Electronic Properties of the Materials: Computational Approach
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Lecture: 23
Origin of Band Gaps Part 3

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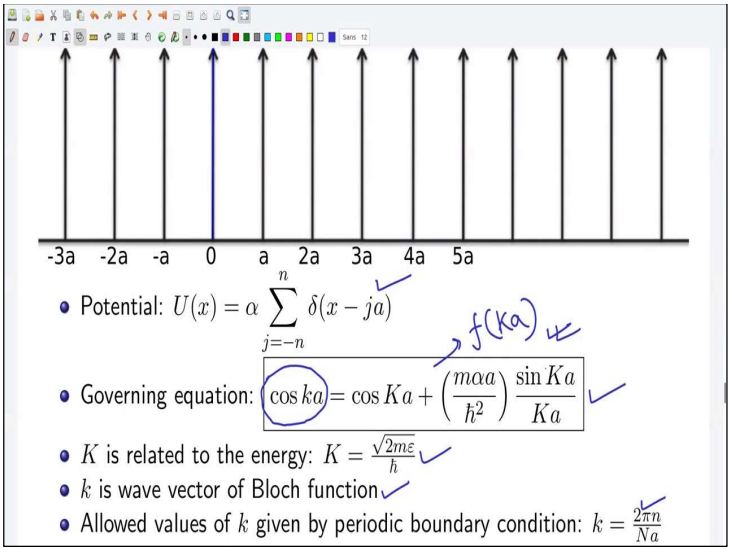

Hello friends in this lecture we continue our discussion on Kronig-Penny model using our Dirac comb and derive the allowed energy values in a 1D lattice. Lattice we have derived the governing equation in the previous lecture. In the left hand side of the governing equation we have cos small k times a and in the right hand side of the governing equation we have a function of capital Ka let me call this as f of is related to the energy and small k is the wave Vector of the block function.

Allow value of K is given by the periodic boundary condition using the governing equation we are going to find the energy eigenvalues of block electrons in 1D lattice where the potential is given by the Dirac comb. Next we take the right hand side of the governing equation and plot f of k as a function of k.

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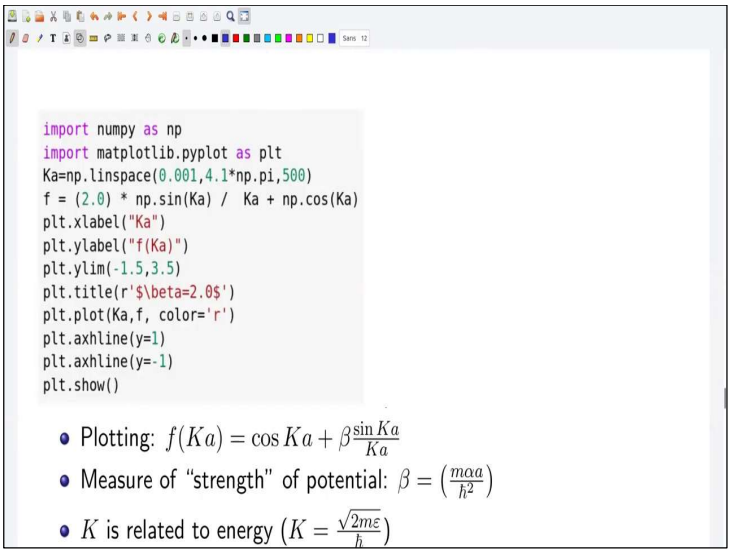

Using a python code let us plot the right hand side of the governing equation. Note that beta is the measure of the strength of the potential higher the value of beta stronger is the potential. We are going to plot f of Ka for different values of beta. The function to be plotted is defined here in the code. This is the code for plotting the right hand side of the governing equation defined in this line.

The value of capital K times a is varied from 0 to 4 pi first we run the code for beta is equals to 2 now let us run the code for another value of beta and let us take beta is equals to 4.

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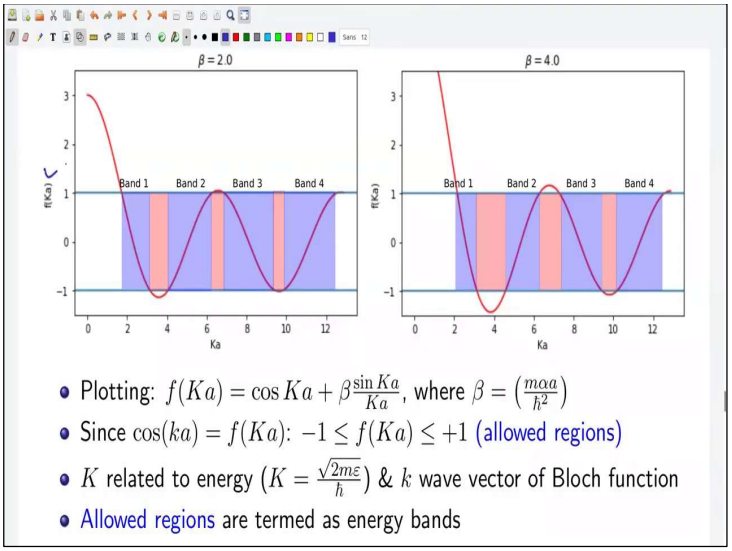

This is the plot of f of ka for beta equal to 2 and this is the plot for f of k for beta equal to 4. In the left-hand side of the governing equation, we have cos Ka note that f of Ka values shown by the red line in the plot has no restriction for example in case of beta equal to 2 the

maximum value of f of Ka is around 3. in case of beta equal to 4 it is even higher but cos K lies in a range of +1 and -1 thus the regions where f of Ka lies between -1 and +1 are the allowed regions. Allowed regions are shaded in blue in the figures.

Remember that capital K is related to the energy and small k is wave Vector of block function allowed regions are termed as energy bands and I have marked them as band 1 band 2 band 3 band 4 etc in the ascending order according to their energy.

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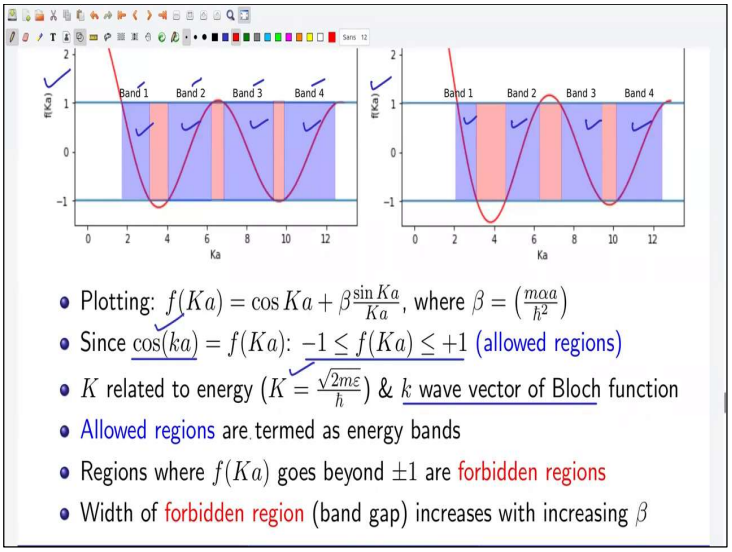

Regions where f of Ka goes beyond + 1 and -1 are forbidden regions and they are shaded in red in the figure. So, these are the forbidden regions because f of Ka is either more than one or less than one in these regions. Forbidden regions are related to the band gap and their width increases with the increasing value of beta for example in case of beta is equals to 2 this is the width of one of the forbidden regions.

And this is the width of the one of the forbidden regions for beta is equals to four note that the width is much higher when beta is equals to 4 thus a stronger potential leads to wider band gap as expected.

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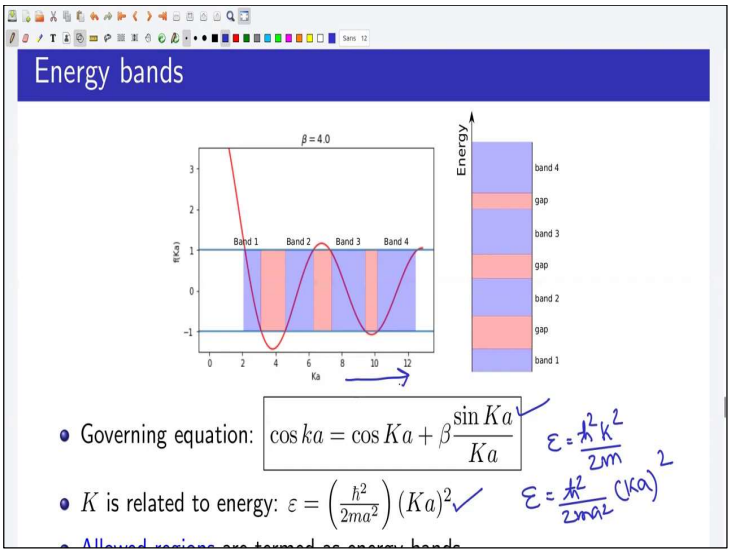

So, this is our governing equation which determines the allowed and forbidden regions. Capital K is related to energy e is equals to h cross Square capital K Square by 2m and multiply and dividing by A square we can rewrite A square h cross square by 2m a square times capital Ka whole Square thus as capital Ka increases the energy is increasing in this direction. If we plot the energy along the vertical axis then this is what we get.

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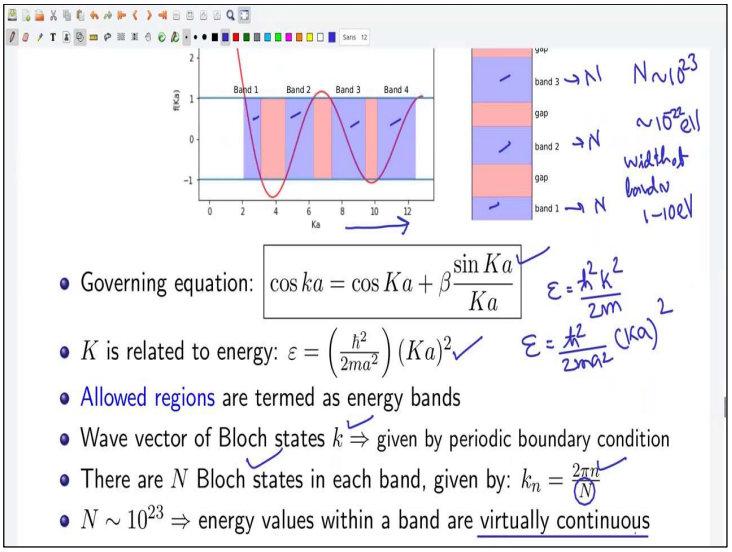

The allowed regions shaded in blue are termed as energy banks they are shown in ascending order that is band 2 has higher energy than Band 1 Band 3 has higher energy than band 2 Etc remember that small k are the wave Vector of the block states given by the periodic boundary condition. If there are capital N number of lattice points in the 1D lattice allow values are Kn is equals to 2 pi small n divided by capital N that is there are capital N allowed values of K this implies that there are N block states in each band.

So, that means Band 1 has N states band 2 has N states band 3 has N states and. So, on and if we apply Pauli's Exclusion Principle then we can put maximum 2N electrons in the first band we can put maximum 2N electrons in second band and so on width of each band generally varies from 1 to 10 EV in a solid capital N is 10 power 23. this implies that gap between energy levels within a band is very small and this is of the order of 10 power -22 electron volt. Thus energy values within a band are virtually continuous.

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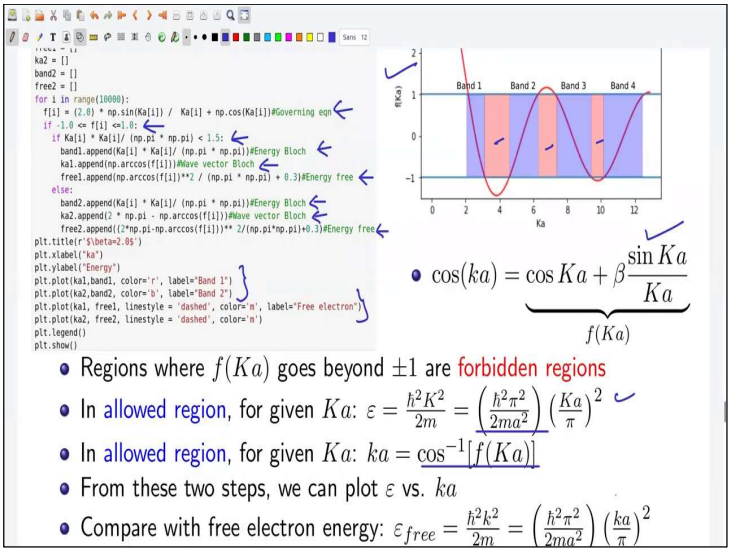

Now we are going to plot energy versus the wave vector small k this is the governing equation and we already have plotted f of Ka as a function of Ka regions where f of Ka goes beyond +1 and -1 are forbidden regions. For a given K we calculate f of Ka here in the code and determine whether it is in the allowed or forbidden region in this line. If f of Ka is in the allowed region we calculate the energy.

We write the energy in this form and set this term equal to 1. Such that energy is equals to Ka by pi whole square. In the code we find energy in this step. For a given K the wave Vector of the block function is given by cos inverse f of Ka if the energy lies in the first band we calculate the energy we calculate the wave vector at we calculate the corresponding free electron energy here in the code.

All the values are stored in different lists. Similarly if the energy value lies in the second band we calculate energy we calculate the wave vector and we calculate the corresponding free electron energy here in the code. Finally we plot energy versus the wave vector and compare

with the free electron energy. Note that free electron energy is obtained from the calculated value of the wave vector small k.

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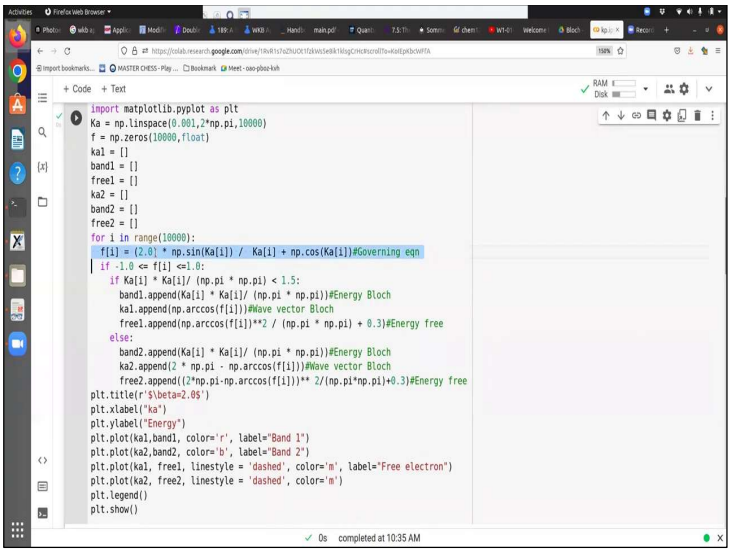

```
import matplotlib.pyplot as plt
Ka = np.linspace(0.001,2*np.pi,10000)
f = np.zeros(10000,float)
ka1 = []
band1 = []
free1 = []
ka2 = []
band2 = []
free2 = []
for i in range(10000):
  f[i] = (2.0) * np.sin(Ka[i]) /  Ka[i] + np.cos(Ka[i])#Governing eqn
  if -1.0 <= f[i] <=1.0:
    if Ka[i] * Ka[i]/ (np.pi * np.pi) < 1.5:
      band1.append(Ka[i] * Ka[i]/ (np.pi * np.pi))#Energy Bloch
      ka1.append(np.arccos(f[i]))#Wave vector Bloch
      free1.append(np.arccos(f[i])**2 / (np.pi * np.pi) + 0.3)#Energy free
    else:
      band2.append(Ka[i] * Ka[i]/ (np.pi * np.pi))#Energy Bloch
      ka2.append(2 * np.pi - np.arccos(f[i]))#Wave vector Bloch
      free2.append((2*np.pi-np.arccos(f[i]))** 2/(np.pi*np.pi)+0.3)#Energy free
plt.title(r'$\beta=2.0$')
plt.xlabel("ka")
plt.ylabel("Energy")
plt.plot(ka1,band1, color='r', label="Band 1")
plt.plot(ka2,band2, color='b', label="Band 2")
plt.plot(ka1, free1, linestyle = 'dashed', color='m', label="Free electron")
plt.plot(ka2, free2, linestyle = 'dashed', color='m')
plt.legend()
plt.show()
```

This is the code to plot energy versus K this is the governing equation to determine allow dot forbidden region. We determine the allow dot forbidden region using the; if loop here we calculate the energy and wave vector of the first band here we calculate the energy and wave vector of the second band. Let us run the code for beta is equals to 2.

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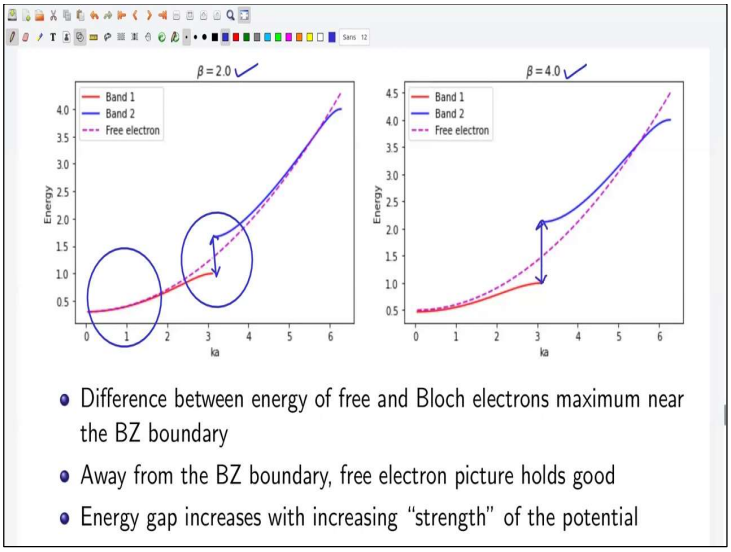

Now let us calculate for some other value of beta for example beta is equals to 4. The dash line denotes the energy of the free electrons solid red light shows the energy of the block electron in the first bank and solid blue line shows the energy of the electron in the second

band this is the plot of energy versus K for beta equal to 2 and this is the plot of energy versus K for beta equal to 4.

From the plots it is clear that the energy of the block and free electrons differ mainly in a region close to the Brillouin zone boundary. Away from the Brillouin zone boundary free electron picture holds good. We also notice that energy gap increases with increasing strength of the potential. For example, for beta equal to 2 this is the energy gap at for beta equal to 4 the energy gap is much larger than beta equal to 2.

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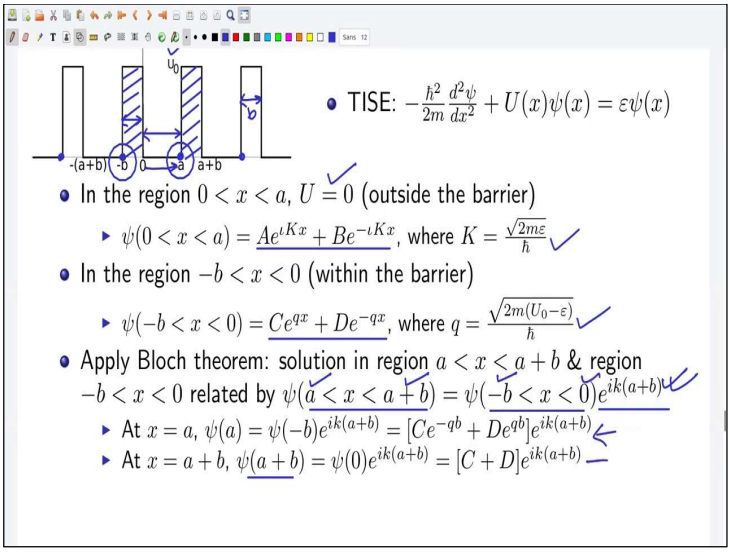

For mathematical convenience we have used the Dirac comb type potential. So, far however actual Kronig-Penny model uses periodic potential barriers of finite width not the Dirac delta type of potential. As shown here the barriers have a width of b and a is the lattice translation vector, height of the barrier is U naught. Consider the region between x equal to 0 and x equal to a this region is located outside the barrier that is U is equals to 0.

In that case the solution is a e power ikx + b e power - ikx where K is equals to square root of 2 me divided by h bar. Now consider the region between -b and 0. This is a region located inside the barrier in this case the solution is C e power qx + D e power - qx where q is equal to square root of 2m u naught - epsilon divided by h bar. So, far this looks exactly like what we did for the tunnelling problem.

Now because of the periodicity of the potential we can apply Bloch theorem. For example consider solution in the region between a and a + b that is this region this has to be related to

the solution between –b and 0 that is this region they are related because of the periodic potential and they are related by this phase factor e power i k e + b note that we can put the lattice points here, here and here thus the lattice point located at -b can be mapped to the lattice point located at +a via a lattice translation vector of a + b.

That is why the block function satisfies this equation. At x equal to a psi of a is real psi of –b by this equation and at x equal to a + b psi of a + b is related to psi of 0 by this equation.

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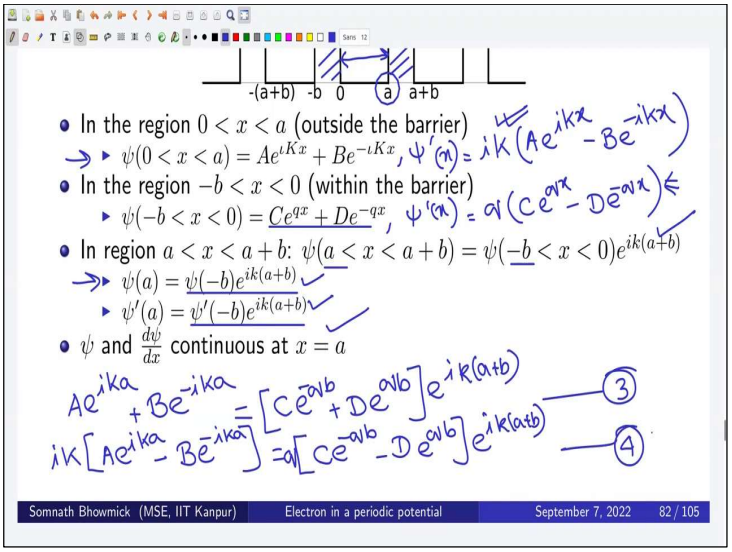

In the region between x equal to 0 and x equal to a the wave function is a e power i kx + b power - i kx that is the first derivative of the wave function is A e power i k x - B e power - i k x now in the region between -b and 0 the solution is C e power qx + D e power - qx and the first derivative is psi dashed is equals to C e power qx - D e power - qx both psi and D psi dX is continuous at x equal to 0.

Note that since we are dealing with a potential barrier of finite width there is no discontinuity of the first derivative thus putting x equal to 0 and equating the wave function we get a + b is equals to C + D. Now we put x equal to 0 and liquid d psi dx in that case we get i K A - B is equals to q times C – D. Now we match the wave function and its first derivative at x equal to a in the region x lying between 0 and a the wave function is A e power i k x + B e power - i k x and it is first derivative is i k A e power i k h - B e power - i k.

In the region x between -b and 0 the Y function is C e power qx + D e power - qx and it is first derivative is q C e power qx - D e power – qx. Now we already know that the wave

function in this region lying between a and a + b and lying between -b and 0 are related via Bloch theorem and satisfy this equation. Applying Bloch theorem the wave function and its first derivative fact x equal to a and x equal to -b are related by these two equations.

Now we have to equate the wave function at x equal to a. So, we put x equal to a in this equation and write the left hand side as A e power i Ka + B e power - i Ka and this part is equal to psi a given by this expression psi of - b times the phase factor e power i Ka + b from this equation psi of -b is C e power qb + q e power q times b and then we have the phase factor e power i k a + b.

Now we have to equate the first derivatives. So, left hand side we just put x is equals to a in this equation such that we get i k A e power i k a – B e to the power – i ka and in the right hand side we put this term. So, where psi dashed of -b we can get from here this is equal to q times C e power - qb - B e power qb times the phase Factory power i k a + b.

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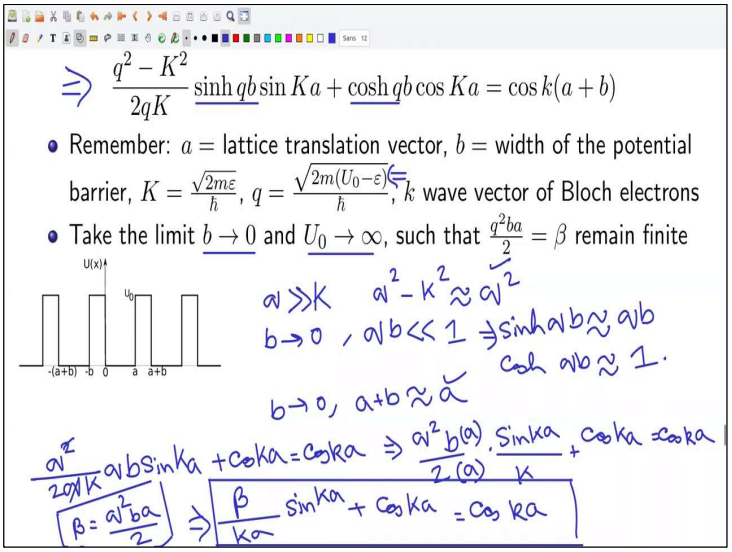

Now we have four equations and four unknowns A B C and D. Solution exists if determinant of the coefficients of A B C and D vanishes if you apply this condition then you get this equation. Note that in this equation a is the lattice translation vector B is the width of the potential capital K is related to the energy small q is related to the height of the potential as well as the energy and small k is the wave vector of block electrons.

Equation 5 that is this equation is qualitatively similar to the governing equation we derive for the Dirac comb. Let us prove that. Let us take the limit b going to 0 that is width of the

potential is vanishing and U naught tends to Infinity that is the height of the potential barrier becomes very high in the limit U naught going to infinity we see from this equation that q becomes much much larger than capital K such that we can write q Square - K Square is almost equal to q Square.

Now since b tends to 0 we have q times b is much less than less than equal to 1. And in this limit sine hyperbolic qb is approximately equal to qb and cos hyperbolic qb is approximately equal to 1. Also in the limit b tends to 0 a + b can be approximated to be equal to a now we substitute all these in equation 5 that is this equation. So, q Square - K square is approximately equal to q Square.

So, we put it and then we have divided by 2q K sine hyperbolic qb this is approximately equal to q times b then we have psi k + cos hyperbolic qb is approximately equal to 1 and then we have cos of k this is equal to cos of small k times a because a + b is approximately equal to a and then we just rearrange the terms q square b divided by 2 because 1 q gets cancelled and then we just multiply and divide by a times sine Ka divided by K and then we have + cos Ka this is equal to cos of small k times a.

And then we can rewrite this equation as beta where beta is equals to q square b a divided by 2 and then I have K times a beta is equals to q Square b a divided by 2. So, now we have sine of K + cos of Ka is equals to cos of small k times a. Note that this equation is exactly same as the equation we got for the Dirac comb.

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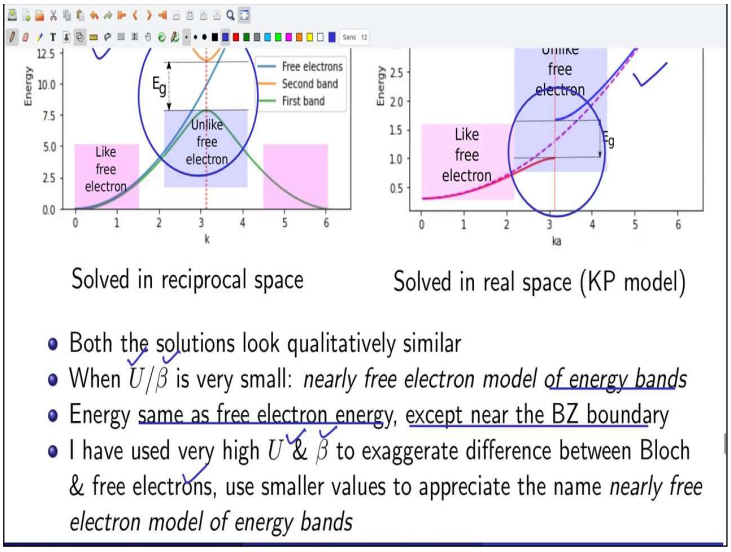

We have completed our discussion on how to solve time independent Schrodinger equation in a periodic potential. This has been a long discussion and let me summarize the most important steps. The first step is to write some generic form of the oil function in a periodic potential this is given by the Bloch theorem let me quote block himself I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation.

Then we solved in two different roots. First one is a solution in reciprocal space we do a Fourier series expansion of the potential and of the wave function. Using the Fourier components we can express the time independent Schrodinger equation in the form for system of linear equations energy eigenvalues are obtained from the determinant of this Matrix. In the second method we solve the time independent Schrodinger equation in real space using Kronig-Penny model.

It is assumed that a potential barrier exists at every lattice point we derive a governing equation by matching the wave function and its first derivative at every lattice point energy eigenvalues are obtained from the governing equation both the methods yield qualitatively similar results. For example this is how the energy versus K diagram looks like when solved in reciprocal space and this is how it looks like when solved in real space using Kronig-Penny model.

When U or beta is very small we call it a nearly free electron model of energy bands. The name originates from the fact that energy of the Bloch electrons is same as free electron energy except near the Brillouin zone boundary for example in this case the energy of block and free electrons differ mainly in this region and in this case the energy of the free electron and the block electrons differ mainly in this region which is close to the Brillouin zone boundary.

Otherwise the energy of the block and free electron energies are identical. Note that I have used very high U and beta to exaggerate difference between block and free electrons. You are advised to use smaller values to appreciate the name nearly free electron model of energy bands.