

Introduction to Solid State Physics
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Lecture – 57

Applying perturbation theory to free electron wavefunctions and creation of energy gap at zone boundaries

(Refer Slide Time: 00:13)

The image shows a digital whiteboard with handwritten notes. At the top, it states the periodic potential condition $V(x) = V(x+a)$ and the Bloch wave function $\psi(x) = e^{ikx} u_k(x)$. Below this, it defines Bloch's theorem as $u_k(x) = u_k(x+a)$. The notes then describe the 'Nearly free electron model for weak periodic potentials' and mention that 'we could use perturbation theory'. Finally, it shows the potential expansion $V(x) = V_0 + \sum_{G \neq 0} e^{iGx} V_G$, with an arrow pointing from the V_0 term to a '0' below it, indicating that $V_0 = 0$.

So, let me summarize what we have done so far. We have said that if particles or electrons are moving in a periodic potential then the wave function satisfies the form; it has the form $e^{ikx} u_k(x)$ where $u_k(x)$ is periodic $u_k(x+a)$ this is known as Bloch's theorem. Keep in mind when I write, Bloch is b l o c h. Lot of people make a mistake of writing as block. It's b l o c h. Second thing we did is did nearly free electron model for weak periodic potentials so that we could use perturbation theory

For this, what we did was wrote $V(x) = V_0 + \sum_{G \neq 0} e^{iGx} V_G$ and took this V_0 to be 0 and therefore, the first order change in the energy comes out to be 0 and what mattered was the second order energy change.

(Refer Slide Time: 01:59)

Notation: $\langle e^{-ik'x} | V | e^{ikx} \rangle$
 $\langle k' | V | k \rangle$
 $\langle x | k' \rangle = e^{ik'x}$
 $\langle k' | x \rangle = e^{-ik'x}$

Just A bit about notation I have been little careless in writing the notation. I have used things like $e^{-ik'x}$ whatever the V is e^{ikx} . Actually what this refers to, is the matrix element $k' V k$ and the space representation of k' is $e^{ik'x}$ and therefore, space representation of k becomes $e^{-ik'x}$ and this is what I have used directly in writing my matrix elements. In case you wonder, I just wanted to clarify that.

So, I will be using this back and forth. Just follow this as it is.

(Refer Slide Time: 02:53)

$$E_k^{(2)} = \sum_G \frac{|V_G|^2}{E_k - E_{k+G}}$$

$$\psi_k^{(0)}(x) = \frac{1}{\sqrt{L}} e^{ikx}$$

$$\langle k' | \sum_G V_G e^{iGx} | k \rangle$$

$$= \frac{1}{L} V_G \int e^{-ik'x} e^{iGx} e^{ikx} dx$$

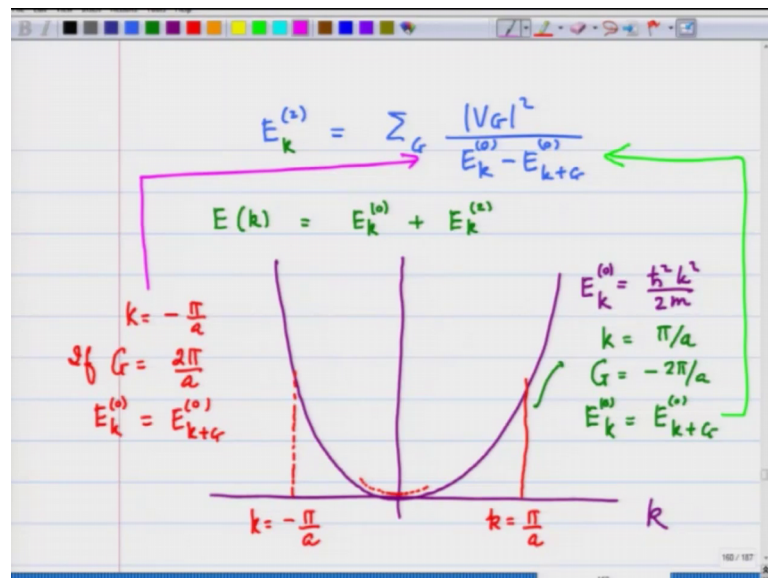
$$= \frac{V_G}{L} \int_0^L e^{i(k+G-k')x} dx = V_G \delta_{k, k+G}$$

So back to second order energy change; which we found to be equal to summation $G V G$ over E_k minus E_{k+G} and this is energy change for the k th level. Let me just go over this calculation once more. So, that you are very clear about the normalization things like that.

Remember the zeroth order wave function size $0 \times$ is 1 over root $L e$ raised to $i k x$. This is $i k x$ and when I take the expectation value, k prime summation $G V G e$ raised to $i G x$ k , it turns out to be 1 over L integral e raised to $minus i k$ prime x . There is a $V G$ here, e raised to $i G x$, e raised to $i k x$ $d x$ and this is nothing but, $V G$ over L integral of E raised to $i k$ plus G minus k prime x $d x$. And this integral is over the length over which the periodic boundary condition is applied.

Therefore, this is equal to 0 . If k prime is not equal to plus G and it is equal to integral of $d x$ over L when it is equal to k prime is equal to k plus G . So, this you can write very easily as $V G \delta_{k \text{ prime } k + G}$. This is what we used earlier; so, I just wanted to clarify how it is obtained.

(Refer Slide Time: 04:44)



In any case, E second order then comes out to be summation $G V G$ square over E_k minus E_{k+G} and I will put a 0 on top to show that these E_k and E_{k+G} are being calculated at unperturbed level.

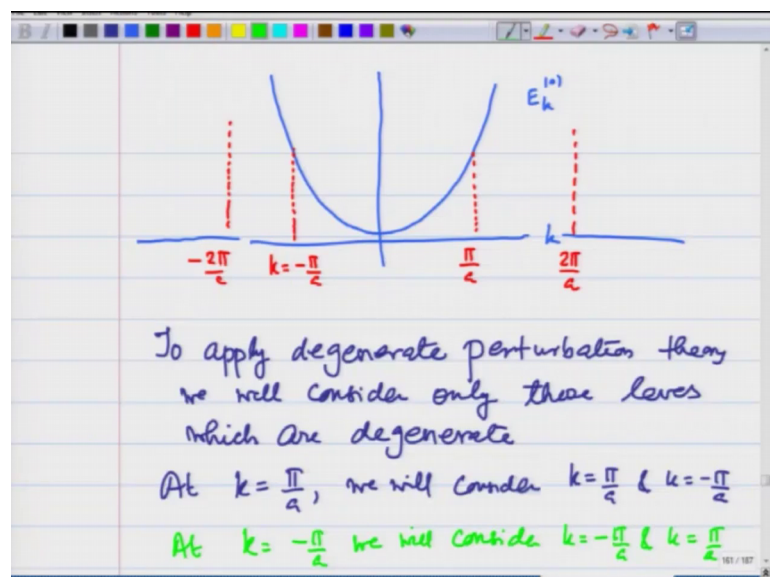
So that the total energy of the system for k th level, I will put k here is equal to E_k^0 plus E_k^2 . Remember the first order is already taken to be 0 because that was just background constant shift of the potential. Now when I plot the total energy E_k with respect to k , E_k^0 is parabolic and when I add the second order energy to it; we will have some value near k equals 0 and around it, but the main point is that when I come to k equals π/a or k equals minus π/a , what happens then? And let me show this on the side.

On the right hand side, I will show when k equals π/a and if I take G equals minus $2\pi/a$ then E_k equals E_k^0 plus G . And therefore, let me put a 0 here the denominator here becomes 0 and therefore, E_k^2 blows up. It becomes infinitely large. Let me show it for k equals minus π/a also. If G equals $2\pi/a$ then, E_k^0 becomes E_k^0 plus G 0 and again we see that the denominator blows up. E_k^2 becomes infinitely large.

That cannot happen; where did we go wrong? Where we went wrong is that at these case; the case at the Brillouin zone boundary when E_k^0 is equal to E_{k+G}^0 , the energies are the same the two levels. E_k and E_{k+G} are degenerate; and when we calculated E_k^2 we used perturbation theory which is applicable only to the levels when they are not degenerate.

So, to calculate energy at these points; I must use degenerate perturbation theory then only I will get the right answer. So, we will do that now.

(Refer Slide Time: 08:09)



So what we figured out by looking at E_2 is that let me make this $E_{k=0}$ again. What we figured out is that near k equals minus π/a and π/a ; the levels become degenerate and therefore, I cannot apply the perturbation theory; non degenerate perturbation theory that I used. Same thing would happen at any Brillouin zone boundary or any multiple of these case.

So, even at k equals minus $2\pi/a$ or k equals $2\pi/a$, again we will have a G that will have energy level degenerate with k plus G and we have to apply degenerate perturbation theory and let us see now what happens when we do that? To apply theory, we will consider only those levels which are degenerate. Why because other levels are far away. So, they are not going to have effective mixing at the zeroth level; so we will consider only those levels that are degenerate.

So, at k equals π/a , we will consider levels k equals π/a and k equals minus π/a . Similarly, at k equals minus π/a we will consider k equals minus π/a and k equals π/a . These are the levels which are degenerate because energy depends on k square and k is equal to k plus G .

(Refer Slide Time: 10:34)

$|k\rangle, |k'\rangle$ which are degenerate
 $E_k = E_{k'}$
 $H = H_0 + V(x)$
 $= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \sum_G V_G e^{iGx}$
 If the energy of the state formed by making linear combination of $|k\rangle$ & $|k'\rangle$
 $\hookrightarrow E$
 $H|\psi\rangle = E|\psi\rangle$

So, how do we apply degenerate perturbation theory? What we do is; so I have two levels k and k' which are degenerate and; that means, that E_k equals $E_{k'}$. Given the Hamiltonian which is H_0 plus $V(x)$ which is minus \hbar^2 cross square over $2m$ d^2 by dx^2 plus this summation $\sum_G V_G e^{iGx}$ I will consider only two levels

k and k' what we do is if the energy of the states formed by making linear combination of k and k' is E . then I should have H the linear combinations ψ equals $E \psi$.

Let us see what does it lead to.

(Refer Slide Time: 12:03)

The image shows a whiteboard with the following handwritten equations:

$$\begin{aligned} |\psi\rangle &= a|k\rangle + b|k'\rangle \\ &= a|k\rangle + b|k+G\rangle \\ (H_0 + V(x))|\psi\rangle &= E|\psi\rangle \\ [H_0 + V(x)](a|k\rangle + b|k+G\rangle) &= E \times (a|k\rangle + b|k+G\rangle) \end{aligned}$$

Below these equations, two rows of terms are boxed in red:

$$\begin{aligned} \langle k| & a E_k^0 |k\rangle + a V(x)|k\rangle + b E_{k+G}^0 |k+G\rangle \\ \langle k+G| & + b V(x)|k+G\rangle = a E|k\rangle + b E|k+G\rangle \end{aligned}$$

So, I make a linear combination, ψ which is equal to some constant a k plus b k' and let me write this as a k plus b $k + G$ I know is $k + G$ for some G . G could be 2π by a minus 2π by a whatever. Wherever the degeneracy is there; then if I take H_0 plus V acting on ψ ; it gives me $E \psi$.

Then what do we do? We write H_0 plus V acting on a k plus b $k + G$ is equal to E times a k plus b $k + G$ and that gives me $a E_k^0$ when H_0 acts on k times k plus $a V$ k plus $b E_{k+G}^0$ $k + G$ plus $b V$ acting on $k + G$ is equal to $a E$ k plus $b E$ $k + G$. This is the working equation for the second order perturbation theory.

From this, I will once take the expectation value with respect to k and once with respect to $k + G$ and I will get two equations. Let us do that now.

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$$\begin{aligned}
 & \left. \begin{aligned}
 a E_k^{(0)} |k\rangle + a V(x) |k\rangle \\
 + b E_{k+G}^{(0)} |k+G\rangle + b V(x) |k+G\rangle
 \end{aligned} \right\} = E a |k\rangle + E b |k+G\rangle \\
 \langle k| & \quad a E_k^{(0)} + b \langle k|V(x)|k+G\rangle = a E \\
 & \quad a (E_k^{(0)} - E) + b V_G = 0 \quad \text{--- (I)} \\
 \langle k+G| & \quad b (E_{k+G}^{(0)} - E) + a V_G = 0 \\
 & \quad a V_G + b (E_{k+G}^{(0)} - E) = 0 \quad \text{--- (II)} \\
 \text{For } a \neq 0, & \quad b \neq 0 \quad \left| \begin{array}{cc} E_k^{(0)} - E & V_G \\ V_G & E_{k+G}^{(0)} - E \end{array} \right| = 0
 \end{aligned}$$

So, the equation I am working at is $a E_k^{(0)} |k\rangle + a V(x) |k\rangle + b E_{k+G}^{(0)} |k+G\rangle + b V(x) |k+G\rangle = E a |k\rangle + E b |k+G\rangle$. So, this whole thing is equal to $E a |k\rangle + E b |k+G\rangle$. If I take the expectation value or multiply this by $\langle k|$ I get, $a E_k^{(0)} + b \langle k|V(x)|k+G\rangle = a E$ gives me V_G which we have taken to be 0 plus k plus G inner product is 0 and I get plus $b k V(x) |k+G\rangle$ is equal to $a E$ which I can write as $a E_k^{(0)} - E + b V_G = 0$ and this expectation value would be V_G . Let us say k should be equal to, it will be $V - G$ is equal to 0.

Similarly, if I take the expectation value $k+G$, I will get $b E_{k+G}^{(0)} - E + a V_G = 0$. Let me rewrite this bringing a first. So, I will rewrite this as $a V_G + b (E_{k+G}^{(0)} - E) = 0$, the same equation. So, I have equation, this is my equation number 2, this is my equation number 1 and if a and b have to be non-zero the determinant of the coefficient must vanish. And therefore, for $a \neq 0$ $b \neq 0$, I should have $(E_k^{(0)} - E)(E_{k+G}^{(0)} - E) - V_G^2 = 0$ and that will give me the energy eigenvalues. Let us see what these are.

(Refer Slide Time: 16:59)

$$\begin{vmatrix} E_k^0 - E & V_{-G} \\ V_G & E_{k+G}^0 - E \end{vmatrix} = 0$$

$$(E_k^0 - E)(E_{k+G}^0 - E) - \underbrace{V_G \cdot V_{-G}}_{V_G = V_G^*} = 0$$

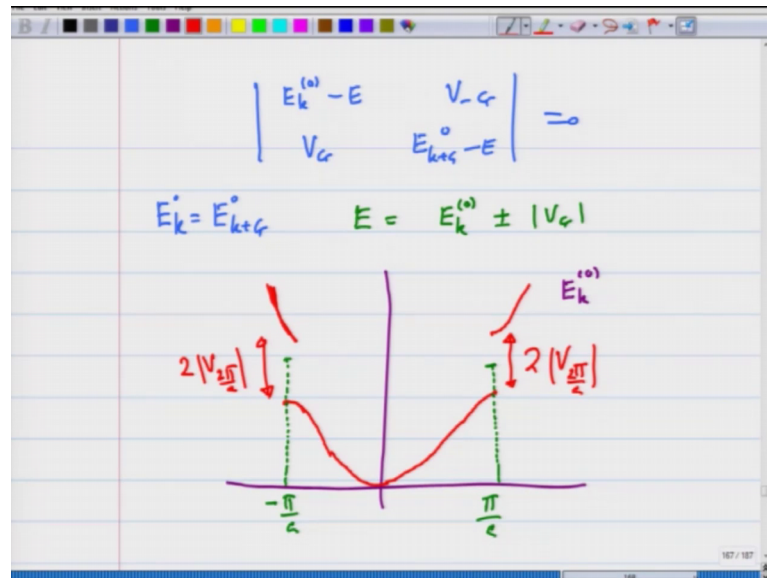
$$(E_k^0 - E)(E_{k+G}^0 - E) - |V_G|^2 = 0$$

Since $E_k^0 = E_{k+G}^0 \Rightarrow (E_k^0 - E) = \pm |V_G|$
 $E = E_k^0 \pm |V_G|$

So, I have to determine energy eigenvalues $E_k^0 - E$, V_{-G} , $E_{k+G}^0 - E$, V_G , $E_{k+G}^0 - E$ minus V_G times V_{-G} is equal to 0. Recall from earlier because the reality of V_x ; we have $V_{-G} = V_G^*$ and therefore, this equation becomes $(E_k^0 - E)(E_{k+G}^0 - E) - |V_G|^2 = 0$. This is a quadratic in E and therefore, it gives me two eigenvalues.

So, let us now look at that. What it gives me? It gives me since $E_k^0 = E_{k+G}^0$. This implies that I get $E_k^0 - E = \pm |V_G|$ or $E = E_k^0 \pm |V_G|$.

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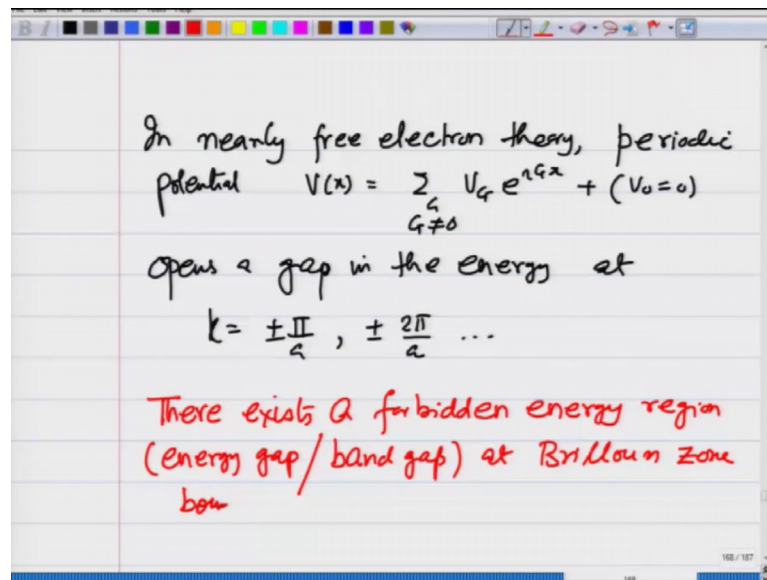


So let us see when I solve this, $E_k = E_{k+G}^{(0)}$ and $E = E_k^{(0)} \pm |V_G|$. I am taking into account that we have $E_k = E_{k+G}^{(0)}$ at the zeroth level, I get $E = E_k^{(0)} \pm |V_G|$; that means, I get two eigenvalues.

So, if I will go back to that curve which I had plotted at zeroth level which was $E_k = E_{k+G}^{(0)}$ and we had problems at $k = \pm \frac{\pi}{2}$. The energies actually is not equal to this $H = \frac{\hbar^2 k^2}{2m}$ at these two eigenvalues because these two k values; because energies are degenerate. What happens instead is that this energy starts deviating and goes low. This energy starts deviating and goes low. Whatever I have done here for k , it applies equally well to $k = \frac{\pi}{2}$ or $k = -\frac{\pi}{2}$ taking appropriate G and the other eigen value opens from the top and this energy becomes like this, this energy becomes like this other places it is not affected.

So, now I am going to erase the middle thing and show you what the energy structure now looks like. I am going to erase this part and plot the energy like this and it opens up here and again goes on top whereas, where this gap is $2|V_{\pi/2}|$. This gap here also $2|V_{\pi/2}|$. You can show similar thing for other case where they are near the Brillouin zone boundary.

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So what have you learnt? In nearly free electron theory periodic potential $V(x)$ equals summation G ; G not equal to 0 $V_G e^{iGx} + V_0$ we have taken to be 0 because shift in the potential opens a gap in the energy at k equals plus minus π by a . It will also open it at plus minus 2π by a because I can add G equals 4π by a and get degenerate eigenvalues and so on.

So, now the energy eigenvalues are no longer continuous; they are discontinuous at Brillouin zone boundaries. So, there exists a forbidden energy region or a energy gap or a band gap at Brillouin zone boundaries. This is the conclusion of this lecture; we will make it more rigorous in coming lectures.

Thank you.