Homework 2 - Solutions

Carbon Nanotubes

Part 4)

We can write the wavefunction of the graphene sheet within the tight-binding model in the usual way

$$\psi(\vec{R}) = \bar{\psi} e^{i\vec{k}\cdot\vec{R}} \tag{1}$$

Then, to impose periodic boundary condition we want to ensure that our wavefunction satisfies the constraint

$$\psi(\vec{R} + \vec{W}) = \psi(\vec{R}) \tag{2}$$

That is, the winding vector $\vec{W}$ is a vector which wraps completely around the periodic axis of the carbon nanotube so that when we move from a site $\vec{R}$ by the vector $\vec{W}$, we end up at the same site $\vec{R}$. So then, we write

$$\psi(\vec{R} + \vec{W})\psi(\vec{R}) \tag{3}$$

$$\bar{\psi} e^{i\vec{k}\cdot(\vec{R}+\vec{W})} = \bar{\psi} e^{i\vec{k}\cdot\vec{R}} \tag{4}$$

$$\Rightarrow \quad \vec{k}\cdot(\vec{R} + \vec{W}) = \vec{k}\cdot\vec{R} + 2\pi\ell \qquad \ell \in \mathbb{Z} \tag{5}$$

$$\Rightarrow \quad \vec{k}\cdot\vec{W} = 2\pi\ell \qquad \ell \in \mathbb{Z} \tag{6}$$

Then, enforcing the periodic boundary conditions of the carbon nanotube means the our reciprocal lattice vectors $\vec{k}$ must satisfy the condition $\vec{k}\cdot\vec{W} = 2\pi\ell$.

Part 5)

a) The 2d honeycomb lattice of graphene has the same lattice structure as the hexagonal lattice, but with a two atom basis. The lattice is bipartite, so it can be split into A and B sublattices, with each sublattice forming a hexagonal lattice. The three unit vectors which point between the two sublattices are given by:

$$\vec{e}_1 = a(\frac{\sqrt{3}}{2}, \frac{1}{2}), \quad \vec{e}_2 = a(0, -1) \quad \text{and} \quad \vec{e}_3 = a(-\frac{\sqrt{3}}{2}, \frac{1}{2}) \tag{7}$$

Then, the primitive basis vectors are given by the two vectors $\vec{a}_1$ and $\vec{a}_2$

$$\vec{a}_1 = \vec{e}_1 - \vec{e}_3 = \sqrt{3}a(1, 0) \tag{8}$$

$$\vec{a}_2 = \vec{2}_3 - \vec{e}_2 = \sqrt{3}a(-\frac{1}{2}, \frac{\sqrt{3}}{2}) \tag{9}$$

Then, we can find our reciprocal space basis vectors by finding the vectors which satisfy the relationship

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{i,j} \tag{10}$$

These vectors are

$$\vec{b}_1 = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, \frac{1}{3}) \tag{11}$$

$$\vec{b}_2 = \frac{2\pi}{a}(0, \frac{2}{3}) \tag{12}$$

Using these vectors we can draw the 1st Brillouin zone by bisecting the vectors $\{\pm\vec{b}_1, \pm\vec{b}_2, \pm(\vec{b_1} - \vec{b_2}\}$

Now, in class it was seen that the two sublattice structure of graphene leads to an energy dispersion of the type

$$\varepsilon_{\pm}(k) = \varepsilon_0 \pm |f(k)| \qquad \text{with} \quad f(k) = -\gamma \sum_{i=1}^{3} e^{i\vec{k}\cdot e_i} \tag{13}$$

Using our values of e_1, e_2 and e_3 above, setting the lattice constant $a = 1$, gives

$$\begin{aligned} f(k) &= -\gamma[e^{ik_y} + e^{i(\frac{\sqrt{3}}{2}k_x + \frac{1}{2}k_y)} + e^{i(\frac{-\sqrt{3}}{2}k_x + \frac{1}{2}k_y)} && (14)\\ &= -\gamma[e^{-ik_y} + 2\cos(\frac{\sqrt{3}}{2}k_x)e^{i\frac{1}{2}k_y}] && (15)\\ &= -\gamma e^{i\frac{k_y}{2}}\left[e^{-\frac{3}{2}ik_y} + 2\cos(\frac{\sqrt{3}}{2}k_x)\right] && (16) \end{aligned}$$

Clearly, the energy given above is split into two bands, one each for the plus and minus values of $|f(k)|$. Now, the graphene lattice has two atoms per primitive unit cell, since the honeycomb lattice contains a two lattice basis. This tells us that the first energy band is completely filled while the second band is empty. Then, the Fermi energy is the energy which splits the two bands, which occurs when $|f(k)| = 0$. To find when $f(k) = 0$, we must set the real and imaginary parts of the r.h.s. of Eq. (16) to zero and solve. This is done in the lecture notes and the result is the two equations

$$\sin(\frac{3}{2}k_y) = 0 \quad \Rightarrow \quad k_y = 0, \pm\frac{2\pi}{3} \tag{17}$$

$$\cos(\frac{3}{2}k_y) + 2\cos(\frac{\sqrt{3}}{2}k_x) = 0 \tag{18}$$

subbing in our solutions for k_y gives

$$\pm 1 + 2\cos(\frac{\sqrt{3}}{2}k_x) = 0 \quad \Rightarrow \quad k_x = \pm\frac{4\pi}{3\sqrt{3}}, \pm\frac{2\pi}{3\sqrt{3}} \tag{19}$$

Therefore, this gives six points where $f(k) = 0$ so that $\varepsilon(k) = \varepsilon_F$

$$(k_x, k_y) = (\pm\frac{4\pi}{3\sqrt{3}}, 0)\ ,\ (\pm\frac{2\pi}{3\sqrt{3}}, \pm\frac{2\pi}{3}) \tag{20}$$

To verify that these points lie on the corners of the first Brillouin zone, note that the corners of the 1st B.Z., are at the points $\{\pm\frac{2}{3}(2\vec{b}_1 - \vec{b}_2), \pm\frac{2}{3}(\vec{b}_1 + \vec{b}_2), \pm\frac{2}{3}(2\vec{b}_2 - \vec{b}_1)\}$. That is, the corners of the B.Z. lie two thirds the way to the second nearest neighbor lattice points. Plugging in the values of $\vec{b}_1$ and $\vec{b}_2$ shows that the six Fermi points given above coincide with the corners of the 1st B.Z.

b) Note: this solution is written for the *first* version of the homework. The solution for the corrected homework (with definition of m,n changed) is easier. It is left as an exercise.

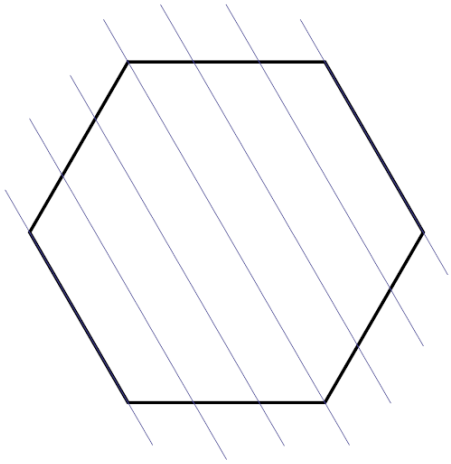
The lines given in part 4 are the values of $\vec{k}$ which satisfy the equation $\vec{k} \cdot \vec{W} = 2\pi\ell$ for any integer ℓ.

For the winding vector $(m, n) = (3, 3)$, we have $\vec{W} = 6\vec{a}_1 + 3\vec{a}_2 = 9(\frac{\sqrt{3}}{2}, \frac{1}{2})$ Then

$$\vec{k} \cdot W = 2\pi\ell \quad \Rightarrow \quad \sqrt{3}k_x + k_y = \frac{4\pi\ell}{9} \tag{21}$$

$$\Rightarrow \quad k_y = -\sqrt{3}k_x + \frac{4\pi\ell}{9} \tag{22}$$

We can plot these lines within the first B.Z. (for all values of ℓ such that the lines fall within the B.Z.) and find that the allowed k-points fall along the lines in the figure below:



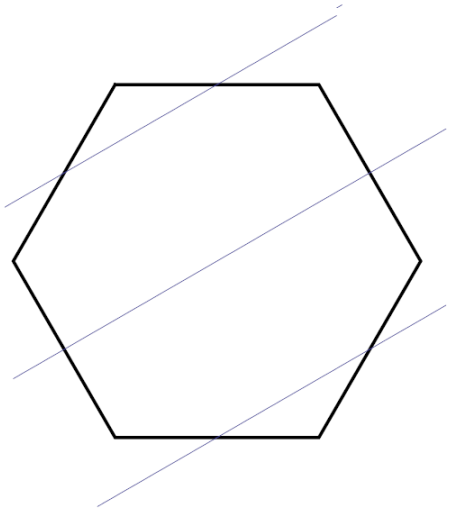
For the winding vector $(m, n) = (-2, 2)$, we have $\vec{W} = 2\vec{a}_2 = (-\sqrt{3}, 3)$ Then

$$\vec{k} \cdot W = 2\pi\ell \quad \Rightarrow \quad -\sqrt{3}k_x + 3k_y = 2\pi\ell \tag{23}$$

$$\Rightarrow \quad k_x = \sqrt{3}k_y - \frac{2\pi\ell}{\sqrt{3}} \tag{24}$$

$$\Rightarrow \quad k_y = \frac{k_x}{\sqrt{3}} + \frac{2\pi\ell}{3} \tag{25}$$

Again, plotting these lines for different ℓ within the first B.Z. looks like:



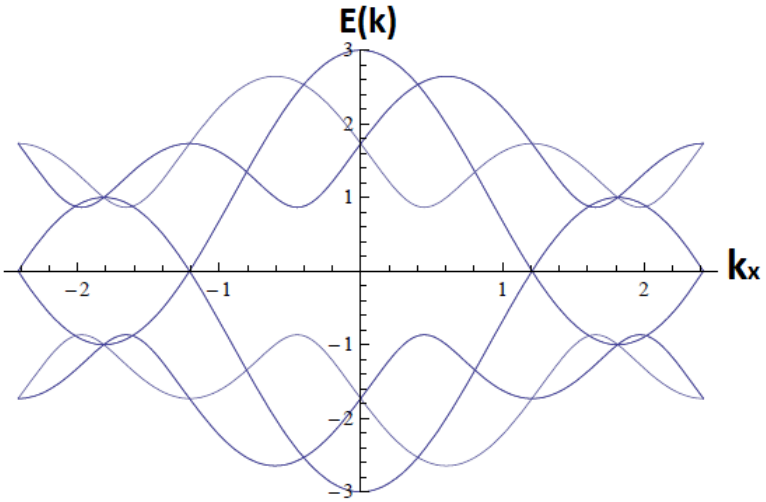
Part 6)

For the $(m, n) = (3, 3)$ tube, the allowed k_y wavevectors for a given k_x must obey the restriction $k_y = -\sqrt{3}k_x + 4\pi\ell/9$. These lines fall within the first B.Z. for $\ell \in \{0, \pm1, \pm2, \pm3\}$. The energy is found by taking

the absolute value of Eq. (16) to get

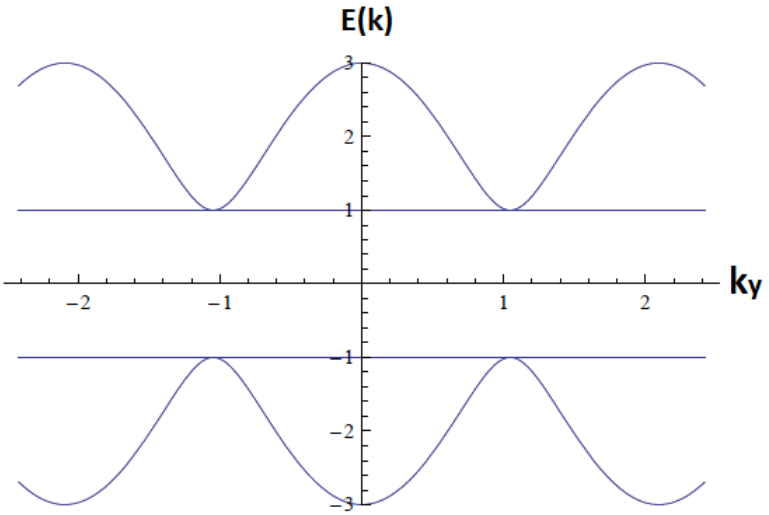
$$\varepsilon(k) = \pm|f(k)| = \sqrt{1 + 4\cos(\sqrt{3}k_x/2)\Big(\cos(\sqrt{3}k_x/2) + cos(-3k_y/2)\Big)} \tag{26}$$

Subbing in our equation for k_y and plotting in Mathematica gives



The two dispersion bands at individual points. Therefore, the (3,3) nanotube is metallic.

For the $(m, n) = (2, -2)$ tube, the allowed k_x wavevectors are given by $k_x = \sqrt{3}k_y - 2\pi\ell/\sqrt{3}$. Subbing this into the equation for energy and plotting $\varepsilon(k)$ as a function of k_y gives:



Here, the upper and lower band never touch, and so the $(2, -2)$ carbon nanotube is insulating according to band theory.

part 7)

For a general winding vector (m, n), the vector $\vec{W}$ has the form

$$\vec{W} = (m+n)\vec{a}_1 + n\vec{a}_2 = \sqrt{3}(m + n - \frac{n}{2}, \frac{\sqrt{3}n}{2}) = \sqrt{3}(m + \frac{n}{2}, \frac{\sqrt{3}n}{2}) \tag{27}$$

The only allowed wavevectors in reciprical space, $\vec{k}$, are those which satisfy the condition condition $\vec{k} \cdot \vec{W} = 2\pi\ell$. Note, that there are only two independent corners of the Brillouin zone, those at wavevectors $(\frac{-2\pi}{3\sqrt{3}}, \frac{2\pi}{3})$ and $(\frac{2\pi}{3\sqrt{3}}, \frac{2\pi}{3})$. The other four corners of the B.Z. are translations of these corners by some combination of basis vectors, so that if $\vec{k} \cdot \vec{W} = 2\pi\ell$ for one of these two corners, then $veck' \cdot \vec{W}$ will also equal $2\pi\ell$ for the other four corners of the B.Z. (since $\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{i,j}$ and $\vec{W} = (m+n)\vec{a}_1 + n\vec{a}_2$).

Then, for the corner point $\vec{k} = (\frac{-2\pi}{3\sqrt{3}}, \frac{2\pi}{3})$ we have

$$\vec{k} \cdot \vec{W} = 2\pi\ell \tag{28}$$

$$\Rightarrow \quad \sqrt{3}(\frac{-2\pi}{3\sqrt{3}}, \frac{2\pi}{3}) \cdot (m + \frac{n}{2}, \frac{\sqrt{3}n}{2}) = 2\pi\ell \tag{29}$$

$$\Rightarrow \quad \frac{-m}{3} - \frac{n}{6} + \frac{n}{2} = \ell \tag{30}$$

$$\Rightarrow \quad -2m - n + 3n = 6\ell \tag{31}$$

$$\Rightarrow \quad (n - m) = 3\ell \tag{32}$$

And, for the corner point $\vec{k} = (\frac{2\pi}{3\sqrt{3}}, \frac{2\pi}{3})$ we have

$$\vec{k} \cdot \vec{W} = 2\pi\ell \tag{33}$$

$$\Rightarrow \quad \sqrt{3}(\frac{2\pi}{3\sqrt{3}}, \frac{2\pi}{3}) \cdot (m + \frac{n}{2}, \frac{\sqrt{3}n}{2}) = 2\pi\ell \tag{34}$$

$$\Rightarrow \quad \frac{m}{3} + \frac{n}{6} + \frac{n}{2} = \ell \tag{35}$$

$$\Rightarrow \quad 2mn + 3n = 6\ell \tag{36}$$

$$\Rightarrow \quad (2n + m) = 3\ell \tag{37}$$

But, now notice that these are actually the same condition. Start with

$$2n + m = 3\ell \tag{38}$$

$$\Rightarrow \quad 3n - n + m = 3\ell \tag{39}$$

$$\Rightarrow \quad -n + m = 3(\ell - n) \tag{40}$$

$$\Rightarrow \quad n - m = 3\ell' \quad \text{where } \ell' = (n - \ell) \text{ is an arbitrary integer} \tag{41}$$

Therefore, in order for an allowed wavevector for a nanotube cylinder with $\vec{W}$ given by (m, n), to lie on a Brillouin zone corners, (m, n) must satisfy the conditions

$$2n + m = 3\ell' \tag{42}$$

It is obvious that the tubes satisfying this condition are metallic as we have already shown in part 5) that the corners of the Brillouin zone correspond to the points where $f(k) = 0$. Since graphene has a two particle basis, this implies that the primitive unit cell contains two atoms and so the first Brillouin zone is exactly filled with two particles per state. This means that the first band is exactly filled and the second band is empty. Since the energy dispersion is given by the relation

$$\varepsilon(k) = \varepsilon_0 \pm |f(k)| \tag{43}$$

Then, the system is metallic if and only if an allowed k vector lies on the point where $f(k) = 0$. So then, any nanotube where the Brillouin zone corners are allowed wavevectors contains a point where $|f(k)| = 0$ and so is metallic.

part 8)

Now, we have

$$f(k) = -\left(t' \sum_{\text{vert.}e_i} e^{i\vec{k}\cdot\vec{e}_i} \; - \; t \sum_{\text{diag.}e_i} e^{i\vec{k}\cdot\vec{e}_i} \right) \tag{44}$$

Both the armchair and the zig-zag tubes differentiate between the $\vec{e}_1$ and $\vec{e}_2/\vec{e}_3$ bonds (since the vector W is either parallel or perpendicular to the $\vec{e}_1$ bond in these cases. The band structure of the nanotubes is then given by

$$\varepsilon \;\; = \;\; \varepsilon_0 \pm |f(k)| \tag{45}$$

To solve for the points when $f(k) = 0$, let's let's assume that the vertical $\vec{e}_i$ bond with hopping t' is the bond $e_2 = (0, a)$. This will make solving for $f(k) = 0$ convenient and ocne we find these points we can rotate our axes so that $\vec{e}_1 \to \vec{e}_2$. Using this choice we can write

$$f(k) \;\; = \;\; e(-t'e^{-\frac{1}{2}ik_y} \; - te^{\frac{i(\sqrt{3}}{2}k_x + \frac{1}{2}k_y)} - te^{i(-\frac{\sqrt{3}}{2}ik_x + \frac{1}{2}k_y)} \Big) = 0 \tag{46}$$

$$0 \;\; = \;\; e^{\frac{1}{2}ik_y} \Big(- t'e^{-\frac{3}{2}ik_y} \; - te^{\frac{\sqrt{3}}{2}ik_x} - te^{-\frac{\sqrt{3}}{2}ik_x} \Big) \tag{47}$$

$$\text{Im}[f(k)] = 0 \;\; \Rightarrow \;\; \sin(-\frac{3}{2}k_y) = 0 \tag{48}$$

$$\text{Re}[f(k)] = 0 \;\; \Rightarrow \;\; t'\cos(-\frac{3}{2}k_y) + 2t\cos(\frac{\sqrt{3}}{2}k_x) = 0 \tag{49}$$

The solutions to Eq. (48) are

$$k_y = 0, \pm\frac{2\pi}{3} \tag{50}$$

We can sub this into Eq. (49) to get:

$$\pm t' + 2t\cos(\frac{\sqrt{3}}{2}k_x) = 0 \tag{51}$$

$$\pm 1 + \frac{2t}{t'}\cos(\frac{\sqrt{3}}{2}k_x) = 0 \tag{52}$$

$$\frac{\sqrt{3}}{2}k_x = \cos^{-1}\left(\mp \frac{t'}{2t} \right) \tag{53}$$

$$\Rightarrow \qquad k_x = \frac{2}{\sqrt{3}}\cos^{-1}\left(\mp \frac{t'}{2t} \right) \tag{54}$$

Eq.'s (50) and (54) give us the Dirac points for our modified Hamiltonian, when e_2 has hopping t'. To find the solution when bond $\vec{e}_1$ has hopping t' we want to rotate our axes, so that what we defined as k_y above becomes $\vec{e}_1 = \frac{1}{2}k_x + \frac{\sqrt{3}}{2}k_y$. That is we want to rotate our axes clockwise by angle $\pi/6$, to let

$$k_x \to \frac{1}{2}k_x - \frac{\sqrt{3}}{2}k_y \quad \text{and} \quad k_y \to \frac{\sqrt{3}}{2}k_x + \frac{1}{2}k_y \tag{55}$$

Then in our new basis, our Dirac points given by (50) and (54) must satisfy:

$$\frac{\sqrt{3}}{2}k_x + \frac{1}{2}k_y = 0 \ \left(\text{ or } \frac{2\pi}{3} \right) \tag{56}$$

$$\frac{1}{2}k_x - \frac{\sqrt{3}}{2}k_y = \frac{2}{\sqrt{3}} \cos^{-1}\left(\frac{t'}{2t}\right). \tag{57}$$

Solving this system of equations for k_x and k_y gives

$$k_x = \frac{1}{\sqrt{3}} \cos^{-1}\left(-\frac{t'}{2t}\right) \tag{58}$$

$$k_y = -\cos^{-1}\left(-\frac{t'}{2t}\right) \tag{59}$$

Now, recall that for the $(3,3)$ armchair nanotube, our wavevectors k_x, k_y had to satisfy the requirement

$$k_y = -\sqrt{3}k_x + \frac{4\pi\ell}{9} \tag{60}$$

Subbing Eq. (58) into this condition gives

$$k_y = -\sqrt{3}\left[-\frac{1}{\sqrt{3}} \cos^{-1}\left(\frac{-t'}{2t}\right)\right] + \frac{4\pi\ell}{9} \tag{61}$$

$$= \cos^{-1}\left(\frac{-t'}{2t}\right) + \frac{4\pi\ell}{9} \tag{62}$$

For $\ell = 0$ this is exactly the k_y coordinate of the Dirac point we just found above. Therefore, for the armchair nanotube, the Dirac points alway fall along one of the quatized wavevectors. Therefore, the modifications of the hopping term doesn't affect the metalicity of the nanotube in this case.

Now, for the$(-2,2)$ zig-zag nanotube, our wavevectors had to satisfy the condition

$$k_x = \sqrt{3}k_y - \frac{2\pi\ell}{\sqrt{3}} \tag{63}$$

Subbing in Eq. (58) and (59) gives

$$\frac{1}{\sqrt{3}} \cos^{-1}\left(\frac{-t'}{2t}\right) = -\sqrt{3} \cos^{-1}\left(\frac{-t'}{2t}\right) - \frac{2\pi\ell}{3} \tag{64}$$

$$\Rightarrow \quad 4 \cos^{-1}\left(\frac{-t'}{2t}\right) = \frac{2\pi\ell}{\sqrt{3}} \tag{65}$$

$$\Rightarrow \quad t' = -2t \cos\left(\frac{\pi\ell}{2\sqrt{3}}\right) \tag{66}$$

Therefore, the allowed wavevectors of the zig-zag nanotube will not in general cross the Dirac points unless the hopping parameters satisfy the above condition. If the above condition is satisfied by the specific values of t and t' then the system will be metalic, otherwise it will be insulating. For $\ell = 1$, the condition above is $t' \approx 1.2t$ must be satisfied for the nanotube to be metallic.