Electronic Properties of the Materials: Computational Approach
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Lecture: 21
Origin of Band Gaps Part I

Hello friends we are going to continue our discussion on block electrons. In the previous lecture we solved the energy eigenvalues of block electrons we found that unlike free electrons energy spectrum of block electron is capped. We define band gap as the energy gap between the two bands at the first billowing zone boundary. In this lecture let us try to understand the origin of band gap in a 1d lattice.

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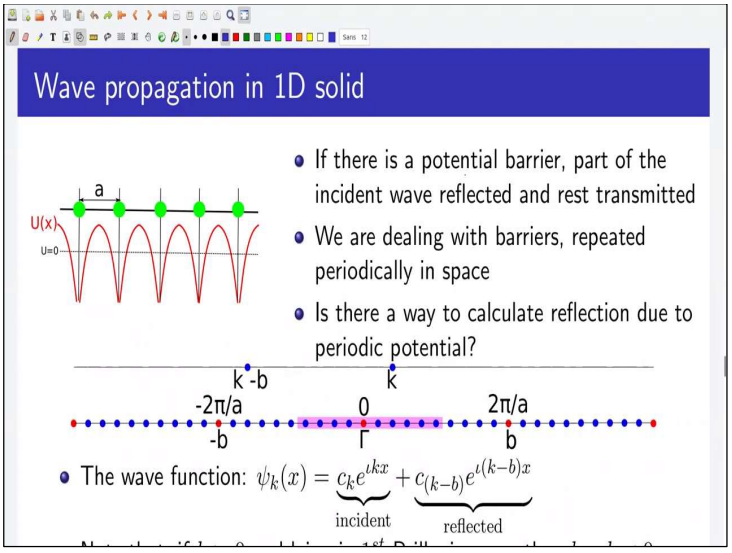

Remember what we discussed in basic quantum mechanics lecture if there is a potential barrier part of the incident wave gets reflected and the rest is transmitted. In the lattice we are dealing with barriers repeated periodically in space as shown in the diagram. Let us try to calculate reflection due to the periodic potential.

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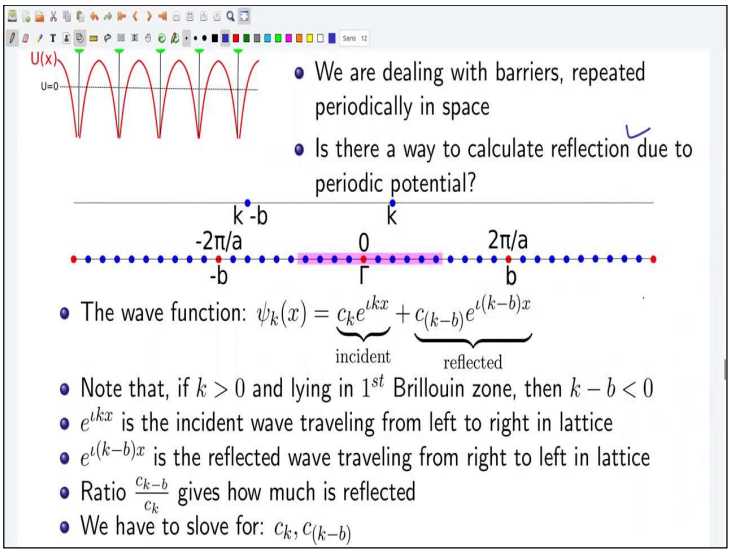

We expand the wave function in terms of just two Fourier components e power i kx and e power i k - b x. Note that if k is greater than 0 and lying in the first below in zone then k - b is less than 0 in that case e power i kx is the incident wave travelling from left to right in the lattice e power i k - bx is the reflected wave travelling in the opposite direction of the incident wave. To estimate how much is reflected we need to calculate the ratio of c k - b and c k and for that we need to solve c k and c k – b.

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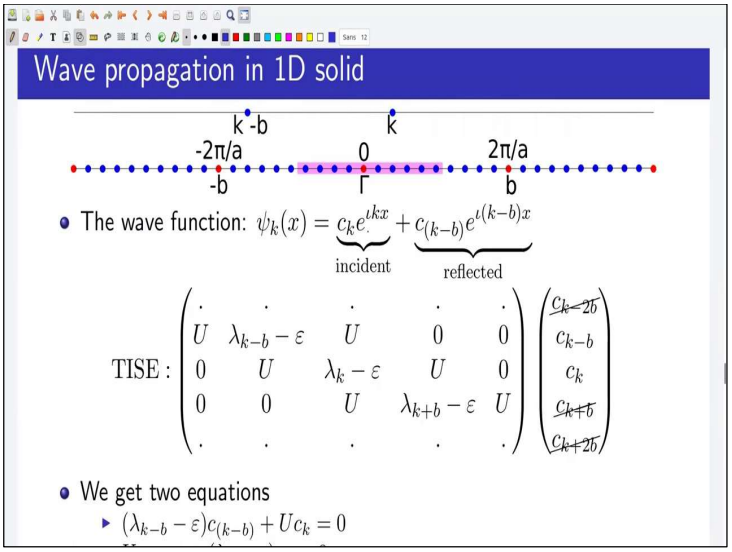

We are writing the Fourier series expansion of the wave function keeping just two terms e power i k e power i k - b x time independent Schrodinger equation is converted to a system of linear equations in case of block electrons. Note that other than c k - b and c k rest of the coefficients are zero because we have decided to keep only two terms in the Fourier series expansion of sine.

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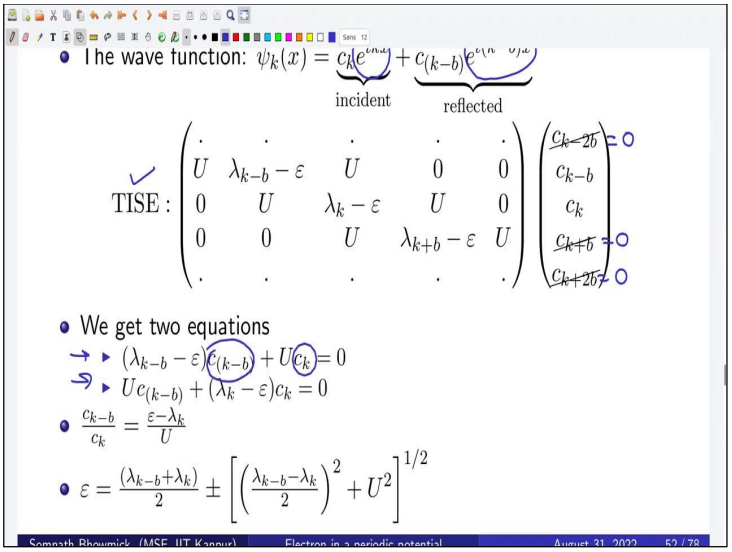

We get two equations and we have to solve two unknowns c k - b and c k. From the second equation we can write $Uc_{k-b} = (\varepsilon - \lambda_k)c_k$which implies that $\frac{c\_b}{c_k} = \frac{\varepsilon-\lambda_k}{U}$ we also get the energy eigenvalues of block electrons from the system of linear equations as given here.

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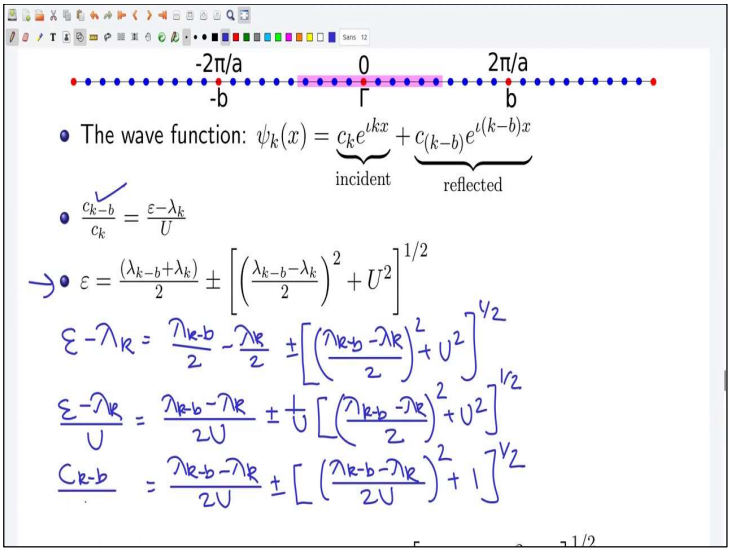

Now let us calculate this ratio from this equation we can write

$$\frac{c_{k-b}}{c_k} = \frac{\lambda_{k-b}-\lambda}{2U} \pm \left[\left(\frac{\lambda_{k-b}-\lambda}{2U}\right)^2 + 1\right]^{1/2}$$

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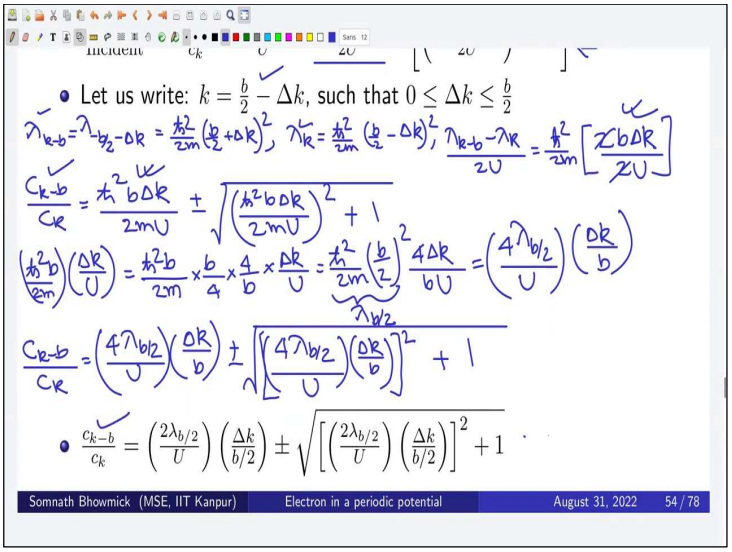

So, $\frac{c_{k-b}}{c_k}$ tells us how much of the incident wave is getting reflected because of the periodic potential. Now we write k is equals to b by 2 - delta k where delta k is the distance from the first Brillouin zone boundary shown by the green line in this diagram, we are going to rewrite this equation in terms of delta k. This is equivalent to changing our reference point in the reciprocal space.

If we express in terms of k the reference point is the gamma point this one which is the origin of the reciprocal space. If we express in terms of delta k the reference point is the first Brillouin zone boundary shown by the green vertical line in the diagram. If we write lambda k - b in terms of delta k then we get

$$\lambda_{k-b} = \lambda_{-b/2-\Delta k} = \frac{\hbar}{2m}\left(\frac{b}{2} + \Delta k\right)^2$$

Similarly, we write

$$\lambda_k = \frac{\hbar^2}{2m}\left(\frac{b}{2} - \Delta k\right)^2$$

subtracting λ_{k-b} and $\lambda_k$we get this term. So let us do that

$$\frac{\lambda_{k-b} - \lambda_k}{2U} = \frac{\hbar^2}{2m}\left[\frac{2b\Delta k}{2U}\right]$$

$$\frac{c_{k-b}}{c_k} = \frac{\hbar^2 b\Delta k}{2mU} \pm \sqrt{\left(\frac{\hbar b\Delta k}{2mU}\right)^2 + 1}$$

$$\frac{\hbar^2 b}{2m}\frac{\Delta k}{U} = \frac{\hbar^2 b}{2m}\frac{b}{4}\frac{4}{b}\frac{\Delta k}{U} = \frac{\hbar^2}{2m}\left(\frac{b}{2}\right)^2\frac{4\Delta k}{bU} = \left(\frac{4\lambda_{b/2}}{U}\right)\frac{\Delta k}{b}$$

Now we can slightly rearrange the terms and express $\frac{c_{k-b}}{c_k}$ in this form.

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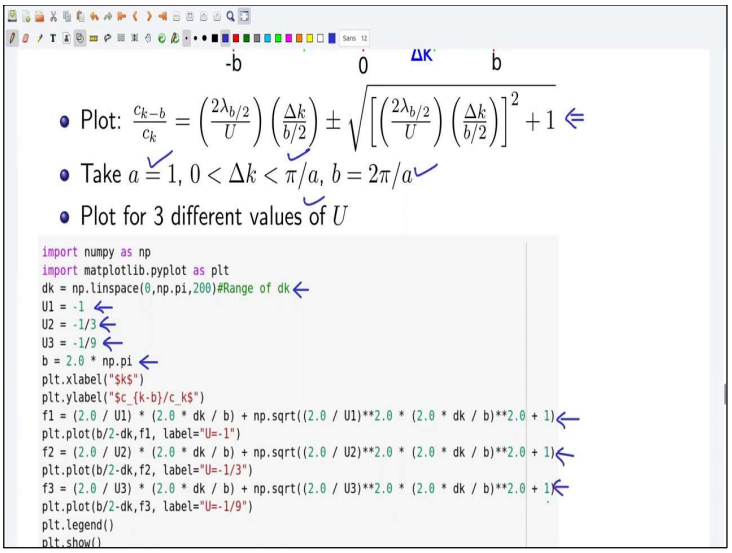

Using a simple python code let us plot this equation which tells us how much of the incident wave is getting reflected because of the periodic potential. We take a to be equal to 1 and delta k lies in the range of 0 and pi by a as defined here and b is equals to 2 pi by a as defined here we plot for 3 different values of U, U equal to - 1 - 1 third and -1 by 9. The functions to be plotted for three different use are defined here in the code.

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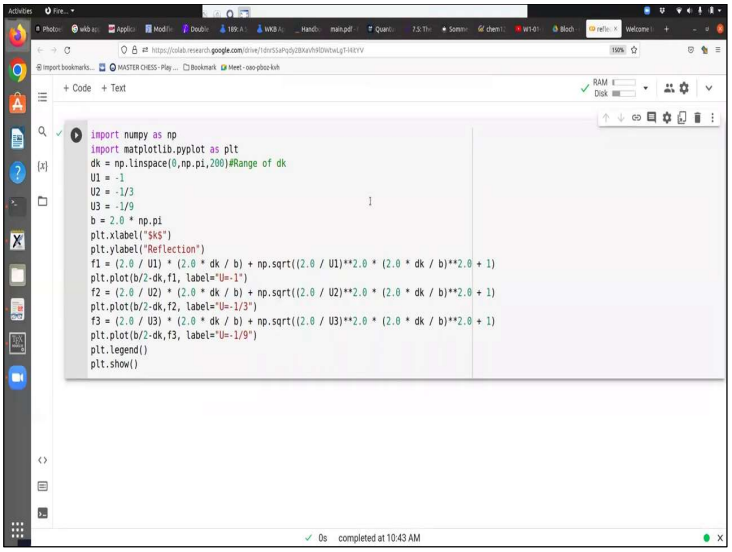

This is the code for plotting reflection due to a periodic potential. So, this is the range of delta k we are going to find the reflection for three different potentials and the functions to be plotted are defined here. So, let us run the code and see the output.

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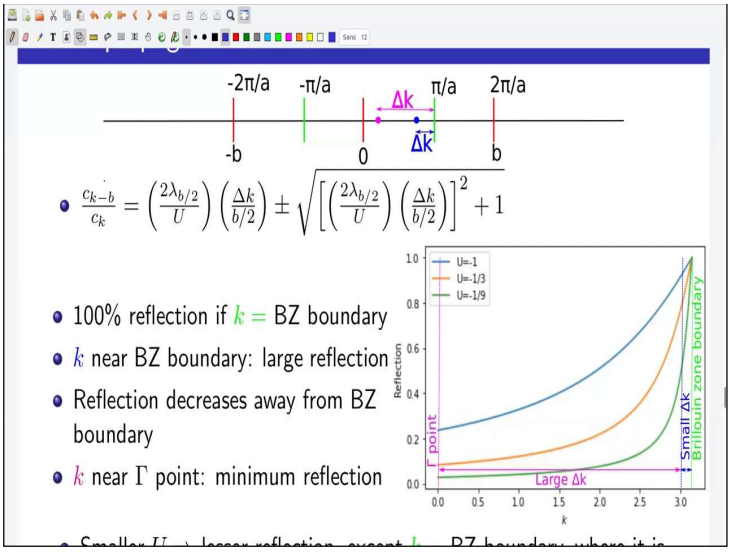

Using a python code we have plotted the ratio of c k - b and c k. The green dotted line shows the Brillouin zone boundary the blue dotted line marks the region where k is very close to the Brillouin zone boundary. The purple dotted line shows the location of the gamma point. Now we find that if k is exactly equal to the Brillouin zone boundary then there is 100% reflection as shown here. If k lies near the below zone boundary the reflection is very large.

As we move away from the Brillouin zone boundary the reflection decreases. When k is near the gamma point the reflection is minimum.

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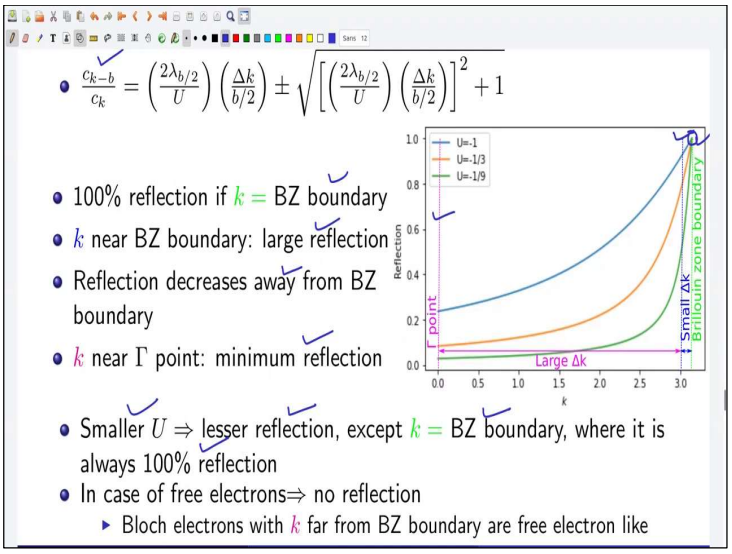

We find that for a given k smaller the value of U lesser is the reflection. However there is a notable exception if k is exactly equal to the Brillouin zone boundary we always get 100% reflection irrespective of the value of U. We know that in case of free electrons there exists no reflection thus we conclude that block electrons with k far from the Brillouin zone boundary are free electron like.

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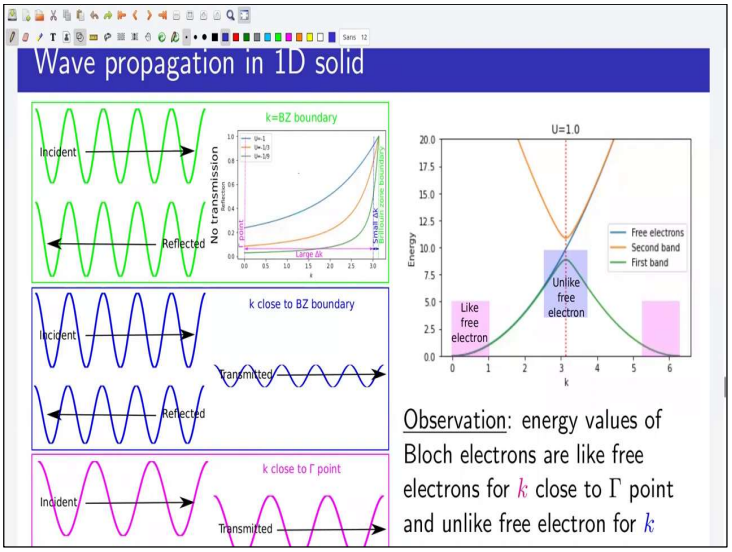

In this slide I summarize our main findings from the numerical codes we have calculated reflection of block electrons due to the periodic potential. We have found that how much of the incident wave is reflected depends mainly on the wave vector k of the block electrons. If the block electron has a wave vector equal to the first pillowing zone boundary it cannot propagate inside the crystal.

This is true irrespective of the value of U it does not matter whether U is small or large block electrons with wave vector equal to the first Brillouin zone boundary gets reflected 100% due to the periodic potential. If the effector is close to the Brillouin zone boundary the lattice allows a small part of the wave to be transmitted. Amount of transmission depends on the value of U.

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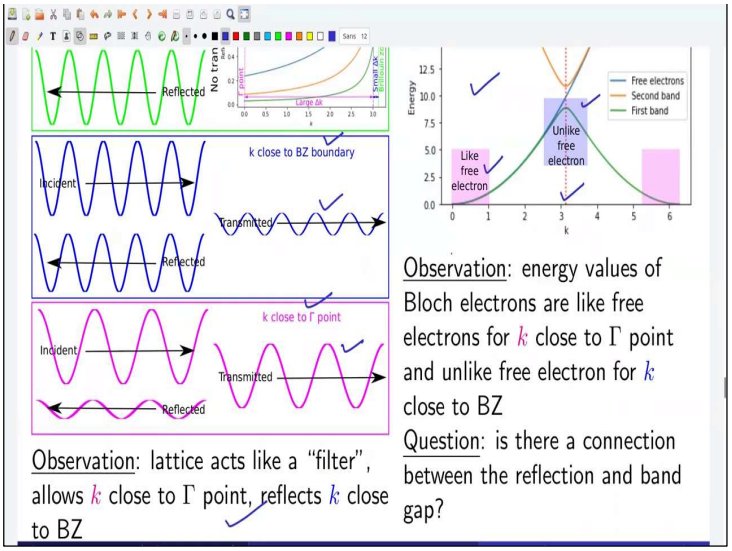

If the wave vector is close to the gamma point that is the center of the reciprocal lattice then a large part of the incident wave is allowed to be transmitted. In conclusion the lattice acts like a filter allowing block electrons having k close to the gamma point to pass and not letting block electrons having k close to the Brillouin zone boundary. Thus block electrons with k close to the gamma points are more like free electrons.

However as k value of block electrons move closer to the Brillouin zone boundary its behavior starts deviating from that of free electrons. Comparing the energy of free and block electrons we find a similar trend. Close to the Brillouin zone boundary as shown by the red dotted line in the figure energy of block electrons and free electrons differ significantly. However close to the gamma point energy of the block electrons is very similar to the energy of the free electrons.

In conclusion when the block electrons can propagate like free electrons their energies are very similar however when block electrons cannot propagate like free electrons their energies differ significantly. Propagation of block electrons are stopped because of the reflection by periodic potential and we observe a gap in the energy spectrum of the block electrons. Is there any connection between the reflection and band cap let us investigate.

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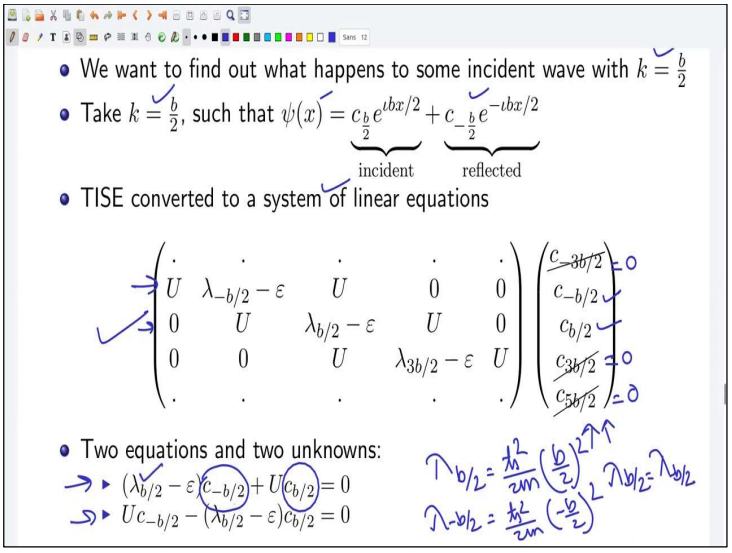

So, far we did a Fourier series expansion of psi in this form. Now we want to find out what happens to some incident wave with k equal to the first Brillouin zone boundary that is k equal to b by 2 substituting k equal to b by 2 in this equation we get psi of x is equals to c b by 2 e power i bx by 2 + c - b by 2 e power - i bx by 2. Time independent Schrodinger equation is converted to a system of linear equations of this form.

We set all the c is to equal to 0 except for c - b by 2 and c b by 2 multiply the second row with the column we get this equation and multiply the third row with the column we get this equation thus we have two equations and there are two unknowns c - b by 2 and c + b by 2.

Note that

$\lambda_{b/2} = \frac{\hbar^2}{2m}\left(\frac{b}{2}\right)^2$ and $\lambda_{-b/2} = \frac{\hbar^2}{2m}\left(\frac{-b}{2}\right)^2$

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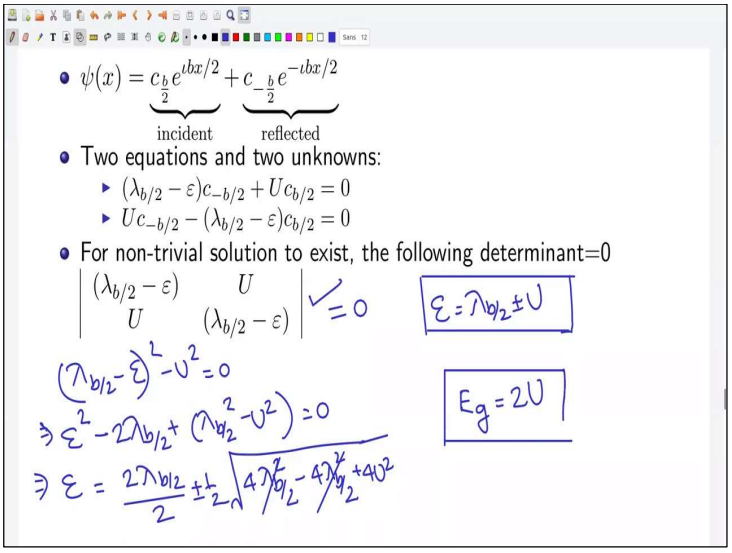

For non-trivial solution to exist the determinant should be equal to 0 let us expand the determinant

$$\left(\lambda_{b/2} - \varepsilon\right)^2 - U^2 = 0$$

$$\Rightarrow \varepsilon^2 = 2\lambda_{b/2} + \left(\lambda_{b/2}^2 - U^2\right) = 0$$

$$\Rightarrow \varepsilon = \frac{2\lambda_{b/2}}{2} \pm \frac{1}{2}\sqrt{4\lambda_{b/2}^2 - \lambda_{b/2}^2 + 4U^2}$$

$$\varepsilon = \lambda_{b/2} \pm U$$

Thus at k equal to b by 2 the difference of energy between the first and second band which is defined as the band gap is equal to $E_g = 2U$

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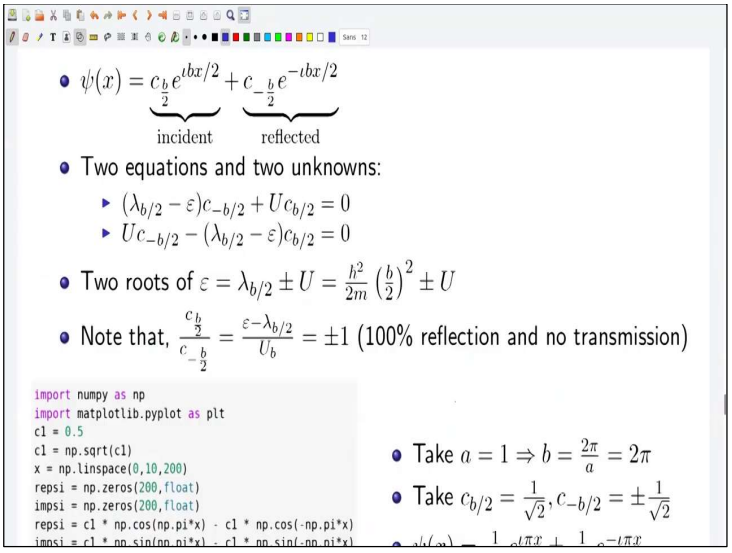

Let us write a code and plot the wave functions we take the distance between adjacent direct lattice points to be equal to 1 such that the reciprocal lattice points are 2 pi apart from each other we assume that c b by 2 is equals to 1 by square root of 2 such that c - b by 2 is + 1 by root 2 in one case and c - b by 2 is equals to - 1 by root 2 in the other case. We plot psi x is equals to 1 by square root of 2 e power i pi x + 1 by square root of 2 e power - i pi x in one case and psi x is equals to 1 by square root of 2 e power i pi x - 1 by square root of 2 e power - i pi x in the other case.

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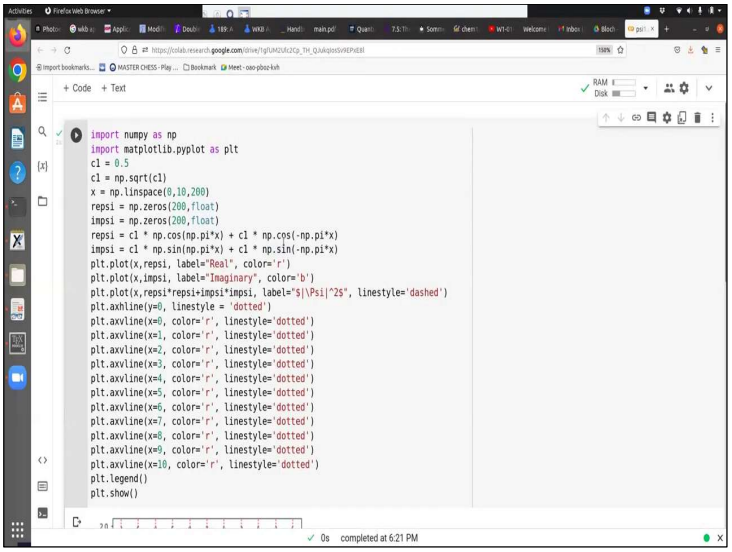

This is the code for plotting the wave functions first we plot for plus as shown here let us run the code. The solid red line is the real part of the wave function the solid blue line is the imaginary part of the wave function the dashed blue line is the probability density and the red dotted vertical lines denote the location of the lattice points. Next we plot for the other wave function by changing + to -.

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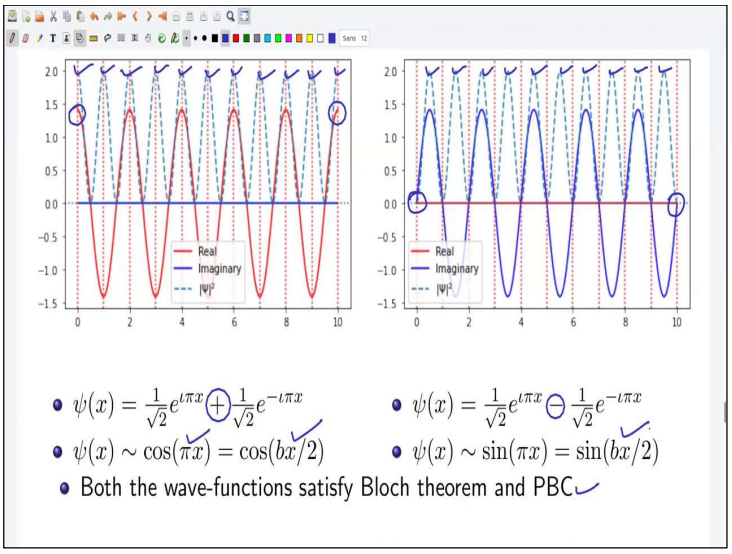

Let us run the code. Thus we have plotted for psi x is equals to 1 by square root of 2 e power i pi x + 1 by square root of 2 e power - i pi x and psi x is equals to 1 by square root of 2 e power i pi x - 1 by square root of 2 e power - i i x clearly both the wave functions satisfy Bloch Theorem as well as periodic boundary condition. Bloch Theorem is satisfied because the probability density has the periodicity of the lattice.

Periodic boundary condition is satisfied as the wave function and its first derivative is continuous at the boundary. Clearly the first wave function is cos of pi x, if we write in terms of the reciprocal lattice points we can write as cos bx by 2 on the other hand the second wave function is sine bx by 2. We get the wave functions in this form because of complete reflection at the Brillouin zone boundary. In the next lecture we shall discover the link between such wave functions and band gap.