Introduction to Solid State Physics
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Lecture – 56
Applying perturbation theory to free electron wavefunctions and nearly free electron model

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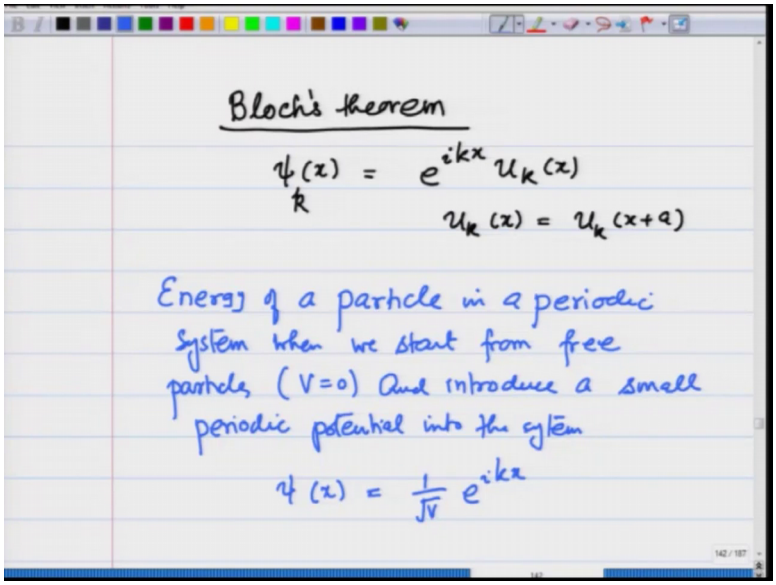

Recall from the previous lecture that I had stated what Bloch's theorem for wave function is for a single particle, it says that psi x is going to depend on a parameter k is going to be of the form e raised to i k x U k x, where u k is a periodic function. As I said in the previous lecture, I am focusing only on one-dimensional cases. Now, this is the form of the wave function. This is mathematically proved and I argued it from the symmetry that if you move the lattice by its periodicity nothing really changes in the system from that we argued, and then we proved Bloch's theorem.

Now, I am going to take a slightly different route, and build up to it again from a different root. So, we are now going to focus on energy of a particle in a periodic system, when we start from free particles or electrons, which means V equals 0 and introduce a small periodic potential into the system.

So, now I am coming from a very different approach and earlier I actually showed that what the wave function form should be like. Now, I am approaching this problem from the point of view, I have a system which has free particles, and now I introduce a very small periodic potential in the system. So, to start with I have wave function psi x, which is 1 over root V e raised to i k x. And now I introduce this potential. So, what happens, let us see what happens.

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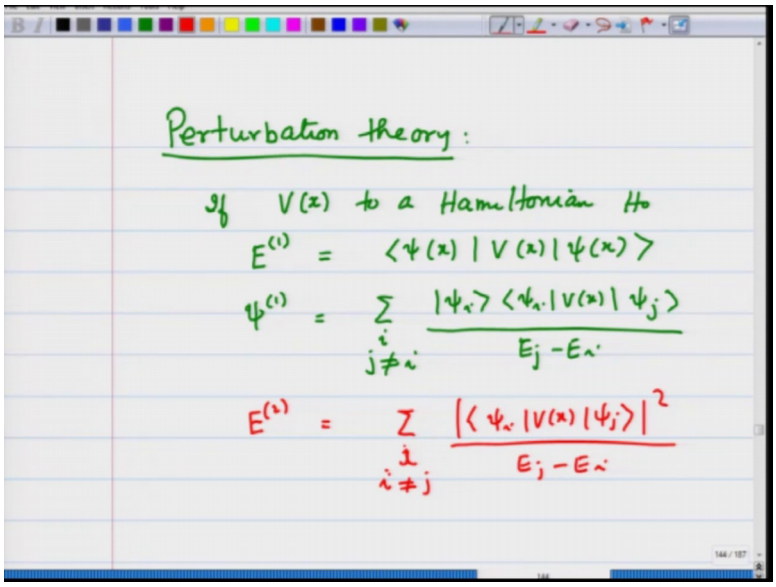

So, we are going to use the method of perturbation theory in quantum mechanics, which says that f a small potential V x is introduced to a Hamiltonian H 0, then the first order energy change in the system, I will write it as V is equal to the wave function psi x V x psi x. The first order wave function is summation i psi i psi i V x and I started with let us say j divided by E j minus E i j not equal to i.

And the second order change in the energy is equal to summation i psi i V x psi j mod squared over E j minus E i i not equal to j. So, I am summing over all these is all the states and finding out what the second-order changes. So, this is how I can calculate the energy up to the second order when I apply a small perturbation. Let us see what happens in the case of this crystal.

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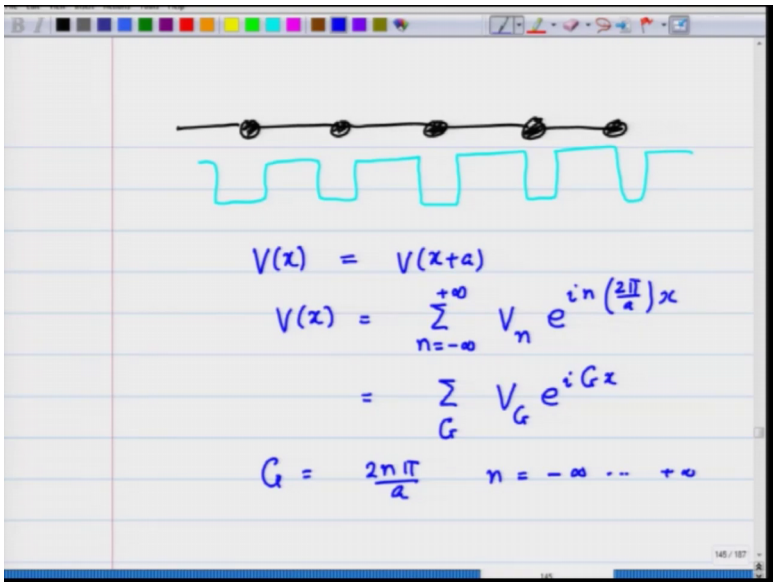

So, in this crystal, I have this periodic potential, which I keep making with the potential being periodic, I am really making it flat, it does not matter its only symbolic and so on. V x, since it is periodic with period a can be written as V x equals summation n equals minus infinity to plus infinity V n e raised to i n 2 pi by a x. Let, me write this as summation G, where G is the reciprocal space vector V G e raised to i G x, where G is 2 n pi over a, and going from minus infinity to plus infinity, this is the potential.

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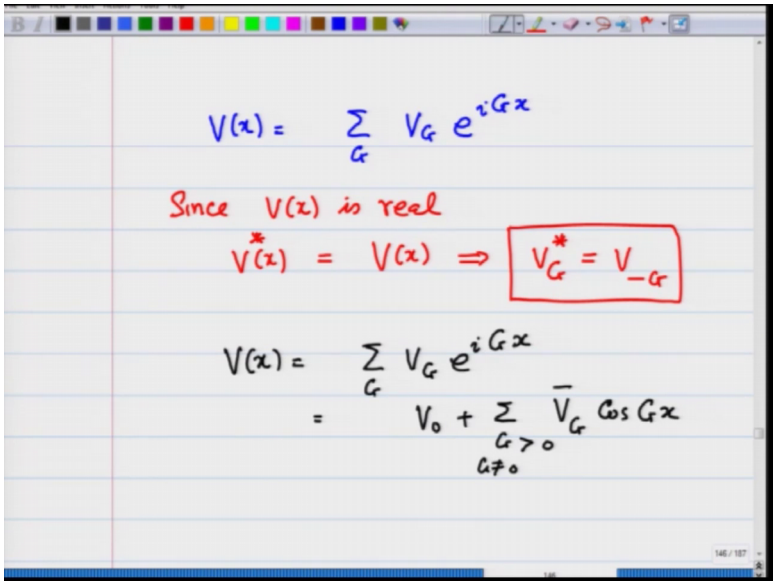

So, let me write it again since the potential is periodic, I can write V x as summation G, G spans all the reciprocal space vectors V G e raised to i G x. Now, since V x is real that means, V x star a complex conjugate is same as V x. So, this implies V G star is going to be equal to V minus G this follows from the potential being real. So, I have this periodic potential with vg equals minus G, I could also have written this in a slightly different form, I could have written this as V x is equal to which is summation G V G e raised to i G x.

I could have written this as some other constants. Let us call them V bar G, some V 0 plus summation G G naught equal to 0, 0 and G only greater than 0 0 some V bar G cosine of G x is the same thing, because V x is real. So, V G bar would be something there you are. So, I could have written these two forms, which is a periodic potential. Now, I am applying this periodic potential to the homogeneous gas or free electron gas.

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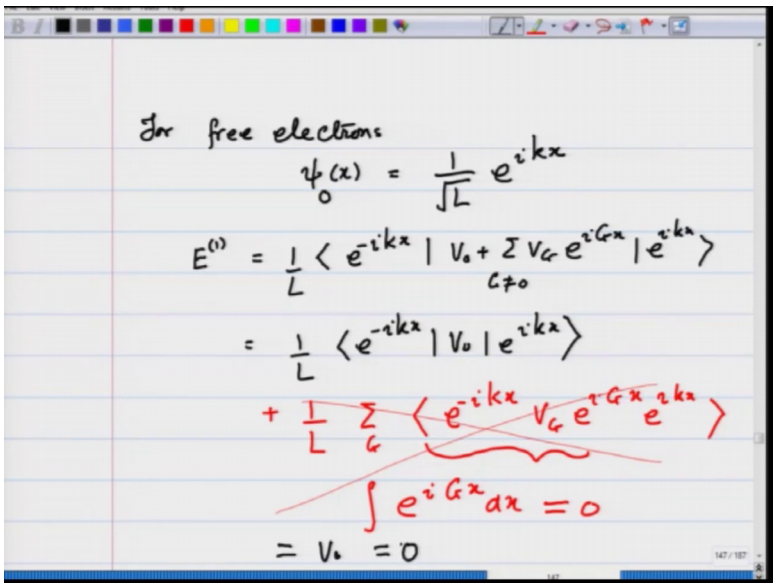

So, for free electrons, the wave function size 0 0 in the language of perturbation theory was equal to 1 over root L e raised to i k x. And therefore, E 1 is going to be 1 over L e raised to minus i k x V 0 plus summation V G G naught equal to 0 e raised to i G x e raised to i k x. This I can write as 1 over L e raised to minus i k x V 0 e raised to i k x that is the first term plus the second term 1 over L summation over G e raised to minus i k x V G e raised to i G x e raised to i k x, this expectation value, G is not equal to 0.

Since G is not equal to 0, we have this term, which is like the integral e raised to i G x dx, and for G naught equal to 0 over, the length with periodic boundary condition this is going to be 0. And therefore, all these terms that I have taken they give me 0. And E 1 comes out to be just a constant E 1 comes out to be a constant equal to V 0. So, the first order energy change in this periodic potential is just a shift of the energy, and I may as well take this V 0 to be 0, because shift of energy by a constant does not really matter, potential anyway is defined up to a constant. So, I can take this constant to be 0.

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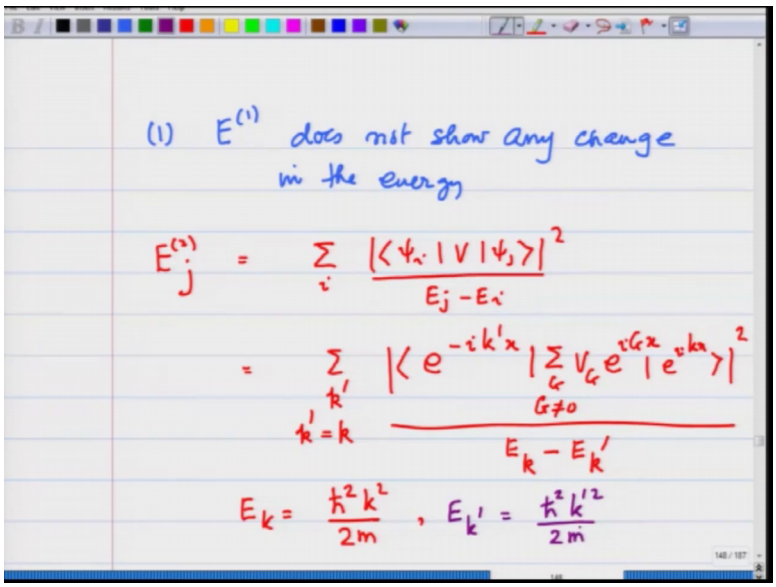

So, point number 1, E 1 does not show any change in the energy. So, I have to go to the next order. Let us go to the next order. Let us calculate e 2, which is equal to summation i psi i V psi j mod square over E j minus E i, and this is for j at level, so which in the language of the case and all that we are talking about is going to be summation k prime k prime not equal to k e raised to minus i k prime x summation g vg e raised to i G x.

And I can now write G not equal to 0, because I have excluded that using the first order perturbation theory e raised to i k x mod square divided by E k minus E k prime, where E k is equal to h cross square k square over 2 m and E k prime is equal to h cross square k prime square over 2 m.

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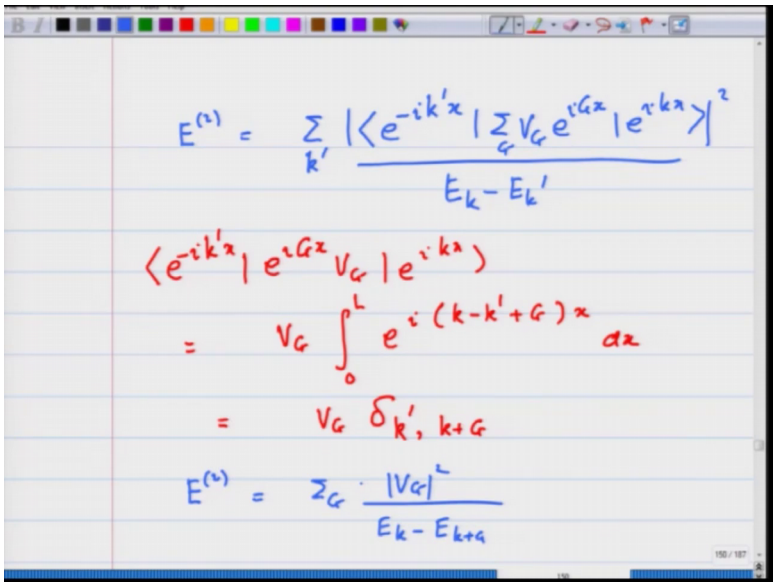

So, I am writing second order change in the energy as E 2 is equal to summation over k prime e raised to minus i k prime x summation G V G e raised to i G x e raised to i k x divided by E k minus E k prime, which I can write or mod square here, which I can write in the form of the integral. So, let me write that now. So, I am going to write e raised to minus i k prime x e raised to i G x V G e raised to i k x is equal to V G integral e raised to i k minus k prime plus G x dx, where the integral dx is over this entire length over, which I apply the periodic boundary conditions.

So, I can write this as 0 to L. This you have done again and again in your free electron theory. So, I am not going to actually go over how to evaluate this integral, but I know this is going to be V G times delta k prime comma k plus G with all the normalization 1 over L and everything taken care of. So, this is non-zero only when k prime equals k plus G. So, I can write energy E 2 as summation G V G square over E k minus E k plus G summed over all the Gs, this is the second order energy.

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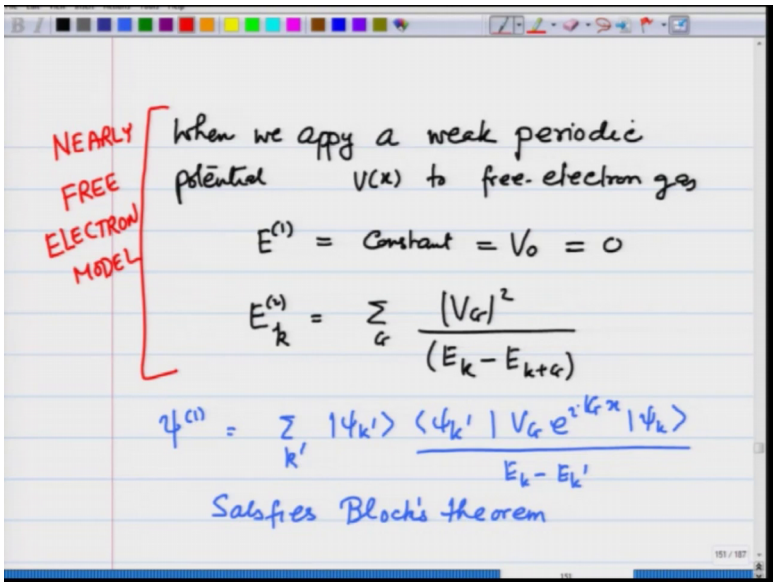

So, to summarize this lecture, I am going to write that when we apply a weak periodic potential, V x to free electron, yes, E 1 comes out to be a constant equals V 0. And we take this V 0 to be 0. E 2 comes out to be summation over G V G squared over E k, this is energy for kth level minus E k plus G. And we are going to see its repercussions in the next lecture.

By the way I should also mention that if I calculate psi 1, which is nothing but summation k prime psi k prime psi k prime V G e raise to i G x psi k over E k minus E k prime, you can easily show that this satisfies theorem. And now let me give all this a technical name, when we take this potential to be weak, this is known as nearly free electron model. And it works well for metals where this potential can really be weak. We will slowly build up from here and go to cases when the potential becomes strong what happens, but this is a good learning example as to what happens when you introduce a weak potential how the energies are affected.