in two of the six M–points, $\boldsymbol{k}_M = (0, \pm 2\pi/\sqrt{3}a)$
- $\cos(\alpha/2) = 0$ and $\cos(\sqrt{3}\beta/2) = 0$ yields the remaining four saddle points $E_M = -8\gamma$ in $\boldsymbol{k}_M = (\pm\pi/a, \pm\pi/\sqrt{3}a)$
- $\sin(\sqrt{3}\beta/2) = 0$ and $\cos(\alpha/2) = -(1/2)\cos(\sqrt{3}\beta/2)$ yields the six energy maxima $E_K = -9\gamma$ at the K–points $\boldsymbol{k}_K = (\pm 4\pi/3a, 0)$ and $\boldsymbol{k}_K = (\pm 2\pi/3a, \pm 2\pi/\sqrt{3}a)$.

A 3D plot, viewed down the E–axis, and with a somewhat extended region of k–space, could be illustrative:



Question 2

In Exercise 1, Question 2, we found reciprocal lattice vectors $\boldsymbol{b}_1 = (2\pi/a)(\hat{x} - \sqrt{3}\hat{y})$ and $\boldsymbol{b}_2 = (2\pi/a)(\hat{x}+\sqrt{3}\hat{y})$ for the hexagonal graphene lattice. Hence, the 6 midpoints M of the edges of the hexagonal 1BZ are located at $\boldsymbol{k}$ values $\pm\boldsymbol{b}_1/2$, $\pm\boldsymbol{b}_2/2$, and $\pm(2\pi/3a)\hat{x}$. The 6 corners K of the 1BZ are located at $\pm(4\pi/3\sqrt{3}a)\hat{y}$, $\pm(b_{2x}\hat{x} + (1/3)b_{2y}\hat{y}) = \pm((2\pi/3a)\hat{x} + (2\pi/3\sqrt{3}a)\hat{y}$, and $\pm(b_{1x}\hat{x} + (1/3)b_{1y}\hat{y}) = \pm((2\pi/3a)\hat{x} - (2\pi/3\sqrt{3}a)\hat{y}$. (See figure in Solution1.) Hence, by making a 3D plot of E^+ and E^- in the range $-2\pi/3 < k_x a < 2\pi/3$ and $-4\pi/3\sqrt{3} < k_y a < 4\pi/3\sqrt{3}$, we cover the 1BZ (plus a little extra, 4/12 of the 2BZ, actually). We set $E_0 = 0$ and $\gamma = -1$ and obtain the following valence band $E^- \leq 0$ and conduction band $E^+ \geq 0$, showing clearly how the VB and the CB touch at the six K–points:



If we imagine the various energy bands of graphene being constructed from atomic orbitals in carbon, and taking into account that each primitive cell contains two carbon atoms, each giving rise to one band pr atomic orbital, we will end up with the two bands 1σ and $1\sigma^*$ from the $1s$ state. Next, we have "hybridized" sp^2 bands, constructed as linear combinations of the atomic $2s$, $2p_x$, and $2p_y$ states of the two carbon atoms. The sp^2 bands are responsible for the strong C–C bonds, and the corresponding wave functions are "directional", pointing towards the three nearest neighbours of any given carbon atom. As discussed in the lectures, each primitive cell will contribute 2 electronic states to each energy band. Hence, 10 of the 12 electrons in each primitive cell will occupy the 1σ and $1\sigma^*$ bands and three sp^2 bands. We are left with 2 electrons pr primitive cell (one from each C atom), and these electrons have precisely the energy bands E^- and E^+ of the present problem at their disposal. It is the $2p_z$ atomic orbital that is the basis for constructing these two energy bands. In chemistry, they are typically referred to as π and π^* bands. (The notion of π bonding is probably well known from molecules like ethylene and benzene, I guess.)

At zero temperature, the electrons will be in the ground state of the system, i.e., the valence

band E^- will be filled and the conduction band E^+ will be empty. Hence, graphene may be considered a semiconductor, with zero bandgap, $E_g = 0$.
Graphene, a single layer of graphite, was first made experimentally in 2004, using simple equipment like Scotch tape. Since then, it has been a hot research topic, both experimentally and theoretically. One important reason is the rather peculiar band structure in the vicinity of the K–points. We will come back to graphene in the next Exercise. The nearest neighbour tight binding solution of graphene (and graphite) was published already more than sixty years ago (P. R. Wallace, *Phys Rev* **71**, 622 (1947)).