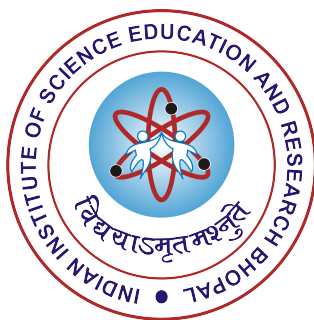


Report on

# **Tight Binding Approximation on Graphene**

submitted by

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## DECLARATION

We hereby declare that the material, which we now submit for assessment under the report title "Tight Binding Approximation on Graphene ", is entirely our own work and has not been taken from the work of others except to the extent that such work has been cited and acknowledged within the text of this report.

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IISER Bhopal  
April 2022

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# 1 Abstract

Graphene is a very unusual material with carriers(massless fermions) that exhibit an effective "speed of light" in the low energy range of  $<0.5$  eV; these massless fermions exhibit various Quantum electrodynamics(QED) phenomena at this energy range which many researchers are exploring. But before doing that, we should understand and stimulate the band structure of graphene. In this project, we propose to study the band structure of graphene using the tight-binding model. Initially, we will consider only the nearest neighbour hopping and analyse the band structure. Further, we can also consider the second nearest neighbour hopping and study the difference it causes to the band structure. We first explore the electronic properties by obtaining the analytical solution of the wave function by solving the Schrodinger equation. We construct the Hamiltonian matrix using the nearest neighbour interaction and use this Hamiltonian to get the energy dispersion relation. We have used Wolfram Mathematica and python programming language to draw the band structure of graphene using tight binding approximation method.

## 2 Introduction

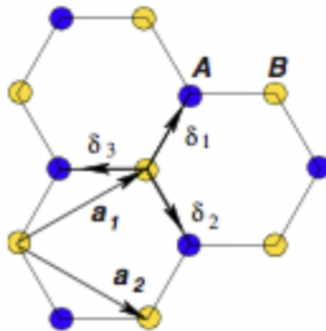
### 2.1 Graphene

Graphene is an allotrope of carbon in the form of  $sp^2$  - bonded atoms. The molecular bond length is 0.142 nm. We can make Graphite by stacking up graphene layers on top of each other. The interplanar spacing of the layers is 0.335 nm.[5] Van der Waals forces are responsible for holding the different graphene layers together in Graphite. Graphene is one atom thick, and therefore it is the thinnest material known to humanity to date. Some other notable properties of graphene that make the graphene system attractive are the following :

- Strongest compound, 100 to 300 times stronger than steel with a tensile strength of 130 GPa and young's modulus of 1 TPa to 1.034 TPa.[5]
- Lightest material, 1 sq.meter weighs only 0.77 mg.[5]
- Good conductor of heat and electricity at room temperature.
- Uniform absorption of light across the visible and near-infrared parts of the spectrum.
- Potential suitability for use in spin transport.

### 2.2 Graphene : Structure

Graphene has a honeycomb lattice structure. Graphene unit cell has two types of lattice site, which we represent using A and B.



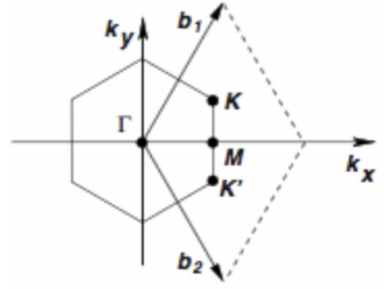
Graphene honeycomb lattice structure[2]

In the above figure  $a_1$  and  $a_2$  are lattice vectors,  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  are the nearest neighbor vectors. The vectors can be represented as

$$\begin{aligned} a_1 &= \frac{a}{2}(3, \sqrt{3}) \\ a_2 &= \frac{a}{2}(3, -\sqrt{3}) \\ \delta_1 &= \frac{a}{2}(1, \sqrt{3}) \\ \delta_2 &= \frac{a}{2}(1, -\sqrt{3}) \\ \delta_3 &= -\frac{a}{2}(1, 0) \end{aligned}$$

The Brillouin Zone (BZ) of Graphene is hexagonal, and corner points are known as Dirac points. At this point, band energy is zero. We represent Dirac points by K and K'. Here M represents the midpoint of the line joining K and K' point. These vectors can also be represented as

$$\begin{aligned} K &= \frac{2\pi}{3a}(1, \frac{1}{\sqrt{3}}) \\ M &= \frac{2\pi}{3a}(1, 0) \\ K' &= \frac{2\pi}{3a}(1, -\frac{1}{\sqrt{3}}) \end{aligned}$$



1st BZ of Graphene [2]

### 3 Tight Binding Model

The tight binding model is found accurate and less computationally expensive in the simulation of the band structure of the material. It assumes that there exists strong crystal or ionic potentials. This implies that, when an electron is captured while traveling through the lattice, it remains bound to the ion for a long period of time before it moves ahead. Thus, during this period, the electron is tightly bound. In tight binding model, we observe how wavefunctions of atom or ions will interact as we bring them together.

let's consider crystal with  $N$  number of atoms. Assume that there is one atom per unit cells. Each atom has only one orbital  $\phi(\mathbf{r})$ . Then we can form wavefunction using Bloch function as follow

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_m \exp(\iota \mathbf{k} \cdot \mathbf{R}_m) \phi(\mathbf{r} - \mathbf{R}_m)$$

By taking translation of this wave function, we can clearly see that this wave function satisfy the Bloch function condition.

$$\psi_k(\mathbf{r} + \mathbf{T}) = \frac{1}{\sqrt{N}} \sum_m \exp(\iota \mathbf{k} \cdot \mathbf{R}_m) \phi(\mathbf{r} - \mathbf{R}_m + \mathbf{T})$$

Let's take  $\mathbf{T}$  as translation vector.

$$\psi_k(\mathbf{r} + \mathbf{T}) = \frac{1}{\sqrt{N}} \exp(\iota \mathbf{k} \cdot \mathbf{T}) \sum_m \exp(\iota \mathbf{k} \cdot \mathbf{R}_m - \mathbf{T}) \phi(\mathbf{r} - (\mathbf{R}_m - \mathbf{T}))$$

$$\psi_k(\mathbf{r} + \mathbf{T}) = \exp(\iota \mathbf{k} \cdot \mathbf{T}) \psi_k(\mathbf{r})$$

So, This wavefunction satisfies the Bloch function.

Now, we take  $\mathbf{H}$  as Hamiltonian of the system. We applying tight binding approximation by assuming that Hamiltonian  $\mathbf{H}$  is interact with onsite atom and nearest neighbour atoms. Let's find expectation value of Hamiltonian,

$$\langle \psi_k(\mathbf{r}) | \mathbf{H} | \psi_k(\mathbf{r}) \rangle = \frac{1}{\sqrt{N}} \sum_m \sum_n \exp(\iota \mathbf{k} \cdot (\mathbf{R}_m - \mathbf{R}_n)) \langle \phi_m | \mathbf{H} | \phi_n \rangle \quad (1)$$

by applying tight binding approximation , we get

$$\langle \phi_n | \mathbf{H} | \phi_n \rangle = \alpha$$

$$\langle \phi_m | \mathbf{H} | \phi_n \rangle = \gamma$$

if n and m are nearest neighbours.

$$\langle \phi_m | \mathbf{H} | \phi_n \rangle = 0$$

is n and m are not nearest neighbours.

Here,  $\alpha$  is onsite energy term and  $\gamma(\gamma < 0)$  is the hopping term.

From equation 1, we can write

$$E = \langle \psi_k(\mathbf{r}) | \mathbf{H} | \psi_k(\mathbf{r}) \rangle$$

$$E = \alpha + \gamma \sum_n \exp(i\mathbf{k} \cdot \mathbf{R}_n)$$

Where, the sum is over nearest neighbour only and,  $\mathbf{R}_n$  is a vector joining an atom to its nearest neighbour.



## 4 Hamiltonian for Tight binding model : Graphene

### 4.1 Nearest neighbour Hopping

In this case, we assume only the nearest neighbour hopping, therefore the required Hamiltonian for this case is

$$\hat{H} = -t \sum_{\langle ij \rangle} \left[ \hat{a}_i^\dagger \hat{b}_j + \hat{b}_j^\dagger \hat{a}_i \right]$$

Here,  $a_i^\dagger$  creates and  $a_i$  annihilates an electron at the A sites and similarly for the B site case. Using the  $\delta$  vectors mentioned in the Graphene structure section we can write  $j = i + \delta$  and hence we can rewrite the above Hamiltonian as

$$\hat{H} = -t \sum_{i \in A} \sum_{\delta} \left[ \hat{a}_i^\dagger \hat{b}_{i+\delta} + \hat{b}_{i+\delta}^\dagger \hat{a}_i \right]$$

Here,  $\sum_{\delta}$  represents summation over all the three  $\delta$  vectors  $\delta_1, \delta_2, \delta_3$ . We can write the  $\hat{a}_i^\dagger$  operator as

$$\hat{a}_i^\dagger = \frac{1}{\sqrt{\frac{N}{2}}} \sum_k e^{ik \cdot r_i} \hat{a}_k^\dagger$$

Similarly,  $\hat{b}_j$  can be written as

$$\hat{b}_j = \hat{b}_{i+\delta} = \frac{1}{\sqrt{\frac{N}{2}}} \sum_{k'} e^{-ik' \cdot (r_i + \delta)} \hat{b}_{k'}$$

By using above two equation we can rewrite the Hamiltonian as

$$\hat{H} = \frac{-t}{2} \sum_{i \in A} \sum_{\delta, k, k'} \left( e^{i(k-k') \cdot r_i} e^{-ik' \cdot \delta} \hat{a}_k^\dagger \hat{b}_{k'} + H.c. \right)$$

Here H.c. represents hermitian conjugate. Also,

$$\sum_{i \in A} e^{i(k-k') \cdot r_i} = \frac{N}{2} \delta_{kk'}$$

Using the above equation we can further simplify the Hamiltonian as

$$\begin{aligned} \hat{H} &= \frac{-t}{2} \sum_{\delta, k, k'} \left( \frac{N}{2} \delta_{kk'} e^{-ik' \cdot \delta} \hat{a}_k^\dagger \hat{b}_{k'} + H.c. \right) \\ &= -t \sum_{\delta, k} \left( e^{-ik \cdot \delta} \hat{a}_k^\dagger \hat{b}_k + H.c. \right) \\ &= -t \sum_{\delta, k} \left( e^{-ik \cdot \delta} \hat{a}_k^\dagger \hat{b}_k + e^{ik \cdot \delta} \hat{b}_k^\dagger \hat{a}_k \right) \end{aligned}$$

So in the basis ,

$$\Psi \equiv \begin{bmatrix} \hat{a}_k \\ \hat{b}_k \end{bmatrix} \Rightarrow \Psi^\dagger \equiv [\hat{a}_k^\dagger \quad \hat{b}_k^\dagger]$$

We can represent Hamiltonian in this basis as

$$\hat{H} = \sum_k \Psi h(k) \Psi^\dagger$$

In our graphene system,  $h(k)$  can be represented as a matrix given by

$$h(k) = -t \begin{bmatrix} 0 & \Delta_k \\ \Delta_k^* & 0 \end{bmatrix}$$

Energy bands can be obtained by calculating the eigenvalue of the above matrix which is given by  $E = -t\sqrt{\Delta_k \Delta_k^*}$  [2] Where  $\Delta_k$  can be written as

$$\begin{aligned} \Delta_k &= e^{ik \cdot \delta_1} + e^{ik \cdot \delta_2} + e^{ik \cdot \delta_3} \\ &= e^{ik \delta_3} \left[ 1 + e^{ik(\delta_1 - \delta_3)} + e^{ik(\delta_2 - \delta_3)} \right] \\ &= e^{ik_x a} \left[ 1 + e^{i3k_x a/2} e^{i\sqrt{3}k_y a/2} + e^{i3k_x a/2} e^{-i\sqrt{3}k_y a/2} \right] \\ &= e^{ik_x a} \left[ 1 + e^{i3k_x a/2} \left( e^{i\sqrt{3}k_y a/2} + e^{-i\sqrt{3}k_y a/2} \right) \right] \\ &= e^{ik_x a} \left[ 1 + e^{i3k_x a/2} \left( 2 \cos\left(\frac{\sqrt{3}k_y a}{2}\right) \right) \right] \end{aligned}$$

Hence the energy band is given by

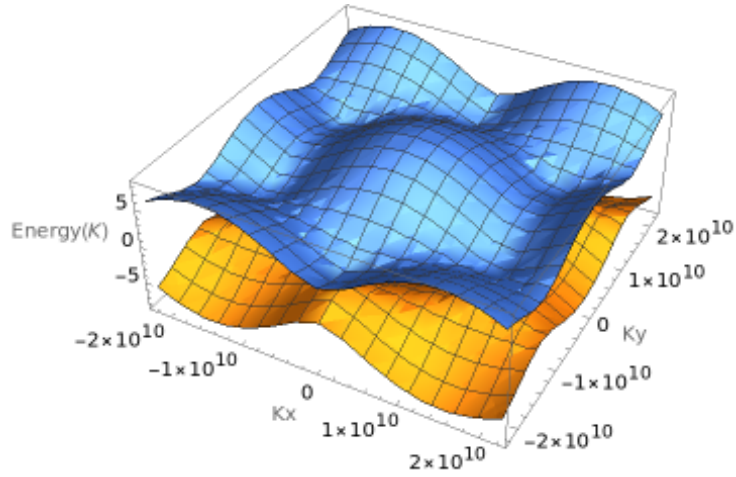
$$\begin{aligned} E &= -t\sqrt{\Delta_k \Delta_k^*} \\ &= -t\sqrt{e^{ik_x a} \left[ 1 + e^{i3k_x a/2} \left( 2 \cos(\sqrt{3}k_y a/2) \right) \right] e^{-ik_x a} \left[ 1 + e^{-i3k_x a/2} \left( 2 \cos(\sqrt{3}k_y a/2) \right) \right]} \\ &= -t\sqrt{\left[ 1 + e^{i3k_x a/2} \left( 2 \cos(\sqrt{3}k_y a/2) \right) \right] \left[ 1 + e^{-i3k_x a/2} \left( 2 \cos(\sqrt{3}k_y a/2) \right) \right]} \\ &= -t\sqrt{\left[ 1 + e^{i3k_x a/2} \left( 2 \cos(\sqrt{3}k_y a/2) \right) + e^{-i3k_x a/2} \left( 2 \cos(\sqrt{3}k_y a/2) \right) + \left( 4 \cos^2(\sqrt{3}k_y a/2) \right) \right]} \\ &= -t\sqrt{\left[ 1 + \left( 2 \cos(\sqrt{3}k_y a/2) \right) (e^{i3k_x a/2} + e^{-i3k_x a/2}) + \left( 4 \cos^2(\sqrt{3}k_y a/2) \right) \right]} \\ &= -t\sqrt{\left[ 1 + \left( 2 \cos(\sqrt{3}k_y a/2) \right) (2 \cos(3k_x a/2)) + \left( 4 \cos^2(\sqrt{3}k_y a/2) \right) \right]} \\ &= -t\sqrt{\left[ 1 + 4 \cos(\sqrt{3}k_y a/2) \cos(3k_x a/2) + 4 \cos^2(\sqrt{3}k_y a/2) \right]} \end{aligned}$$

$$E = -t\sqrt{\left[3 + 4\cos(\sqrt{3}k_y a/2)\cos(3k_x a/2) + 2\cos(\sqrt{3}k_y a)\right]} \quad (2)$$

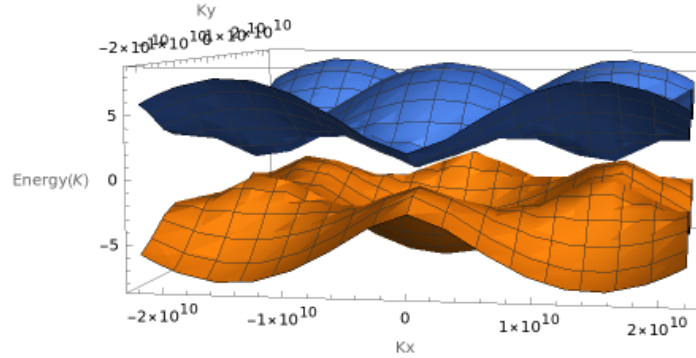
#### 4.1.1 Graphs and Plots

Using Equation (2), We plotted energy band structure in 3D using Wolfram Mathematica programming language.

In the code, We use hopping parameter  $t = -2.8$  eV, lattice constant  $a = 1.42 \times 10^{-10}$ m and range of  $k_x$  and  $k_y$  is from  $-\frac{\pi}{a}$  to  $\frac{\pi}{a}$ . 3D plots of graphene band structure are attached below:

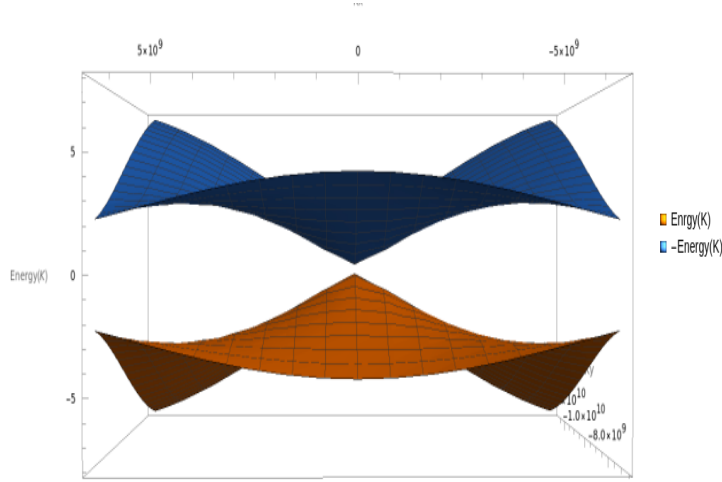


(a) Top View



(b) Side View

Graphene band Diagram in 3D

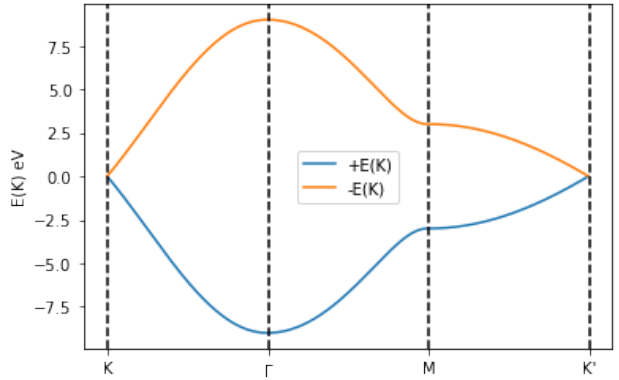


One Dirac point of graphene band structure

From the graph we see that there are points where the bands come very close to each other. This points are called Dirac points and can be calculated mathematically too. Also near this Dirac point the bands take a conical shape, which is clear from the above graphs.

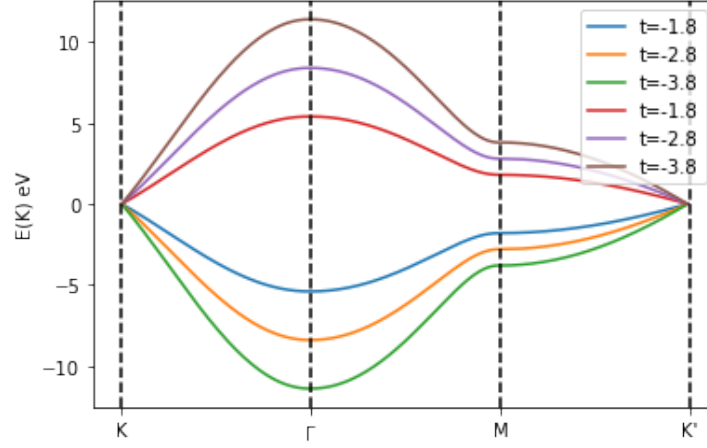
We can also plot the band diagram in special direction for more insights as shown by the graphs attached below. The code for this graph was written in python. In the code, we took direction of band structure along the high symmetry points as  $K \rightarrow \Gamma \rightarrow M \rightarrow K'$ .

From the above graph it is more clear that at the Dirac point the band energy is zero, and the conduction and valence band just touch each other.



Band diagram plotted along the line joining high symmetry point

We also analysis the effect of hopping term ( $t$ ) on the band structure of graphene by taking different value of  $t$ .



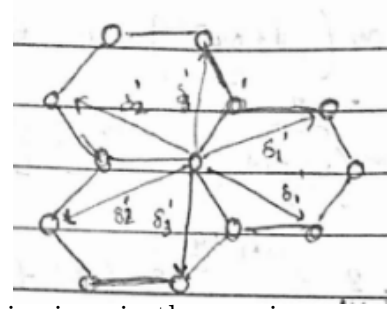
band structure of graphene with different hopping parameters

In the code, we take value of hopping parameter is -1.8 eV, -2.8 eV and -3.8 eV. As we can see in the figure, band structure along the line joining of high symmetry points is become more wide with increasing value of hopping parameter. We can say that the distance between valance band and conduction band along the line joining of high symmetry point is increase with the hopping parameter. But, there is no change at the Dirac points (K and K').

## 4.2 Second Nearest neighbour hopping

In this case, we take next nearest neighbour hopping also into account. There are total 6 next nearest neighbour sites in graphene lattice.  $\delta'$  vectors represent the position of the next nearest neighbour in graphene lattice, and they are the following.

$$\begin{aligned}\delta'_1 &= \pm a_1 \\ \delta'_2 &= \pm a_2 \\ \delta'_3 &= \pm(a_2 - a_1)\end{aligned}$$



Here value of  $a_1, a_2, a_3$  in terms of lattice constant  $a$  is given in the previous section (graphene : structure). Again  $t$  represents the nearest neighbour hopping energy, and  $t'$  represents the next nearest neighbour hopping energy. So the Hamiltonian for this case can be written as below [3]

$$\hat{H} = -t \sum_{\langle ij \rangle} [\hat{a}_i^\dagger \hat{b}_j + H.c.] - t' \sum_{\langle\langle ij \rangle\rangle} [a_i^\dagger a_j + b_i^\dagger b_j + H.c.]$$

It can be rewritten in matrix form as

$$H = \begin{bmatrix} h_0 & h_1 - ih_2 \\ h_1 + ih_2 & h_0 \end{bmatrix}$$

$$h_1 = t \sum_{j=1}^3 \cos(\delta_j k)$$

$$h_2 = -t \sum_{j=1}^3 \sin(\delta_j k)$$

$$h_0 = -t' \sum_{j=1}^6 \cos(\delta'_j k)$$

Again, we can calculate the band energy by finding the eigenvalues of the above matrix. Since the matrix looks little cumbersome, we used wolfram mathematica to find the eigenvalues and then simplified it to desired form by hand. The code is attached below :

```

In[360]:= avector = {{3 a / 2, (Sqrt[3] a) / 2}, {-3 a / 2, (-Sqrt[3] a) / 2}, {(3 a) / 2, (-3 a) / 2}, {(3 a) / 2, (Sqrt[3] a) / 2}, {-3 a / 2, (Sqrt[3] a) / 2}, {a 0, -a Sqrt[3]}, {a 0, a Sqrt[3]}};
kvector = {k_x, k_y};
bvector = {{a / 2, a Sqrt[3] / 2}, {a / 2, -a Sqrt[3] / 2}, {-a, a 0}};
h0 = -t' Total[Cos[avector.kvector]];
h1 = -t Total[Cos[bvector.kvector]];
h2 = -t Total[Sin[bvector.kvector]];
H = {{h0, h1 - I h2}, {h1 + I h2, h0}} // MatrixForm;
Eigenvalues[{{h0, h1 - I h2}, {h1 + I h2, h0}}] // Simplify

```

```

Out[367]= {-Sqrt[t^2 (3 + 4 Cos[3 a k_x / 2] Cos[1/2 Sqrt[3] a k_y] + 2 Cos[Sqrt[3] a k_y]) - 2 (Cos[Sqrt[3] a k_y] + Cos[1/2 a (3 k_x - Sqrt[3] k_y)] + Cos[1/2 a (3 k_x + Sqrt[3] k_y)])] t',
Sqrt[t^2 (3 + 2 Cos[Sqrt[3] a k_y] + 2 Cos[1/2 a (3 k_x - Sqrt[3] k_y)] + 2 Cos[1/2 a (3 k_x + Sqrt[3] k_y)]) + 2 (Cos[Sqrt[3] a k_y] + Cos[1/2 a (3 k_x - Sqrt[3] k_y)] + Cos[1/2 a (3 k_x + Sqrt[3] k_y)])] t'}

```

|

In the above equation the term,

$$\cos \left[ \frac{1}{2} a \left( 3k_x - \sqrt{3}k_y \right) \right] + \cos \left[ \frac{1}{2} a \left( 3k_x + \sqrt{3}k_y \right) \right]$$

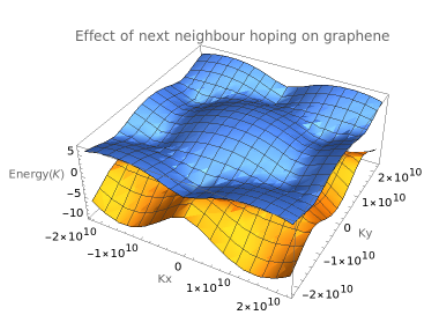
can be simplified further and get energy equation as below,

$$\begin{aligned} \cos \left[ \frac{a}{2} \left( 3k_x - \sqrt{3}k_y \right) \right] + \cos \left[ \frac{a}{2} \left( 3k_x + \sqrt{3}k_y \right) \right] &= \left( \cos \left[ \frac{3ak_x}{2} \right] \cos \left[ \frac{\sqrt{3}ak_y}{2} \right] + \sin \left[ \frac{3ak_x}{2} \right] \sin \left[ \frac{\sqrt{3}ak_y}{2} \right] \right) \\ &+ \left( \cos \left[ \frac{3ak_x}{2} \right] \cos \left[ \frac{\sqrt{3}ak_y}{2} \right] - \sin \left[ \frac{3ak_x}{2} \right] \sin \left[ \frac{\sqrt{3}ak_y}{2} \right] \right) \end{aligned}$$

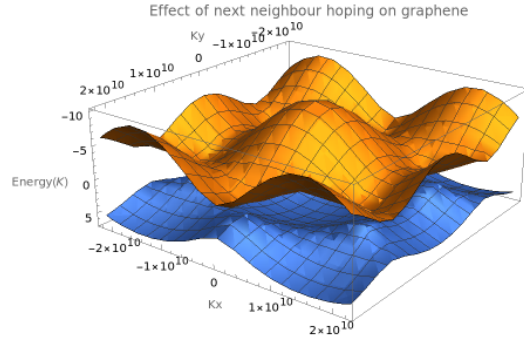
$$\Rightarrow E_{\pm}(k) = \pm t \sqrt{3 + 2\cos(\sqrt{3}k_y a) + 4\cos\left(\frac{\sqrt{3}}{2}k_y a\right)\cos\left(\frac{3}{2}k_x a\right) - t' \left(2\cos(\sqrt{3}k_y a) + 4\cos\left(\frac{\sqrt{3}}{2}k_y a\right)\cos\left(\frac{3}{2}k_x a\right)\right)}$$

#### 4.2.1 Graphs and Plots

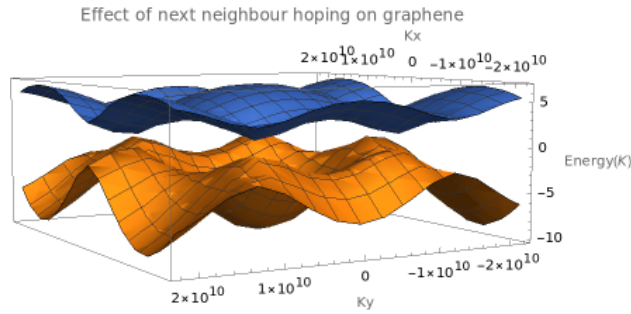
We plotted 3D band structure of graphene using the above energy band equation . In the code, we have taken hopping parameter  $t = -2.8\text{eV}$  and next nearest hopping term  $t' = -0.28\text{eV}$ .



(a) Top View



(b) Back View



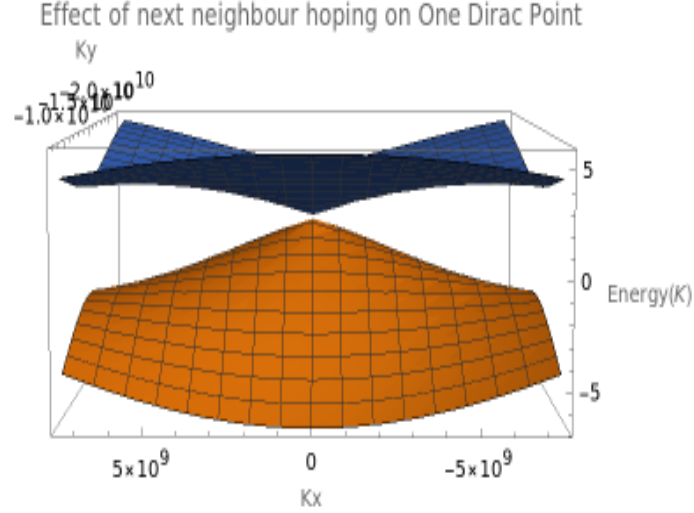
(c) Side View

#### Graphene band Diagram in 3D

We can see the top view, back view and side view of band structure



of graphene. When we include the effect of next nearest neighbour hopping, the conduction band become more flatten and the valance band become more curved.

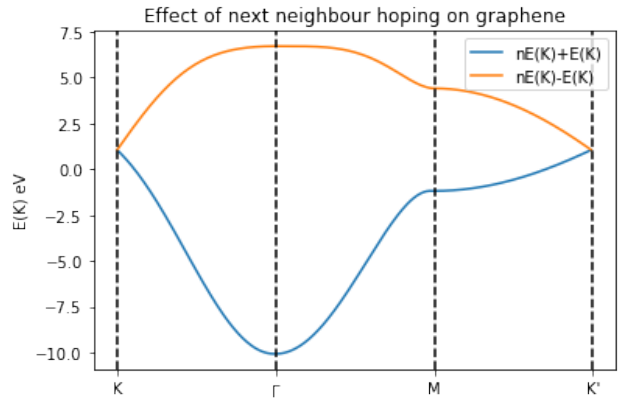


Effect of next nearest neighbour hopping on single Dirac point of graphene

In this figure, we can see the single Dirac point of graphene structure. There is no effect of next nearest neighbour hopping on Dirac points. There is no band gap between conduction band and valance band at Dirac points.

We can also plot the band diagram in special direction for more insights as shown by the graphs attached. In the code, we took direction of band structure along the high symmetry points as  $K \rightarrow \Gamma \rightarrow M \rightarrow K'$ .

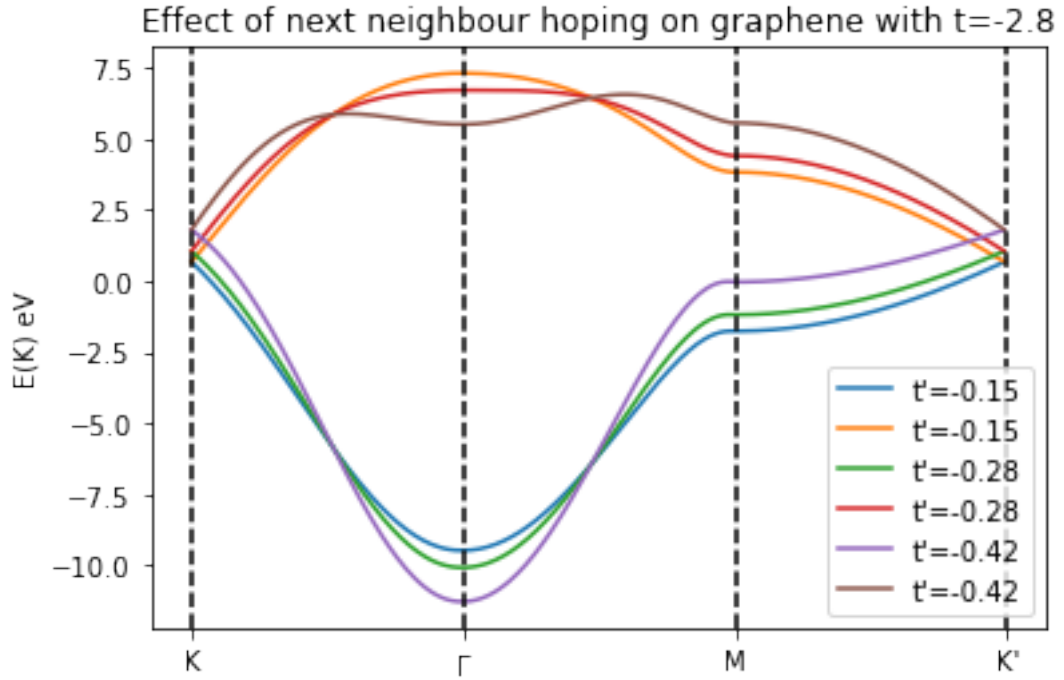
From the above graph it is more clear that at the Dirac point the band energy is zero, and the conduction and valance band just touch each other. But, the symmetry between conduction band and valance band along the line joining to the high symmetry point is break. We can see that the conduction band become more flatten and valance band



Band diagram plotted along the line joining high symmetry point

become more curved as compare to the previous plot where  $t'=0$

Now, We do further analysis of band structure of graphene using different next nearest neighbour hopping parameter ( $t'$ ).



band structure of graphene for  $t=-2.8$  with different  $t'$

In the above graphs, the nearest neighbour hopping factor is  $t = -2.8$  eV and the next neighbour hopping factor is set to be  $-0.15$  eV,  $-0.28$  eV,  $-0.42$  eV. As you can see, when you change the next nearest neighbour hopping parameter( $t'$ ) by keeping the nearest neighbour hopping parameter constant, the conduction band becomes more and more flatter. In contrast, the valence band becomes more and more curved about the Dirac point. Also, when  $t' = 0$  was symmetric, that is  $E = -E$ , but when  $t' \neq 0$ , the symmetry is lost, which is clear from the above graphs. We also observed that the touching point of both band at the Dirac points is goes up on energy scale for different value of  $t'$ . But when  $t'=0$ , there is no such kind of shift in band structure.

## 5 Berry Curvature

Berry connection is defined as [3]

$$A_k = \sum_{\text{occupied state}} \langle \psi | i \partial_{\mathbf{k}} | \psi \rangle$$

and Berry curvature as

$$\Omega_{k_x, k_y} = \partial_{k_x} A_{k_y} - \partial_{k_y} A_{k_x}$$

Near Dirac points we can approximate the next nearest neighbour Hamiltonian to

$$H = v (\zeta q_x \sigma_x + q_y \sigma_y) - 3t' I$$

Here

$$v = \frac{\sqrt{3}}{2} at \quad \sigma_x = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \zeta = \pm 1$$

For one K point we have 2 component wave function which is called pseudo spinor wave function.

$$\Psi = \frac{1}{2} (\pm) e^{i\theta_q}$$

Here,  $\theta_q = \tan^{-1} \left( \frac{q_y}{q_x} \right)$  So we can solve the above berry connection equation for this  $\Psi$  and get

$$A_{q_y} = \frac{-q_x}{2(q_y^2 + q_x^2)}$$

$$A_{q_x} = \frac{q_y}{2(q_y^2 + q_x^2)}$$

So from the above two equations we get [3]

$$\partial_{q_x} A_{q_y} = \frac{-2q_y^2}{4(q_y^2 + q_x^2)^2}$$

$$\partial_{q_y} A_{q_x} = \frac{-2q_y^2}{4(q_y^2 + q_x^2)^2}$$

$$\implies \Omega_{q_x, q_y} = \partial_{q_y} A_{q_x} - \partial_{q_x} A_{q_y}$$

$$= 0$$

But berry phase is [3]

$$\phi_{berry} = \oint_0^{2\pi} \langle \Psi | i \partial_\theta | \Psi \rangle d\theta = \pm \pi$$

The rotation of  $2\pi$  in  $k$  space causes a change in phase of  $\pi$ , i.e. a sign change. As far as these models are concerned, where nearest neighbour hopping or next nearest neighbour hopping is taken into consideration, there is still an unintentional degeneracy that causes the particle-like band of one flavor to be degenerate at the K (K) with the antiparticle-like (hole-like) band of the other flavor.

By application of perpendicular electric field we can easily lift this degeneracy and break the inversion symmetry of our system.

## 6 Conclusion and Future work

So, in this project, we learned about the graphene model using a tight-binding model approximation. We took the nearest neighbour hopping and next-nearest neighbour hopping case and analytically derived its band energy equation. From the band equation, we learned about how hopping factors affect band structure. We used programming software such as Wolfram Mathematica and python to plot 3D and 2D graphs. We also used Wolfram Mathematica to find eigenvalues of complex Hamiltonian. We also observed that we could increase the distance between conduction band and valance band along the line joining to high symmetry point by changing the nearest neighbour hopping parameter. We also observed that there is no change on Dirac points with change in hopping parameter. By changing the second nearest neighbour hopping parameter, we can increase the curvature of the bands, i.e. make the conduction band flatter and the valence band more curved. We observed that there is not effect the next nearest neighbour hopping on the Dirac Cone.

In the future, we would like to further work on this topic and obtain a plot for the density of states for both cases and analyze that graph. We would also like to learn more about berry curvature and berry phase and how it affects the band diagram. Also, consider the next to next neighbour hopping into account and see what new physical features it unravels.

## 7 Codes

### 7.1 Matematica Codes

Equation use in code:

```
c = 0.246*10^(-9); (*Distance between adjacent Graphene Layers*)
a = 1.42*10^(-10); (*Graphene Lattice Constant*)
```

```
Energy[Kx_, Ky_, t_] := t Sqrt[ 3+ 2 Cos[Sqrt[3]*Ky*a]
                               +4 Cos[Sqrt[3]*Ky*a/2] Cos[3*Kx*a/2]];
```

for the plot of 3D band structure,

```
P1=Plot3D[{Energy[kx,ky,-2.8],-Energy[kx,ky,-2.8]},{kx,-\[Pi]/a,\[Pi]/a},
           {ky,-\[Pi]/a,\[Pi]/a},AxesLabel->{Kx,Ky,Energy[K]},
           PlotLegends->{Energy[K],-Energy[K]},Axes->True]
```

Plot of Single Dirac point:

```
P1=Plot3D[{Energy[kx,ky,-2.8],-Energy[kx,ky,-2.8]},{kx,-\[Pi]/(3a),\[Pi]/(3a)},
           {ky,-\[Pi]/a,-\[Pi]/(3a)},AxesLabel->{Kx,Ky,Energy[K]},
           PlotLegends->{Energy[K],-Energy[K]},Axes->True,PlotLabel->"One Dirac Point"]
```

Code for next nearest neighbour hopping:

```
Energy[Kx_, Ky_, t_] := t Sqrt[ 3+ 2 Cos[Sqrt[3]*Ky*a]
                               +4 Cos[Sqrt[3]*Ky*a/2] Cos[3*Kx*a/2]];
```

```
NEnergy[Kx_,Ky_,v_]=v(4 Cos[Sqrt[3]*a*Ky/2]Cos[3*Kx*a/2]+2 Cos[Sqrt[3]*Ky*a]);
```

```
P2=Plot3D[NEnergy[kx,ky,-0.28]},{kx,-\[Pi]/a,\[Pi]/a},{ky,-\[Pi]/a,\[Pi]/a},
           AxesLabel->{Kx,Ky,Energy[K]},Axes->True]
```

Plot of Single Dirac point for next nearest neighbour hopping:

```
P1=Plot3D[{NEnergy[kx,ky,-0.28]+Energy[kx,ky,-2.8],
           NEnergy[kx,ky,-0.28]-Energy[kx,ky,-2.8]},
           {kx,-\[Pi]/(3a),\[Pi]/(3a)},{ky,-\[Pi]/a,-\[Pi]/(3a)},
           AxesLabel->{Kx,Ky,Energy[K]},Axes->True,
           PlotLabel->"Effect of next neighbour hoping on One Dirac Point"]
```

## 7.2 Python Code

Code for band structure of graphene along the line joining to high symmetry points:

```
import numpy as np
import matplotlib.pyplot as plt

def Energy(t,a,Kx,Ky):
    return(t*np.sqrt(3+2*np.cos(np.sqrt(3)*Ky*a)
    +4*np.cos(np.sqrt(3)*Ky*a/2)*np.cos(3*Kx*a/2)))
```

Direction K to  $\Gamma$ :

```
Kx1=np.linspace(2*np.pi/(3*a),0,100)
Ky1=np.linspace((2*np.pi/(3*np.sqrt(3)*a)),0,100)
n1=np.size(Kx1)
E1=np.zeros(n1)
for i in range(n1):
    E1[i]=Energy(t,a,Kx1[i],Ky1[i])
```

Direction  $\Gamma$  to M:

```
Kx2=np.linspace(0,(2*np.pi/(3*a)),100)
Ky2=0
n2=np.size(Kx2)
E2=np.zeros(n2)
for i in range(n2):
    E2[i]=Energy(t,a,Kx2[i],Ky2)
```

Direction M to K':

```
Kx3=(2*np.pi/(3*a))
Ky3=np.linspace(0,-2*np.pi/(3*np.sqrt(3)*a),100)
n3=np.size(Ky3)
E3=np.zeros(n3)
for i in range(n3):
    E3[i]=Energy(t,a,Kx3,Ky3[i])
```

For the Plot band structure:

```

n=n1+n2+n3
I=np.zeros(n)
E=np.zeros(n)
for i in range(n):
    I[i]=i
for i in range(n1):
    E[i]=E1[i]
    E[n1+i]=E2[i]
    E[n1+n2+i]=E3[i]
plt.plot(E,label="+E(K)")
plt.plot(-E,label="-E(K)")
plt.xticks([])
plt.axvline(0,color="k",linestyle="dashed")
plt.axvline(100,color="k",linestyle="dashed")
plt.axvline(200,color="k",linestyle="dashed")
plt.axvline(300,color="k",linestyle="dashed")
plt.xticks([0,100,200,300],['K','$\Gamma$', 'M', 'K'])
plt.legend()
plt.ylabel("E(K) eV")
plt.show()

```

plot for different hopping parameters in Band structure:

```

t=[-1.8,-2.8,-3.8] #ev
a = 0.246e-9 #Graphene Lattice Constant
c = 1.42e-10 #Distance between adjacent Graphene Layers

```

Direction K to  $\Gamma$ :

```

Kx1=np.linspace(2*np.pi/(3*a),0,100)
Ky1=np.linspace((2*np.pi/(3*np.sqrt(3)*a)),0,100)
n1=np.size(Kx1)
E1=np.zeros((3,n1))
for j in range(3):
    for i in range(n1):
        E1[j][i]=Energy(t[j],a,Kx1[i],Ky1[i])

```

Direction  $\Gamma$  to M:

```

Kx2=np.linspace(0,(2*np.pi/(3*a)),100)
Ky2=0

```



```

n2=np.size(Kx2)
E2=np.zeros((3,n2))
for j in range(3):
    for i in range(n2):
        E2[j][i]=Energy(t[j],a,Kx2[i],Ky2)

Direction M to K':

Kx3=(2*np.pi/(3*a))
Ky3=np.linspace(0,-2*np.pi/(3*np.sqrt(3)*a),100)
n3=np.size(Ky3)
E3=np.zeros((3,n3))
for j in range(3):
    for i in range(n3):
        E3[j][i]=Energy(t[j],a,Kx3,Ky3[i])

For the plot:

n=n1+n2+n3
I=np.zeros(n)
E=np.zeros((3,n))
for i in range(n):
    I[i]=i
for j in range(3):
    for i in range(n1):
        E[j][i]=E1[j][i]
        E[j][n1+i]=E2[j][i]
        E[j][n1+n2+i]=E3[j][i]
plt.plot(E[0][:],label="t=-1.8")
plt.plot(E[1][:],label="t=-2.8")
plt.plot(E[2][:],label="t=-3.8")
plt.plot(-E[0][:],label="t=-1.8")
plt.plot(-E[1][:],label="t=-2.8")
plt.plot(-E[2][:],label="t=-3.8")
plt.xticks([])
plt.axvline(0,color="k",linestyle="dashed")
plt.axvline(100,color="k",linestyle="dashed")
plt.axvline(200,color="k",linestyle="dashed")
plt.axvline(300,color="k",linestyle="dashed")
plt.xticks([0,100,200,300],['K','$\Gamma$', 'M', 'K'])
plt.legend()

```

```
plt.ylabel("E(K) eV")
plt.figure(figsize=(10,12))
plt.show()
```

Code for next nearest neighbour hopping:

```
def nEnergy(v,a,Kx,Ky):
    return(v*(4*np.cos(np.sqrt(3)*Ky*a/2)*np.cos(3*Kx*a/2)
    +2*np.cos(np.sqrt(3)*Kx*a)))
```

Direction K to  $\Gamma$ :

```
Kx1=np.linspace(2*np.pi/(3*a),0,100)
Ky1=np.linspace((2*np.pi/(3*np.sqrt(3)*a)),0,100)
n1=np.size(Kx1)
E1=np.zeros(n1)
E11=np.zeros(n1)
for i in range(n1):
    E1[i]=nEnergy(v,a,Kx1[i],Ky1[i])+Energy(t,a,Kx1[i],Ky1[i])
    E11[i]=nEnergy(v,a,Kx1[i],Ky1[i])-Energy(t,a,Kx1[i],Ky1[i])
```

Direction  $\Gamma$  to M:

```
Kx2=np.linspace(0,(2*np.pi/(3*a)),100)
Ky2=0
n2=np.size(Kx2)
E2=np.zeros(n2)
E22=np.zeros(n2)
for i in range(n2):
    E2[i]=nEnergy(v,a,Kx2[i],Ky2)+Energy(t,a,Kx2[i],Ky2)
    E22[i]=nEnergy(v,a,Kx2[i],Ky2)-Energy(t,a,Kx2[i],Ky2)
```

Direction M to K':

```
Kx3=(2*np.pi/(3*a))
Ky3=np.linspace(0,-2*np.pi/(3*np.sqrt(3)*a),100)
n3=np.size(Ky3)
E3=np.zeros(n3)
E33=np.zeros(n3)
for i in range(n3):
    E3[i]=nEnergy(v,a,Kx3,Ky3[i])+Energy(t,a,Kx3,Ky3[i])
    E33[i]=nEnergy(v,a,Kx3,Ky3[i])-Energy(t,a,Kx3,Ky3[i])
```

For the Plot band structure:

```

I=np.zeros(n)
E=np.zeros(n)
EE=np.zeros(n)
for i in range(n):
    I[i]=i
for i in range(n1):
    E[i]=E1[i]
    E[n1+i]=E2[i]
    E[n1+n2+i]=E3[i]
    EE[i]=E11[i]

    EE[n1+i]=E22[i]
    EE[n1+n2+i]=E33[i]
plt.plot(E,label="nE(K)+E(K)")
plt.plot(EE,label="nE(K)-E(K)")
plt.xticks([])
plt.axvline(0,color="k",linestyle="dashed")
plt.axvline(100,color="k",linestyle="dashed")
plt.axvline(200,color="k",linestyle="dashed")
plt.axvline(300,color="k",linestyle="dashed")
plt.xticks([0,100,200,300],['K','$\Gamma$', 'M', 'K'])
plt.legend()
plt.title("Effect of next neighbour hopping on graphene")
plt.ylabel("E(K) eV")
plt.figure(figsize=(10,12))
plt.show()

```

plot for different next nearest neighbour hopping parameters by keeping hopping term at -2.8 eV in Band structure:

```

t=-2.8 #eV
v=[-0.15,-0.28,-0.42] #eV

```

Direction K to  $\Gamma$ :

```

Kx1=np.linspace(2*np.pi/(3*a),0,100)
Ky1=np.linspace((2*np.pi/(3*np.sqrt(3)*a)),0,100)
n1=np.size(Kx1)
E1=np.zeros((3,n1))
E11=np.zeros((3,n1))

```

```

for j in range(3):
    for i in range(n1):
        E1[j][i]=nEnergy(v[j],a,Kx1[i],Ky1[i])+Energy(t,a,Kx1[i],Ky1[i])
        E11[j][i]=nEnergy(v[j],a,Kx1[i],Ky1[i])-Energy(t,a,Kx1[i],Ky1[i])

```

Direction  $\Gamma$  to M:

```

Kx2=np.linspace(0,(2*np.pi/(3*a)),100)
Ky2=0
n2=np.size(Kx2)
E2=np.zeros((3,n2))
E22=np.zeros((3,n2))
for j in range(3):
    for i in range(n2):
        E2[j][i]=nEnergy(v[j],a,Kx2[i],Ky2)+Energy(t,a,Kx2[i],Ky2)
        E22[j][i]=nEnergy(v[j],a,Kx2[i],Ky2)-Energy(t,a,Kx2[i],Ky2)

```

Direction M to K':

```

Kx3=(2*np.pi/(3*a))
Ky3=np.linspace(0,-2*np.pi/(3*np.sqrt(3)*a),100)
n3=np.size(Ky3)
E3=np.zeros((3,n3))
E33=np.zeros((3,n3))
for j in range(3):
    for i in range(n3):
        E3[j][i]=nEnergy(v[j],a,Kx3,Ky3[i])+Energy(t,a,Kx3,Ky3[i])
        E33[j][i]=nEnergy(v[j],a,Kx3,Ky3[i])-Energy(t,a,Kx3,Ky3[i])

```

For the plot:

```

I=np.zeros(n)
E=np.zeros((3,n))
EE=np.zeros((3,n))
for i in range(n):
    I[i]=i
for j in range(3):
    for i in range(n1):
        E[j][i]=E1[j][i]
        E[j][n1+i]=E2[j][i]
        E[j][n1+n2+i]=E3[j][i]

```

```

EE[j][i]=E11[j][i]
EE[j][n1+i]=E22[j][i]
EE[j][n1+n2+i]=E33[j][i]
plt.plot(E[0][:],label="t'=-0.15")
plt.plot(EE[0][:],label="t'=-0.15")
plt.plot(E[1][:],label="t'=-0.28")
plt.plot(EE[1][:],label="t'=-0.28")
plt.plot(E[2][:],label="t'=-0.42")
plt.plot(EE[2][:],label="t'=-0.42")
plt.xticks([])
plt.axvline(0,color="k",linestyle="dashed")
plt.axvline(100,color="k",linestyle="dashed")
plt.axvline(200,color="k",linestyle="dashed")
plt.axvline(300,color="k",linestyle="dashed")
plt.xticks([0,100,200,300],['K','$\Gamma$', 'M', 'K'])
plt.legend()
plt.title("Effect of next neighbour hopping on graphene with t=-2.8")
plt.ylabel("E(K) eV")
plt.figure(figsize=(10,12))
plt.show()

```

## References

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