Electronic Properties of the Materials: Computational Approach
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Lecture – 20
Bloch Electrons in 1D Solid: Part 3

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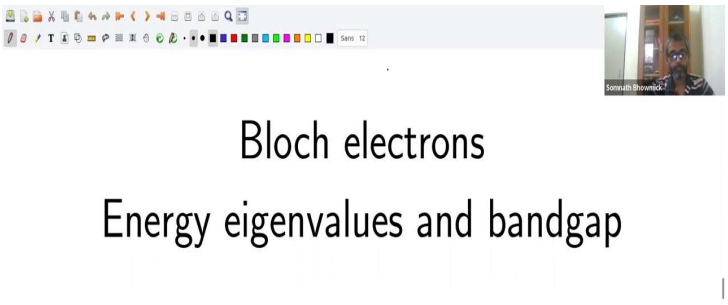

Hello friends, we are going to continue our discussion on Bloch electrons. In the previous lecture, we converted time independent Schrodinger equation to a system of linear equations. In this lecture, I am going to solve the system of linear equations to get the energy eigenvalues and show that energy values are not continuous but gapped in case of Bloch electrons.

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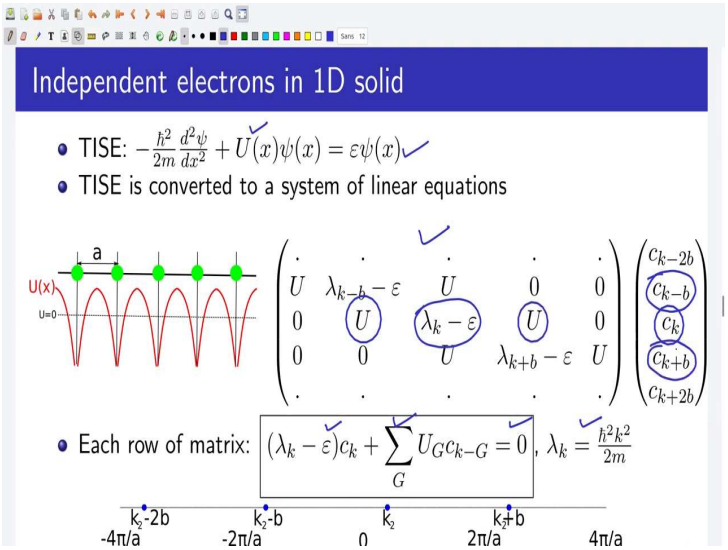

This is the form of time independent Schrodinger equation we are familiar with when U of x is a periodic potential time independent Schrodinger equation is converted to a system of linear equations shown in the form of a matrix here. Note that each row of the matrix can be expressed as lambda k – epsilon times c k + sum over G U G c k – G = 0, where lambda k = h + square k square divided by 2m which is equal to the energy of a free electron with wave vector k.

Let us verify the third row of the matrix. We have lambda k – epsilon times c k+ U times c k – p + U times c k+ b.

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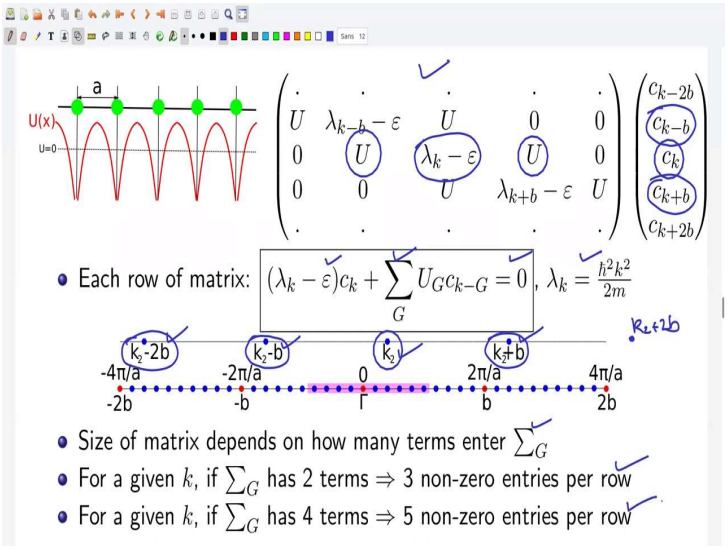

Note that size of the matrix depends on how many terms enter the sum over G? For example, for a given k say sum over G has 2 terms that is, if this is the k point we are talking about then we have to consider 2 terms k 2 – b and k 2 + b. In that case, there are 3 non-zero entries per row. If sum over G has 4 terms that is, if we take k 2 then we have to also consider k 2 – b k 2 – 2b k 2 + b and somewhere there will be another point k 2 + 2b. In that case there are 5 non-zero entries per row.

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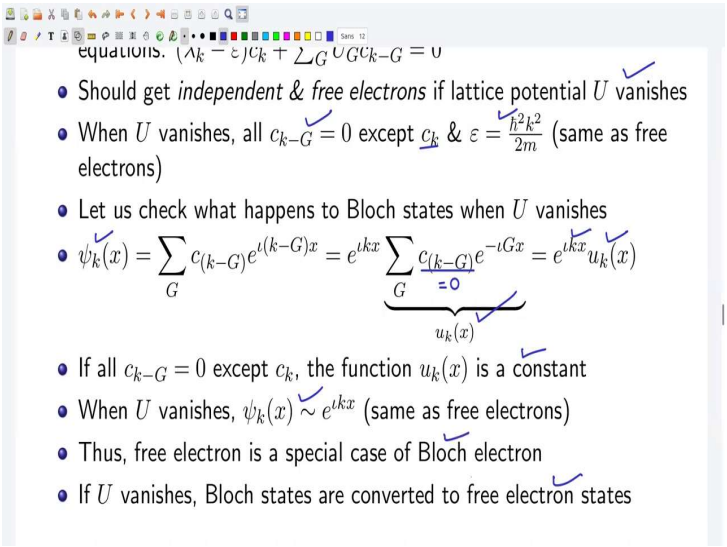

So, we have a system of linear equations representing time independent Schrodinger equation for independent electrons in a lattice. Note that these are not free electrons because we have non-zero potential U which has the periodicity of the lattice. Assume that potential U vanishes in that case, we should get back the free electron results, let us verify that thing. Clearly, when u vanishes all c k – G = 0, except for c k and E = h square k square divided by 2m.

Thus, energy eigenvalue is same as the free electron value when u vanishes. Let us also check whether Bloch states are converted to free electron eigen functions when u vanishes. We know that the Bloch state psi k of x is e power ikx times U k of x, where U k of x is given by this sum. If all c k – G = 0 except c k the function U k of x is a constant. Note that any constant function also has the periodicity of the lattice. So that Bloch theorem is still valid from mathematical point of view.

But this is only a mathematical argument, as we really do not mean a constant potential when we talk about the periodic potential in a solid. Since U k of x is a constant when potential vanishes psi k of x is e power ikx which is same as the eigen functions of free electrons. Whatever we reduce for Bloch electrons will coincide with free electron results if we make potential U = 0. Thus, we can say that free electron is a special case of Bloch electron.

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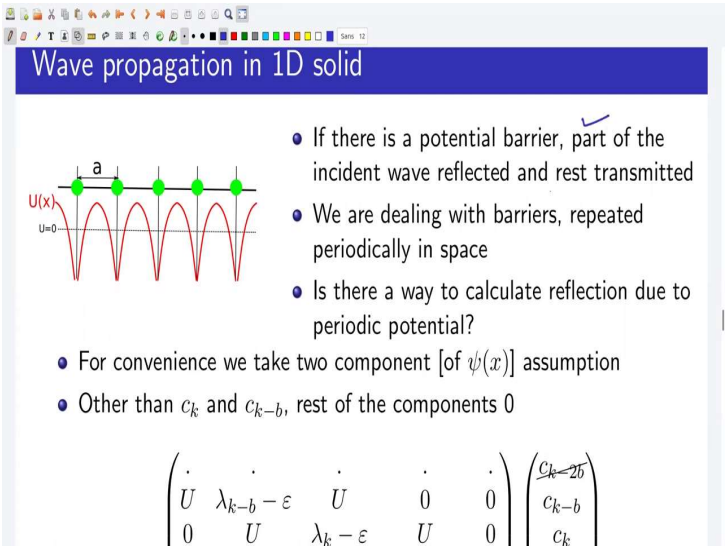

When we discussed basics of quantum mechanics, we have seen that if there is a potential barrier part of the incident wave function is reflected and part of it is transmitted depending on the barrier, height and barrier width. Now, we are dealing with barriers which are repeated periodically in space. Can you estimate the amount reflected due to the periodic potential.

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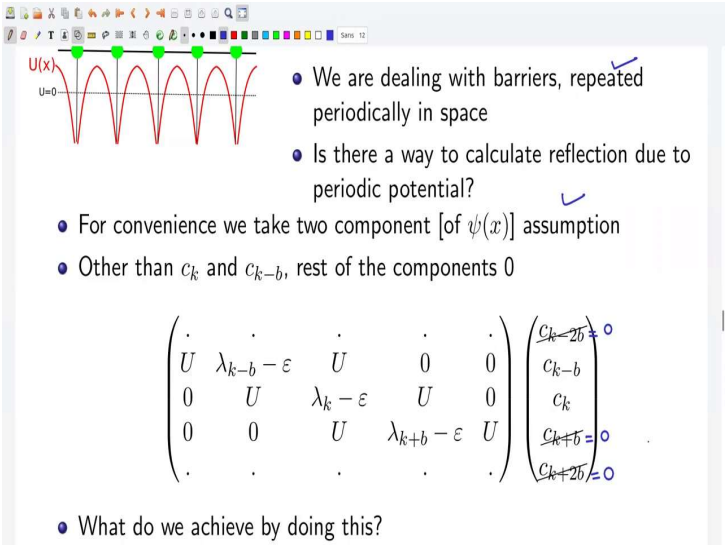

For this purpose, let us design a simplest possible model. We just take 2 Fourier components of psi of x that means we make c k – 2b = 0 c k+ b = 0 and c k+ 2b = 0 and we have only 2 non-zero c k – b and c k. Let us understand what is the purpose of doing so?

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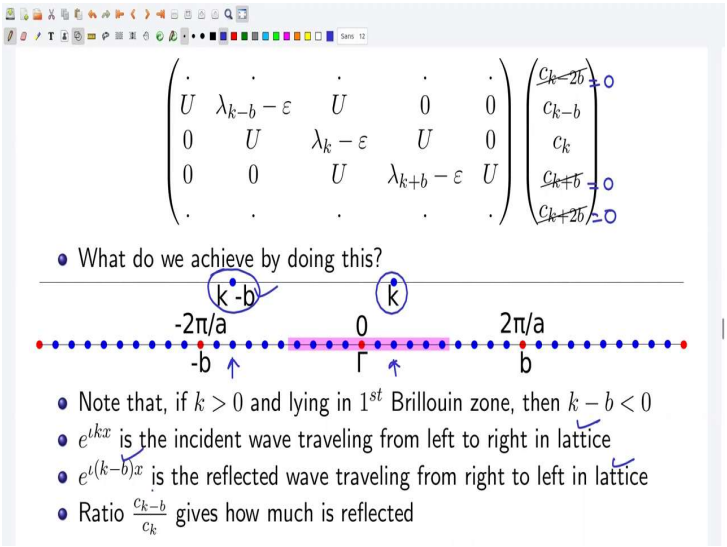

Note that if we select some k point greater than 0 and lying in the first Brillouin zone, for example, this point. In that case k – b is less than 0. Thus, e power ikx is the incident wave traveling from the left to right in the lattice. Since k – b is less than 0 e power i k – b x is the reflected wave travelling from left to the right in the lattice. If we calculate the ratio of the coefficients c k – b divided by c k that will tell us how much is reflected due to the periodic potential?

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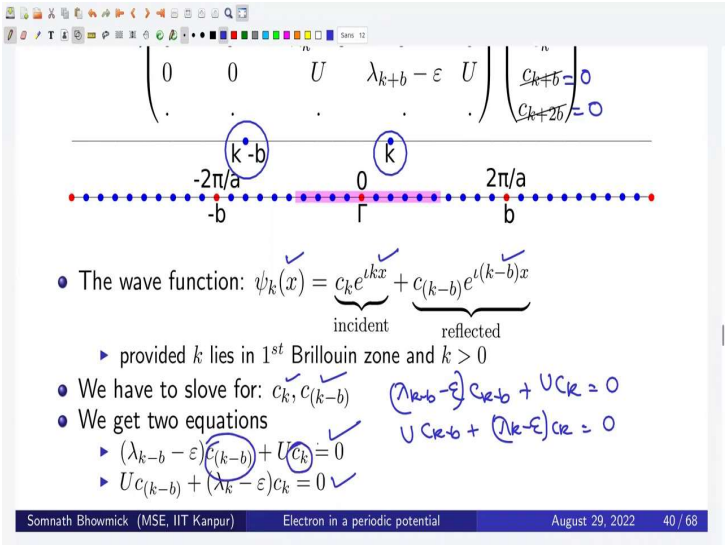

Thus, the wave function is psi k of x = c k e power ikx + c k – b e power i k – b x. Note that we have taken k to be positive and lying in the first Brillouin zone that means ck times e power ikx is a wave traveling from the left to the right of the lattice. On the other hand k – b is less than 0. Thus, the reflected wave e power i k – b x is travelling from the right to the left of the lattice. We are looking to solve for c k at c k – b.

Let us multiply the matrix with the column vector. So, if we multiply this row with the column vector then the first term is 0 because c k – 2b = 0. Then we have a non-zero term that is lambda k – b – epsilon times c k – b plus we have U times c k this is equal to 0. Then we multiply this row with the column vector, so, the first term is 0, the second term is U times c k – b + lambda k – epsilon times c k = 0. Thus, we get 2 equations and we have two unknowns to solve.

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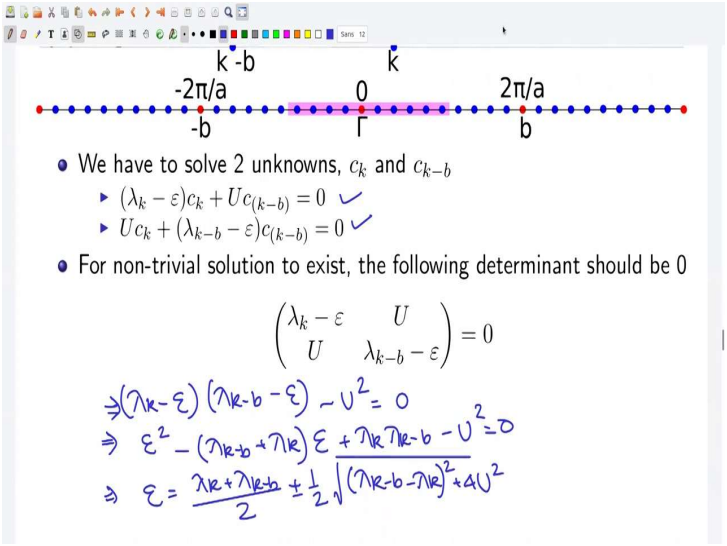

It is very easy to solve two unknowns from two equations. We know that for non-trivial solution to exist, the determinant must be equal to 0. So, let us expand the determinant and find the solution. So, lambda k – epsilon times lambda k – b – epsilon – U square = 0 which can be written as epsilon square – lambda k – b + lambda k times epsilon + lambda k lambda k – b – U square = 0 which implies that epsilon = lambda k+ lambda k – b divided by 2 + – half square root of lambda k – b – lambda k whole square + 4 U square.

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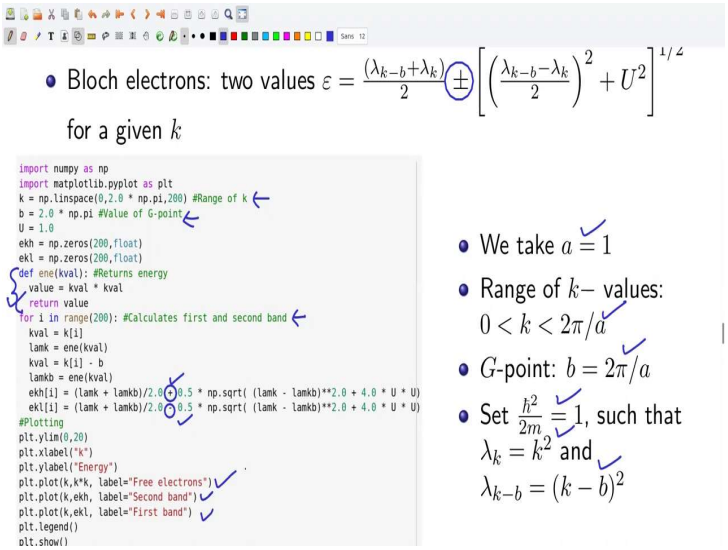

In case of free electrons, we have only one value e of k = h + square k square by 2m for a given k. In case of Bloch electrons for a given k value we have two energy values, one for plus and another for minus using a code. Let us plot the energy values of Bloch electrons as a function of k. We are going to plot energy values for k ranging from 0 to 2pi by a. Note that we take a = 1. The range of k values is defined here in the code.

The G point is taken to be 2pi by a which is defined here in the code we said h cross square by 2m = 1 such that lambda k = k square and lambda k – b = k – b whole square. Lambda values are calculated using a user divide function here in the code. Using a for loop, we calculate the energy value for the first band and for the second band. For a given value of k the first band has lower energy.

And the second band has higher energy. Then we plot the first and second band and compare with the free electron values.

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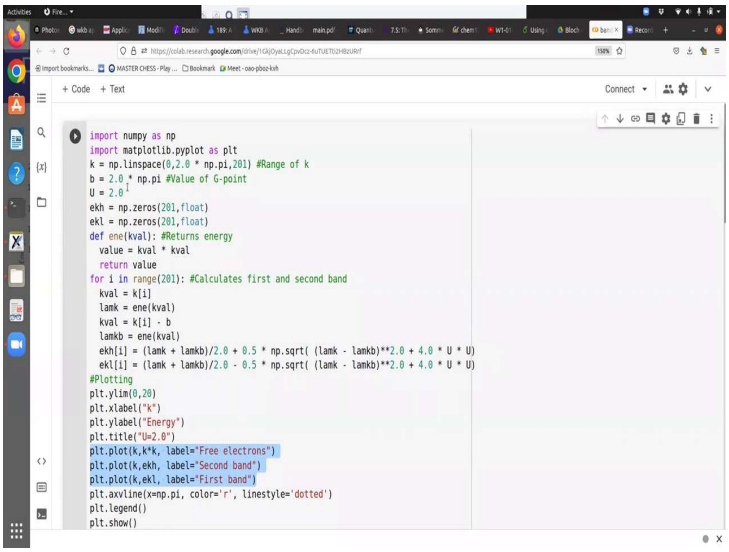

```
import numpy as np
import matplotlib.pyplot as plt
k = np.linspace(0,2.0 * np.pi,201) #Range of k
b = 2.0 * np.pi #Value of G-point
U = 2.0
ekh = np.zeros(201,float)
ekl = np.zeros(201,float)
def ene(kval): #Returns energy
  value = kval * kval
  return value
for i in range(201): #Calculates first and second band
  kval = k[i]
  lamk = ene(kval)
  kval = k[i] - b
  lamkb = ene(kval)
  ekh[i] = (lamk + lamkb)/2.0 + 0.5 * np.sqrt( (lamk - lamkb)**2.0 + 4.0 * U * U)
  ekl[i] = (lamk + lamkb)/2.0 - 0.5 * np.sqrt( (lamk - lamkb)**2.0 + 4.0 * U * U)
#Plotting
plt.ylim(0,20)
plt.xlabel("k")
plt.ylabel("Energy")
plt.title("U=2.0")
plt.plot(k,k*k, label="Free electrons")
plt.plot(k,ekh, label="Second band")
plt.plot(k,ekl, label="First band")
plt.axvline(x=np.pi, color='r', linestyle='dotted')
plt.legend()
plt.show()
```

This is the code for plotting the first and second band as a function of k ranging between 0 and 2pi. We define a and b here. We define the value of U here. The 2 bands are calculated at different k points using the for loop. We plot the bands and compare with free electron values here. Let us run the code for different values of U we start with U = 2.

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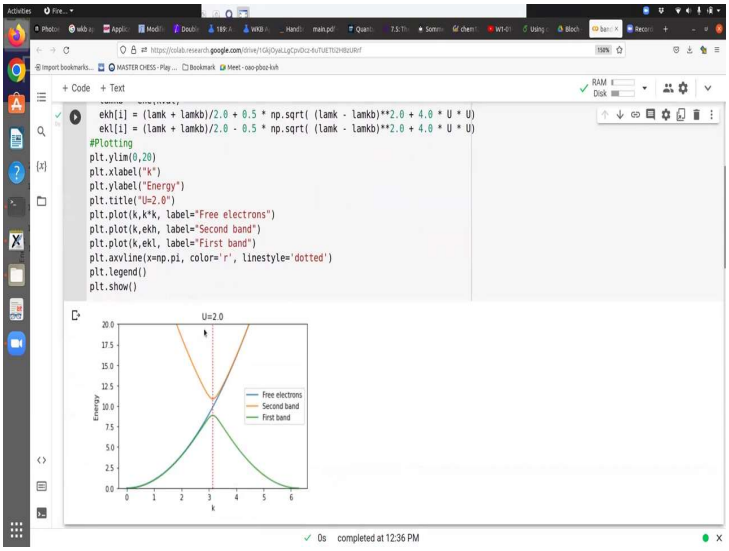

The blue line is for free, electrons, green and orange line is for the first and second band respectively. The vertical red dotted line shows the first Brillouin zone boundary lying in the middle of the 2 reciprocal lattice points. The gap between the first band shown in green and the second band shown in red is minimum at the Brillouin zone, boundary that is at the red dotted line. Now, let us run it for U = 1.

This is how the plot looks like for U = 1. And now, finally, let us run it for U = 0. This is how the plot looks for U = 0.

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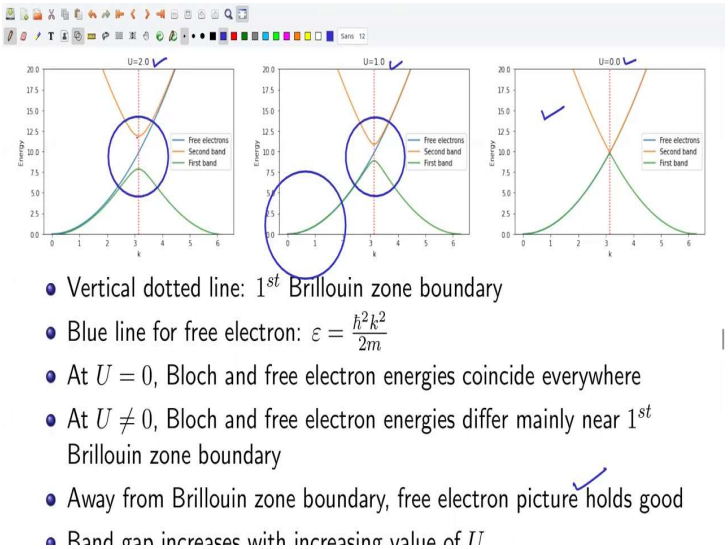

We compare 3 cases, U = 2, U = 1 and U = 0. Clearly for U = 0 Bloch and free electron energies coincide everywhere as expected. At U not = 0 Bloch and free electron energies differ from each other, mainly near the first Brillouin zone, boundary shown by the red dotted line that is, they differ mainly in this region. Otherwise, as we move closer to k = 0 point that is here, they coincide.

Thus, away from the Brillouin zone boundary free electron picture holds good. Note that band gap is defined as the energy gap between the first and second band at the Brillouin zone boundary that is, this is the band gap. The value of band gap increases with increasing U.

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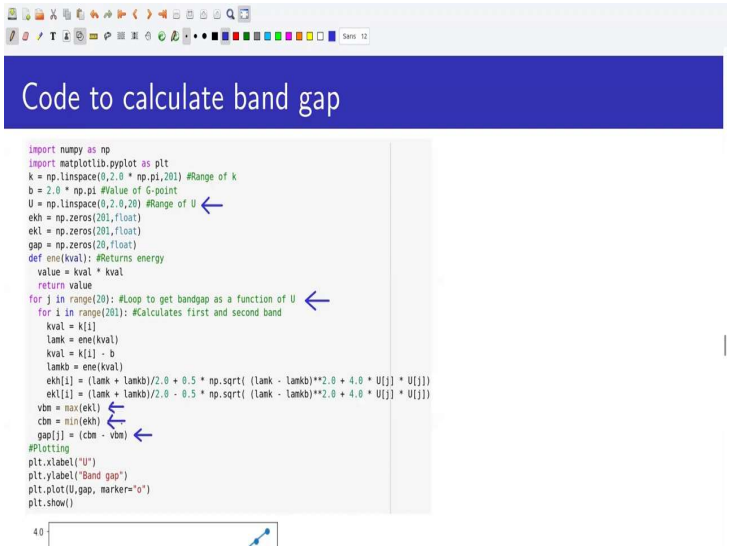

With a very small modification of the previous code, we can plot band gap as a function of U. We vary U from 0 to 2, using a follow. Band gap is the energy difference between the maximum of the first band and the minimum of the second band.

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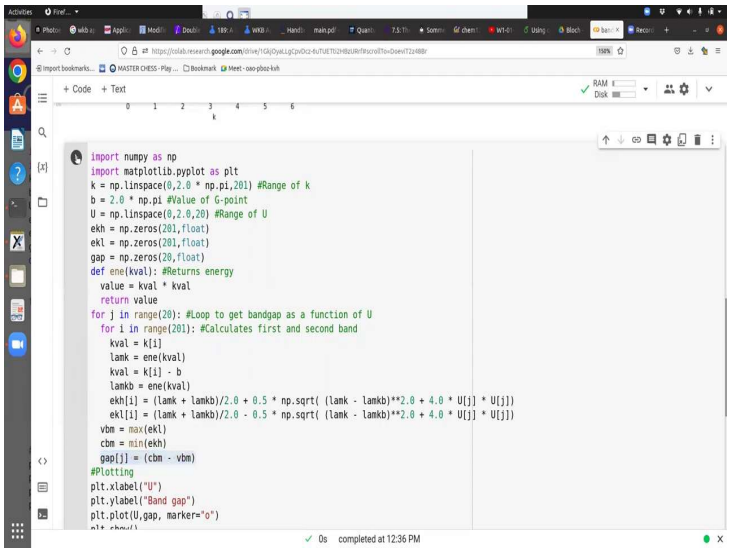

This is the code for plotting band gap as a function of U. Band gap is calculated by varying U between 0 and 2, using a follow. We calculate the maximum of the first band and minimum of the second band and calculate their difference here. The difference between the maximum of the first band and the minimum of the second band gives the value of band gap. Let us run the code.

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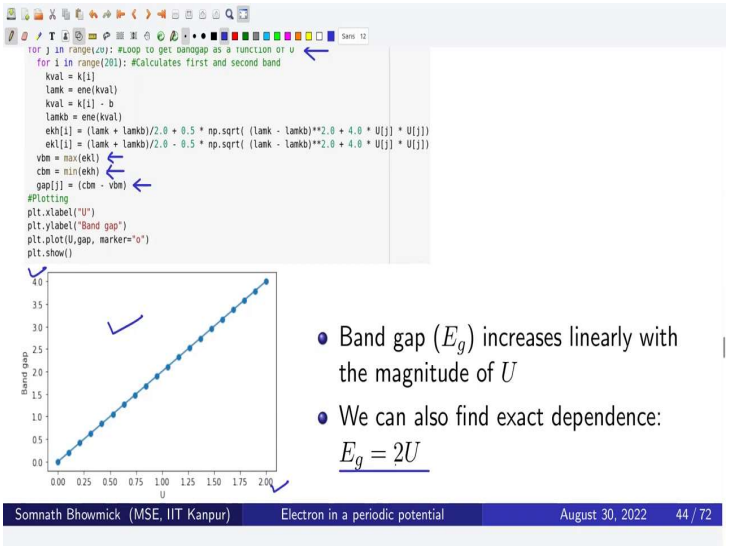

From the plot of band gap as a function of U clearly, band gap increases linearly with the magnitude of U. Note that increasing the value of U from 0 to 2 increases the band gap from 0 to 4. Thus, we can say that E G the band gap is equals to 2 times U.

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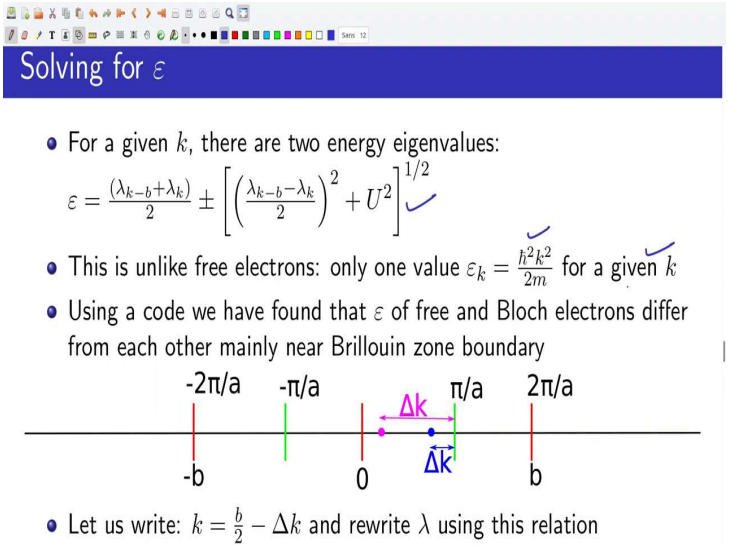

In case of Bloch electrons, for a given k there are 2 energy eigenvalues, as shown here. This is unlike free electrons, where we get only one value E of k = h + square k square divided by 2m for a given value of k using a code we have found that epsilon of free and Bloch electrons differ from each other, mainly near the Brillouin zone boundary. Let us see whether we can analytically verify this or not.

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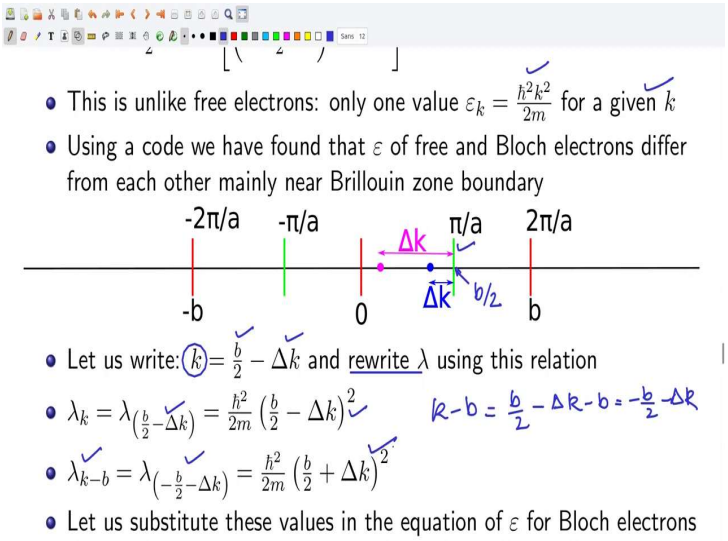

We redefine k in terms of it is distance from the first Brillouin zone boundary shown by the green line. We write k = b by 2, so, this green line is located at b by 2 and delta k is the distance from the Brillouin zone boundary and we write k as b by 2 – delta k. And then we rewrite lambda using this relation, so, lambda k will be equal to lambda b by 2 – delta k because that is how we define k now and this is equal to h cross square by 2m b by 2 – delta k whole square.

Similarly, k – b will be equal to b by 2 – delta k – b which is equal to – b by 2 – delta k. Thus, lambda k – b will be equal to lambda – b by 2 – delta k and which is equal to h cross square by 2m b by 2 + delta k whole square. Let us substitute these values in the equation of energy for Bloch electrons.

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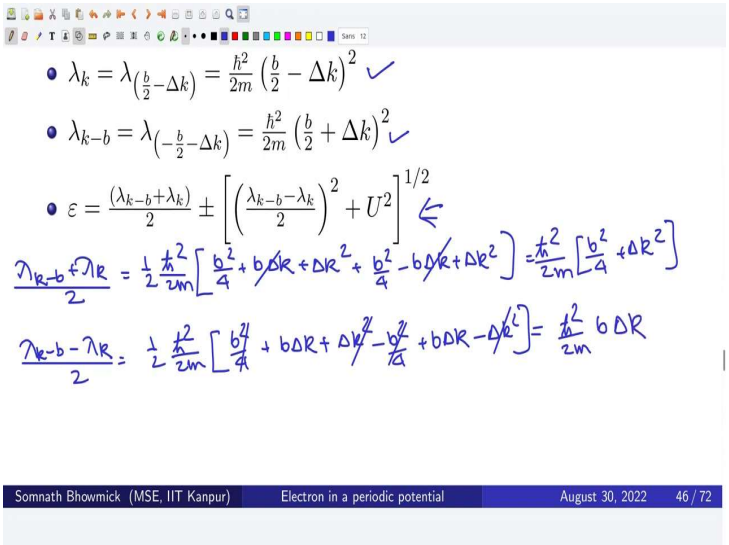

We have redefined k in terms of it is distance from the first Brillouin zone boundary given by delta k. Now, we have to rewrite lambda k and lambda k – b in terms of delta k and substitute in this equation, let us do that. So, we have lambda k – b + lambda k divided by 2 = half h cross square by 2m and we have b square by 4 + b delta k+ delta k square + b square by 4 – b delta k+ delta k square.

These two terms cancel out and this is equal to h square by 2m b square by 4 + delta k square. Similarly, lambda k – b – lambda k divided by 2 = half h + square by 2m b square by 4 + b delta k+ delta k square – b square by 4 + b delta k – delta k square which is equal to h cross square by 2m b delta k.

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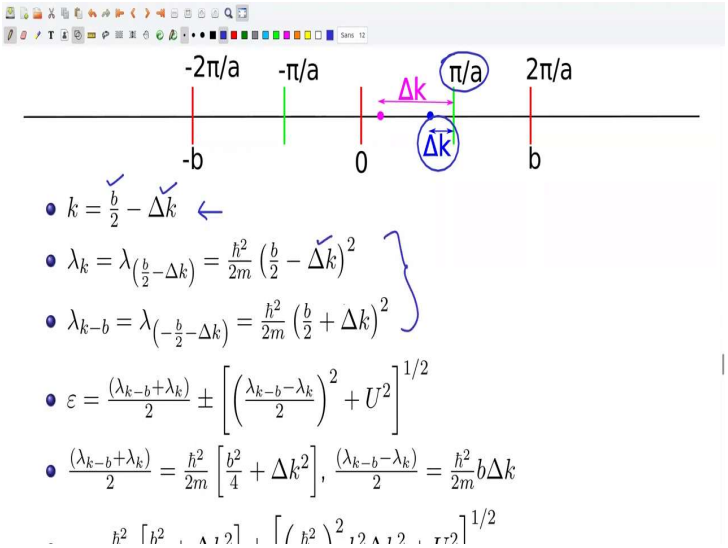

Let me quickly summarize what we have done so, far. We have redefined k in terms of it is distance delta k from the first Brillouin zone boundary located at pi by a. So, this is how we write k in terms of b by 2, the first Brillouin zone boundary and delta k the distance of k from the first Brillouin zone boundary. Then we rewrite the lambdas in terms of delta k.

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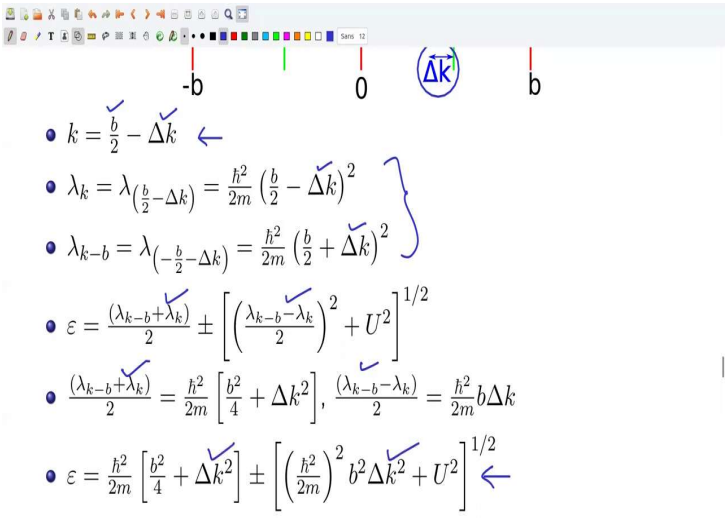

Then we substitute in this equation the values of lambda and if we do that then we can rewrite the energy eigenvalues in terms of delta k.

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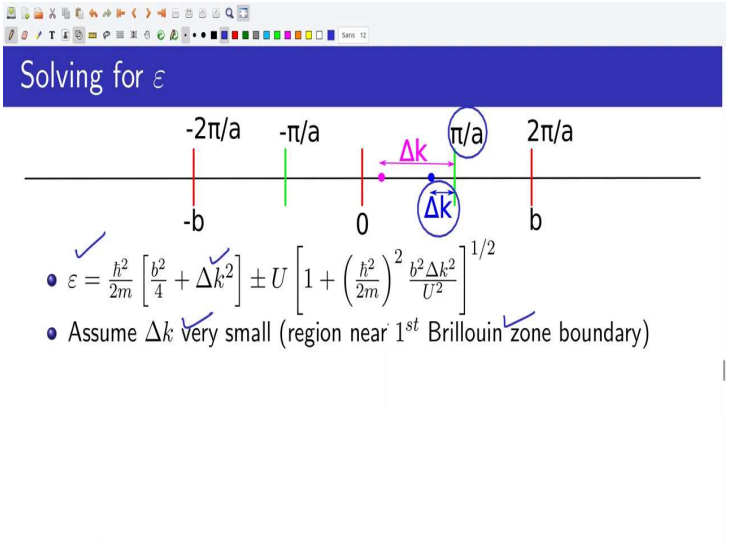

This is how the energy eigenvalues of Bloch electrons, look like if we express it in terms of delta k where delta k is the distance of the k point from the first Brillouin zone boundary. Assume delta k to be very small that is, it is very close to the first Brillouin zone boundary. Why we are doing this? Because we found from our numerical code that energy values between Bloch and free electrons differ mainly in a region close to the first Brillouin zone boundary and we want to check it analytically.

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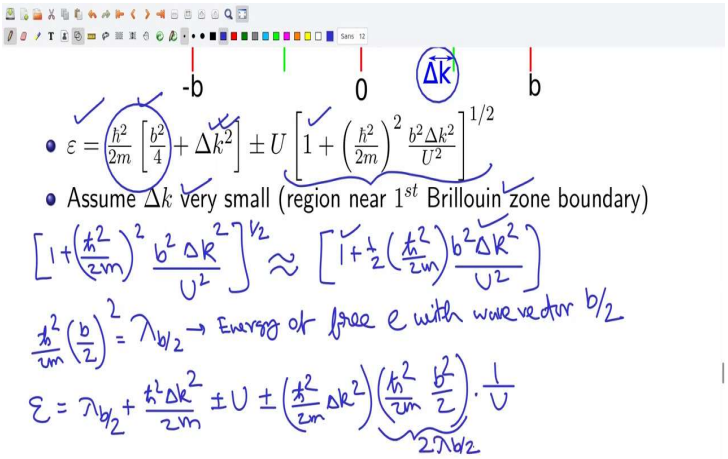

In case of very small k we can write this term that is 1 + h cross square by 2m whole square b square delta k square divided by U square whole power half. So, when delta k is very small, we can write it approximately as 1 + half h + square by 2m b square delta k square divided by U square. Now, note that the first term h cross square by 2m times b by 2 whole square = lambda b by 2 that is the energy of free electron with wave vector b by 2.

Thus, we can write energy is equals to so the first term is lambda b by 2. The second term is + h cross square delta k square divided by 2m. The third term is + – U times 1 and then we have plus minus so, we use the small k approximation and then this turns out to be h cross square by 2m delta k square times h cross square by 2m b square by 2 times. So, 1 U gets cancelled so, this is 1 by U. Note that this term is 2 times lambda b by 2.

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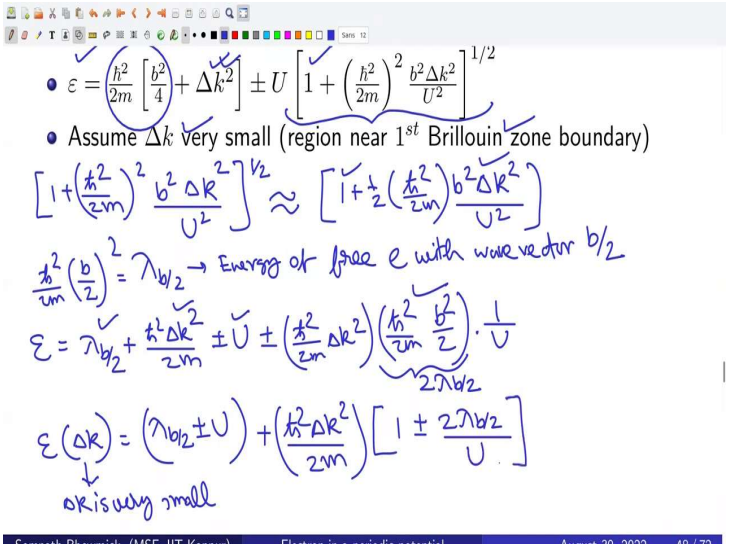

Thus, we can rewrite the energy in terms of delta k when remember that delta k is very small that is k is located very close to the first Brillouin zone boundary. So, in that case, energy is lambda b by 2 + – U. So, these two terms + h cross square delta k square by 2m. So that means we take this term and this term and then this is like 1 + – 2 lambda b by 2, divided by U.

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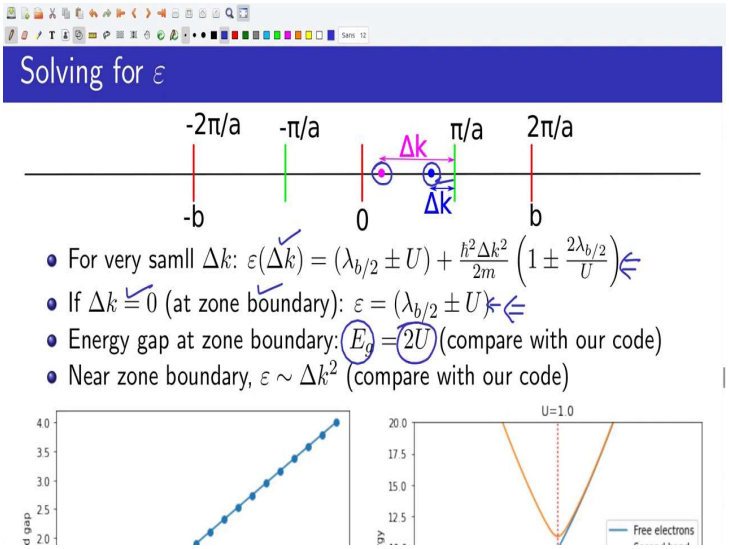

Thus, we have found the approximate form of energy eigenvalues, when k is very close to the first Brillouin zone boundary. That means this equation will hold good in case of this blue point because this is closer to the first Brillouin zone boundary. But it will not hold good for the magenta point which is far away from the Brillouin zone boundary. Now, let us put delta k = 0.

In that case, the second term will vanish completely and the energy eigenvalues exactly at the zone boundary is equal to lambda b by 2 + – U. We know that the energy gap at the zone boundary between the first band and second band is defined as the band cap and from this expression we find that the band gap is equal to 2U.

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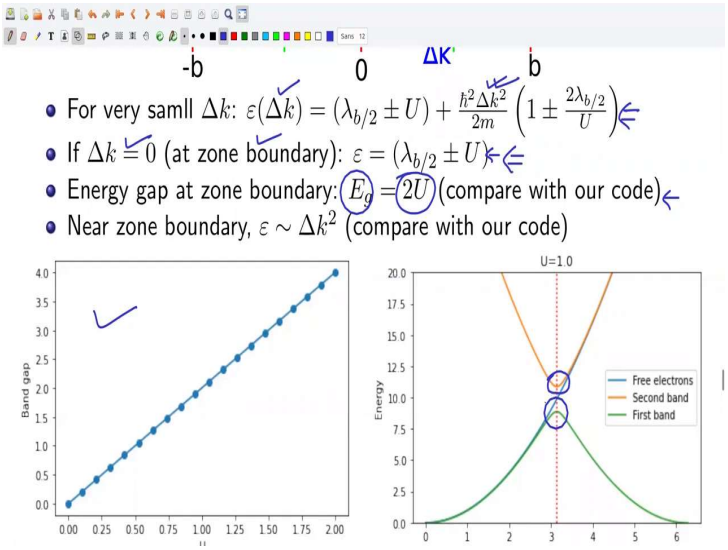

Thus, if we compare with our code then it matches exactly what we have found in our code? Similarly, from our analytical result we find that energy varies as delta k square near the Brillouin zone boundary. You compare with our code and then we see that indeed, the energy eigenvalues vary as k square near the Brillouin zone boundary. Thus, whatever we have observed with our numerical code is matching very well, with the analytical expression.