Electronic Properties of the Materials Computational Approach

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Module No # 08
Lecture No # 36
Tight-Binding Method: Part 3

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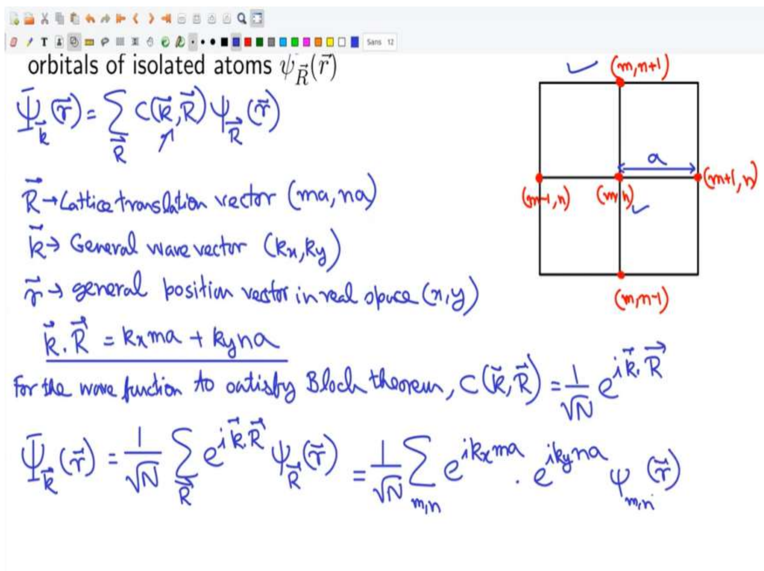

I already have derived the energy dispersion relation for a 1D lattice using type by day model. In this lecture, I am going to do it for a 2D Square lattice this is a 2d square lattice every point is indexed by 2 integers m n every lattice Point has four nearest neighbours. Wave function of the whole crystal is a linear combination of atomic orbital’s of isolated atoms.

Such that we can write Psi k of R = sum over r c k R psi R of r

$$\Psi_{\vec{k}}(\vec{r}) = \sum_{\vec{R}} c(\vec{k},\vec{R})\psi_{\vec{R}}(\vec{r})$$

note that big psi is the wave function of the whole crystal and psi is the atomic orbital of an isolated atom. Let me define the notations first R is a lattice translation vector denoted by (ma, na). Where a; is the lattice parameter a; is a general wave vector having 2 components (k_x, k_y), r is some general position vector in real space.

We can also write $\vec{k}.\vec{R} = k_x ma + k_n na$

For the wave function to satisfy block theorem this constant

$$C(\vec{k},\vec{R}) = \frac{1}{\sqrt{N}} e^{i\vec{k}.\vec{R}}$$

Such that we can rewrite the wave function as

$$\Psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}.\vec{R}}\, \psi_{\vec{R}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{m,n} e^{ik_x ma} . e^{ik_y na} \psi_{m,n}(\vec{r})$$

Note that N is the total number of lattice points now in place of k dot R I replace this such that the wave function can be expressed as 1 by the square root of N sum over m n e power I k x ma times e power i k y n psi m n of r.

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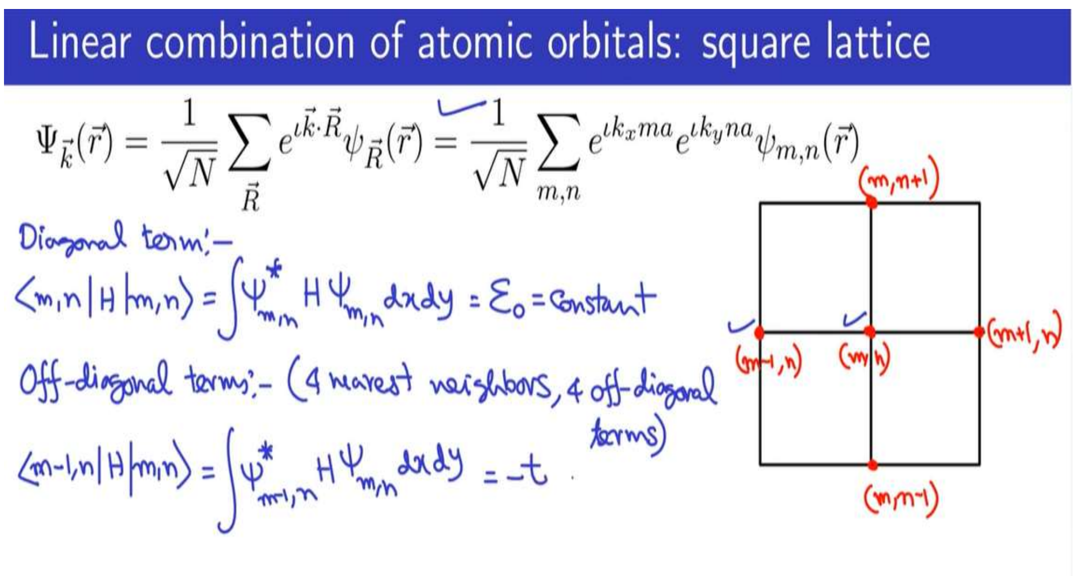

Thus we have defined the wave function for the whole crystal which satisfies the block theorem. Now let me define the overlap of atomic orbitals. I assume that only the orbitals of the nearest neighbour's overlap. Let us start with the diagonal term

$$\langle m,n|H|m,n\rangle = \int \psi^*_{m,n} H\, \psi_{m,n} dxdy = \varepsilon_0 = \text{constant}$$

Now let us find the off-diagonal terms there are 4 nearest neighbours and as a result, there are 4 non-zero of diagonal terms.

So let us derive them one by one. The first term is between m n and its left nearest neighbor that is

$$\langle m-1, n|H|m, n\rangle = \int \psi^*_{m-1,n} H\, \psi_{m,n} dxdy = -t$$

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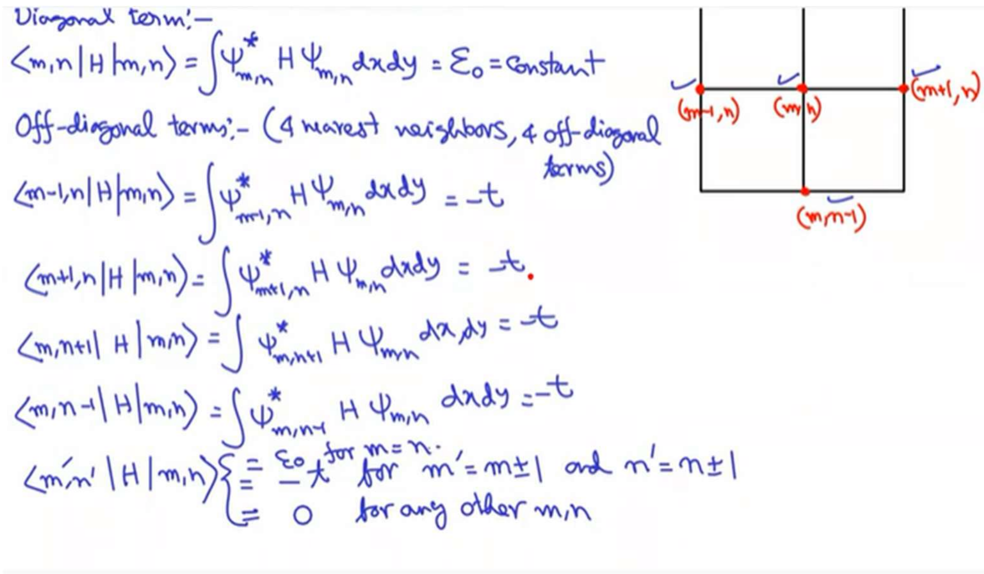

Similarly, we can define it for the right-hand side neighbor and that is equal to

$$\langle m+1, n|H|m, n\rangle = \int \psi^*_{m+1,n} H\, \psi_{m,n} dxdy = -t$$

Now we do it for the top neighbor such that

$$\langle m, n+1|H|m, n\rangle = \int \psi^*_{m,n+1} H\, \psi_{m,n} dxdy = -t$$

And then we do it for the bottom neighbor such that

$$\langle m, n-1|H|m, n\rangle = \int \psi^*_{m,n-1} H\, \psi_{m,n} dxdy = -t$$

Thus, we can generalize as

$$\langle m', n'|H|m, n\rangle = -t$$

for $m' = m \pm 1$ and $n' = n \pm 1$. And this term equals to 0 for any other *m,n*

Of course, this term equals to e naught for *m* = *n*.

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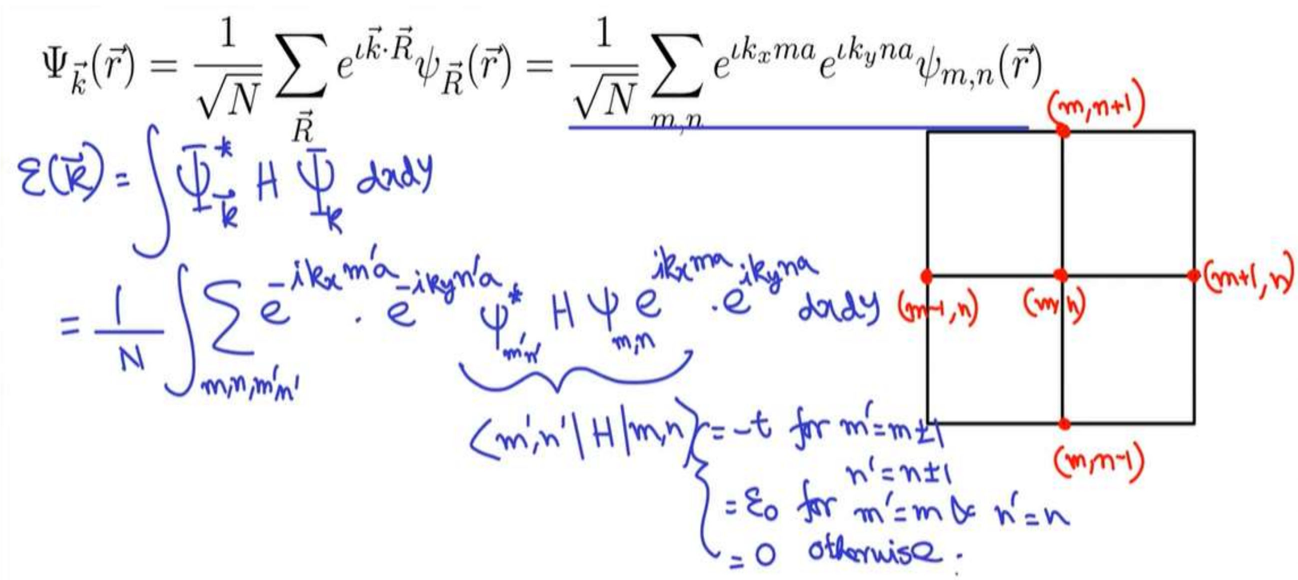

Now let me calculate a energy expectation value e k is equal to the integral psi k star H psi k dx, dy. I am going to use this form of the wave function such that I have 1 by N integral. First I write psi star sum over m n m dashed, n dashed so psi dashed is equal to e power - i k x m dashed a times e power - i k y n dashed a psi star of m dashed n dashed. Then I have the Hamiltonian and then I write psi that is psi of m n e power i k x m a times e power i k y n a dx, dy.

Note that this term is m dashed n dashed H m n and we know that this is equal to - t for m dashed = m plus minus 1 and n dashed = n plus minus 1. This term is equal to e naught for m dashed = m and n dashed = n and this term is equal to 0 otherwise.

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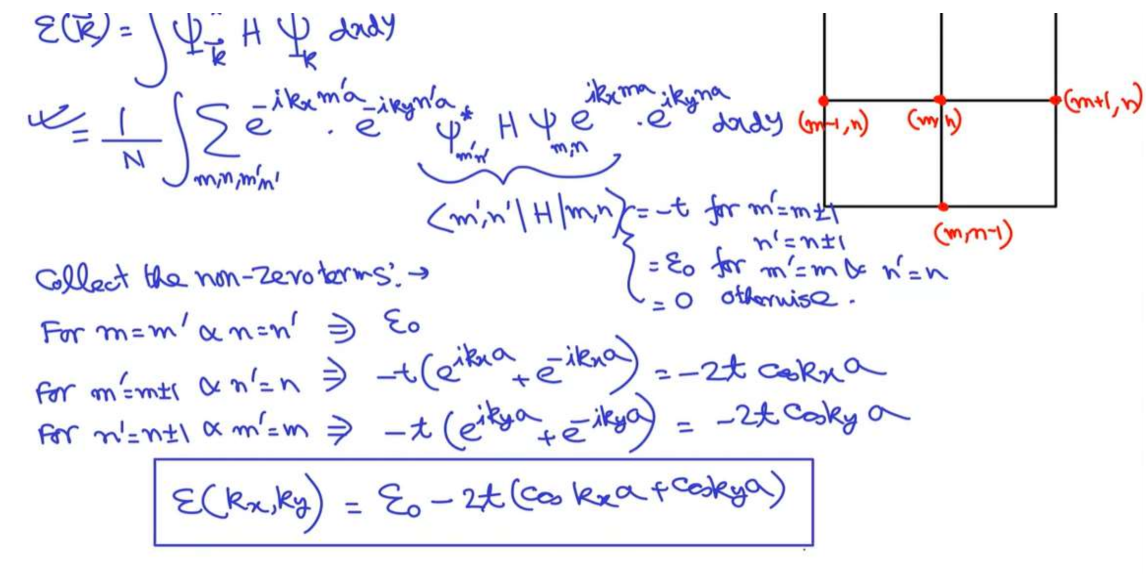

Now let us collect the non-zero terms from this sum for m = m dashed and n = n dashed, we have a non-zero turn which is equal to Epsilon naught for m dashed = m plus minus 1 and n dashed = n. We have - t e power i k x a + e power - i k x a; which is equal to – 2t Cos x a. Similarly for n dashed = n plus or minus 1 and m dash = m we have - t e power i k y k + e power - i k y a; which is equal to – 2 t Cos k y a. Thus we have that energy expectation value which is equal to e naught – 2 t Cos k x a + Cos k y a; this is the energy dispersion relation in case of a 2d Square lattice.

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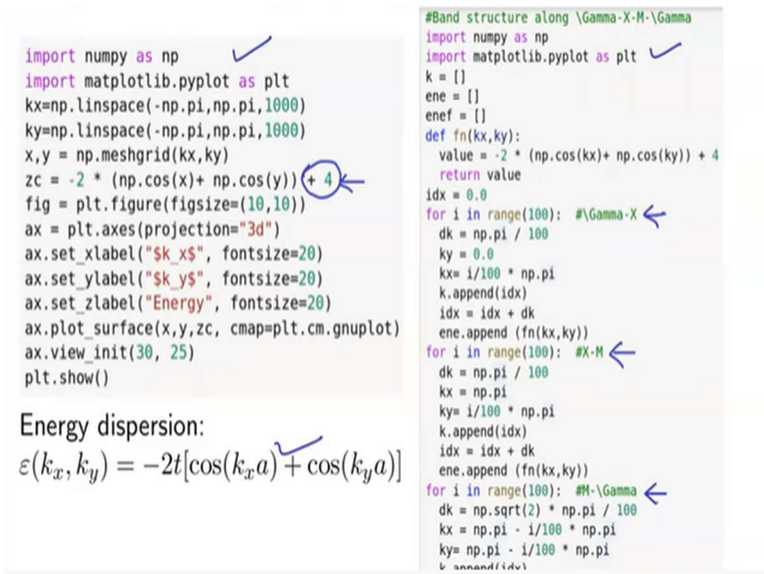

We got the type binding energy dispersion relation of 2D Square lattice energy is a quadratic surface given by this expression. Let us plot the quadratic surface as well as the e k plots along various high symmetry directions, This is the code to plot the quadratic surface the energy dispersion is defined in this line I have added + 4 such that the energy minimum is at 0 this is the code to plot a e k curve along different high symmetry directions. I am going to plot along gamma X, X M and M comma directions.

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```python
import numpy as np
import matplotlib.pyplot as plt
kx=np.linspace(-np.pi,np.pi,1000)
ky=np.linspace(-np.pi,np.pi,1000)
x,y = np.meshgrid(kx,ky)
zc = -2 * (np.cos(x)+ np.cos(y)) + 4
fig = plt.figure(figsize=(10,10))
ax = plt.axes(projection="3d")
ax.set_xlabel("$k_x$", fontsize=20)
ax.set_ylabel("$k_y$", fontsize=20)
ax.set_zlabel("Energy", fontsize=20)
ax.plot_surface(x,y,zc, cmap=plt.cm.gnuplot)
ax.view_init(30, 25)
plt.show()
```

```python
import numpy as np
import matplotlib.pyplot as plt
kx=np.linspace(-np.pi,np.pi,1000)
ky=np.linspace(-np.pi,np.pi,1000)
x,y = np.meshgrid(kx,ky)
zc = -2 * (np.cos(x)+ np.cos(y)) + 4
zf = 0.7 * (x ** 2 + y ** 2)
fig = plt.figure(figsize=(10,10))
ax = plt.axes(projection="3d")
ax.set_xlabel("$k_x$", fontsize=20)
ax.set_ylabel("$k_y$", fontsize=20)
ax.set_zlabel("Energy", fontsize=20)
ax.plot_surface(x,y,zf-zc, cmap=plt.cm.gnuplot)
ax.view_init(30, 25)
plt.show()
```

This is the code to plot the quadratic energy surface k x k y is taken within the first Bellowing zone. In this line, I define the energy dispersion relation and this is where I plot the energy dispersion relation let us run the code.

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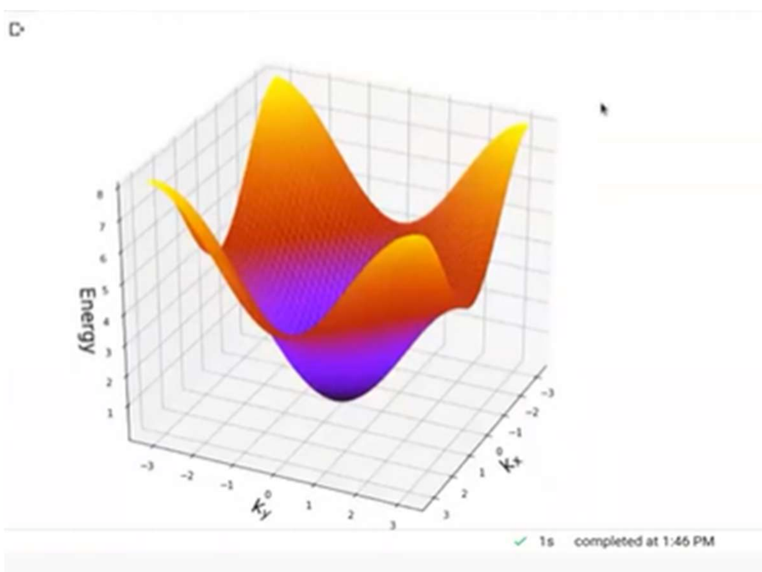

This is what the quadratic surface looks like.

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This is the code to get the e k curves along various high symmetry directions in a square lattice. This is where I define the energy dispersion relation. Then I vary K along the gamma X line I vary k along the XM line and I vary K along M comma line. Then the energy dispersion relations are plotted along various asymmetric directions let us run the code.

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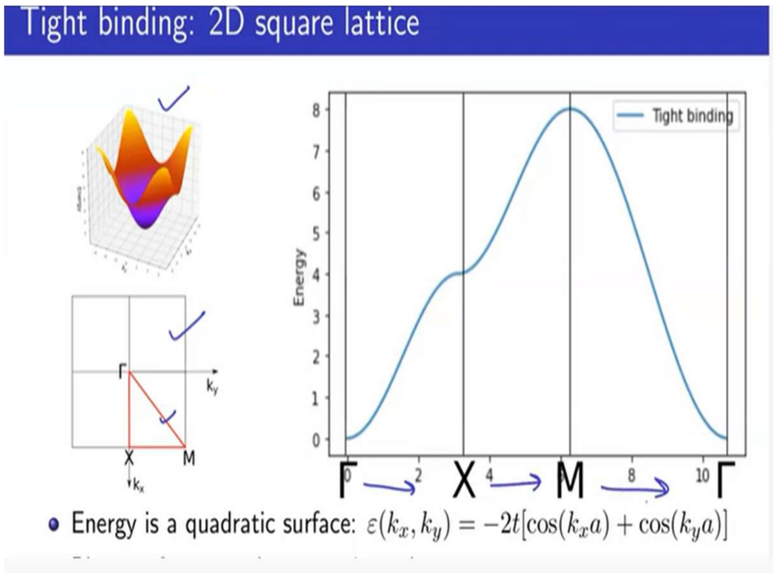

This is the quadratic energy surface for a square lattice obtained from a tight binding model. These are the high symmetry points and high symmetry paths in the first bellowing zone of a square lattice shown by the red line because symmetry is sufficient to plot energy along gamma to X, X to M and M to gamma.

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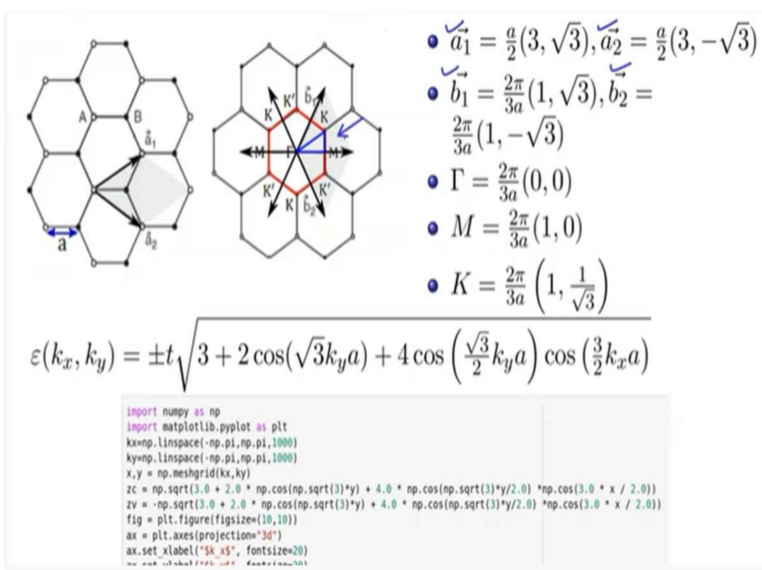

Finally, Let me show the band structure of graphene which is a 2d allotrope of carbon. Graphene was the first 40 materials to be experimentally exfoliated graphene has a honeycomb lattice, which is a hexagonal lattice with a 2 atom basis. These are the vectors in the real lattice and these are the corresponding vectors in the reciprocal lattice the first bellowing zone is shown by the red hexagon in this figure other than the gamma point. There are 2 high symmetry points K and M we are going to plot e k curves along the gamma K M gamma direction.

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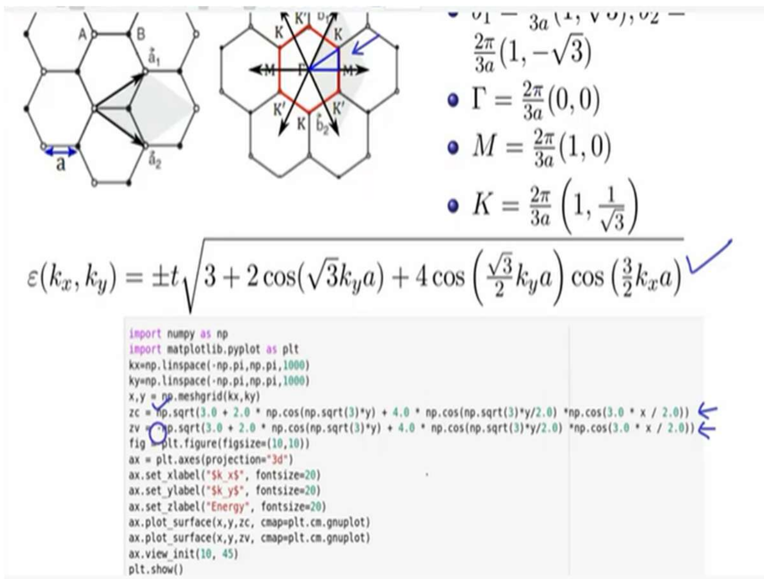

This is the energy dispersion relation for grapheme in the code we define the energy dispersion in these 2 lines. The plus side as the energy for conduction band and the minus sign is the energy for the valence band.

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This is the code to plot the energy dispersion relation for graphene in the code. We define the energy dispersion for the conduction band in this slide and the energy dispersion for the balance band in this line. Finally, we plot the energy dispersion for balance and conduction band here let us run the code. This is how the quadratic energy surface for graphene looks like. If, we plot along gamma K M gamma direction we get these e k curves. Note that the valence and conduction band is touching each other at the K point. And there are 6 such points in the first bellowing zone 1, 2, 3, 4, 5, 6 these are known as Dirac points.

Since the valence band and conduction band touch each other graphene is known as a zero band gap semiconductor. Most of the spectacular properties of graphene originate from the unique energy dispersion relation near the Dirac points.

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