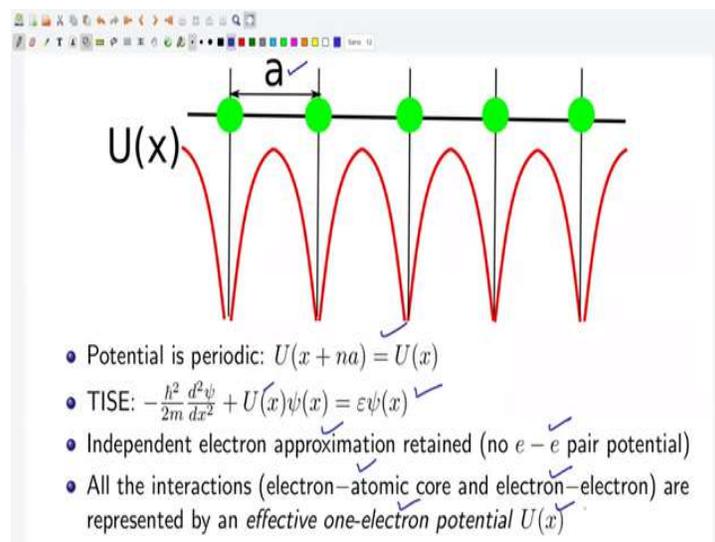


Electronic Properties of the Materials: Computational Approach
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Lecture – 18
Bloch Electrons in 1D Solid: Part I

Hello friends, we already have discussed about Bloch theorem which gives us some generic form for eigen function of an electron in a periodic potential. In this lecture we are going to study several features of Bloch electrons in detail, assuming a 1-dimensional solid.

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- Potential is periodic: $U(x + na) = U(x)$
- TISE: $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi(x) = \epsilon\psi(x)$
- Independent electron approximation retained (no $e - e$ pair potential)
- All the interactions (electron-atomic core and electron-electron) are represented by an effective one-electron potential $U(x)$

The lattice points are arranged in a linear chain. Spacing between adjacent lattice points is a . The potential is periodic. We want to solve time independent Schrodinger equation for a periodic potential U of x . Let us try to understand the nature of the periodic potential. Electrons in a solid is in principle a many body problem. We have one-electron potential, describing the interaction of electrons with massive atomic cores.

In addition to that we also have pair potentials describing electron-electron interaction. We stick to independent electron approximation such that we do not consider electron-electron pair potential. All the interactions including electron atomic core and electron-electron are represented by an effective one-electron potential U of x .

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- Potential is periodic: $U(x + na) = U(x)$
- TISE: $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi(x) = \epsilon\psi(x)$
- Independent electron approximation retained (no $e - e$ pair potential)
- All the interactions (electron-atomic core and electron-electron) are represented by an effective one-electron potential $U(x)$
- How to design effective one-electron potential is outside the scope of our discussion

Designing such effective one-electron potential is a complicated problem and outside the scope of our discussion.

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- 1D solid of length $L = Na$, a : spacing of adjacent lattice points
- Spacing between two reciprocal lattice points (G points): $\frac{2\pi}{a}$
- Inside the box $\psi(x)$ must satisfy Bloch theorem

Handwritten equations:

$$\psi_R(x) = e^{ikx} u_k(x) \rightarrow u_k(x+X) = u_k(x) \quad X - \text{Lattice translation vector}$$

$$\psi_R(x+X) = e^{ik(x+X)} u_k(x+X) = e^{ikX} e^{ikx} u_k(x) = e^{ikX} \psi_R(x) = \psi_R(x+X)$$

Examples:

- ▶ Example: $\psi(x+a) = \exp(ika)\psi(x) \Rightarrow |\psi(x+a)|^2 = |\psi(x)|^2$
- ▶ Example: $\psi(x+2a) = \exp(i2ka)\psi(x) \Rightarrow |\psi(x+2a)|^2 = |\psi(x)|^2$
- ▶ Example: $\psi(x+Na) = \exp(iNka)\psi(x) \Rightarrow |\psi(x+Na)|^2 = |\psi(x)|^2$

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Let us work with a 1D solid of length L equal to N times a , where N is the number of lattice points and a , is the spacing between the adjacent lattice points. In this diagram N equal to 10 such that L equal to 10 times a . Note that the last point shown by the open circle is a periodic image of the first point. Since we have a lattice, we are dealing with electrons in a periodic potential and eigen states of the time independent Schrodinger equation must satisfy Bloch theorem.

Thus, the eigen states are $\psi_k(x) = e^{ikx} u_k(x) \Rightarrow u_k(x + X) = u_k(x)$ this function has the periodicity of the direct lattice. That means $U_k(x + X) = U_k(x)$, where X

is a lattice translation vector. A lattice translation vector is a vector which takes a lattice point to some other lattice point, for example, x equal to a , is a lattice translation vector because this will take every lattice point to some other lattice point and nothing is going to change.

Similarly, x is equals to $2a$, is another lattice translation vector because it will again take one lattice point to another lattice point and nothing is going to change. Now, we can write

$$\psi_k(x + X) = e^{ik(x+X)} u_k(x + X)$$

Now, we know that this function small u , this has the periodicity of the direct lattice so that means this term is equal to $u_k(x)$. So that gives us $e^{ikX} e^{ikx} u_k(x)$. But this is equal to ψ_k of x so, this term is ψ_k of x . Thus, we can write, this is equal to

$$e^{ikX} \psi_k(x) = \psi_k(x + X)$$

Now, let us take some example, if we take the lattice translation vector to be a then eigen function must satisfy $\psi(x + a)$ equal to e^{ika} times $\psi(x)$, the phase factor e^{ika} cancels out when we calculate mod square of the complex function and we get $|\psi(x + a)|^2$ equal to $|\psi(x)|^2$. Similarly, if we take the lattice translation vector to be $2a$, the eigen function must satisfy $\psi(x + 2a)$ equal to e^{i2ka} times $\psi(x)$.

The phase factor e^{i2ka} cancels out as we calculate the mod square of the complex wave function and we get $|\psi(x + 2a)|^2$ equal to $|\psi(x)|^2$. Finally, if we take the lattice transition vector to be capital N times a , the eigen function must satisfy $\psi(x + Na)$ equal to e^{iNka} times $\psi(x)$ and $|\psi(x + Na)|^2$ equal to $|\psi(x)|^2$. Thus, the complex wave function does not have the periodicity of the lattice.

As it differs by a phase factor from point to point. However, probability density must have the periodicity of the lattice, as shown here.

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• 1D solid of length $L = Na$, a : spacing of adjacent lattice points
 • Spacing between adjacent reciprocal lattice points (G points): $\frac{2\pi}{a}$
 • At the boundary of the box:

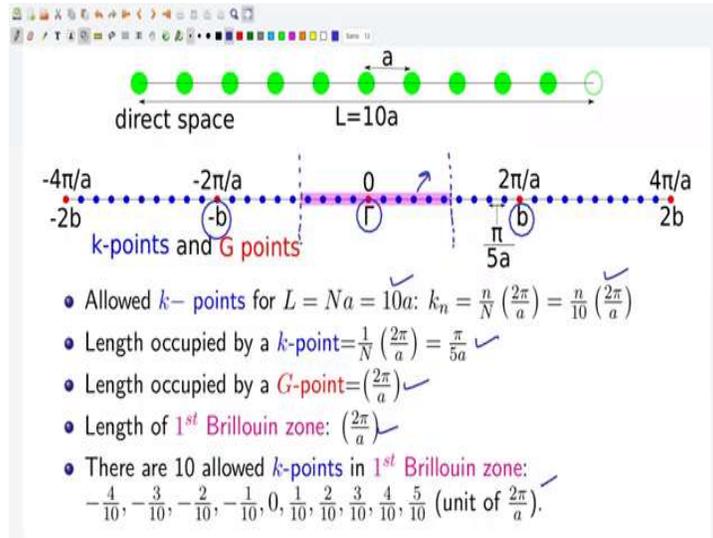
- ▶ $\psi(x)$ must satisfy periodic boundary condition: $\psi(x + Na) = \psi(x)$
- ▶ We know that $\psi(x + Na)$ also follows Bloch theorem:
 $\psi(x + Na) = \exp(iNka)\psi(x)$
- ▶ For $\psi(x + Na)$ to satisfy P.B.C and Bloch theorem simultaneously, the phase factor must be = 1
- ▶ Thus, $\exp(ikNa) = \exp(i2\pi n) \Rightarrow k_n = \frac{n}{N} \left(\frac{2\pi}{a} \right) = \frac{n}{N} b$

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Let us now, focus on the k space since, spacing between two adjacent points in direct space is equal to a , spacing between two adjacent reciprocal lattice points is equal to $2\pi/a$. The reciprocal lattice points or G-points are shown by red dots in this figure. The origin of the reciprocal lattice has a special length it is called the gamma point. At the boundary of the box $\psi(x)$ must satisfy periodic boundary condition that is $\psi(x + Na)$, should be equal to $\psi(x)$.

Since, we have a periodic potential $\psi(x + Na)$, also has to satisfy Bloch theorem, as shown here. For $\psi(x + Na)$ to satisfy periodic boundary condition and Bloch theorem simultaneously, the phase factor shown here must be equal to 1 and this gives us the allowed values of k . Allowed values of k are small n divided by capital N times $2\pi/a$, where capital N is the number of lattice points and small n is some integer. Allowed k values are shown by blue dots in this diagram.

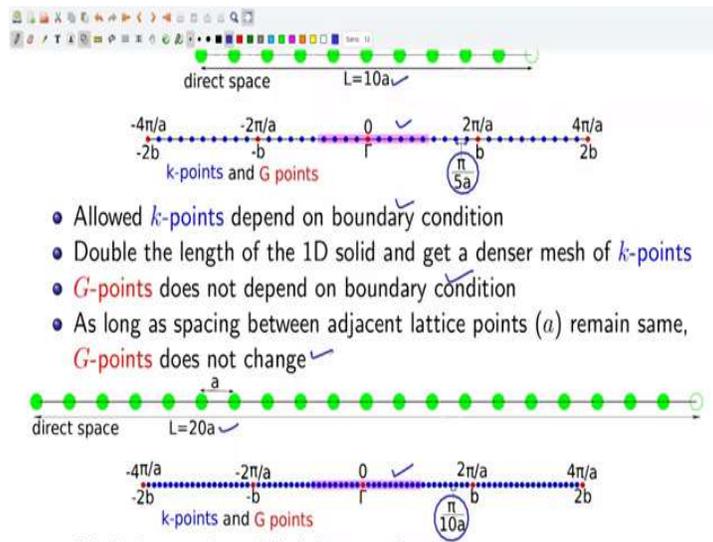
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Thus, for a solid of length equal to $10a$, allowed k -points are small n divided by 10 times 2π by a . Distance between two adjacent allowed k -points which is same as the length occupied by a k point equal to π by $5a$. Distance between two adjacent G -points which is same as the length occupied by a G point equal to 2π by a . Length of the first Brillouin zone is also 2π by a . To get the first Brillouin zone, we have to draw perpendicular bisector of a line joining the gamma point and the b point, and the line will be approximately here.

Similarly, we have to draw another perpendicular bisector of the line joining the gamma point and the minus b point and this is where it will lie approximately. The first Brillouin zone is shown by the magenta shaded region in the figure, in this particular case, there are 10 allowed k -points in the first Brillouin zone.

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Note that both k-points and G-points belong to the reciprocal space, let us clearly understand their difference. Allowed k-points depend on the boundary condition if we double the length of the solid we get a denser mesh of k points. For example, if we increase the length from 10a to 20a, as shown here distance between two adjacent k-points decreases by a factor of 2. For example, in case of L equal to 10a distance between two adjacent k-points is pi divided by 5a.

However, if L equal to 20a then distance between two adjacent k-points is pi divided by 10a, for L equal to 10a, there are 10 allowed k-points in the first Brillouin zone. On the other hand, for L equal to 20a, there are 20 allowed k-points in the first Brillouin zone. For very large value of N, k point mesh becomes so dense that we can consider it to be almost continuous. However, G-points always remain discrete because G-points does not depend on the boundary condition.

As long as spacing between adjacent points in direct lattice remains same, G-points does not change.

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k-points and G points

- Allowed k -points depend on boundary condition
- Double the length of the 1D solid and get a denser mesh of k -points
- G -points does not depend on boundary condition
- As long as spacing between adjacent lattice points (a) remain same, G -points does not change

direct space $L=20a$

k -points and G points

- Bloch theorem is satisfied for every k -point
 - Eigen functions in periodic potential: $\psi_{k_n}(x) = e^{ik_n x} u_{k_n}(x)$; where $k_n = \frac{n}{N} \left(\frac{2\pi}{a} \right)$

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Note that Bloch theorem is satisfied for every k-points and eigen function in a periodic potential can be written in this form for every k-point.

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Free electron vs. Bloch electron (1D)		
	Free electron	Bloch electron
TISE	$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = \epsilon\psi(x)$	$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi(x) = \epsilon\psi(x)$
Eigen function	$\psi_k(x) = \frac{1}{\sqrt{L}} \exp(ikx)$	$\psi_k(x) = \exp(ikx)u_k(x)$
$\hat{p} \equiv -i\hbar \frac{d}{dx}$	$\psi_k(x)$ eigenfn ✓	$\psi_k(x) \neq$ eigenfn ✓
$\hbar k$	Momentum ✓	Crystal momentum ✓
Length scale	Macroscopic (L)	Macroscopic (L) and atomic (a); $L = Na$
Lattice	none ✓	Real lattice a Reciprocal lattice $b = \frac{2\pi}{a}$
P.B.C	$\psi(x) = \psi(x+L)$	$\psi(x) = \psi(x+Na)$
k -points (P.B.C)	$k_n = \frac{2n\pi}{L}$, $n = \text{integer}$ $\Delta k = \frac{2\pi}{L}$	$k_n = \frac{2n\pi}{Na} = \frac{n}{N} \left(\frac{2\pi}{a}\right) = \frac{n}{N} b$ $\Delta k = \frac{2\pi}{Na} = \frac{2\pi}{L}$

Before proceeding further, let us quickly review the main differences between the Bloch electrons and free electrons. In case of Bloch electrons, we have an effective one-electron periodic potential U . This is a one-electron potential because we continue to ignore explicit electron-electron repulsion term that is these electrons are still independent electrons but these are not free electrons anymore. U equal to 0 is a special case known as the free electrons.

In case of free electrons, eigen functions are plane waves. In case of Bloch electrons, eigen functions are plane wave times a function having the periodicity of the direct lattice, ψ of k is eigen function of the momentum operator and $\hbar k$ is the momentum in case of free electrons. However, ψ of k is not eigen function of the momentum operator and $\hbar k$ is called the crystal momentum in case of Bloch electrons.

In case of free electrons, we have only one length scale L , the length of the box. L can be very large and we can take it as a macroscopic length scale. However, in case of Bloch electrons, in addition to L we also have to consider inter atomic distance a which is of the order of 1 angstrom and this is an atomic length scale. In free electrons, we completely ignore the underlying lattice.

However, in case of Bloch electrons, we deal with real as well as reciprocal lattice. Periodic boundary condition is similar in both the cases, in case of Bloch electrons this L is replaced with N times a . Because of periodic boundary condition k points are discrete and allowed k -points are similar in both the cases. However, again in case of Bloch electrons, L is replaced with N types a .

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Eigen function	$\psi_k(x) = \frac{1}{\sqrt{L}} \exp(i k x)$	$\psi_k(x) = \exp(i k x) u_k(x)$
$\hat{p} \equiv -i\hbar \frac{d}{dx}$	$\psi_k(x)$ eigenfn ✓	$\psi_k(x) \neq$ eigenfn ✓
$\hbar k$	Momentum ✓	Crystal momentum ✓
Length scale	Macroscopic (L)	Macroscopic (L) and atomic (a); $L = Na$
Lattice	none ✓	Real lattice a Reciprocal lattice $b = \frac{2\pi}{a}$
P.B.C	$\psi(x) = \psi(x+L)$	$\psi(x) = \psi(x+Na)$
k -points (P.B.C)	$k_n = \frac{2n\pi}{L}, n = \text{integer}$ $\Delta k = \frac{2\pi}{L}$	$k_n = \frac{2n\pi}{Na} = \frac{n}{N} \left(\frac{2\pi}{a}\right) = \frac{n}{N} b$ $\Delta k = \frac{2\pi}{Na} = \frac{2\pi}{L}$
G -points	none ✓	$G_n = n \left(\frac{2\pi}{a}\right) = nb$

Since we ignore the lattice, we do not have G-points in case of free electrons.

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- TISE: $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + U(x)\psi(x) = \epsilon\psi(x)$
- Eigen states are called Bloch functions: $\psi_k(x) = e^{ikx} u_k(x)$
- Allowed values of k are given by periodic boundary condition ✓
- What we do not know so far? ✓
 - ▶ $u_k(x)$ some generic function – what is the exact form of $\psi_k(x)$?
 - ▶ What are the energy eigenvalues of Bloch states?

So, we want to solve the time independent Schrodinger equation for a 1D solid where, U of x is an effective one-electron potential having the periodicity of the direct lattice. The eigen states are given by the Bloch theorem having the form of a plane wave times, some function U of x which has the periodicity of the Bravais lattice. When we consider a solid of finite length L applying periodic boundary condition, we can get the allowed values of k .

Let us see what we do not know so far. U of x is some generic function having the periodicity of the direct lattice. So, what is the exact form of eigen function ψ of x ? We do not know. We

also do not know what are the energy eigenvalues of the Bloch states? Let us try to find these answers.

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Fourier transform of $U(x)$

$-4\pi/a$ $-2\pi/a$ 0 $2\pi/a$ $4\pi/a$
 $-2b$ $-b$ b $2b$

- We can write: $U(x) = \sum_G U_G e^{iGx}$, where $G = nb = n \left(\frac{2\pi}{a}\right)$ in 1D
- Why do we expand in terms of G , but not in terms of k ?
- Because U must have periodicity of lattice: $U(x+a) = U(x)$
- Let us compare \sum_k vs. \sum_G

Using plane waves of wave vector G , we can write the function U of x as sum over G , U of G times e power iGx , where G is a reciprocal lattice point. That is G equal to n times 2π by a , in 1D. This is related to Fourier series or Fourier transform which we are not going to discuss in detail. Rather, I am going to show that if U is expressed in this form then you is guaranteed to have periodicity of the direct lattice.

Before proceeding further, let me discuss an important issue. We have G -points as well as, k points. Why do we expand U in terms of G but not in terms of k ? Note that you must have the periodicity of the direct lattice. That is U of x plus a , should be equal to U of x . Let me prove that if we expand in terms of k , we do not get some U which has the periodicity of the direct lattice.

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• We can write: $U(x) = \sum_G U_G e^{iGx}$, where $G = nb = n \left(\frac{2\pi}{a}\right)$ in 1D
 • Why do we expand in terms of G , but not in terms of k ?
 • Because U must have periodicity of lattice: $U(x+a) = U(x) e^{ika} \neq 1$
 • Let us compare \sum_k vs. \sum_G
 $U(x) = \sum_k U_k e^{ikx} \Rightarrow U(x+a) = \sum_k U_k e^{ik(x+a)} = \sum_k U_k e^{ikx} e^{ika} \neq 1$
 $U(x) = \sum_G U_G e^{iGx} \Rightarrow U(x+a) = \sum_G U_G e^{iG(x+a)} = \sum_G U_G e^{iGx} e^{iGa}$
 $U(x+a) = U(x) = \sum_G U_G e^{iGx} e^{iGa} = 1$
 $e^{iGa} = 1$
 $G = \frac{2\pi n}{a}$
 $Ga = 2\pi n$
 integer

• Thus, for U to have periodicity of lattice, $U(x) = \sum_G U_G e^{iGx}$

If we write U , using k -points then

$$U(x) = \sum_k U(k) e^{ikx} \Rightarrow U(x+a) = \sum_k U_k e^{ik(x+a)} = \sum_k U(k) e^{ikx} e^{ika}$$

Note that this part is U of x . Thus, for U of x plus a , to be equal to U of x , $e^{ika} = 1$. Now, let us see whether we get this or not? We know that $k = \frac{2\pi n}{Na}$, thus, $ka = \frac{2\pi n}{N}$. In that case, we see that $e^{ika} \neq 1$. In that case, we cannot say that U x plus a equal to U x . Thus, if we expand U using the k points, the potential does not have the periodicity of the direct lattice. Now, on the other hand if we write

$$U(x) = \sum_G U_G e^{iGx} \Rightarrow U(x+a) = \sum_G U_G e^{iG(x+a)} = \sum_G U_G e^{iGx} e^{iGa}$$

Thus, if e power $e^{iGa} = 1$ then we can say that $U(x+a) = U(x)$, let us check that. So, we know that G equal to $2\pi n$ divided by a that means $Ga = 2\pi n$, where n is an integer. Thus, we see that indeed $e^{iGa} = 1$, and in that case, we know that U of x plus a equal to U of x . Thus, for U to have the periodicity of the direct lattice, we must expand it in terms of G not in terms of k .

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Fourier transform of $U(x)$

- $U(x) = \sum_G U_G e^{iGx}$, where $G = nb = n \left(\frac{2\pi}{a}\right)$ in 1D
- For every G , there is a $-G$
- Thus, $U(x) = \sum_{G>0} U_G [e^{iGx} + e^{-iGx}] = 2 \sum_{G>0} U_G \cos(Gx)$
- U_0 not important as it provides a constant potential in direct lattice
- We can take $U_0 = 0$ without any loss of generality
- U_G is real (can be proved using symmetry argument)
- How many terms needs to be taken for the sum to converge?

Thus, a periodic potential U of x can be expressed in this form, where G is a reciprocal lattice point. Note that for every G there is a minus G for example, for b we have minus b for $2b$, we have minus $2b$ and so. Thus, we can write U of x is equals to sum over G greater than 0, $U_G e^{iGx} + e^{-iGx}$, where these 2 G 's are always positive. And then we can write it in the form of 2 times sum over G greater than 0 $U_G \cos$ of Gx . Because $e^{i\theta} + e^{-i\theta} = 2 \cos \theta$.

Note that we have used G greater than 0, so, how about this point where G equal to 0. We ignore the term U_0 because it provides a constant potential in the direct lattice. Making U_0 equal to 0 does not make any qualitative difference in the periodic potential. Thus, we can make U_0 equal to 0 without any loss of generality.

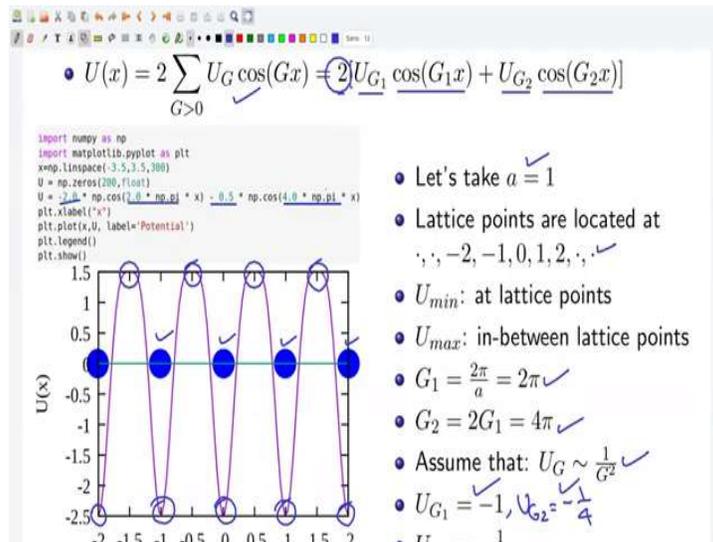
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- $U(x) = \sum_G U_G e^{iGx}$, where $G = nb = n \left(\frac{2\pi}{a}\right)$ in 1D
- For every G , there is a $-G$
- Thus, $U(x) = \sum_{G>0} U_G [e^{iGx} + e^{-iGx}] = 2 \sum_{G>0} U_G \cos(Gx)$
- U_0 not important as it provides a constant potential in direct lattice
- We can take $U_0 = 0$ without any loss of generality
- U_G is real (can be proved using symmetry argument)
- How many terms needs to be taken for the sum to converge?
- Fortunately, not too many as U_G decays rapidly with increasing G
- For Coulomb potential, $U_G \sim \frac{1}{G^2}$ (in 3D)

Note that U of G is real this can be proved using symmetry argument but I shall skip the proof. There are many G points, how many do we need for the sum to converge? Fortunately, not too many because as G increases, U decreases rapidly. For example, in case of coulomb potential, U of G varies as 1 by G square, Thus, contribution of U of G decreases quadratically with increasing G .

For very large value of G , U of G will be so small that it will hardly contribute to the periodic potential U of x .

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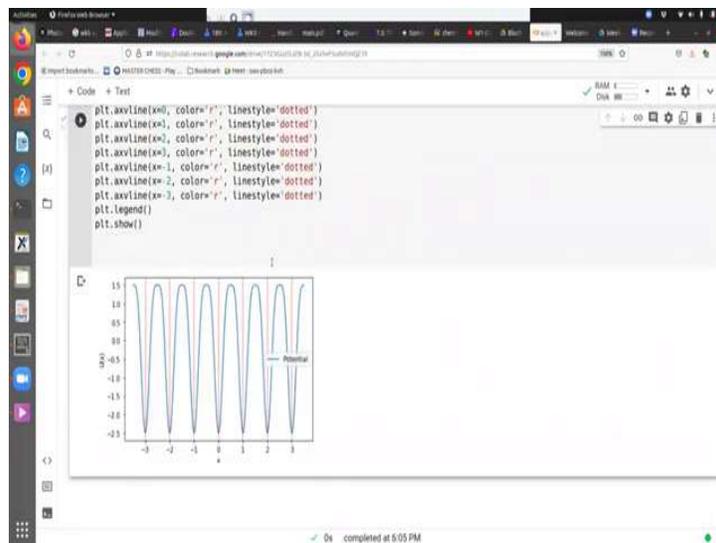
Using a simple python code, let me show that we get a periodic potential by writing U of x in this form. For simplicity, we keep only two terms in the sum G_1 and G_2 , such that U of x equal to 2 times $U_{G_1} \cos G_1$ of x plus $U_{G_2} \cos G_2$ of x . Let us take a equal to 1 , such that the lattice points are located at minus 2 , minus 1 , 0 , 1 , 2 etcetera as shown by blue circles in this diagram. Since the atomic cores are positively charged, negatively charged electrons will see some highly attractive potential near the cores.

As a result, we expect the potential energy to be minimum at the lattice points, as shown here. The attraction decreases as the electron moves away from the lattice point. Thus, we expect the potential to be maximum in the middle of two lattice points, as shown here. Since a equal to 1 , G_1 equal to 2π and G_2 equal to 4π so, this is where we define G_1 equal to 2π and G_2 equal to 4π in the code. We assume that U_G goes as 1 by G square, such that U_{G_1} equal to -1 and U_{G_2} equal to $-1/4$.

After multiplying U G 1 and U G 2 with the factor of 2 we put minus 2 and minus 0.5 in the code, while defining the potential in the code.

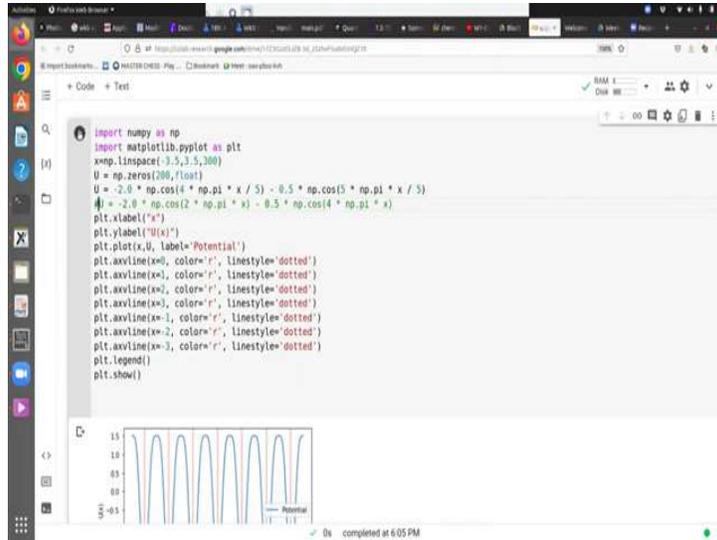
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```
import numpy as np
import matplotlib.pyplot as plt
x=np.linspace(-3.5,3.5,100)
U = np.zeros(100,float)
#U = -2.0 * np.cos(4 * np.pi * x / 5) - 0.5 * np.cos(5 * np.pi * x / 5)
U = -2.0 * np.cos(2 * np.pi * x) - 0.5 * np.cos(4 * np.pi * x)
plt.xlabel("x")
plt.ylabel("U(x)")
plt.plot(x,U, label='Potential')
plt.axvline(x=0, color='r', linestyle='dotted')
plt.axvline(x=1, color='r', linestyle='dotted')
plt.axvline(x=2, color='r', linestyle='dotted')
plt.axvline(x=-1, color='r', linestyle='dotted')
plt.axvline(x=-2, color='r', linestyle='dotted')
plt.axvline(x=3, color='r', linestyle='dotted')
plt.legend()
plt.show()
```



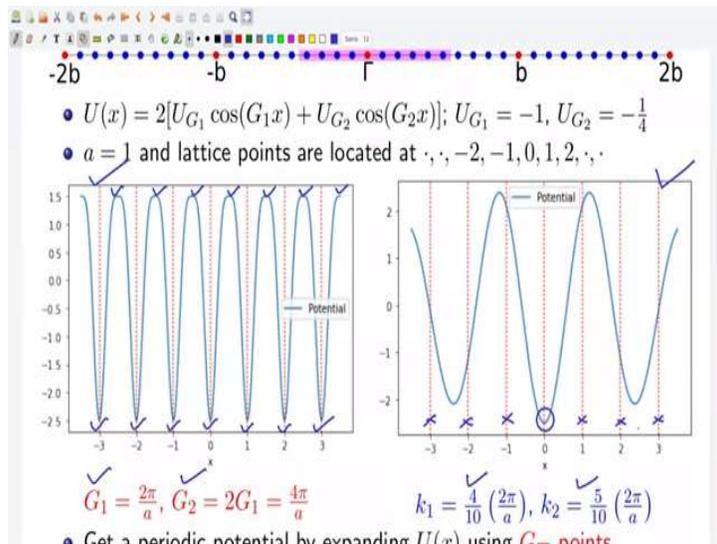
Let us run the code, the blue line shows the periodic potential and vertical red dashed lines show the location of the lattice points.

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Let us take some other value of wave vector for example, 4π by 5 and 5π by 5 and then we generate the plot of U of x again.

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The first figure from the left shows the potential U x when it is expanded in terms of $2 G$ points. Red dashed lines show the location of the lattice points. As expected, the potential has the periodicity of the lattice, potential is minimum at every lattice point and it is maximum in the middle of two lattice points. The second diagram from the left that is this one, shows the potential U x when it is expanded in terms of 2 allowed k points.

Clearly, the value of the potential is not equal at every lattice point. For example, at this lattice point, the value of the potential is this and this is not equal at any other lattice point. Thus, if we expand U of x in terms of allowed k values, we do not get a potential having the periodicity

of the lattice. In conclusion, Fourier series expansion of $U(x)$ must be done in terms of G-points to ensure that $U(x)$ has the periodicity of the underlying lattice.