Electronic Properties of the Materials: Computational Approach
Prof. Somnath Bhowmick
Department of Materials Science and Engineering
Indian Institute of Technology – Kanpur

Lecture – 19
Bloch Electrons in 1D Solid: Part 2

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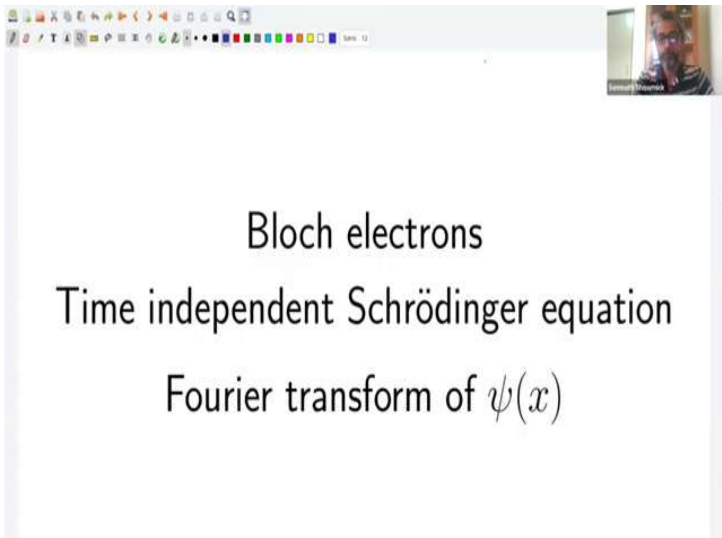

Hello friends, in this lecture, we continue our discussion on solving time independent Schrodinger equation to get energy eigenvalues and eigen functions in a 1D lattice.

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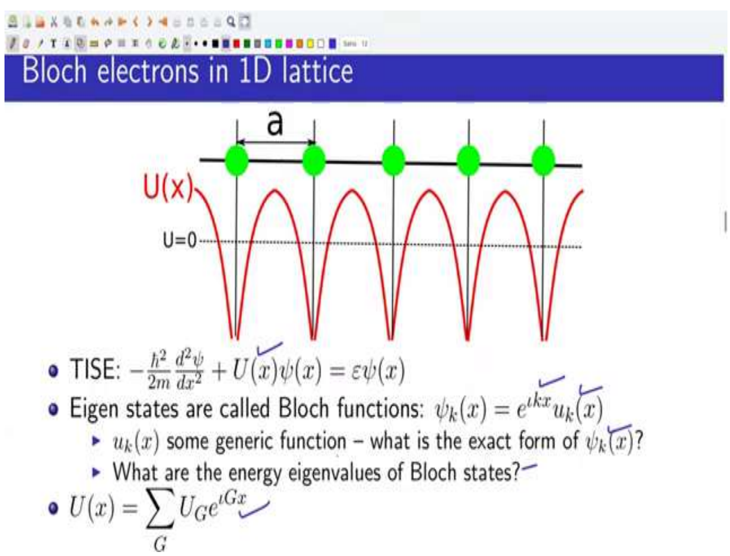

We have to solve time independent Schrodinger equation, where U of x is an effective 1 electron potential having the periodicity of the lattice. According to Bloch theorem, the eigen function is a plane wave times some function U of x which has the periodicity of the lattice. However, U of x is a generic function and thus we do not know the exact form of psi of x. We also do not know the energy eigenvalues. In the previous lecture, we expanded U x in this form where G is reciprocal lattice point.

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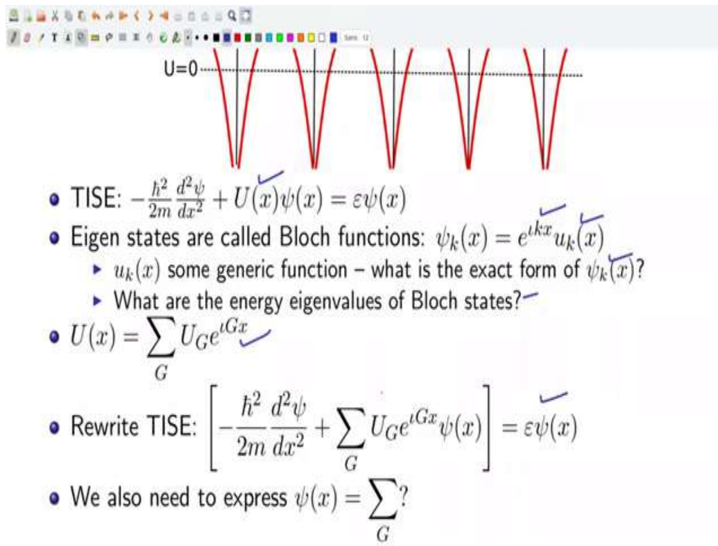

Replacing U of x in time independent Schrodinger equation we rewrite in this form. However, we cannot solve it yet we need to express psi of x also in the form of a Fourier series let us do that.

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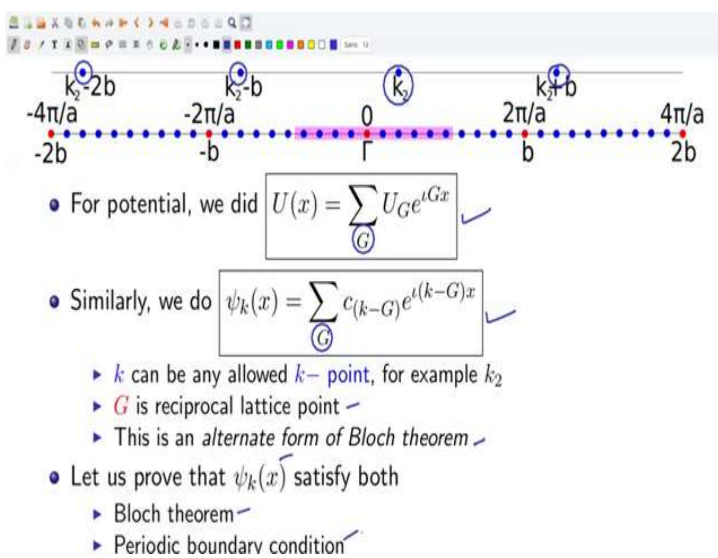

For potential, we wrote the Fourier series of U x using the reciprocal lattice points or G points. Similarly, I claim that we can expand psi k of x the wave function in this form where k can be any allowed k point. For example, we can take this point k 2, G is a reciprocal lattice point, since there is a sum over G we have to consider all the terms which differ from k 2 by G. For example, we have to consider k 2 – b, we have to consider k 2 – 2b, we have to consider k 2 + 2b, etcetera.

This is an alternate form of Bloch theorem. We can accept psi k of x to be a solution of electron in a periodic potential provided psi k of x satisfy both Bloch theorem and periodic boundary condition, let us verify that.

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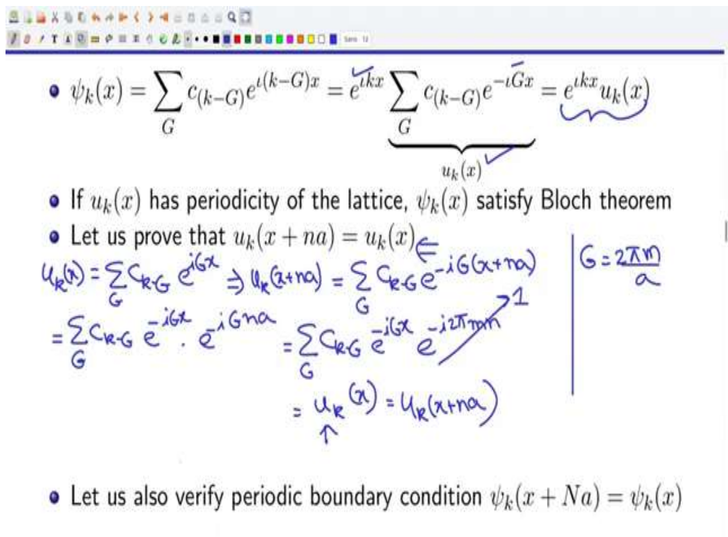

Let us rewrite psi of x by bringing e power ikx outside the sum because the sum is over G. The term sum over G c k – G e power – iGx let us rewrite this as u k of x such that we can write psi k of x as e power ikx u k of x. Now, this will look exactly like Bloch theorem, provided u k of x has the periodicity of the direct lattice. Let us prove that u x + na = u of x where n is some integer and a is spacing between adjacent direct lattice points.

$$U_k(x) = \sum_G c_{kG}\, e^{ikx} \Rightarrow U_k(x+na) = \sum_G c_{k-G} e^{-iG(x+n\ \ )}$$

$$= \sum_G c_{k-G}\, e^{-ik} e^{-iGna} = \sum_G c_{k-G}\, e^{-ik} e^{-iGna} = \sum_G c_{kG} e^{-ik}\ \ e^{-ik}$$

$$U_k(x)$$

Thus, this function $U_k(x)$ has the periodicity of the direct lattice.

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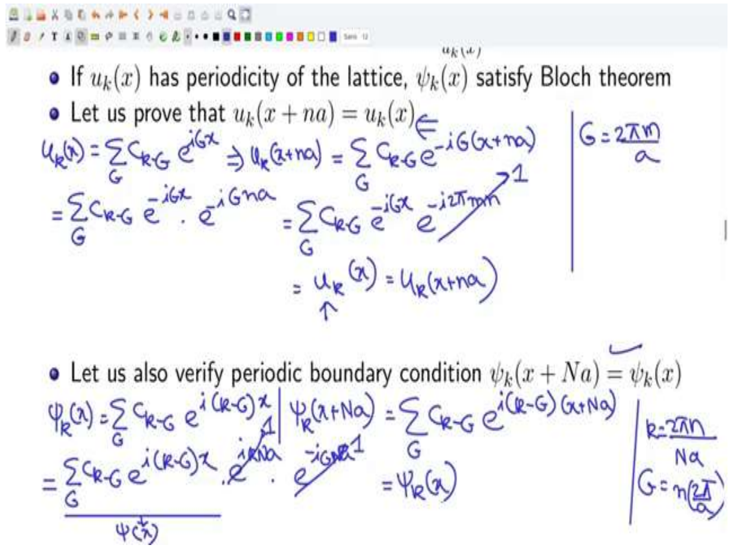

Now that we have proved psi k of x satisfy Bloch theorem, let us also verify whether it satisfies the periodic boundary condition.

$$\psi_k(x) = \sum_G c_{k-G}\, e^{i(k-G)x}$$

$$\psi_k(x+Na) = \sum_G c_{k-G}\, e^{i(k-G)(x+N\ \ )}$$

$$= \sum_G c_{k-G} e^{i(k-G)x}\, e^{ikNa} e^{-iG}$$

And this term is nothing but psi of x and then we have e power ikNa times e power – iGNa. Now, we know that k = 2pi n divided by Na and $G = n\frac{2\pi}{a}$. If we replace k and G in this equation then this term is equal to 1 and this term is equals to 1. And then that gives us the proof that $\psi_k(x+Na) = \psi_k(x)$. Thus, psi k x also satisfies periodic boundary condition.

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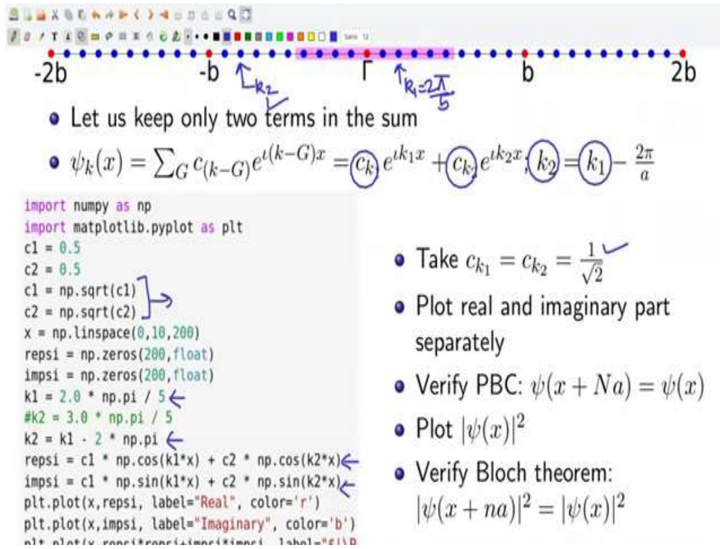

Like we did for the potential, let us understand Fourier series expansion of psi of x using a simple python code. For simplicity, let us keep only two terms in the Fourier series expansion. We take a k point in the first Brillouin zone k 1, for example this point the other k point k 2 = k 1 – 2pi by a, this means k 2 is located here. Let us take the constants c k 1 and c k 2 to be equal that is c k 1 = c k 2 = 1 by square root of 2.

In the code the constants are defined here we take an allowed k point k = 2pi by 5, as shown here. In the diagram, this is the k point, this point lyes in the first brillouin zone which is marked by the magenta shaded region, the other k point k 2 is k 1 – 2pi. Note that I have taken the distance between two adjacent direct lattice points to be equal to 1. In the diagram, the second k point lyes here. And this is outside the first Brillouin zone.

The real part of the complex wave function contains cosine terms and defined here. The imaginary part of the complex wave function contains sin terms and defined here, plotting real and imaginary part separately we can verify the periodicity. For the complex wave function to be periodic both real and imaginary part should be periodic.

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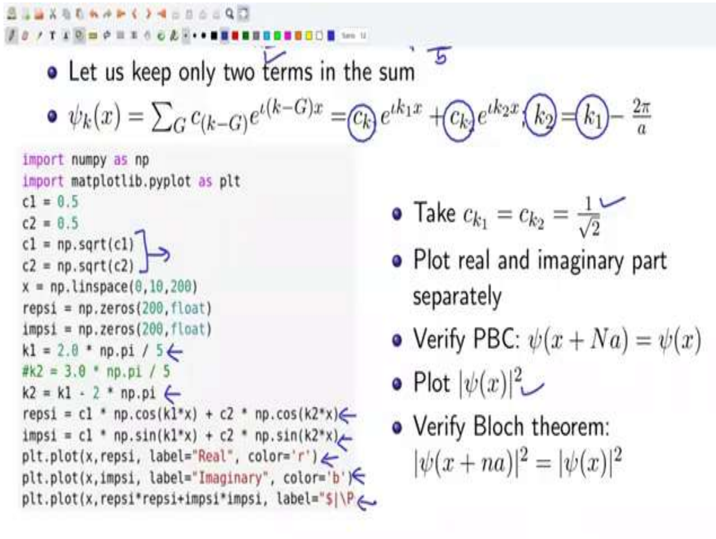

In this code we plot the real and imaginary part here. Then we plot mod psi of x square which tells us whether the wave function satisfies Bloch theorem or not. In the code, we plot mod psi x square here.

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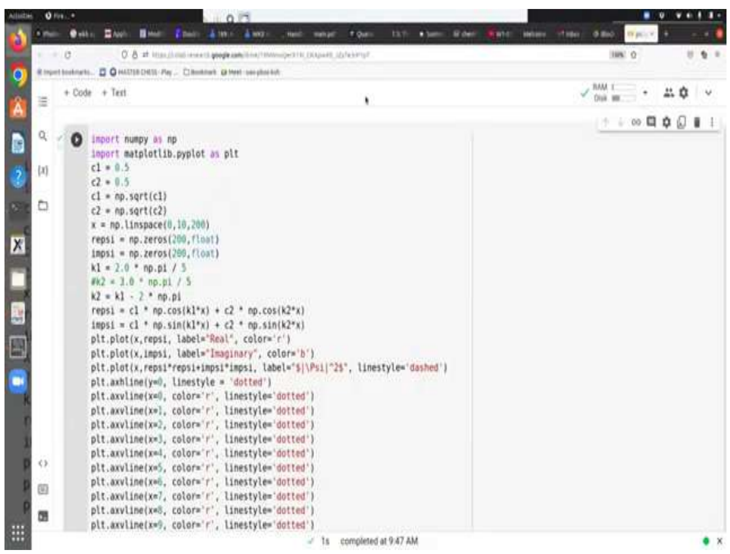

This is the code to plot real and imaginary part of psi as well, as probability density. Length of the periodic box is equal to 10 as shown here. We take k 1 = 2pi by 5 which is one of the allowed k points obtained from the PBC applied on a box of length L = 10 k 1 lyes in the first Brillouin zone. The other point k 2 differs from the point k 1 by a reciprocal lattice vector 2pi. This is where the real part and the imaginary part of the wave function is defined. This is where we plot the real part, this is where we plot the imaginary part and this is where we plot the probability density. Let us run the code.

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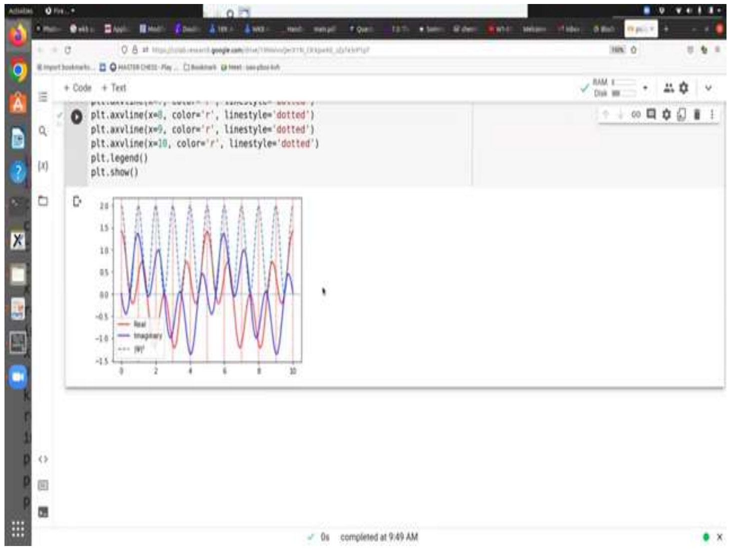

The solid red line is the real part of the complex wave function and the solid blue line is the imaginary part of the complex wave function. The dashed blue line is the probability density vertical red dotted lines show the location of the lattice points. Let us try another set of k values.

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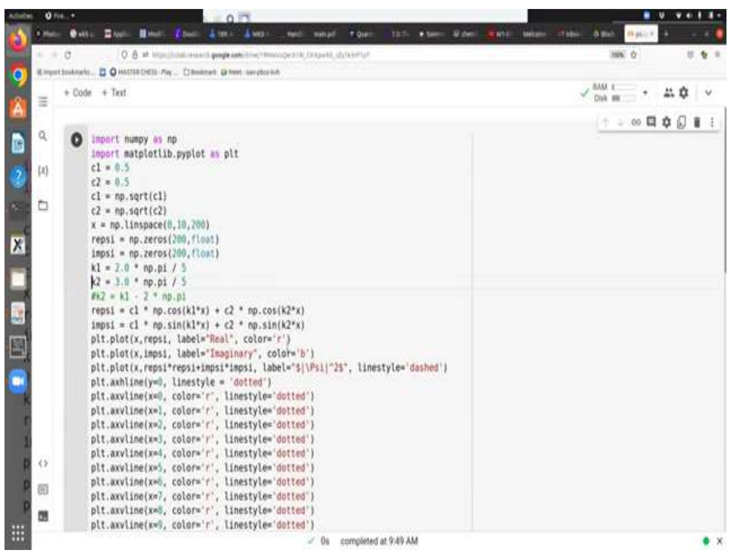

In this case we take k 1 = 2pi by 5 same as before and we take k 2 = 3pi by 5. Note that k 1 and k 2 are just adjacent allowed k points. They are not separated by a lattice vector, unlike we did for the previous case. Now, let us run the code.

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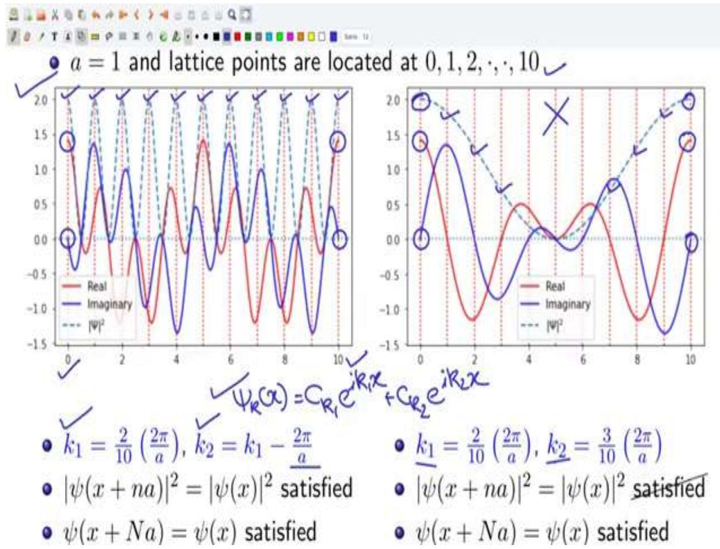

Remember that the solid has a length of L = 10 and distance between two adjacent points in real lattice is equal to 1. Thus, the direct lattice points are located at 0, 1, 2, 3, 4 etcetera, as shown by the vertical red dotted line in the diagrams. First, let us analyze the first diagram from the left that is, this one. The real and imaginary part of psi satisfies periodic boundary condition.

By this I mean that real and imaginary part of the wave function, as well, as it is first derivative, is continuous at x = 0 and at x = 10. At x = 0 this is the real part and this is the imaginary part of the wave function. At x = 10 this is the real part and this is the imaginary part of the wave function. Clearly, the wave function and it is first derivative is continuous at the boundary.

Moreover, probability density is equal at each lattice point, as shown in the diagram. This is the necessary condition for the wave function to satisfy Bloch theorem. Next, let us analyze the second diagram the wave function satisfies the periodic boundary condition. Note that both real and imaginary part of the wave function as well as it is first derivative is continuous at the boundary.

For example, this is the real part of the wave function at the boundary and this is the imaginary part of the wave function at the boundary. However, the probability density is not same at every lattice point. The probability density is maximum at the boundary and it decreases continuously as we move inside the solid. Thus, although the wave function satisfies periodic boundary condition, it does not satisfy Bloch theorem.

So, this one cannot be a valid Bloch function. In conclusion, for psi of x to satisfy Bloch theorem, we need to do a Fourier series expansion of psi of x using allowed k points which differ from each other by some reciprocal lattice vector. Any other choice, for example, adjacent values of allowed k points produce a wave function which satisfies periodic boundary condition but does not satisfy Bloch theorem.

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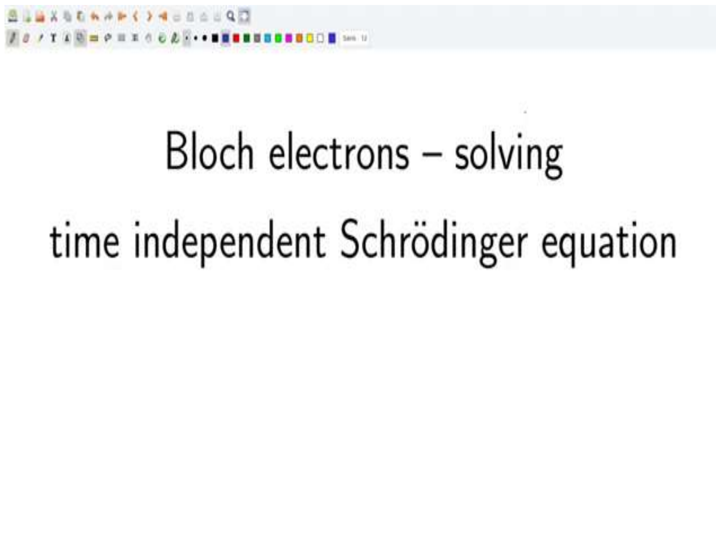

Now, that we have learnt, how to expand the potential U and the wave function, psi in a Fourier series? Let us learn how to solve time independent Schrodinger equation for Bloch electrons?

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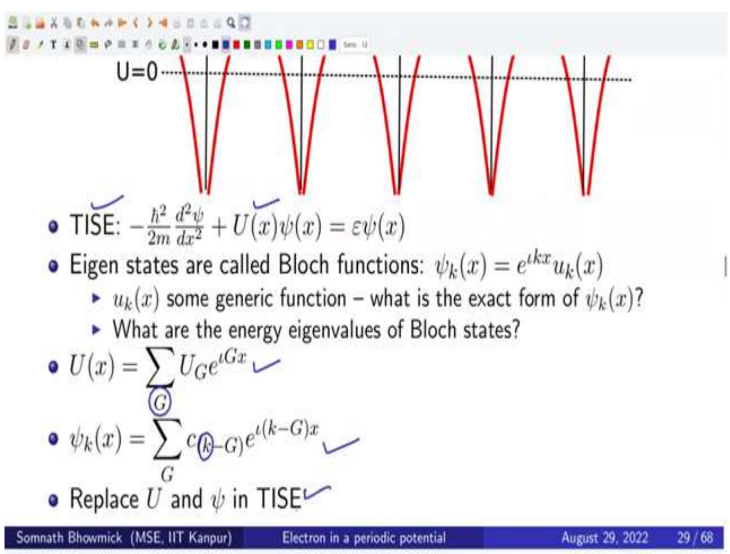

So, we are trying to solve time independent Schrodinger equation for a potential having the periodicity of the 1D lattice. This is the Fourier series of the potential and this is the Fourier series of the wave function. G is a reciprocal lattice point and k is an allowed k point given by the periodic boundary condition. Using python codes, we have verified that if we expand in this way, U of x has the periodicity of the lattice.

And psi of x satisfies periodic boundary condition as well as Bloch theorem. Let us substitute the Fourier series of U and psi in time independent, stronger equation.

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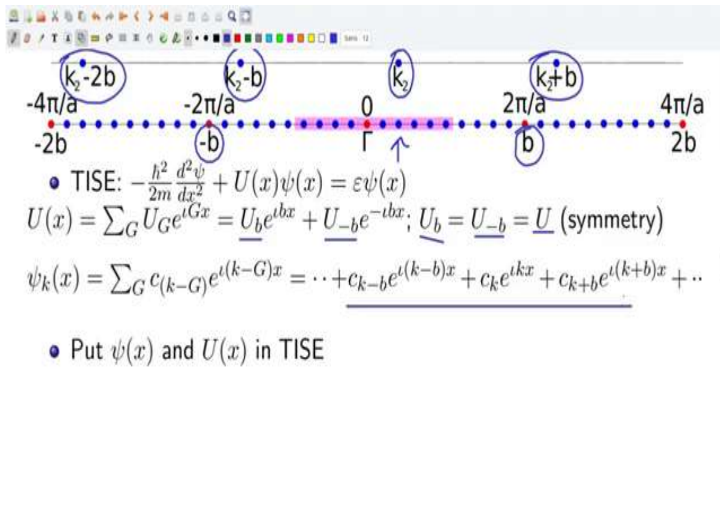

Let us take only two terms in the expansion of U, U of b and U of – b that means these two points b and – b. U 0 gives some constant potential in the direct lattice and we can set it to = 0 because of symmetry we can just take U of b and U of – b to be equal. In case of psi we take some allowed k point in the first Brillouin zone for example, say this point, in the expansion of psi of x terms like k – b.

That means, if we take this point then this term and then the terms like k – 2b and k+ 2b etcetera will enter. There are infinitely many terms and we show only a few here.

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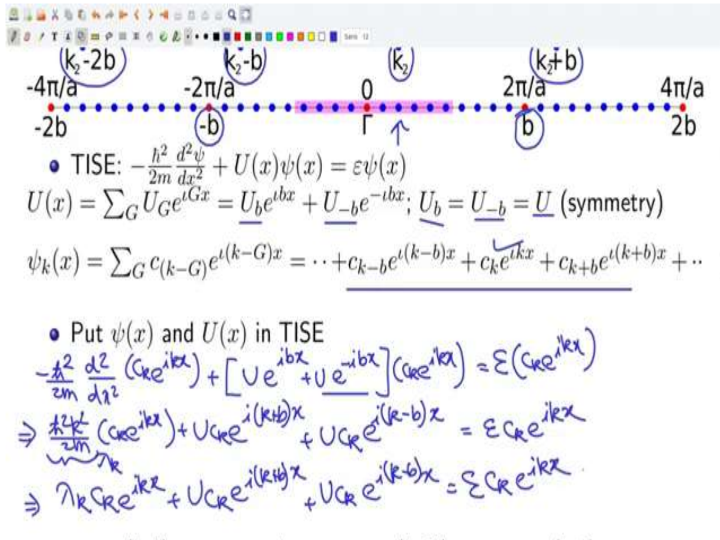

Now, let us put psi of x and u of x in time independent Schrodinger equation. We do it turn by term, starting with this term. So, – h cross square by 2m b 2 dx square and we put c k e power ikx plus we put the potential term U e power ibx + U e power – ibx times c k e power ikx = epsilon times c k e power ikx. Now, we have so if I take derivative twice of this term e power ikx we just get h cross square k square by 2m c k e power ikx + U c k e power i k + b x plus the second term U c k e power i k – b x = epsilon c k e power ikx.

And this term h + square k square by 2m we just call it lambda of k such that we can write the equation as lambda of k c k e power ikx + U c k e power i k + b x + U c k e power i k – b x = epsilon c k e power ikx.

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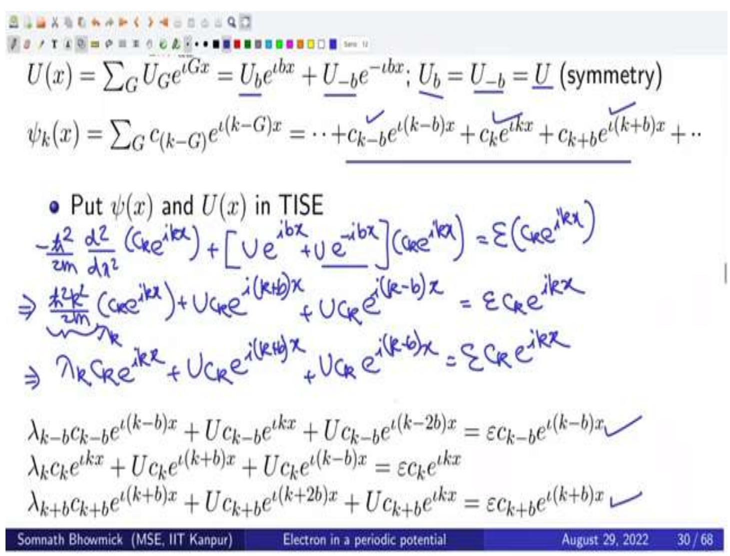

Similarly, for this term c k – b e power i k – b x we get this equation and for the last term c k+ b e power i k + b x we get this equation.

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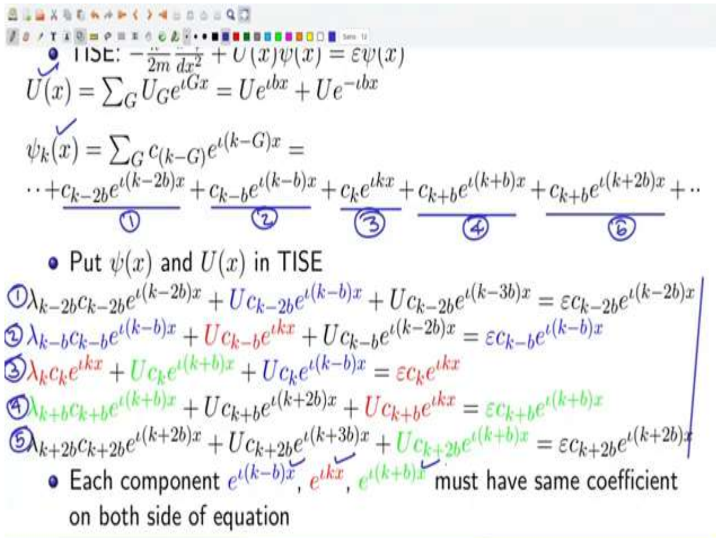

Thus, substituting Fourier series of U x and psi of x in time independent Schrodinger equation we get these equations. I have shown for five terms in Fourier series of psi of x. So, this is the first term and this is the corresponding equation this is the second term and this is the corresponding equation, third term the corresponding equation, fourth term and the corresponding equation, fifth term and the corresponding equation.

I have marked terms containing the components of e power i k – b x in blue and e power ikx in red and e power i k + b x in green. Why we are doing this? Because each component of the Fourier series must have same coefficient in both sides of the equation and we are going to separate them in the next slide.

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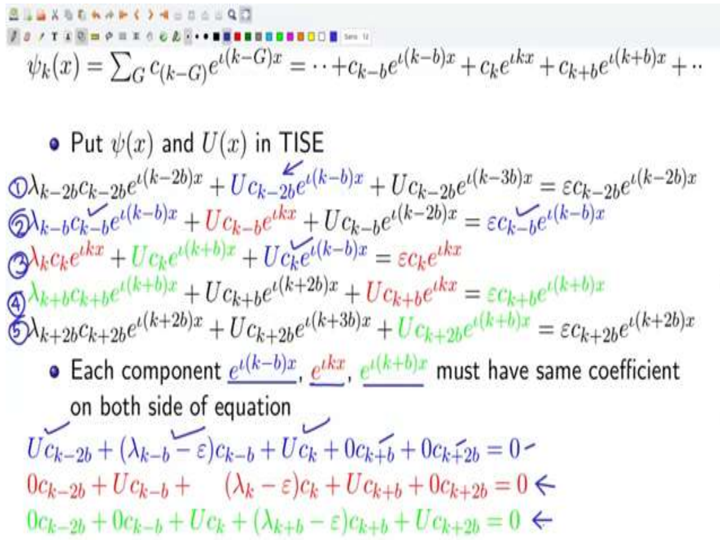

Thus, we have five equations, let us collect all the components of e power i k – b times x from these five equations. So, from equation one we have this term, U c k – 2b from equation two we have two terms this and this. And from equation three we have these terms U times c k note that e power i k – b x does not have components like c k+ b and c k+ 2b. Thus we write them as 0 times c k+ b and 0 times c k+ 2b.

Similarly, we can collect all the components of e power ikx and then we get this equation and we can collect all the components of e power i k + b times x and then we get this equation.

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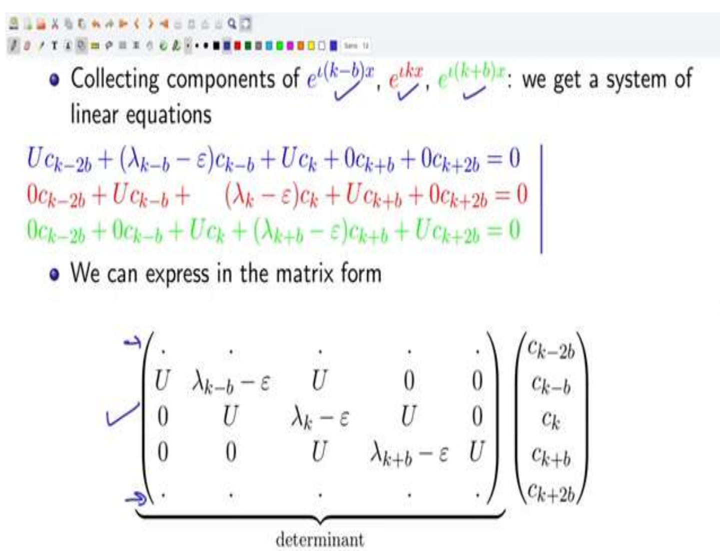

Collecting components of e power i k – b x e power ikx and e power i k + b x. We get a system of linear equations, as shown here. We can express the system of linear equations in the form of a matrix, as shown here. Note that there are some non-0 terms in the first row and in the last row of the matrix as well. I leave it as an exercise for you to complete the first and last row of the matrix.

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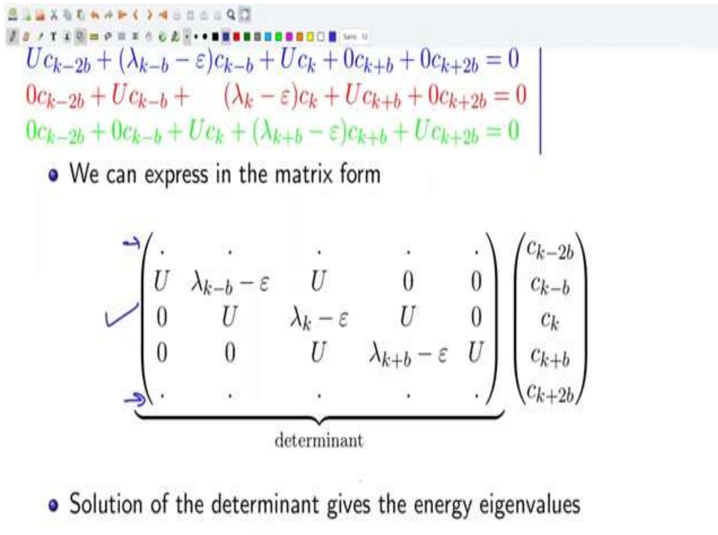

Now, the solution of the determinant gives the energy eigenvalues of the Bloch electrons.

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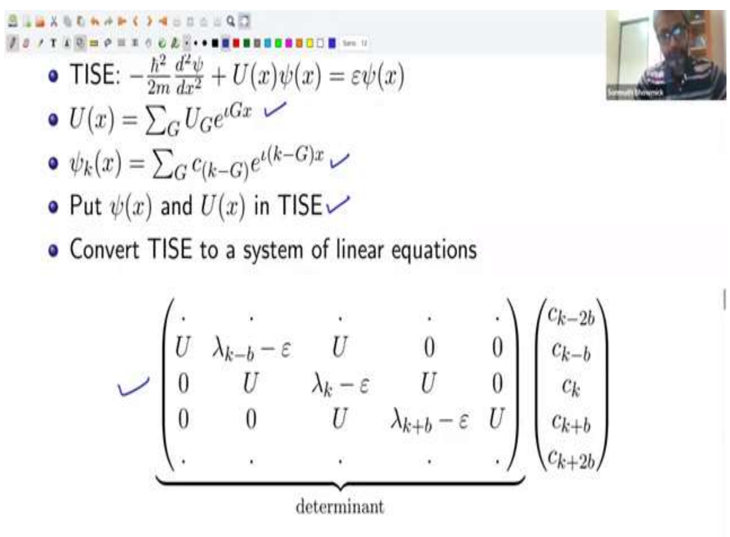

Let me quickly summarize the most important steps for solving time independent Schrodinger equation in case of Bloch electrons. First, we write the Fourier series expansion of U of x and psi of x in this form. Using python codes, we have verified that if we expand in this way U of x has the periodicity of the direct lattice and psi of x satisfies both periodic boundary condition and Bloch theorem.

Putting the Fourier series expansion of U of x and psi of x in time independent Schrodinger equation we convert time independent Schrodinger equation to a system of linear equations. Solution of the determinant gives the energy eigen values.