

It is assumed that the reader has basic knowledge on nanotubes. Mathematically strict and concise introduction can be found in Ref. [1]. All 4 problems have detailed solutions along with the images of *Mathematica* scripts used to generate solutions. Students are encouraged to reproduce and run these simple scripts (I believe that this is a good way to get acquainted with *Mathematica* for novices). All problems exploit screw and rotational symmetry of nanotubes. That makes solutions simple (often analytical), comprehensible and elegant. From looking at large number of publications on nanotubes the author get convinced that only small fraction of researches (even theoreticians) utilizes symmetry properties of nanotubes. No surprise that the authors of *nanohub* tool *CNTBANDS* do not utilize it either. One of the goals pursued by this tutorial is to amend such unfortunate state of affairs.

PROBLEM 1

Nanotube indexes n_1 and n_2 define vector $\vec{R} = n_1 \vec{R}_1 + n_2 \vec{R}_2$, which determines the way how single-wall nanotube (SWNT) is rolled up.

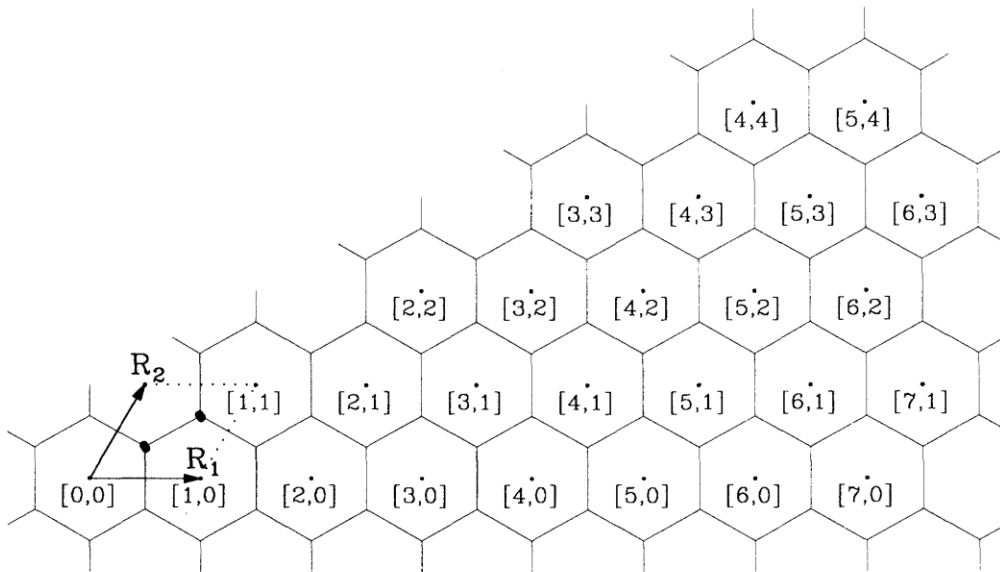


Figure 1

The primitive unit cell of any SWNT contains just two atoms separated by a distance equal to the bond length (two bold dots in Fig. 1). The positions of all other atoms in SWNT can be obtained by applying screw and rotation operations to the coordinates of atoms residing in a single primitive unit cell. Rotation operation rotates atomic positions around SWNT axis by $\frac{2\pi m}{N}$, where N is the greatest common divisor of n_1 and n_2 and m is non-negative integer lesser than N . Screw operation shifts atom along the SWNT axis by $h = \frac{|\vec{H} \times \vec{R}|}{|\vec{R}|}$ and rotates by angle $\alpha = 2\pi \frac{(\vec{H} \cdot \vec{R})}{|\vec{R}|^2}$, where $\vec{H} = p_1 \vec{R}_1 + p_2 \vec{R}_2$, and p_1 and p_2 are integers. Prove that $p_2 n_1 - p_1 n_2 = \pm N$

Solution:

Assumption: when the SWNT is rolled up, Fig. 1 is mapped on the cylinder surface with the radius equal to $r = \frac{|\vec{R}|}{2\pi}$. As a result of such mapping, the interatomic distance changes. We assume that no structural relaxation occurs when graphene sheet is rolled up into SWNT. Therefore we can use plain geometry for expressing the chiral vector \vec{H} through, n_1, n_2, \vec{R}_1 , and \vec{R}_2 . The only additional condition one needs to keep in mind is that all geometrical equations are “modulo \vec{R} ”, i.e. atomic positions separated by vector \vec{R} are equivalent.

The condition for chiral vector \vec{H} can be found from equating area A_{UC} of a primitive unit cell multiplied by N (because there are N equivalent primitive unit cells in the same cross-section of SWNT) to the area on the SWNT corresponding to a single screw operation:

$$\begin{aligned}
 A_{UC} N &= |\vec{R} \times \vec{H}| \Rightarrow \\
 |\vec{R}_1 \times \vec{R}_2| N &= |(n_1 \vec{R}_1 + n_2 \vec{R}_2) \times (p_1 \vec{R}_1 + p_2 \vec{R}_2)| \Rightarrow \\
 |\vec{R}_1 \times \vec{R}_2| N &= |n_1 p_2 \vec{R}_1 \times \vec{R}_2 - n_2 p_1 \vec{R}_1 \times \vec{R}_2| \Rightarrow \\
 N &= |n_1 p_2 - n_2 p_1|
 \end{aligned}$$

The last equation is equivalent to $p_2 n_1 - p_1 n_2 = \pm N$. That finishes the proof. The uncertainty in sign is due to possibility of applying screw operation in either direction along the SWNT axis. If

\vec{H} is a screw vector, then $\vec{H} + m\vec{R}$ is also a valid screw vector (m is integer). This uncertainty is due to the cyclic boundary conditions.

It is worthwhile to make sure that any atom of the graphene sheet can be translated to the primitive unit cell at the origin by applying translation vector (or, equivalently, by applying screw and rotation operations)

$$a \frac{\vec{R}}{N} + b\vec{H} = a \frac{n_1 \vec{R}_1 + n_2 \vec{R}_2}{N} + b(p_1 \vec{R}_1 + p_2 \vec{R}_2),$$

where a and b are integers. If the desired unit cell is located at $x\vec{R}_1 + y\vec{R}_2$ (x and y are integers), then

$$x\vec{R}_1 + y\vec{R}_2 = a \frac{n_1 \vec{R}_1 + n_2 \vec{R}_2}{N} + b(p_1 \vec{R}_1 + p_2 \vec{R}_2).$$

Solving for a and b :

$$a = p_2 x - p_1 y$$

$$b = \frac{n_1 y - n_2 x}{N}$$

Indeed, a and b are integers because x , y , n_1 , n_2 , p_1 , and p_2 are integers, and N is common divisor of n_1 and n_2 .

PROBLEM 2 (Prerequisite: **Problem 1**. α , N and screw operator are defined in **Problem 1**)

Bloch theorem can be extended to 1-D systems with helical and rotational symmetries. Unit cell with indexes $\{m, n\}$ is obtained from the unit cell with indexes $\{0, 0\}$ through application of m

consecutive rotations by angle $\frac{2\pi}{N}$ and n consecutive screw operations. If the wave function inside the primitive unit cell $\{0, 0\}$ is $\psi_{\{0,0\}}[\vec{r}]$, the wave function in the unit cell $\{m, n\}$ is

$$\psi_{\{m,n\}}[\vec{r}] = \psi_{\{0,0\}} \left[\mathfrak{R} \left[-\frac{2\pi m}{N} \right] \mathfrak{R}[-n\alpha] \vec{r} \right] \exp[ikn + 2\pi ilm/N].$$

Here $\mathfrak{R}[\varphi]$ is the operator,

which rotates vector \vec{r} around SWNT axis by angle φ , l is a branch integer index running from 0 to $N - 1$, and k is a real scalar in the range $[-\pi, \pi]$. Show that in the π -orbital tight-binding approximation the two-component wave-function has a form:

$$C_j[m, n; l] = C_j[0, 0; l] \exp[i k m + 2 \pi i l n / N].$$

Here index j denotes atom in the unit cell ($j = 1, 2$), $C_j[0, 0; l]$ is the wave function component in unit cell $\{0, 0\}$ and $C_j[m, n; l]$ is the wave function component in unit cell $\{m, n\}$.

Solution:

Suppose one uses sp^3 localized basis set to solve for electronic states of SWNT and

$$\varphi_{i,j}[\vec{r} - \vec{R}_{i,j}]_{\pi} = \sum_{\lambda=\{x,y,z\}} a[i, j]_{m,n} p_{\lambda}[\vec{r} - \vec{R}_{i,j}]$$

is a linear combination of p -orbitals centered on i -th atom of j -th unit cell, such that the axis of $\varphi_{i,j}[\vec{r} - \vec{R}_{i,j}]_{\pi}$ (which is p -orbital itself) is normal to the SWNT surface. Then, it appears that the contribution of $\varphi_{i,j}[\vec{r} - \vec{R}_{i,j}]_{\pi}$ to the electronic states of SWNT approximately within energy range of ± 2 eV with respect to the Fermi level substantially exceeds contributions from any other sp^3 combinations. Thus, functions $\varphi_{i,j}[\vec{r} - \vec{R}_{i,j}]_{\pi}$ can be chosen as a new basis set with just one p -orbital per atom. If m screw and n rotation operations transform i -th atom residing in the unit cell with index 0 to i -th atom residing in unit cell j , then

$$\varphi_{i,j} \left[\Re \left[-\frac{2\pi m}{N} \right] \Re[-n\alpha] \vec{r} - \vec{R}_{i,j} \right] = \varphi_{i,0} [\vec{r} - \vec{R}_{i,0}].$$

The wave function in the unit cell at the origin (i.e. $m = 0, n = 0$) is a linear combination of two atomic orbitals $\varphi_{i,0}[\vec{r} - \vec{R}_{0,j}]_{\pi}$:

$$\psi_{0,0}[r] = \sum_{j=1}^2 C_j[0, 0; l] \varphi_{i,0}[\vec{r} - \vec{R}_{0,j}].$$

Using Bloch theorem the same wave function in the unit cell with indexes m and n is

$$\begin{aligned}
\psi_{m,n}[\vec{r}] &= \psi_{0,0} \left[\Re \left[-\frac{2\pi m}{N} \right] \Re[-n\alpha] \vec{r} \right] \exp[i k n + 2 \pi i l m / N] = \\
&\sum_{j=1}^2 C_j [0,0;l] \varphi_{0,j} \left[\Re \left[-\frac{2\pi m}{N} \right] \Re[-n\alpha] \vec{r} - \vec{R}_{0,j} \right] \exp[i k n + 2 \pi i l m / N] = \\
&\sum_{j=1}^2 C_j [m,n;l] \varphi_{i,j} \left[\vec{r} - \vec{R}_{i,j} \right]
\end{aligned}$$

Because functions $\varphi_{i,j} \left[\vec{r} - \vec{R}_{i,j} \right]$ (for $j = 1,2$) constitute a complete basis within unit cell, the pre-factors in the second and the third lines of equation above must match for each j . That results in the following equation for wave function components:

$$C_j [m,n;l] = C_j [0,0;l] \exp[i k m + 2 \pi i l n / N]$$

PROBLEM 3 (Prerequisites: **Problems 1** and **2**. N , p_1 , and p_2 are defined in **Problem 1**)

Show that in the π -orbital tight-binding nearest neighbor approximation band structure $E[k]$ of $\{n_1, n_2\}$ SWNT can be expressed analytically (Ref. [1] has this equation, but does not include its complete derivation):

$$E[k] = \pm V \sqrt{3 + 2 \left(\cos \left[\frac{n_1 k - 2\pi l p_1}{N} \right] + \cos \left[\frac{n_2 k - 2\pi l p_2}{N} \right] + \cos \left[\frac{(n_1 + n_2) k - 2\pi l (p_1 + p_2)}{N} \right] \right)}$$

Here l is the index of dispersion brunch running from 0 to $N - 1$, k is a real scalar in the range $[-\pi, \pi]$, and V is Hamiltonian matrix element between nearest neighbors.

Solution:

Electronic states in the infinitely long SWNT are described by an infinite set of complex vectors $\{C^{\varepsilon,k}[l]\}$. The Hamiltonian matrix \mathbf{H} in localized basis representation has infinite dimensions, and vectors $C^{\varepsilon,k}[l]$ have infinite length. Indexes ε and k refer respectively to the energy of electronic state and its k -number associated with screw symmetry. Integer l lying in the range 0, $N - 1$ indexes dispersion branches associated with different rotational symmetries. The compo-

ment of $C^{\varepsilon,k}[l]$ associated with j^{th} atom in the unit cell ($j = 1,2$) is denoted as $C_j^{\varepsilon,k}[m,n;l]$. Indexes m and n denote respectively the number of screw and rotation operations required to transform the unit cell at the origin to the unit cell associated with component $C_j^{\varepsilon,k}[m,n;l]$. The Schrödinger equation can be formally written as

$$H \cdot C^{\varepsilon,k}[l] = \varepsilon C^{\varepsilon,k}[l]$$

From this infinite set of linear equations we select two equations associated with the unit cell at the origin:

$$\begin{aligned} & \begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix} \cdot \begin{pmatrix} C_1^{\varepsilon,k}[0,0;l] \\ C_2^{\varepsilon,k}[0,0;l] \end{pmatrix} + \\ & \sum_{\{m,n\} \in \left\{ \begin{smallmatrix} \text{All Nearest} \\ \text{Neighbors of atom 1} \end{smallmatrix} \right\}} \begin{pmatrix} 0 & V \\ 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} C_1^{\varepsilon,k}[m,n;l] \\ C_2^{\varepsilon,k}[m,n;l] \end{pmatrix} + \\ & \sum_{\{m,n\} \in \left\{ \begin{smallmatrix} \text{All Nearest} \\ \text{Neighbors of atom 2} \end{smallmatrix} \right\}} \begin{pmatrix} 0 & 0 \\ V & 0 \end{pmatrix} \cdot \begin{pmatrix} C_1^{\varepsilon,k}[m,n;l] \\ C_2^{\varepsilon,k}[m,n;l] \end{pmatrix} = \varepsilon \begin{pmatrix} C_1^{\varepsilon,k}[0,0;l] \\ C_2^{\varepsilon,k}[0,0;l] \end{pmatrix} \end{aligned}$$

Using the results obtained in **Problem 2**:

$$\begin{aligned} & \left(\begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix} + \right. \\ & \sum_{\{m,n\} \in \left\{ \begin{smallmatrix} \text{All Nearest} \\ \text{Neighbors of atom 1} \end{smallmatrix} \right\}} \begin{pmatrix} 0 & V \\ 0 & 0 \end{pmatrix} \exp[i k m + 2 \pi i l n / N] + \\ & \left. \sum_{\{m,n\} \in \left\{ \begin{smallmatrix} \text{All Nearest} \\ \text{Neighbors of atom 2} \end{smallmatrix} \right\}} \begin{pmatrix} 0 & 0 \\ V & 0 \end{pmatrix} \exp[i k m + 2 \pi i l n / N] \right) \cdot \begin{pmatrix} C_1^{\varepsilon,k}[0,0;l] \\ C_2^{\varepsilon,k}[0,0;l] \end{pmatrix} = \varepsilon \begin{pmatrix} C_1^{\varepsilon,k}[0,0;l] \\ C_2^{\varepsilon,k}[0,0;l] \end{pmatrix} \end{aligned}$$

The problem has converged to 2×2 eigenproblem. To obtain analytical equation for dispersion we need the expressions for m and n . Figure 2 below uses grey shade to mark unit cells neighboring the unit cell at the origin (with $m = 0, n = 0$). Unit cells are marked with red indexes and blue indexes mark atoms within unit cells.

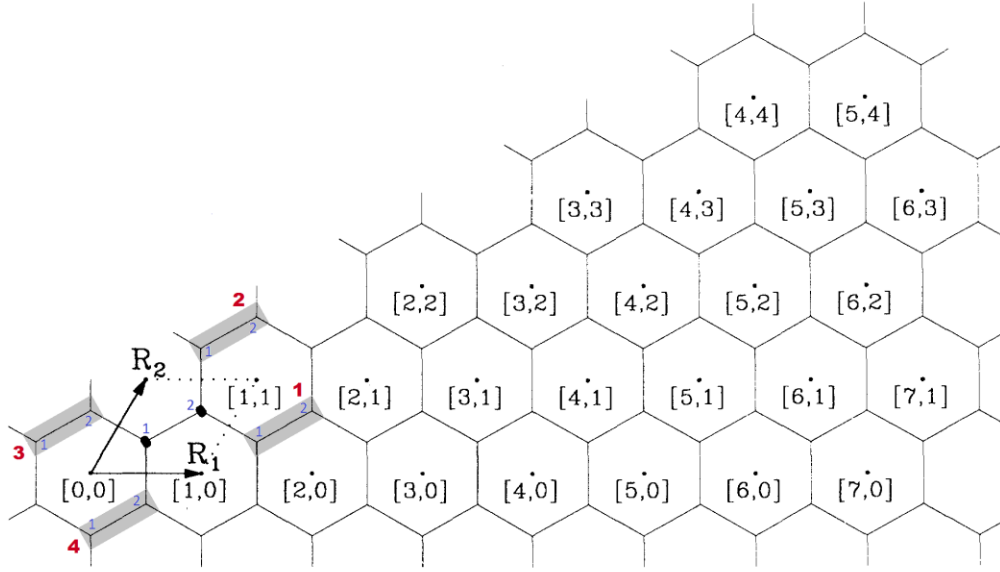


Figure 2

To obtain m and n for unit cell marked in Fig. 2 with index 1 we equate its position with respect to the origin (\vec{R}_1) to the displacement resulting from m screw and n rotation operations

$$\left(m \frac{\vec{R}}{N} + n \vec{H}\right):$$

$$\vec{R}_1 = m \frac{\vec{R}}{N} + n \vec{H} = m \frac{n_1 \vec{R}_1 + n_2 \vec{R}_2}{N} + n (p_1 \vec{R}_1 + p_2 \vec{R}_2).$$

The solution of the linear system above is: $m = p_2$, $n = -n_2/N$. Solutions for m and n for cells marked with indexes 2, 3, and 4 are respectively $\{m = -p_1, n = n_1/N\}$, $\{m = -p_2, n = n_2/N\}$, and $\{m = p_1, n = -n_1/N\}$. Figure 3 presents *Mathematica* script generating these solutions.

```

In[92]:= ExpressNeighborCoordinatesThroughRandHGeneral[n1_, n2_] := Module[{r1234, RoverN, H},
  r1234 = {R1, R2, -R1, -R2};
  RoverN =  $\frac{n1 \times R1 + n2 \times R2}{N}$ ;
  H = (p1 \times R1 + p2 \times R2);

  Table[#[[2]] & /@ (Solve[Table[(r1234[[i]] - (a \times RoverN + b \times H))[[j]] == 0, {j, 1, 2}], {a, b}][[1]]),
    {i, 1, Length[r1234]}]
]

```

```

In[93]:= ExpressNeighborCoordinatesThroughRandHGeneral[n1, n2] /. {n2 p1 - n1 p2 -> -N, -n2 p1 + n1 p2 -> N}

```

Out[93]=

```

{{p2, - $\frac{n2}{N}$ }, {-p1,  $\frac{n1}{N}$ }, {-p2,  $\frac{n2}{N}$ }, {p1, - $\frac{n1}{N}$ }}

```

Figure 3

Substituting the first and the second $\{m, n\}$ sets to the third term of the equation below and the third and fourth sets into the second term

$$\begin{aligned}
 & \begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix} + \\
 & \sum_{\{m,n\} \in \left\{ \begin{smallmatrix} \text{All Nearest} \\ \text{Neighbors of atom 1} \end{smallmatrix} \right\}} \begin{pmatrix} 0 & V \\ 0 & 0 \end{pmatrix} \exp[i k m + 2 \pi i l n / N] + \\
 & \sum_{\{m,n\} \in \left\{ \begin{smallmatrix} \text{All Nearest} \\ \text{Neighbors of atom 2} \end{smallmatrix} \right\}} \begin{pmatrix} 0 & 0 \\ V & 0 \end{pmatrix} \exp[i k m + 2 \pi i l n / N]
 \end{aligned}$$

we obtain 2×2 matrix:

$$V \begin{pmatrix} 0 & 1 + e^{i\left(-\frac{n_1 k}{N} + \frac{2\pi p_1 l}{N}\right)} + e^{i\left(\frac{n_2 k}{N} - \frac{2\pi p_2 l}{N}\right)} \\ 1 + e^{i\left(\frac{n_1 k}{N} - \frac{2\pi p_1 l}{N}\right)} + e^{i\left(-\frac{n_2 k}{N} + \frac{2\pi p_2 l}{N}\right)} & 0 \end{pmatrix}.$$

Figure 4 presents *Mathematica* script generating Hamiltonian matrix above and the expression for its squared eigenvalues. In Figs. 4 and 5 Hamiltonian matrix element V (also called hopping or coupling energy) factors out and is assumed to be unity. To include coupling energy the final equation should be multiplied by V . That finishes the proof.


```

In[82]:= MatrixForm[
  Hk =
  ( 0 1 ) +
  ( 1 0 ) +
  (( 0 0 ) × (Exp[i × (#[[1, 1]] ×  $\frac{2 \times \pi}{N} \times \ell + \#[[1, 2]] \times k$ )] +
    Exp[i × (#[[2, 1]] ×  $\frac{2 \times \pi}{N} \times \ell + \#[[2, 2]] \times k$ )])) +
  ( 0 1 ) × (Exp[i × (#[[3, 1]] ×  $\frac{2 \times \pi}{N} \times \ell + \#[[3, 2]] \times k$ )] +
    Exp[i × (#[[4, 1]] ×  $\frac{2 \times \pi}{N} \times \ell + \#[[4, 2]] \times k$ )])) &[
  ExpressNeighborCoordinatesThroughRandHGeneral[n1, n2] //. {n2 p1 - n1 p2 → -N, -n2 p1 + n1 p2 → N}]
]

Out[82]//MatrixForm=
( 0 1 + ei (  $\frac{k n_1}{N} - \frac{2 p_1 \pi \ell}{N}$  ) + ei (  $-\frac{k n_2}{N} + \frac{2 p_2 \pi \ell}{N}$  ) )
( 1 + ei (  $\frac{k n_1}{N} - \frac{2 p_1 \pi \ell}{N}$  ) + ei (  $-\frac{k n_2}{N} + \frac{2 p_2 \pi \ell}{N}$  ) )

In[83]:= FullSimplify[ExpToTrig[Hk[[1, 2]] × Hk[[2, 1]]]]

Out[83]=
3 + 2 Cos[  $\frac{k n_1 - 2 p_1 \pi \ell}{N}$  ] + 2 Cos[  $\frac{k n_2 - 2 p_2 \pi \ell}{N}$  ] + 2 Cos[  $\frac{k (n_1 + n_2) - 2 (p_1 + p_2) \pi \ell}{N}$  ]

```

Figure 4

Figures 5(a, b) list the *Mathematica* script used to generate the dispersion plots for (30, 6) SWNT. Blue vertical lines mark extrema of dispersion curves. When unit cell is chosen to be translationally symmetric, i.e. include many primitive unit cells, band folding occurs at these lines. Not all lines mark the Brillouin zone boundary for translationally invariant unit cell, but all zone boundaries match these lines (due to the periodicity of dispersion in k -space derivatives of $E[k]$ at zone boundaries are zero).

```

In[1]:= p1p2[n1_, n2_] :=
Module[{p1}, p1 = 0; While[True, If[IntegerQ[ $\frac{\text{GCD}[n1, n2] + p1 n2}{n1}$ ], Break[]]; p1++];
{p1,  $\frac{\text{GCD}[n1, n2] + p1 n2}{n1}$ }]

In[2]:= e[k_, n1_Integer, n2_Integer] := Module[{p1, p2, n}, n = GCD[n1, n2]; {p1, p2} = p1p2[n1, n2];

Join[
Table[
+ $\sqrt{\left(3 + 2 \cos\left[\frac{n1 \times k - 2 \times \pi \times n \times p1}{n}\right] + 2 \cos\left[\frac{n2 \times k - 2 \times \pi \times n \times p2}{n}\right] + 2 \cos\left[\frac{(n1 + n2) \times k - 2 \times \pi \times n \times (p1 + p2)}{n}\right]\right)}$ , {n, 0, n - 1}],
Table[
- $\sqrt{\left(3 + 2 \cos\left[\frac{n1 \times k - 2 \times \pi \times n \times p1}{n}\right] + 2 \cos\left[\frac{n2 \times k - 2 \times \pi \times n \times p2}{n}\right] + 2 \cos\left[\frac{(n1 + n2) \times k - 2 \times \pi \times n \times (p1 + p2)}{n}\right]\right)}$ , {n, 0, n - 1}]]]

In[3]:= {n1Arg, n2Arg} = {30, 6};
ExtremaTbl =
Table[DeleteCases[If[#[[2]]  $\geq -10^{-7}$  && #[[2]]  $\leq \pi + 10^{-7}$ , #[[2]], "X"] & /@
(N[
Reduce[
((n1 Sin[ $\frac{k n1 - 2 n p1 \pi}{n}$ ] + n2 Sin[ $\frac{k n2 - 2 n p2 \pi}{n}$ ] +
(n1 + n2) Sin[ $\frac{k (n1 + n2) - 2 n (p1 + p2) \pi}{n}$ ]) // .
{p1  $\rightarrow$  p1p2[n1Arg, n2Arg][[1]], p2  $\rightarrow$  p1p2[n1Arg, n2Arg][[2]]} // . n  $\rightarrow$  GCD[n1, n2] // .
{n1  $\rightarrow$  n1Arg, n2  $\rightarrow$  n2Arg} == 0, k]] // . C[1]  $\rightarrow$  0 // . Or  $\rightarrow$  List), "X"],
{n, 0, GCD[n1Arg, n2Arg] - 1}] // . True  $\rightarrow$  {0};

```

Figure 5-a

```
In[4]:= Npnts = 300; RGBColorff[x_] := RGBColor[x, If[x < 1/2, x*2, (1-x)*2], 1-x];
```

```
Show[
```

```
Graphics[
```

```
{Table[ListPlot[Transpose[{{Table[N[ $\frac{i-1}{Npnts-1} \times \pi$ ], {i, 1, Npnts}], #[[i]]}],
```

```
PlotStyle -> RGBColorff[ $\frac{i}{\text{Length}[\#]}$ ], Joined -> True, DisplayFunction -> Identity][[1]],
```

```
{i, 1, Length[#]}, {RGBColor[0, 0, 0.6],
```

```
Line[{{#, -3}, {#, 3}}] & /@ Flatten[ExtremaTbl]}], AspectRatio -> GoldenRatio-1,
```

```
Frame -> True] & [Transpose[Table[ $\epsilon$ [N[ $\frac{i-1}{Npnts-1} \times \pi$ ], n1Arg, n2Arg], {i, 1, Npnts}]]]
```

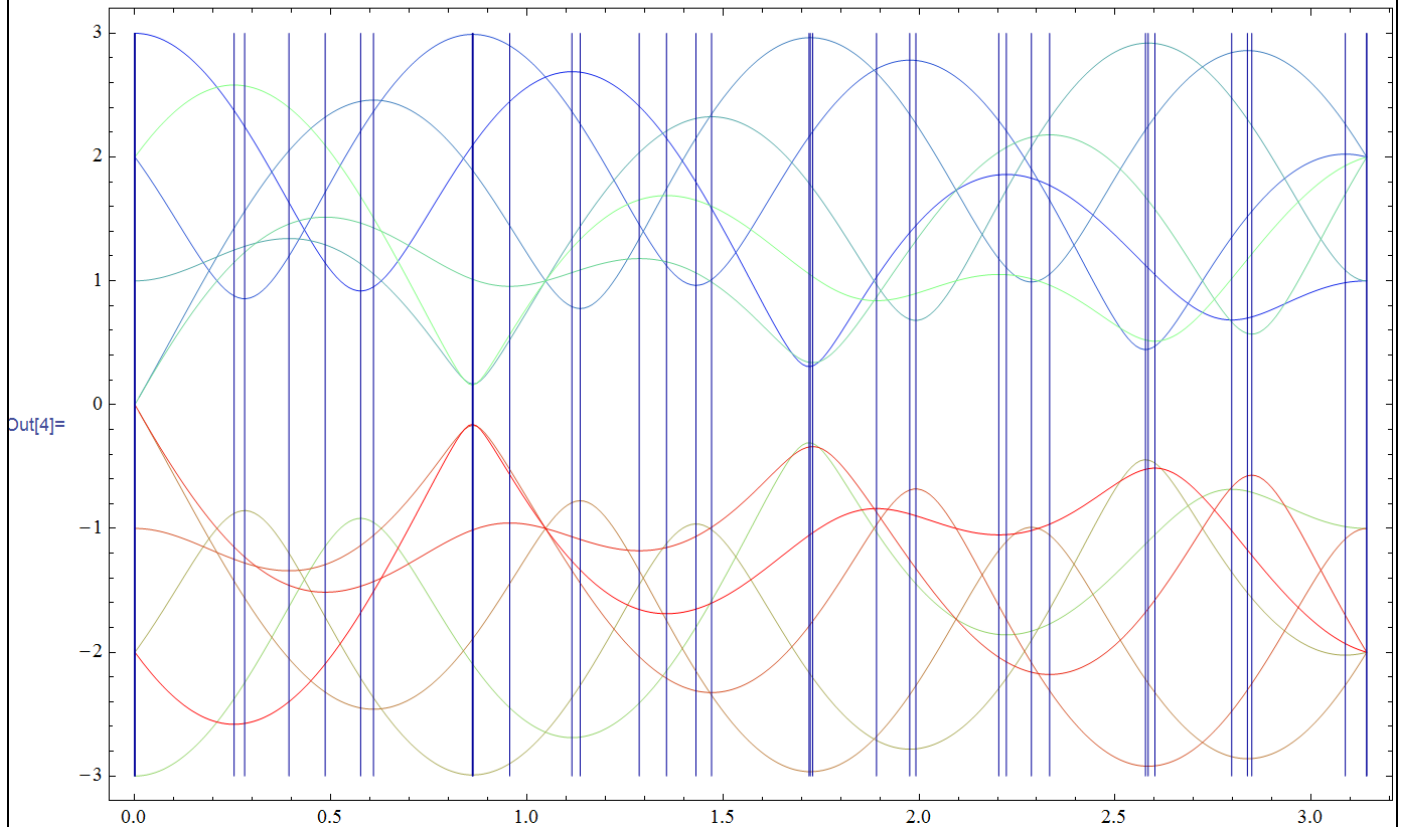


Figure 5-b

PROBLEM 4 (Prerequisites: **Problems 1, 2** and **3**)

Prove that in the π -orbital tight-binding nearest neighbor approximation absolute values of group velocities for electrons with energies equal to the Fermi level are the same in graphene and metallic nanotubes.

Solution:

Note: Only numerical solution for this problem is provided because I was not able to find for all possible $\{n_1, n_2\}$ the analytical dependence of branch index(es) and values of k for which $E[k] = 0$. When n_1 and n_2 are relatively prime (i.e. do not have common integer divisor except 1) there are only two dispersion branches each satisfying condition $E[k] = 0$ only at $k_0 = 2\pi/3$ (provided $n_1 - n_2 = 3q$; q is an integer). When n_1 and n_2 are not relatively prime, for SWNT's with $n_1 - n_2 = 3q$ dispersion $E[k]$ turns to zero at either $k_0 = 0$ or $k_0 = 2\pi/3$. I failed to obtain analytical dependence of k_0 on n_1 and n_2 for that case.

To compare group velocities we need the dispersion law of graphene $E_{gr}[\vec{k}]$ (dispersion law $E[k]$ for arbitrary SWNT has been derived in **Problem 3**). We follow the same approach as in **Problem 3**: determine the nearest neighbors and phase factors of the Bloch functions for them. Then, we collect all non-zero terms in two rows of the infinite Hamiltonian matrix associated with the unit cell at the origin. We can reuse Fig. 2 for this purpose. The only difference is that now \vec{k} is a 2-component vector instead of a scalar.

Translational basis vectors depicted in Fig. 2 are $\vec{R}_1 = \{\sqrt{3}, 0\}$ and $\vec{R}_2 = \{\sqrt{3}/2, 3/2\}$ (for brevity lattice constant is assumed to be 1). As in **Problem 3** the Schrödinger equation for infinite 2D system can be formally written as

$$H \cdot C^{\varepsilon, \vec{k}} = E_{gr}[\vec{k}] C^{\varepsilon, \vec{k}},$$

where H and $C^{\varepsilon, \vec{k}}$ expressed in localized basis have infinite dimensions. Indexes of vectors $C^{\varepsilon, \vec{k}}$ and $H \cdot C^{\varepsilon, \vec{k}}$ run from $-\infty$ to $+\infty$. In this problem only indexes 1 and 2 are important: orbitals with these indexes are located on the corresponding atoms residing in the unit cell at the origin. According to Bloch theorem the only difference between components of $C^{\varepsilon, \vec{k}}$ associated

with unit cell at the origin and unit cell with index 3 in Fig. 2 is the phase factor $e^{-i\vec{R}_1 \cdot \vec{k}}$ (because cell marked with index 3 in Fig. 2 is shifted by $-\vec{R}_1$ with respect to the origin). The corresponding contribution to rows 1 and 2 in vector $H \cdot C^{\varepsilon, \vec{k}}$ is

$$\begin{pmatrix} 0 & V \\ 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} C_1^{\varepsilon, \vec{k}} \\ C_2^{\varepsilon, \vec{k}} \end{pmatrix} e^{-i\vec{R}_1 \cdot \vec{k}},$$

where $C_1^{\varepsilon, \vec{k}}$ and $C_2^{\varepsilon, \vec{k}}$ are wave function components in the unit cell at the origin. Applying the described above operation to unit cells 0, 1, 2, and 4 we obtain:

$$\begin{aligned} & \left(\begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix} + \begin{pmatrix} 0 & V \\ 0 & 0 \end{pmatrix} e^{-i\vec{R}_1 \cdot \vec{k}} + \begin{pmatrix} 0 & 0 \\ V & 0 \end{pmatrix} e^{i\vec{R}_1 \cdot \vec{k}} + \right. \\ & \left. \begin{pmatrix} 0 & V \\ 0 & 0 \end{pmatrix} e^{-i\vec{R}_2 \cdot \vec{k}} + \begin{pmatrix} 0 & 0 \\ V & 0 \end{pmatrix} e^{-i\vec{R}_2 \cdot \vec{k}} \right) \cdot \begin{pmatrix} C_1^{\varepsilon, \vec{k}} \\ C_2^{\varepsilon, \vec{k}} \end{pmatrix} = E_{gr}[\vec{k}] \begin{pmatrix} C_1^{\varepsilon, \vec{k}} \\ C_2^{\varepsilon, \vec{k}} \end{pmatrix} \end{aligned}$$

The terms in parentheses at the left-hand side correspond respectively to interaction within the unit cell at the origin, unit cell at the origin and cells 3, 1, 4, and 2. After assuming that Cartesian components of $\vec{k} = \{k_1, k_2\}$, and substitution of values for \vec{R}_i , the eigenproblem above transforms to:

$$\begin{pmatrix} 0 & V \left(1 + e^{-i\sqrt{3}k_1} + e^{i\left(\frac{\sqrt{3}}{2}k_1 - \frac{3}{2}k_2\right)} \right) \\ V \left(1 + e^{i\sqrt{3}k_1} + e^{-i\left(\frac{\sqrt{3}}{2}k_1 - \frac{3}{2}k_2\right)} \right) & 0 \end{pmatrix} \cdot \begin{pmatrix} C_1^{\varepsilon, \vec{k}} \\ C_2^{\varepsilon, \vec{k}} \end{pmatrix} = E_{gr}[\vec{k}] \begin{pmatrix} C_1^{\varepsilon, \vec{k}} \\ C_2^{\varepsilon, \vec{k}} \end{pmatrix}$$

Analytical expression for eigenvalues $\varepsilon[\vec{k}]$ is:

$$E_{gr}[\vec{k}] = \pm V \sqrt{3 + 2 \cos[\sqrt{3}k_1] + 4 \cos\left[\frac{\sqrt{3}}{2}k_1\right] \cos\left[\frac{3}{2}k_2\right]}$$

Figure 6 below presents the lower dispersion branch of $E_{gr}[\vec{k}]$. The reciprocal vectors corres-

```
In[88]:= Show[
  {Graphics3D[
    {Plot3D[-sqrt[3 + 2 Cos[sqrt[3] K1] + 4 Cos[sqrt[3] K1/2] Cos[3 K2/2]], {K1, -3, 3}, {K2, -3, 3}, PlotPoints -> 300,
      DisplayFunction -> Identity][[1]],
    Table[{RGBColor[0, 1, 0], Line[{0, 0, 0}, 4 pi / (3 sqrt[3]) {Cos[alpha], Sin[alpha], 0}]}, {alpha, 0, 2 pi - pi/3, pi/3}]}],
  BoxRatios -> {1, 1, 0.5}]
```

Out[88]=

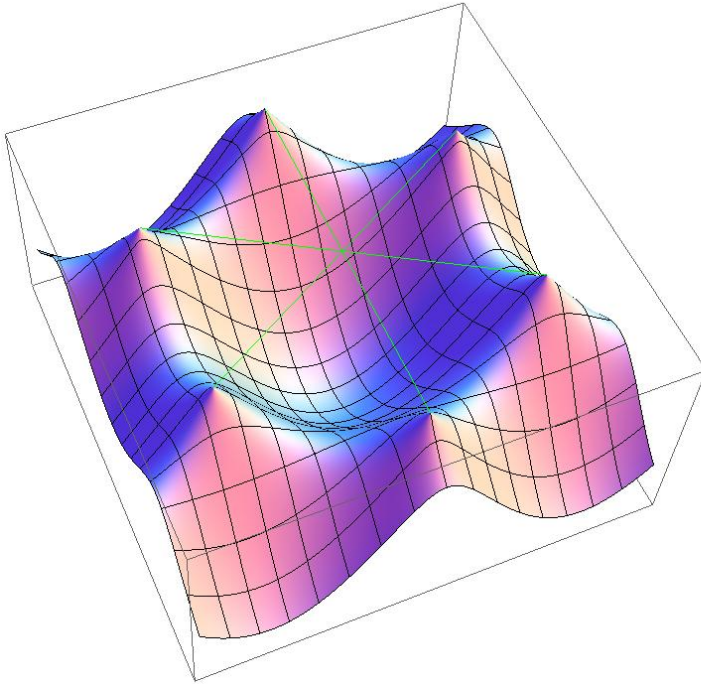


Figure 6

ponding to \vec{R}_1 and \vec{R}_2 are $\vec{K}_1 = \{2\pi/\sqrt{3}, -2\pi/3\}$ and $\vec{K}_2 = \{0, 4\pi/3\}$. The points at which lower and upper dispersion branches touch each other are located at $\vec{K}_F^n = \frac{4\pi}{3\sqrt{3}} \left\{ \cos\left[\frac{\pi n}{3}\right], \sin\left[\frac{\pi n}{3}\right] \right\}$, where integer $n = 0 \dots 5$. Green lines in Fig. 6 are drawn from the origin in k-space to \vec{K}_F^n . Taylor expansion of the upper dispersion branch in the vicinity of \vec{K}_F^0 is

$$E_{gr}[\vec{K}_F^n + \{\delta k_1, \delta k_2\}] = \frac{3}{2} V(\delta k_1 + \delta k_2)$$

That means the gradient of $E_{gr}[\vec{k}]$ (which equals group velocity if $\hbar = 1$) in the vicinity of $\overline{K_F^n}$ is 3/2 in any direction. Figures 7 (a-c) present the above portion of the solution in *Mathematica* format. Hopping energy V factors out and is assumed to be unity.

$\mathcal{R}1$ and $\mathcal{R}2$ are vectors of real space basis:

```
In[14]:=  $\mathcal{R}1 = \{\sqrt{3}, 0\}; \mathcal{R}2 = \left\{\frac{\sqrt{3}}{2}, \frac{3}{2}\right\};$ 
```

$\{\mathcal{K}1, \mathcal{K}2\}$ are vectors of reciprocal basis:

```
In[15]:=  $\{\mathcal{K}1, \mathcal{K}2\} = \text{FullSimplify}[\#, \text{Assumptions} \rightarrow \{\text{Re}[\mathbf{a}] > 0 \ \&\amp; \ \text{Im}[\mathbf{a}] = 0\}] \ \& \ /@$ 
 $(\{\{\mathcal{K}1_1, \mathcal{K}1_2\}, \{\mathcal{K}2_1, \mathcal{K}2_2\}\} //$ 
 $(\text{Solve}[\{\mathcal{R}1.\{\mathcal{K}1_1, \mathcal{K}1_2\} = 2 \times \pi, \mathcal{R}2.\{\mathcal{K}1_1, \mathcal{K}1_2\} = 0, \mathcal{R}1.\{\mathcal{K}2_1, \mathcal{K}2_2\} = 0, \mathcal{R}2.\{\mathcal{K}2_1, \mathcal{K}2_2\} = 2 \times \pi\},$ 
 $\{\mathcal{K}1_1, \mathcal{K}1_2, \mathcal{K}2_1, \mathcal{K}2_2\}][[1]]))$ 
```

```
Out[15]=  $\left\{\left\{\frac{2\pi}{\sqrt{3}}, -\frac{2\pi}{3}\right\}, \left\{0, \frac{4\pi}{3}\right\}\right\}$ 
```

Error Check:

```
In[21]:=  $\text{MatrixForm}[\{\{\mathcal{K}1.\mathcal{R}1, \mathcal{K}2.\mathcal{R}1\}, \{\mathcal{K}1.\mathcal{R}2, \mathcal{K}2.\mathcal{R}2\}\}]$ 
```

```
Out[21]//MatrixForm=
 $\begin{pmatrix} 2\pi & 0 \\ 0 & 2\pi \end{pmatrix}$ 
```

Figure 7-a

Positions of nearest neighbor cells:

$$RA = \mathcal{R}2; RB = \mathcal{R}1; RC = -RA; RD = -RB;$$

Hamiltonian matrix $H[\vec{k}]$

```
In[22]:= H[k1_, k2_, V_] :=  $\begin{pmatrix} 0 & V \\ V & 0 \end{pmatrix}$  + Exp[i × RA . {k1, k2}] ×  $\begin{pmatrix} 0 & 0 \\ V & 0 \end{pmatrix}$  + Exp[i × RB . {k1, k2}] ×  $\begin{pmatrix} 0 & 0 \\ V & 0 \end{pmatrix}$  +  
Exp[i × RC . {k1, k2}] ×  $\begin{pmatrix} 0 & V \\ 0 & 0 \end{pmatrix}$  + Exp[i × RD . {k1, k2}] ×  $\begin{pmatrix} 0 & V \\ 0 & 0 \end{pmatrix}$  ;  
MatrixForm[H[k1, k2, 1]]
```

Out[23]//MatrixForm=

$$\begin{pmatrix} 0 & 1 + e^{-i\sqrt{3}k_1} + e^{i\left(-\frac{\sqrt{3}k_1}{2} - \frac{3k_2}{2}\right)} \\ 1 + e^{i\sqrt{3}k_1} + e^{i\left(\frac{\sqrt{3}k_1}{2} + \frac{3k_2}{2}\right)} & 0 \end{pmatrix}$$

Upper dispersion branch

```
In[10]:= EkGraphene =  $\sqrt{\text{FullSimplify}[\text{ExpToTrig}[H[k1, k2, 1][[1, 2]] H[k1, k2, 1][[2, 1]]]}$ 
```

Out[10]=

$$\sqrt{3 + 2 \text{Cos}[\sqrt{3} k_1] + 4 \text{Cos}\left[\frac{\sqrt{3} k_1}{2}\right] \text{Cos}\left[\frac{3 k_2}{2}\right]}$$

Figure 7-b

Make sure that dispersion surface touches Fermi level at the point $\frac{1}{3} (2 \times \mathbf{K1} + \mathbf{K2})$:

```
In[20]:= DispersionLawGraphene[K1_, K2_] := EkGraphene //. {k1 -> K1, k2 -> K2};
DispersionLawGraphene[#[[1]], #[[2]]] & [1/3 (2 x K1 + K2)]
```

Out[20]= 0

Taylor expansion around point $\frac{1}{3} (2 \times \mathbf{K1} + \mathbf{K2})$

```
{Normal[Series[+DispersionLawGraphene[(1/3 (2 x K1 + K2))[[1]] + delta k1, (1/3 (2 x K1 + K2))[[2]]],
{delta k1, 0, 1}],
Normal[Series[+DispersionLawGraphene[(1/3 (2 x K1 + K2))[[1]], (1/3 (2 x K1 + K2))[[2]] + delta k2],
{delta k2, 0, 1}]]]}
```

Out[19]= $\left\{ \frac{3 \delta k1}{2}, \frac{3 \delta k2}{2} \right\}$

Figure 7-c

Next we compute group velocities in SWNT. To account for helical structure of SWNT we need to recall that the wave function acquires an additional phase factor of e^{ik} when the shift h along SWNT axis constitutes the projection of helical vector on this axis (arrow on top of \vec{H} should prevent the confusion from using the same letter for Hamiltonian and helical vector):

$$h = \frac{|\vec{R} \times \vec{H}|}{|\vec{R}|}.$$

The group velocity for 1D translationally periodic structures is

$$v = \frac{1}{\hbar} \frac{\partial E[k]}{\partial k}.$$

Here k varies within $\left[-\frac{\pi}{a}, +\frac{\pi}{a}\right]$ and a is the translational period. If k scaled to vary within

$[-\pi, +\pi]$, the equation for group velocity includes extra factor a :

$$v = \frac{a}{\hbar} \frac{\partial E[k]}{\partial k}.$$

The wave function $\psi_1[\vec{r}]$ in helical structure inside slice of thickness h normal to SWNT axis is related to the value of the same wave function in the slice shifted by nh along SWNT axis as:

$$\psi[\vec{r} + n\vec{h}] = e^{ikn} \psi[\mathfrak{R}[-n\alpha]\vec{r}].$$

Here vector \vec{h} is collinear to SWNT axis and has length h defined above, operator $\mathfrak{R}[\theta]$ rotates vector \vec{r} around SWNT axis by angle θ , and α is a helical angle (**Problem 1**). If one follows the derivation of the equation for group velocity, it becomes clear that it has the same form regardless of the presence of operator $\mathfrak{R}[-n\alpha]$. In the equation for $E[k]$ derived in **Problem 3**, k varies within $[-\pi, +\pi]$, therefore one needs to include the “slice” thickness in the equation for electron velocity:

$$v = \frac{h}{\hbar} \frac{\partial E[k]}{\partial k}.$$

For SWNT with relatively prime indexes n_1 and n_2 (i.e. $N = 1$ and $l = 0$) the equation for velocity can be derived analytically. For metallic SWNT's with $n_1 - n_2 = 3q$ bands touch or cross (depending on n_1 and n_2) always at $k = 2\pi/3$. This is demonstrated by *Mathematica* script in Fig. 8 below. Given that n_1 and n_2 are relatively prime and $n_1 - n_2 = 3q$, index n_1 can be always written as $n_1 = 3m \pm 1$, where m is an integer (if $n_1 = 3s$, n_1 and n_2 are not relatively prime).

Below we find k -values at which $E[k] = 0$ for metallic ($n_1 - n_2 = 3q$) SWNT's with relatively prime n_1 and n_2 (i.e. $\mathcal{N} = 1$ & $\ell = 0$).

```
In[90]:= Fragment01 =
FullSimplify[
Cos[ $\frac{k n_1 - 2 p_1 \pi \ell}{\mathcal{N}}$ ] + Cos[ $\frac{k n_2 - 2 p_2 \pi \ell}{\mathcal{N}}$ ] + Cos[ $\frac{1}{\mathcal{N}} (k (n_1 + n_2) - 2 (p_1 + p_2) \pi \ell)$ ] // . k  $\rightarrow \frac{2}{3} \pi$  // .
 $\mathcal{N} \rightarrow 1$  // .  $n_2 \rightarrow n_1 - 3 q$  // .  $\ell \rightarrow 0$ ,
Element[n1, Integers] && Element[q, Integers] && Element[p1, Integers] &&
Element[p2, Integers], Assumptions  $\rightarrow \{ \}$ ]
```

```
Out[90]=
2 Cos[ $\frac{2 n_1 \pi}{3}$ ] + Cos[ $\frac{4 n_1 \pi}{3}$ ]
```

```
In[27]:= FullSimplify[Reduce[3 + 2 (Fragment01) == 0, n1]]
```

```
Out[27]=
C[1]  $\in$  Integers && (1 + n1 == 3 C[1] || n1 == 1 + 3 C[1])
```

i.e. when n_1 and n_2 are relatively prime, $n_1 = 3m \pm 1$ (note that integers q and m may differ)

Figure 8

At $k = 2\pi/3$ the dispersion function $E[k]$ has a cusp, so the derivative does not exist at this point. Derivatives at $k = 2\pi/3 + 0$ and $k = 2\pi/3 - 0$ have different signs. Therefore instead of differentiation, we have to perform Taylor expansion at e.g. $k = 2\pi/3 + 0$. *Mathematica* script presented in Fig. 9 is used to compute the derivatives for $n_1 = 3m \pm 1$. The first equation below is for $n_1 = 3m - 1$, the second one is for $n_1 = 3m + 1$.

$$\left. \frac{\partial E[k]}{\partial k} \right|_{\substack{k=2\pi/3+0 \\ n_1=3m-1}} = \sqrt{3} \sqrt{1 + 9m^2 + 3q(q+1) - 3m(2+3q)}$$

$$\left. \frac{\partial E[k]}{\partial k} \right|_{\substack{k=2\pi/3+0 \\ n_1=3m+1}} = \sqrt{3} \sqrt{1 + 9m^2 + 3q(q-1) + 3m(2-3q)}$$

Multiplying these equations by h we get the electron group velocity along SWNT axis.

Below we analytically derive the expression for group velocity in the case when n_1 and n_2 are relatively prime and SWNT is metallic (i.e. $n_1 - n_2 = 3q$)

In[253]:=

```
DispersionNearFermiMutuallyPrimeIndexesSWNTD =
FullSimplify[
  1/δk
  Sqrt[FullSimplify[
    Normal[
      Series[3 + 2 (Cos[k n1 - 2 p1 π ℓ / N] + Cos[k n2 - 2 p2 π ℓ / N] + Cos[k (n1 + n2) - 2 (p1 + p2) π ℓ / N]) // .
        {k -> 2/3 π + δk, N -> 1, ℓ -> 0, n2 -> n1 - 3 q} // . n1 -> 3 m + s // . s -> #, {δk, 0, 2}],
      Element[m, Integers] && Element[q, Integers], Assumptions -> {Im[δk] == 0, Re[δk] > 0}] & /@
    {-1, 1}
  ]
]
```

Out[253]=

$$\left\{ \sqrt{3} \sqrt{1 + 9m^2 + 3q(1+q) - 3m(2+3q)}, \sqrt{3 + 27m^2 + 9m(2-3q) + 9(-1+q)q} \right\}$$

Figure 9

Calculation of $h = \frac{|\vec{R} \times \vec{H}|}{|\vec{R}|}$ requires to use the equation (**Problem 1**) $p_2 n_1 - p_1 n_2 = 1$ (since $N = 1$)

to express either p_1 or p_2 . The first equation below is h for $n_1 = 3m - 1$, the second one is for $n_1 = 3m + 1$.

$$h_{n_1=3m-1} = \frac{1}{2\sqrt{\frac{1}{3} + 3m^2 - m(2+3q) + q(q+1)}}$$

$$h_{n_1=3m+1} = \frac{1}{2\sqrt{\frac{1}{3} + 3m^2 + m(2-3q) + q(q-1)}}$$

Multiplying these equations by respective $\frac{\partial E[k]}{\partial k}$, one gets the group velocities, which are independent of SWNT indexes as long as n_1 and n_2 are relatively prime and $n_1 - n_2 = 3q$. Group ve-

locity equals $3/2$, which coincides with the group velocity in graphene. (the value is unitless because we assumed $\hbar = 1$, $V = 1$, and lattice parameter $a = 1$). If these constants are included,

$$v = \frac{a|V|}{\hbar} \frac{3}{2}.$$

Figure 10 below presents *Mathematica* script completing the proof for the case when n_1 and n_2 are relatively prime.

```
In[254]:=
  solp1 = Solve[p2 n1 - p1 n2 == 1, p1][[1, 1]] // . n2 -> n1 - 3 q // . n1 -> 3 m + s

Out[254]=
  p1 -> (-1 + p2 (3 m + s)) / (3 m - 3 q + s)

In[265]:=
  HProjection =
  FullSimplify[
  FullSimplify[
  Cross[Join[R1 n1 + R2 n2, {0}], Join[R1 p1 + R2 p2, {0}]]][[3]] // . solp1 // .
  n2 -> n1 - 3 q // . n1 -> 3 m + s // . s -> # ] & /@ {-1, 1}

Out[265]=
  { 1 / (2 sqrt(1/3 + m(-2 + 3m) + q - 3mq + q^2)), 1 / (2 sqrt(1/3 + 3m^2 + m(2 - 3q) + (-1 + q)q)) }

In[266]:=
  FullSimplify[HProjection DispersionNearFermiMutuallyPrimeIndexesSWNTD]

Out[266]=
  { 3/2, 3/2 }
```

Figure 10

All metallic SWNT's cross or touch Fermi level either at $k = 2\pi/3$ or $k = 0$. We can numerically compute the group velocities for these points for large range of n_1 and n_2 to make sure that the velocities for all types of metallic SWNT's are indeed equal $3/2$. Figure 11 below presents *Mathematica* script used to test all indexes $3 \leq n_1 \leq 100$ and $0 \leq n_2 \leq n_1$. Because calculations are still symbolic, the results are rational numbers (i.e. $3/2$).

In[277]=

```

Union[
   $\delta k^{-1} \times \#[[5]] \times$ 
  Normal[
    Series[
      + $\sqrt{3 + 2 \text{Cos}\left[\frac{\#[[3, 1]] \times (\#[[2]] + \delta k) - 2 \times \pi \times \#[[1]] \times \#[[4, 1]]}{\#[[6]]}\right]}$  +
      2 Cos $\left[\frac{\#[[3, 2]] \times (\#[[2]] + \delta k) - 2 \times \pi \times \#[[1]] \times \#[[4, 2]]}{\#[[6]]}\right]$  +
      2 Cos $\left[\frac{(\#[[3, 1]] + \#[[3, 2]]) \times (\#[[2]] + \delta k) - 2 \times \pi \times \#[[1]] \times (\#[[4, 1]] + \#[[4, 2]])}{\#[[6]]}\right]$ ),
      { $\delta k$ , 0, 1}] & /@ Flatten[DeleteCases[Table[
      { $p1$ ,  $p2$ } = plp2[n1, n2]; N = GCD[n1, n2];
      h = Abs $\left[\frac{\text{Cross}[\text{Join}[(p1 \times \mathcal{R}1 + p2 \times \mathcal{R}2), \{0\}], \text{Join}[n1 \times \mathcal{R}1 + n2 \times \mathcal{R}2, \{0\}]][[3]]}{\sqrt{(n1 \times \mathcal{R}1 + n2 \times \mathcal{R}2) \cdot (n1 \times \mathcal{R}1 + n2 \times \mathcal{R}2)}}\right]$ ;
      If[Length[#] > 0, Join[#, {{n1, n2}, {p1, p2}, h, N}], {}] & /@ DeleteCases[Table[
      If[#[[1]] < 10-7, { $\ell$ , 0}
      ,
      If[#[[2]] < 10-7, { $\ell$ ,  $\frac{2}{3} \times \pi$ }
      ,
      "X"]
      ] & [
      Abs $\left[3 + 2 \text{Cos}\left[\frac{k n1 - 2 p1 \pi \ell}{N}\right] + 2 \text{Cos}\left[\frac{k n2 - 2 p2 \pi \ell}{N}\right] + 2 \text{Cos}\left[\frac{k (n1 + n2) - 2 (p1 + p2) \pi \ell}{N}\right]\right]$  // .
      k  $\rightarrow$  #] & /@ {0,  $\frac{2}{3} \times \pi$ }]
      ,
      { $\ell$ , 0, N - 1}], "X",  $\infty$ ]
      ,
      {n1, 3, 100}, {n2, 0, n1}], {},  $\infty$ ], 2]]

```

Out[277]=

$$\left\{\frac{3}{2}\right\}$$

Figure 11

REFERENCES:

[1] C.T. White, D.H. Roberrrtson, and J.W. Mintmire “Helical and rotational symmetries of nanoscale graphitic tubules”, PRB v. **47**, p.5485 (1993).