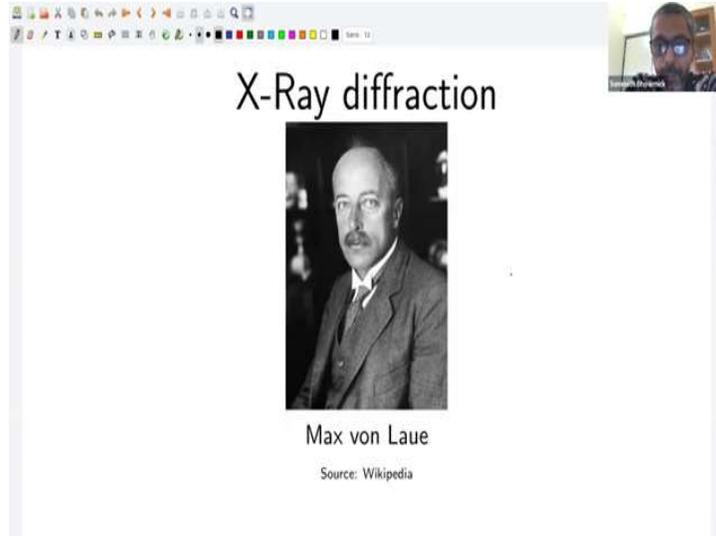


\Electronic Properties of the Materials: Computational Approach
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Lecture – 17
X-ray Diffraction, Periodic Potential, Bloch Theorem

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Hello friends, in the last lecture we have learned about Real Lattice and Reciprocal Lattice. In this lecture we are going to discuss about a related topic X-ray Diffraction. Students of material science and engineering are familiar with Bragg's law of x-ray diffraction. However, in this lecture I am going to talk about Von Laue condition of x-ray diffraction.

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Each atom/ions arranged in a Bravais lattice re-radiate the incident radiation in all directions. Find condition for constructive interference.

Source: Wikipedia

- Take two atoms separated by distance d
- $\vec{k} = \frac{2\pi}{\lambda} \hat{n}, \vec{k}' = \frac{2\pi}{\lambda} \hat{n}'$
- Projection of \vec{d} along $\vec{k} = \vec{d} \cdot \hat{n}$
- Projection of \vec{d} along $\vec{k}' = -\vec{d} \cdot \hat{n}'$
- Path difference:
 $d \cos \theta + d \cos \theta' = \vec{d} \cdot (\hat{n} - \hat{n}')$
- Condition for constructive interference: $\vec{d} \cdot (\hat{n} - \hat{n}') = m\lambda$
- Multiply both sides by $\frac{2\pi}{\lambda} \Rightarrow \vec{d} \cdot (\vec{k} - \vec{k}') = 2\pi m$
- Must be satisfied not by just two, but all lattice points \vec{R}
- $\vec{R} \cdot (\vec{k} - \vec{k}') = 2\pi m \Rightarrow \exp[i(\vec{k} - \vec{k}') \cdot \vec{R}] = 1$

You are shining x-rays on the material. So, the incoming x-rays are coming in this direction of \hat{n} , and each atom or ion arranged in a Bravais lattice they are re-radiating the incident radiation in all possible directions. Let us take one of them, right so, let us assume that the incoming wave, the incoming radiation is in the direction of \hat{n} and the outgoing condition is in the direction of \hat{n}' , right.

So, these are the like 2 unit vectors in those two directions. Okay, we have to find the condition for constructive interference. Let us take 2 atoms separated by a distance of d . So, we have like atom 1 and atom 2 and they are separated by a distance of d . Now, we define the wave vector k , correct. So, this is the wave vector of the incoming wave right k is the wave vector of the incoming wave, right

So, we take the magnitude that is equal to $2\pi/\lambda$ times each direction, \hat{n} . And k' is the magnitude of the or k' is related to the wave that is going in this direction and then again its magnitude is like $2\pi/\lambda$ times direction is \hat{n}' . Okay Note that because of elastic scattering both the like both k and k' , both of them has same wavelength. Now, again we know that this d is the separation between these 2 atoms.

So, what we do is that, now, we calculate the projection of d along k , right. So, to do that what we have to take a dot product, right. So, $d \cdot \hat{n}$, \hat{n} is the unit vector along k . So, this will give the projection of d along k . Similarly, we can get the projection of d along k' which is given by $-d \cdot \hat{n}'$. Now, you see that these two waves right the first wave that is coming in this direction and then this is like going out in this direction.

Similarly, if you look at this wave right, so, this is the incoming and this is the outgoing. right So, if you compare these two waves right this and then this then you see that this way right this particular wave is travelling more path than the second one and and then what we can do is that, we can just find out the path difference between this and between this, how do we do that? The path depends and you see that the extra path that this wave is travelling is given by this plus this, right.

So, this is the extra path that is being travelled by this way right and we already have found out uh right what that is? right That is just the projection of d along this right and then we can just add add these two terms to get the path difference and that is given by this equation.

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Source: Wikipedia

- $\vec{k} = \frac{2\pi}{\lambda} \hat{n}, \vec{k}' = \frac{2\pi}{\lambda} \hat{n}'$
- Projection of \vec{d} along $\vec{k} = \vec{d} \cdot \hat{n}$
- Projection of \vec{d} along $\vec{k}' = -\vec{d} \cdot \hat{n}'$
- Path difference: $d \cos \theta + d \cos \theta' = \vec{d} \cdot (\hat{n} - \hat{n}')$
- Condition for constructive interference: $\vec{d} \cdot (\hat{n} - \hat{n}') = m\lambda$
- Multiply both sides by $\frac{2\pi}{\lambda} \Rightarrow \vec{d} \cdot (\vec{k} - \vec{k}') = 2\pi m$
- Must be satisfied not by just two, but all lattice points \vec{R}
- $\vec{R} \cdot (\vec{k} - \vec{k}') = 2\pi m \Rightarrow \exp[i(\vec{k} - \vec{k}') \cdot \vec{R}] = 1$
- Compare with $\exp[i\vec{G} \cdot \vec{R}] = 1$
- Laue condition for diffraction: $\Delta\vec{k} = \vec{k} - \vec{k}' = \vec{G}$

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Now, what is the condition for the constructive interference between these two waves? The path difference should be equal to some integer times the wavelength. Okay, and then what we do is that? We take this equation and multiply both sides by 2 pi by lambda and then we can rewrite the equation as this, right. So, d dot k minus k dash equal to 2 pi m so, this is the condition for constructive interference.

Now, you see that d is the distance between these two points right any vector that takes me from one lattice point to the other lattice point is a lattice vector, right. So, d is some lattice vector but now, we can generalize right and then we can just put in place of d we can just write it as R Right because this must be true for all lattice points, right. So, d is replaced by R in this equation and then we just write it as R dot k minus k dash equal to 2 pi m.

And then, if we just take exponential right so, e power, this is equals to e power i 2 pi m right but now 2 pi m right so, this is like m is an integer, so that must be equal to 1. So that means we can get this equation Okay e power i k minus k dash dot R equal to 1. Now, we compare this with what we already know, right. We have already derived this right e power i G dot R equal to 1, right. So, if we compare these two equations then we we can just conclude that k minus k dash that is equal to delta k that must be equal to G. Where G is some reciprocal, lattice vector and this is known as the Laue condition for diffraction.

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Bragg planes

Source: Wikipedia

- Laue condition for diffraction: $\Delta \vec{k} = \vec{k} - \vec{k}' = \vec{G}$
- $|\vec{k}'| = |\vec{k} - \vec{G}| = |\vec{k}|$, as scattering does not change wave length
- Squaring the above equation: $\vec{k} \cdot \vec{G} = \frac{1}{2} |\vec{G}|^2$
- Component of incident wave vector \vec{k} along reciprocal lattice vector

So, we can take the Laue condition, $\Delta \vec{k} = \vec{k} - \vec{k}' = \vec{G}$ and represent it in a diagram. So, we can just rewrite this equation as $\vec{G} + \vec{k}' = \vec{k}$, right so, we just use the vector sum. So, this is like $\vec{G} + \vec{k}' = \vec{k}$, right this is the \vec{k} vector. And then you see that the magnitude of \vec{k}' at magnitude of \vec{k} they are same as the scattering does not change the wavelength, right these are like elastic scatterings.

So, in that case, what we can write is that we can take this equation right and just square it, right. So, if we just square this equation, what we get is the following, right, $k^2 = k'^2$ right So, this is what we are saying, right. The scattering does not change the wavelength, so, their magnitude must be same. So, we are just taking square of the magnitude and then what we do is that? We just rewrite this equation, right

So, this this is equal to right this is equal to k^2 . What is $k^2 - k'^2$ right So, this is like $k^2 - k'^2 = k^2 - (k^2 - 2\vec{k} \cdot \vec{G} + G^2)$, okay. And this implies that we can just write this right $\vec{k} \cdot \vec{G}$, right. So, this is like $\vec{k} \cdot \vec{G} = \frac{1}{2} G^2$, so, this term cancels out from both the sides. So, this is half of G^2 , correct, and then what we do is that? We can just rewrite this equation. So, we just divide this vector \vec{G} by its magnitude so that we can just write rewrite it as $\vec{k} \cdot \hat{G} = \frac{1}{2} |\vec{G}|$, okay.

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Source: Wikipedia

- Laue condition for diffraction: $\Delta \vec{k} = \vec{k} - \vec{k}' = \vec{G}$
- $|\vec{k}'| = |\vec{k} - \vec{G}| = |\vec{k}|$, as scattering does not change wave length
- Squaring the above equation: $\vec{k} \cdot \vec{G} = \frac{1}{2} |\vec{G}|^2$
- Component of incident wave vector \vec{k} along reciprocal lattice vector \vec{G} = half the length of \vec{G}
- Tip of \vec{k} equidistant from O & tip of \vec{G}
- Tip of \vec{k} lies in plane perpendicularly bisecting line joining O and \vec{G}
- Such \perp bisector planes of \vec{G} vectors in k -space called **Bragg planes**

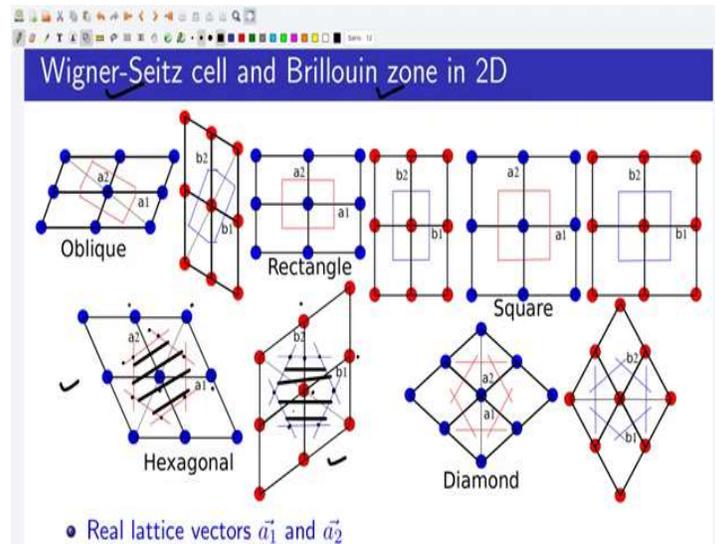
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So, this is what. So Laue condition we can just rewrite this, as this Laue condition is given by this, right. We can just rewrite We are just rewriting this equation like this. Now, if you look at this diagram then you see that this component of the incident wave vector k along reciprocal lattice vector G right that is given by this. right. So, $k \cdot \hat{G}$ what is this? This is the component of the incident wave vector k along the reciprocal lattice vector G , okay, and that is equal to half the length of G .

So that is what we conclude from this equation. right And then, if you look at this diagram carefully then you see that the tip of k is equidistance from O and the tip of G . right. So, this is the tip of k so, this is equidistance from O so, this is the this O point right some point in reciprocal space and then this is the G point and the tip of k is equidistance from both the these points like O and G .

So that means, if we draw a plane right, you see a series blue plane, right if we draw a plane which is like ah perpendicularly bisecting, the line joining O and G , right. Then what will happen? The tip of this vector k will lie on that plane, okay, and this plane has a special name such perpendicular bisector planes of G vectors in k space. These are known as the Bragg planes.

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Let us draw the perpendicular bisectors in case of 2d. We can do it in real lattice as well as reciprocal lattice. For example, let me show the example for a hexagonal lattice, okay. So, these are the so, this is one vector right a_1 correct and this is joining like two real lattice points correct this and this, correct. So, what we do is that? We just draw this perpendicular bisector, right, and this we are doing in the real space.

And then we can again take this point and this point and right and then ah we join them with a line and draw the perpendicular bisector right which is this. And we can do it again for this point and this point and then we get another perpendicular bisector which is given by this and so on, right, and then you see that this is how the, so then you see that we have like built a small cell correct within this right small cell which has the boundaries are given by these red lines.

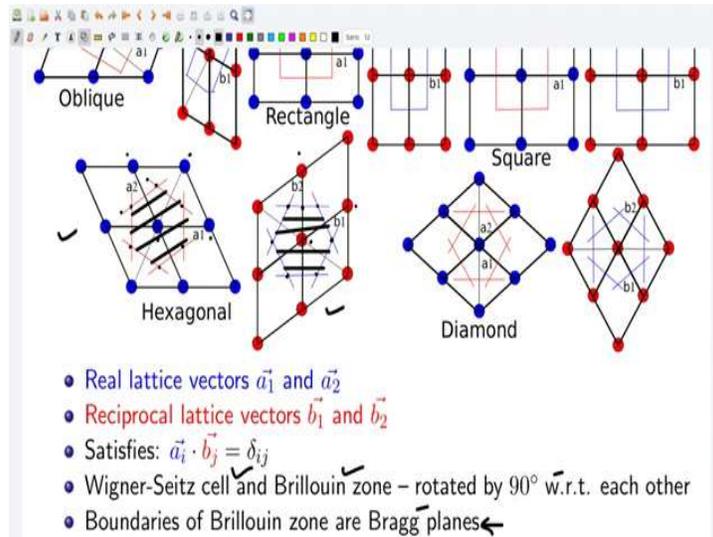
We have built a small cell by joining the perpendicular bisectors. In case of real lattice, these are known as the Wigner-Seitz cell. Now, this is the corresponding reciprocal lattice for the hexagonal lattice and then these are the vectors right b_1 and b_2 . And then you see that you take 2 points in the reciprocal lattice and then you, you draw the perpendicular bisector, right, and you do the same thing right again you take these two lattice points and you draw this perpendicular bisector correct this one, correct.

And then you do again the same thing and then you see that again you built a small cell inside and then right this cell is known as the Brillouin zone, right. So, the principle is same you just joined you just draw the perpendicular bisectors and that will give you a cell, either in real

lattice or in reciprocal lattice and this cell has a name in case of real lattice, this cell right maybe I can just, right so, this is the cell that I am talking about.

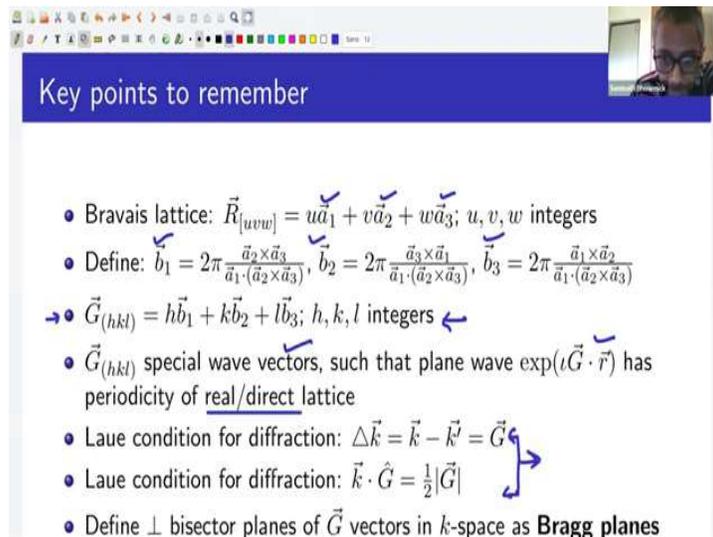
This is known as the Wigner- Seitz cell in case of real lattice and if you look at the reciprocal lattice then this is the cell correct and then this is known as the Brillouin zone.

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You notice like if you look at these figures, you notice one uh interesting thing is that this Wigner-Seitz cell and Brillouin zone they are rotated by 90 degree with respect to each other. Okay, and now, you see this the boundaries of the Brillouin zone right we just have read about like Bragg planes in the previous slide now, we just have learned about that. And then you see that these boundaries of the Brillouin zones these are the Bragg planes.

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Finally, let me just summarize the most important concepts in this lecture. So, we have defined like three basis vectors for real lattice or Bravais lattice and based on them we have defined three basis vectors for the reciprocal lattice. okay, and then we can write a general vector in reciprocal lattice in this form and this G vectors these are like special wave vectors such that the plane wave $e^{i\vec{G}\cdot\vec{r}}$ has the periodicity of the real or direct lattice.

Now, we also learned about Laue condition for this diffraction and they can be represented in two different forms. right. So, $\Delta\vec{k} = \vec{k} - \vec{k}' = \vec{G}$ or $\vec{k} \cdot \hat{G} = \frac{1}{2}|\vec{G}|$, okay.

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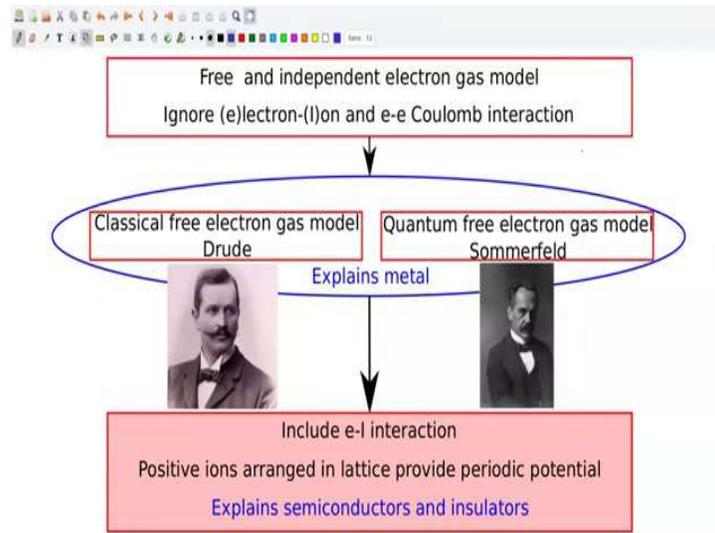
Key points to remember

- Bravais lattice: $\vec{R}_{[uvw]} = u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$; u, v, w integers
- Define: $\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$, $\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$, $\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$
- $\vec{G}_{(hkl)} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$; h, k, l integers ←
- $\vec{G}_{(hkl)}$ special wave vectors, such that plane wave $\exp(i\vec{G} \cdot \vec{r})$ has periodicity of real/direct lattice
- Laue condition for diffraction: $\Delta\vec{k} = \vec{k} - \vec{k}' = \vec{G}$
- Laue condition for diffraction: $\vec{k} \cdot \hat{G} = \frac{1}{2}|\vec{G}|$
- Define \perp bisector planes of \vec{G} vectors in k -space as **Bragg planes**
- Boundaries of Brillouin zone are Bragg planes

Where \vec{G} is a reciprocal lattice vector and \vec{k} is some general wave vector and then what we did is that we defined like perpendicular bisector planes of \vec{G} vectors and they have a name like they are the Bragg planes. And then we have also defined something called Brillouin zones and then these Brillouin zones are the boundaries of the Brillouin zone they are the Bragg planes okay. Why did we learn about this uh Brillouin zone and Bragg planes?

Because they will play some important role when we try to understand the electron in a periodic potential.

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After learning the concept of real and reciprocal lattice let us get back to our discussion on electronic properties of solids. We have discussed free electron theory in great detail and realized that there are certain anomalies which cannot be explained even at the level of quantum theory. Thus, we decided to include electron ion interaction. Our discussion on lattice also taught us that the atomic cores or ions are periodically repeated in space.

We have to solve time independent Schrodinger equation by taking into account the periodic potential because of the underlying lattice. This will not only help us to understand the electronic properties of semiconductors and insulators but also explain the sin anomaly of Hall coefficient of divalent and trivalent metals.

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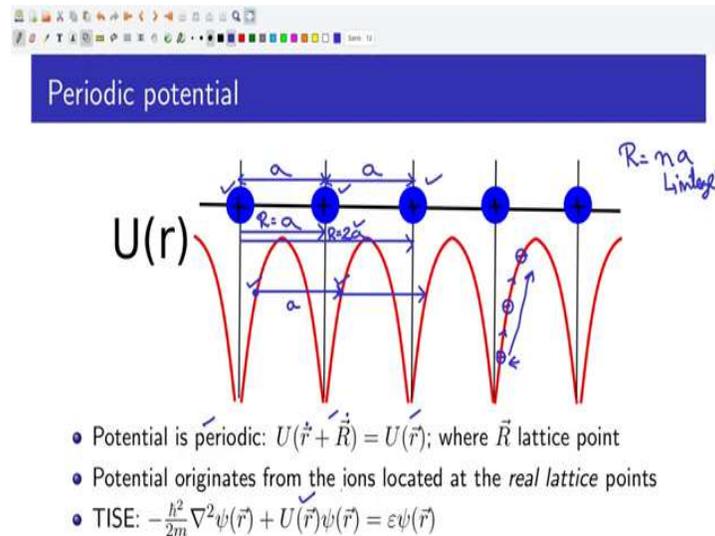
Electrons in a crystal: Bloch theorem

Felix Bloch

Source: Wikipedia

We shall start our discussion with Bloch theorem before we do that. Let us have a feeling that how does a periodic potential look like.

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A schematic diagram of a periodic potential is shown here, blue points are lattice points and the red line is value of potential energy which changes periodically in space. The lattice points are arranged in a distance of a . Starting from a lattice point you can reach another lattice point by moving by a vector R where R equal to n times a , right, n is an integer. For example, to move from the first lattice point to the second lattice point we have to move by a vector R equal to a .

Similarly, to go from the first lattice point to the third lattice point you have to move by a vector R equal to $2a$. The potential is periodic that is U of r plus R equal to U of small r where small r is some general point and capital R is some lattice point or lattice translation vector. So, what does this imply? This implies that if I am say at this point which is not a lattice point and then I move by a lattice translation vector a and reach at this point.

And the potential at this point and this point must be equal because of the periodic nature of the potential. Remember that valence electrons get detached from the atomic core which is made of nucleus and core electrons. Since the atomic cores are positively charged close to the cores the valence electrons see some highly attractive potential. As it moves away from the core the attraction gets weaker.

We have to solve time independent Schrodinger equation for a periodic potential U of r. We have some experience of solving time independent Schrodinger equation for some given potential like harmonic potential, but solving for periodic potential is more complicated than solving for a harmonic potential.

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Electrons in periodic potential: Bloch electrons

- Wave function of free e: $\psi_{\vec{k}}(\vec{r}) \sim \exp(i\vec{k} \cdot \vec{r})$ (plane wave)
- Wave function of Bloch e: $\psi_{\vec{k}}(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) u_{\vec{k}}(\vec{r})$ (Bloch theorem)
 - ▶ u has periodicity of Bravais lattice: $u_{\vec{k}}(\vec{r} + \vec{R}) = u_{\vec{k}}(\vec{r})$; \vec{R} lattice point

Handwritten derivation:

$$\psi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot (\vec{r} + \vec{R})} u(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{r}} e^{i\vec{k} \cdot \vec{R}} u(\vec{r}) = e^{i\vec{k} \cdot \vec{R}} \psi(\vec{r})$$

- Alternate form of Bloch theorem: $\psi_{\vec{k}}(\vec{r} + \vec{R}) = \exp(i\vec{k} \cdot \vec{R}) \psi_{\vec{k}}(\vec{r})$
- Let $\psi(\vec{r})$ be the wave function at some point \vec{r} in a crystal
- Let's move by a Bravais lattice vector \vec{R} from the above point \vec{r}
- What is the relation between the wave function at \vec{r} & $\vec{r} + \vec{R}$:
 $\psi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi(\vec{r})$

For solving time independent Schrodinger equation in periodic potential we need to learn Bloch theorem. This theorem is so important that electrons in the periodic potential is referred to as Bloch electron. I shall not try to prove the theorem but just explain its consequences. Let us try to memorize Bloch theorem by starting from something we already know that is the wave function for free electrons, given by e power i k dot r, where k is some wave vector and r is some general point in space.

Wave function for Bloch electrons is given by the wave function for free electrons multiplied by u of r, where u has the periodicity of the Bravais lattice that is u of small r plus capital R equal to u of r, where capital R is some point in the Bravais lattice. Let us try to calculate psi of r plus capital R. This is equal to e power i k dot r plus capital R times u of small r plus capital R. We can rewrite this as and since this has the periodicity of the Bravais lattice.

We can write it in this form and note that this is nothing but psi of r thus psi of r plus capital R equal to e power i k dot R times psi of r where capital R is some Bravais lattice vector.

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• Wave function of Bloch e : $\psi_{\vec{k}}(\vec{r}) = \exp(i\vec{k} \cdot \vec{r}) u_{\vec{k}}(\vec{r})$ (Bloch theorem)

▶ u has periodicity of Bravais lattice: $u_{\vec{k}}(\vec{r} + \vec{R}) = u_{\vec{k}}(\vec{r})$; \vec{R} lattice point

$$\psi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot (\vec{r} + \vec{R})} u_{\vec{k}}(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} e^{i\vec{k} \cdot \vec{r}} u_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{R}} \psi(\vec{r})$$

• Alternate form of Bloch theorem: $\psi_{\vec{k}}(\vec{r} + \vec{R}) = \exp(i\vec{k} \cdot \vec{R}) \psi_{\vec{k}}(\vec{r})$

→ • Let $\psi(\vec{r})$ be the wave function at some point \vec{r} in a crystal
 → • Let's move by a Bravais lattice vector \vec{R} from the above point \vec{r}

• What is the relation between the wave function at \vec{r} & $\vec{r} + \vec{R}$:
 $\psi(\vec{r}) \stackrel{?}{=} \psi(\vec{r} + \vec{R}) \leftarrow |\psi(\vec{r} + \vec{R})|^2 = e^{-i\vec{k} \cdot \vec{R}} \psi^*(\vec{r}) e^{i\vec{k} \cdot \vec{R}} \psi(\vec{r}) = |\psi(\vec{r})|^2$

• Every lattice point in crystal equivalent \Rightarrow probability density at every lattice point equivalent $\Rightarrow |\psi(\vec{r})|^2 = |\psi(\vec{r} + \vec{R})|^2$

• Wave function at \vec{r} and $\vec{r} + \vec{R}$ differ by a phase factor: $\exp(i\vec{k} \cdot \vec{R})$

Now, we can restate the Bloch theorem like this and let us use this form to understand the meaning of Bloch theorem. Let ψ of r be the wave function at some point r in a crystal. Now, let us move by a Bravais lattice vector R from the above point r . Now, what is the relation between the wave function at small r and small r plus capital R ? Are they equal or not? Or alternately, you can ask the question whether the wave function also has the periodicity of the Bravais lattice?

Because if ψ of small r equal to ψ of small r plus capital R then we have to conclude that the wave function has the periodicity of the Bravais lattice. Clearly that is not the case because the wave function at r and small r plus capital R differ by a phase factor of e power $i k \cdot R$. Thus, the wave function does not have the periodicity of the Bravais lattice. However, you try to calculate the mod square.

This is equal to e power minus $i k \cdot R$ ψ^* of r e power $i k \cdot R$ ψ of r and this term cancels out and we can write it as ψ of r square. Thus, we find that although the wave function does not have the periodicity of the Bravais lattice but the probability density that has the periodicity of the Bravais lattice because ψ of r square equal to mod ψ of r plus R square.

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Significance of \vec{k} for Bloch electrons

- Wave vector \vec{k} of Bloch electron: similar to \vec{k} of free electrons
- But there is a difference:
 - ▶ Plane waves are eigen states of momentum $\hbar\vec{k}$
 - ▶ Bloch states are *not* eigen states of momentum
 - ▶ Easy to verify: $-i\hbar\nabla\psi_{\vec{k}} = \hbar\vec{k}\psi_{\vec{k}} - e^{i\vec{k}\cdot\vec{r}}i\hbar\nabla u_{\vec{k}}(\vec{r})$

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u(\vec{r})$$

$$(-i\hbar\nabla)\psi(\vec{r}) = \hbar\vec{k} e^{i\vec{k}\cdot\vec{r}} u(\vec{r}) - e^{i\vec{k}\cdot\vec{r}} \nabla u$$

- A term is used showing the similarity, but also highlighting difference
 - ▶ For free electrons: $\hbar\vec{k}$ is *momentum* eigen value

Let us try to understand the significance of k for Bloch electrons. Wave vector k of Bloch electrons are similar to the wave vector k of free electrons but there is a difference. We know that the plane waves are eigen states of momentum operator with eigenvalue $\hbar k$. However, Bloch states are not eigen states of momentum operator. This is very easy to verify, so, Bloch states are given by $\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u(\vec{r})$.

Now, I write the momentum operator in 3D minus $i\hbar$ cross times the gradient operator and then this operates on ψ . And this can be written as $\hbar\vec{k} e^{i\vec{k}\cdot\vec{r}} u(\vec{r})$ and now, I take a derivative of $u(\vec{r})$ so, $e^{i\vec{k}\cdot\vec{r}} \nabla u$. Clearly, $\psi(\vec{r})$ is not an eigen function or eigen state of the momentum operator.

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- ▶ Bloch states are *not* eigen states of momentum
- ▶ Easy to verify: $-i\hbar\nabla\psi_{\vec{k}} = \hbar\vec{k}\psi_{\vec{k}} - e^{i\vec{k}\cdot\vec{r}}i\hbar\nabla u_{\vec{k}}(\vec{r})$

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u(\vec{r})$$

$$(-i\hbar\nabla)\psi(\vec{r}) = \hbar\vec{k} e^{i\vec{k}\cdot\vec{r}} u(\vec{r}) - e^{i\vec{k}\cdot\vec{r}} \nabla u$$

- A term is used showing the similarity, but also highlighting difference
 - ▶ For free electrons: $\hbar\vec{k}$ is *momentum* eigen value ←
 - ▶ For Bloch electrons: $\hbar\vec{k}$ is called *crystal momentum* ←
- Dynamics of Bloch and free electrons differ in general
 - ▶ Velocity of free electrons: $\vec{v} = \frac{\hbar\vec{k}}{m}$
 - ▶ Velocity of Bloch electrons: $\vec{v} = \frac{1}{\hbar} \frac{\partial \epsilon(\vec{k})}{\partial \vec{k}}$

Sonnath Bhowmick (MSE, IIT Kanpur) Electron in a periodic potential July 23, 2022 6 / 44

Now, a term is used showing the similarity but also highlighting the difference. For free electrons we know that the $\hbar k$ is the momentum eigenvalue. For Bloch electrons $\hbar k$ is not the momentum eigenvalue but we use a term which sounds familiar or which sounds similar and that term is the crystal momentum. We will see later that dynamics of Bloch and free electrons differ in general.

In case of free electrons, the velocity is given by $\hbar k$ divided by m , $\hbar k$ is the momentum divided by mass and you get the velocity. However, velocity for Bloch electrons given by v equal to $\frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon(\mathbf{k})$.

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Periodic boundary condition for Bloch electrons

- For free electrons, we chose cubic box of vol $V = L^3$
- However, completely ignored underlying lattice in free ϵ discussion

• Now, take any primitive unit cell of Bravais lattice and repeat it

We solved the problem of free electrons in a periodic box of volume V . Let us now try to do the same for Bloch electrons in a periodic box.

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- For free electrons, we chose cubic box of vol $V = L^3$
- However, completely ignored underlying lattice in free e discussion

- Now, take any primitive unit cell of Bravais lattice and repeat it
- Volume of the box: $V = N_1 N_2 N_3 \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = Nv$
- PBC: $\psi(\vec{r} + N_1 \vec{a}_1) = \psi(\vec{r}), \psi(\vec{r} + N_2 \vec{a}_2) = \psi(\vec{r}), \psi(\vec{r} + N_3 \vec{a}_3) = \psi(\vec{r})$
- Two length scales: macroscopic (L_1) and atomic a_1 ; $L_1 = N_1 a_1$

In case of Bloch electrons, the big box of volume V is made of small-small unit cells representing the underlying lattice. The volume of the big box V is given by the number of unit cells present in that box times volume of each unit cell that is N times v . If you look at the periodic boundary condition then it looks same for the free electron as well as Bloch electrons.

However, one should keep in mind in case of Bloch electrons that we have to consider two length scales, one is microscopic length scale and another is atomic length scale. The macroscopic length scale is given by the length of the side of the big box L_1 and the atomic length scale is given by the lattice translation vector a_1 . So that is where the Bloch electrons differ from free electrons because in case of free electrons, we only consider the macroscopic length scale and completely ignore the atomic length scale.

(Refer Slide Time: 26:20)

Allowed values of Bloch wave vector \vec{k}

- In case of free e , allowed values of \vec{k} determined by P.B.C.
- Bloch electrons must satisfy both Bloch theorem and P.B.C
- According to Bloch theorem: $\psi(\vec{r} + N_1 \vec{a}_1) = \exp(i N_1 \vec{k} \cdot \vec{a}_1) \psi(\vec{r})$
- Now, $\vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3$ and $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$
 - ▶ x_1, x_2, x_3 are real numbers
- Thus, $\psi(\vec{r} + N_1 \vec{a}_1) = \exp(i N_1 2\pi x_1) \psi(\vec{r})$
- But P.B.C: $\psi(\vec{r} + N_1 \vec{a}_1) = \psi(\vec{r}) \Rightarrow \exp(i N_1 2\pi x_1) = 1 = \exp(i 2\pi n_1)$
- Thus, $x_1 = \frac{n_1}{N_1}$ and $\vec{k} = \frac{n_1}{N_1} \vec{b}_1 + \frac{n_2}{N_2} \vec{b}_2 + \frac{n_3}{N_3} \vec{b}_3$; $n_i = \text{integer}$
- Vol occupied by a k -point: $\Delta k = \frac{\vec{b}_1}{N_1} \cdot \left(\frac{\vec{b}_2}{N_2} \times \frac{\vec{b}_3}{N_3} \right) = \frac{1}{N} \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)$

Let us find out the allowed values of Bloch wave vector k . In case of free electrons allowed values of k are determined by periodic boundary condition. This is true even for the Bloch electrons, however, in case of Bloch electrons, they must also satisfy Bloch theorem. Now, let us take the periodic boundary condition along the direction of vector a_1 . So, according to Bloch theorem, we know that $\psi(\vec{r} + \vec{R}) = e^{i\vec{k} \cdot \vec{R}} \psi(\vec{r})$.

Now, in this case, \vec{r} equal to $N_1 a_1$. Thus, we can write $\psi(\vec{r} + N_1 a_1)$ in this form. Now, we write the wave vector k as a linear combination of b_1, b_2 and b_3 the vectors in the reciprocal lattice. Here x_1, x_2, x_3 are real numbers now we also know that $a_i \cdot b_j = 2\pi \delta_{ij}$ that means when I try to calculate this term $k \cdot a_1$. The only term that will be non-zero is $b_1 \cdot a_1$, rest of the terms will be equal to 0 because $b_2 \cdot a_1 = 0$ and $b_3 \cdot a_1 = 0$.

Thus, we can write $\psi(\vec{r} + N_1 a_1) = e^{iN_1 2\pi x_1} \psi(\vec{r})$, but according to periodic boundary condition $\psi(\vec{r} + N_1 a_1)$ must be equal to $\psi(\vec{r})$ and then you can compare this equation and this equation and the only way it can satisfy both of them is if $e^{iN_1 2\pi x_1} = 1$. And then we can write x_1 as n_1 / N_1 . And similarly, we can find the value of x_2 and we can find the value of x_3 .

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- According to Bloch theorem: $\psi(\vec{r} + N_1 \vec{a}_1) = \exp(i N_1 \vec{k} \cdot \vec{a}_1) \psi(\vec{r})$
- Now, $\vec{k} = x_1 \vec{b}_1 + x_2 \vec{b}_2 + x_3 \vec{b}_3$ and $\vec{a}_i \cdot \vec{b}_j = 2\pi \delta_{ij}$
 x_1, x_2, x_3 are real numbers
 $\vec{R} = N_1 \vec{a}_1$
 $\psi(\vec{r} + \vec{R}) = e^{i \vec{k} \cdot \vec{R}} \psi(\vec{r})$
- Thus, $\psi(\vec{r} + N_1 \vec{a}_1) = \exp(i N_1 2\pi x_1) \psi(\vec{r})$
- But P.B.C: $\psi(\vec{r} + N_1 \vec{a}_1) = \psi(\vec{r}) \Rightarrow \exp(i N_1 2\pi x_1) = 1 = \exp(i 2\pi n_1)$
- Thus, $x_1 = \frac{n_1}{N_1}$ and $\vec{k} = \frac{n_1}{N_1} \vec{b}_1 + \frac{n_2}{N_2} \vec{b}_2 + \frac{n_3}{N_3} \vec{b}_3$; $n_i = \text{integer}$
- Vol occupied by a k -point: $\Delta \vec{k} = \frac{\vec{b}_1}{N_1} \cdot \left(\frac{\vec{b}_2}{N_2} \times \frac{\vec{b}_3}{N_3} \right) = \frac{1}{N} \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3)$
- Vol of reciprocal lattice primitive cell = $\frac{8\pi^3}{v}$; $v = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \frac{V}{N}$
- Thus, $\Delta \vec{k} = \frac{1}{N} \vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{8\pi^3}{V}$
- Note the similarity with the case of free e !!

And then we can write the wave vector as k is equals to $n_1 / N_1 b_1$ plus $n_2 / N_2 b_2$ plus $n_3 / N_3 b_3$. From this equation we can also find the volume occupied by a k point and that is given by this. So, this is nothing

but the volume of the primitive cell of the reciprocal lattice, divided by the number of the unit cells.

And if you calculate this number, this number turns out to be $8\pi^3$ divided by V , which is same as we as what we found for the free electrons. However, keep in mind that in case of free electrons, we did not talk about reciprocal lattice.