Electronic Theory of Solids
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Lecture - 04
Schrodinger Equation: Boundary Conditions

Hello welcome to today's lecture. Today what we will do is we will now come out of this relaxation time approximation and free electron gas and try to understand the physics of electrons in a material, in a condensed system; at the moment we will only consider solids. So, why do you want to abandon the free electron model? Not that we are abandoning it, but there are so many results that did not come out right using classical gas approximation for electrons along with relaxation time approximation, that one realized that this is not the correct approximation, the correct theory of metals electrons in metals and then of course, one has to go beyond. And, the first signature that this theory of classical gas is not the right theory came when the specific heat of many metals were measured and it was found that the estimate from classical theory is hugely large very large. It is hugely overestimating the specific heat in most cases and then of course, there are many other issues that came out.

For example: the magneto-resistance. Magneto-resistance in this theory, we did the hall effect and we showed that it should not be that the rho of x x, the magnetoresistance isa function of field, in the longitudinal direction: the resistance along the direction of current in transverse field should not be field dependent; should have no field dependence in it. Whereas, the actual measurements show that there is indeed a field dependence to the rho x x.

So, there are so many such problems, then there is the conductivity for example. Drude model gave as a conductivity formula n e square tau by m for dc conductivity and of course, also gave ac conductivity formula, but those formulas were not fitting the experiment. There are temperature dependences, there are frequency differences; that means, energy dependences which were not coming out to be correct.

So, the obvious solution, when quantum mechanics came in around 1925, was that use quantum mechanics to describe these systems, these collection of electrons, and it was because electrons are fermions - spin half fermions and one immediately realized that a classical approximation would not do. Then Sommerfeld of course, was the first to pick up the cue and did a calculation for the specific heat which we will show at later class. And, came out with at least the temperature dependence, the linear temperature dependence correctly: though the coefficient was still not agreeing with many experimental facts.

Now, to do a quantum mechanical theory of a large number of electrons, one has to make again some assumptions and the obvious assumptions people did in the beginning was that these electrons are independent again. They are just like the gas of electrons that we were doing, but in with a quantum mechanics. That means, Pauli principle built into it. Then what you have to do is to solve the Schrodinger equation instead of any classical equation, Newton's law for example.

Instead of taking a collection of electrons which are interacting with each other and interacting with the lattice, one still works with the assumption that these electrons are free, they are independent, but they obey quantum mechanics; that is the first approximation that we are going to do now.

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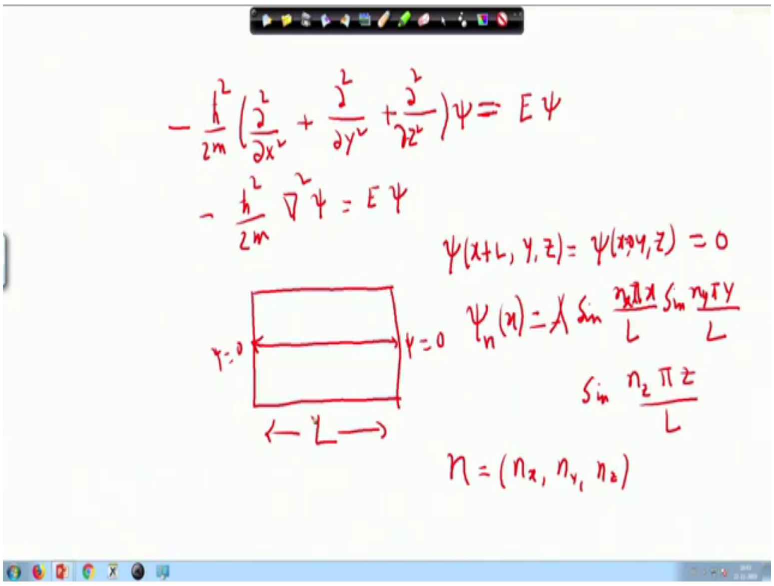

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$$

$$\psi(x+L, y, z) = \psi(x=0, y, z) = 0$$

$$\psi_n(x) = A \sin\frac{n_x \pi x}{L} \sin\frac{n_y \pi y}{L} \sin\frac{n_z \pi z}{L}$$

$$n = (n_x, n_y, n_z)$$

So, the equation that the electrons are now supposed to follow is basically Schrodinger equation. This is the del square operator psi equal to E psi. So, then of course, we know that this can be written as the del square of psi equal to E psi. The solution to this will be the one that we are after, but this solution is quite straightforward because there is no potential here. So, energy is constant. So, we know the solution will depend on the boundary condition, either it will be a standing wave or it will be a travelling wave. One can choose the solution depending on the boundary condition.

The obvious boundary conditions that one can think of are basically two; one is suppose this is my solid and these are the two boundaries and the electron is confined within this boundary. It is 0 outside and it is whatever is the solution of Schrodinger equation inside. Now, this we know gives us a standing wave kind of solution and that solution is a standard solution which let me write down for this boundary condition.

So, this boundary condition is psi at x. So, this is suppose the length of the system, it is extended in three directions, it is a cube. So, x plus L y z equal to psi of x y and z and psi for both are equal to 0 because at x equal to 0 and at x equal to L, psi is zero. So, at the two boundaries the wave function vanishes. It is like putting an infinite potential at the boundary.

Now, if this is the solution then of course, the wave function is psi (x) equal to some constant, which has to be determined from the normalization, times sin n_x pi x by L. Similar conditions in the y and z direction give sin n_y p y/L and sin n_z pi z/l. So, let me write it sin (n_x pi x/L)sin (n_y pi y/L) sin (n_z pi z/L) where n x, n y, and nz are integers. So, I put an n here. This number n = (n x, n y, n z) and these are positive integers other than 0.

Now, this solution is a standing wave solution. It had to be because the wave function has to vanish here and vanish here and it bounces back and forth. So, it forms a standing wave, but this is not very useful for calculating, for example, transport where you have to carry charges from one side to the other, carry energy, and so, one chooses a different boundary condition which is more handy and more useful.

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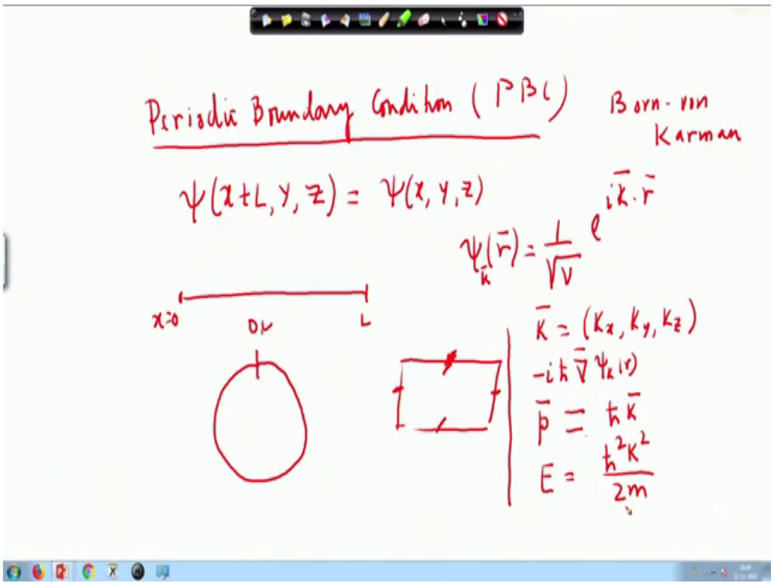

Periodic Boundary Condition (PBC) Born-von Karman

$$\psi(x+L, y, z) = \psi(x, y, z)$$

$$\psi_{k}(\bar{r}) = \frac{1}{\sqrt{V}} e^{i\bar{k}\cdot\bar{r}}$$

$$\bar{K} = (K_x, k_y, k_z)$$

$$-i\hbar\bar{\nabla}\psi_k(r)$$

$$\bar{p} = \hbar\bar{K}$$

$$E = \frac{\hbar^2 K^2}{2m}$$

So, let me just do that. That is called the periodic boundary condition. It is also called Born -von Karman boundary condition, PBC or Born von Karman boundary condition. Now, this boundary condition, let me write down again in terms of psi of x plus L, then I will explain what it means: psi(x+L, y, z) = psi(x, y, z). So, what does it mean? Let us just look at in one dimension.

So, at any value, x equal to 0 this equates 0 to L. So, as if the electron moves from here; suppose it moves from x equal to 0 to L, it leaves L and then reappears through x equal to 0. That means, there is no boundary anymore right. The effect of boundary is already gone in this way of looking at things even under these boundary conditions. Not that the boundaries are not important, they have become important in the last fifteen years or so.

Nevertheless this is the one that we will use and so, this boundary condition basically connects the two sides; that means, a line now becomes a circle. So, whatever was 0 is also the L. So, the electron moves in a circle and I can have a travelling wave solution similarly for y and z direction. So, in two dimension for example, I can still imagine the geometry the topology of this boundary condition. So, what I will do is that I will equate this boundary with this boundary and that boundary with that boundary.

So, it is like a torus, but in three dimension of course, the topology is too complicated and we cannot sort of imagine it, but assume that that is the boundary condition. So, in that situation, the wave functions can be chosen as we did in one dimensional quantum mechanics. We can choose a wave function psi of r vector r is equal to 1 by root v e to the power i k dot r. Now, the value of the k is basic is k x k y k z. So, from here I can easily find out certain quantities because I know the operator for example, for momentum. Momentum operator is minus i h cross grad. So, if that operates on this psi. Let me put a k index here because it also depends on k; k is something we will determine from the boundary condition. It has the dimension of momentum of course.

So, i h cross grad psi of psi k r will give you p as h cross k. So, p will become h cross k and energy is basically that from the Schrodinger equation it itself. You can get operating by del square operator is becoming h cross or you can also use h cross p square by twice m h cross cross square k square by twice m. So, this is still a free particle. Its momentum is h cross times k and its dimension is inverse of wavelength and this is inverse of length basically. So, k is 1 by lambda, usually we write 2 pi by lambda.

Now, p is h cross times k and E is equal to h cross square k square by twice m. So, this is what these things are, that we will be using.

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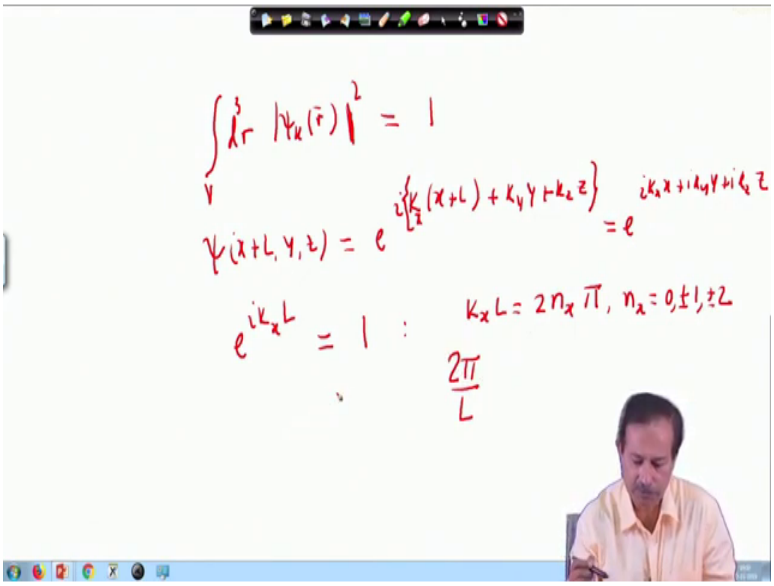

$$\int_V d^3r \, |\psi_k(\bar{r})|^2 = 1$$

$$\psi(x+L, y, z) = e^{i\{k_x(x+L) + k_y y + k_z z\}} = e^{ik_x x + ik_y y + ik_z z}$$

$$e^{ik_x L} = 1 \; : \quad k_x L = 2 n_x \pi, \; n_x = 0, \pm 1, \pm 2$$

$$\frac{2\pi}{L}$$

So, the other thing that I wanted to mention was that the way I have chosen this wave function is such that d 3 r mod psi k square over a volume v is equal to 1. So, that is the normalization 1 by root v that I chose. So, that this integral becomes 1. The electron is somewhere in the volume v where we do not know it is a plane wave solution because you can see that, it is h cross e to the i k dot r. Now, I have to determine the allowed values of k from the boundary condition.

Now, why did I say allowed values of k? Because we already knew from one dimension: one dimensional examples that not all k values are allowed. So, let us see what k which k values do we get from the boundary conditions x plus L y z equal to e to the power i kx x plus L plus ky y plus kz z equal to e to the power i kx x plus i ky y plus i kz z. That means, e to the power i kx L is equal to 1 which means simply that k dot L k x into L equal to 2 n x into pi where n x can now be 0 plus minus 1 plus minus 2 and so on integer,

So, similarly k y and k z will be give me the same relation. So, the so boundary condition now tells me that there are these each k value is restricted should be it between n x equal to 1 and n x equal 2. So, there is a distance of 2 pi by L for each 2 pi by L distance, I will get 1 k value. So, in one dimension and in 2 and three dimension, it will become a become area two pi by L into two pi by L and then 2 pi by L cube. So, this actually very is important because I will start counting the number of states in d k space.

So, that is something that is an extremely important quantity is often called density of states and that that counting is useful in calculating integrals involving physical properties of solid electrons in solids ok. So, my 2 pi by L is. So, let me just show you in a view graph, how does it look like.

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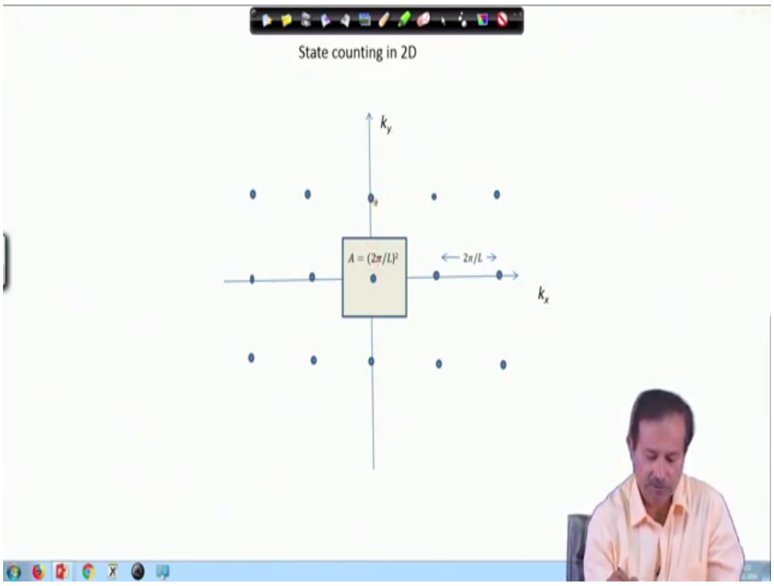
State counting in 2D

Here for example, this is the state counting. So, we are counting the state. What did this previous page tell us? It told us that there are these points in the k x direction for example, though this is a two dimensional case. So, along kx in each 2 pi by L distance, there is one point and these are allowed values of kx, no kx values between these two points are allowed.

Similarly along the ky direction between two ky values, there are no other ky values allowed; that means, this shaded area which has area 2 pi by L square contains only one allowed k = (kx, ky) value. So that means, in two dimensions for 1 k value, I need an area of 2 pi by L square. Similarly, in three dimensions for 1 allowed k value, I will need a volume of 2 pi by L cube. So, 8 pi cube by L cube. Now L cube is the volume. So, let us just go back to what we were doing.

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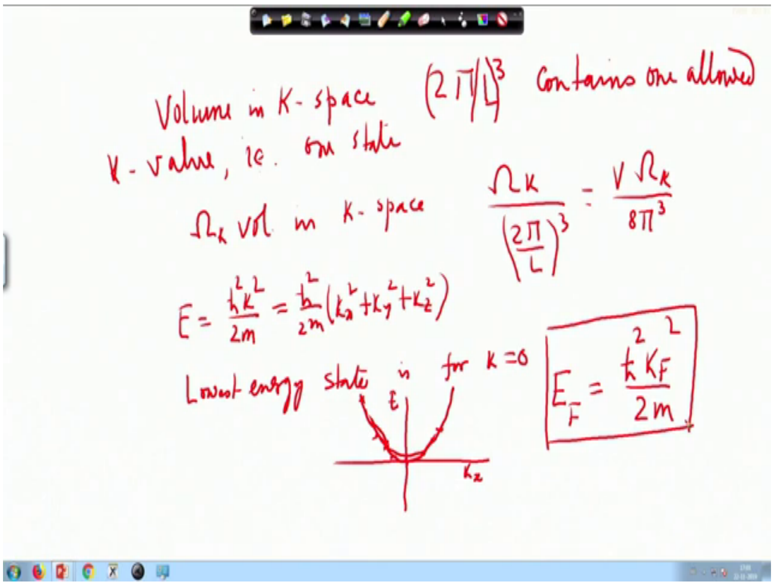

Volume in K-space $\left(\frac{2\pi}{L}\right)^3$ contains one allowed k-value, ie. one state

Ω_k vol in k-space

$$\frac{\Omega_k}{\left(\frac{2\pi}{L}\right)^3} = \frac{V\Omega_k}{8\pi^3}$$

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

Lowest energy state is for $k=0$

$$\boxed{E_F = \frac{\hbar^2 k_F^2}{2m}}$$

What I will do now is that, as I just showed that 2 pi by L, a volume in k space 2 pi by 2 pi by L cube contains one allowed k value; that means, one state. So, that means, for each state I need this volume; this value contains one state. So, suppose I have omega k volume in k space. How many states will that contain will simply be this divided by 2 pi by L cube which is V times omega k times 8 pi cube

That gives me the number of allowed states in a volume omega k in the k space. Remember, this V is the real space volume. Now the interesting thing is that how do I now put the electrons in these allowed states? Since E equal to h cross square k square by twice m, two things are interesting.. Two things have to be noted: one is that the Energy h cross square by twice m into k x square plus k y square plus k z square. So, the constant energy surfaces are surfaces of a sphere in the momentum space.

Since the energy just depends quadratically on a k, it is like take any sphere of radius k, on the surface of that sphere the energy value does not change although k x, k y, k z will change. So, for all k's on that surface the energy remains the same. The other thing is that the k, the lowest energy state is for k equal to 0 which is the 0 energy state. So, we are looking at the ground state (at 0 temperature) and this is the first state that we have to fill in because that is the lowest energy state. And we know for example, in one dimension this k square spectrum is like a parabola, E versus k. Suppose I am working in one dimension, then my allowed k values are here, here… suppose these are my allowed k values. So, how do I fill in these states? All I do is that I put electrons in each of the k space starting from the lowest allowed k-state.

So, if k equal to 0 is allowed, then I will put in k equal to 0. So, in this way 0 energy state is the k equal to 0 state. I go ahead and fill in. This is called the filling of the states. I basically fill up all these states from the lowest energy. Now, the interesting thing is that again in three dimension for example, all the k's you fill up which correspond to same k square will give me the same energy. So, that is something we have to remember.

Now, if we go on filling very large number of states, like I mean there are 10 to the power 23 order of particles. So, that many atoms, each atom contributing at least even one state will give me a very large number of states. The other way to put it is 2 pi by L cube; L cube is the volume. So, that volume is very large compared to the dimensions we are discussing, the wavelength of electrons.

The number of states that we are having here is exceedingly large and then they are extremely densely packed in the sense that the difference between k states is very very small and in such case, it will look very symmetric; there is no anisotropy in any direction as the energy goes as k square. So, the way I fill up the states in momentum space is basically like a sphere.

So, if I fill up all the states that I needed to fill to occupy my n electrons, then the final surface, the highest energy surface in the momentum space, will be a sphere; obviously. This spherical surface; suppose its energy is E_F, then E_F is called the Fermi energy and that surface that separates the unoccupied states from the occupied states in the momentum space is called the Fermi surface. In this case, it is a spherical top surface of a sphere.

Now, if so, I can write down the E_F in terms of h plus square K_F square by 2 m. So, the argument is now I suppose it is clear that I have very large number of states and the separation between states is 2 pi by L which is exceedingly small compared to the volumes we are talking about and so many states have to be filled up. And then it will look like a sphere and the spectrum is a quadratic spectrum.

So, the way you fill it in will finally be the occupied part of the allowed states in the momentum space and it will look like a sphere. And, the highest energy which is the energy of the last occupied states on this sphere is called the Fermi energy and this surface in the momentum space of that sphere is separating the occupied from the unoccupied states and it is called the Fermi surface.

Now, these two things, Fermi energy and Fermi surface, have a lot of bearing on almost every calculation you do with electronic properties of solids and we will use some of these things now. First thing I have to do is to count the number of states because they are very densely packed. I can define a density of states: how many states are there between two spheres radius k and k plus dk, for example. That gives me the number of allowed momentums in an annulus whose width is just dk.

Similarly, I can also calculate the number of states between two energies which is E and E plus dE and these number of states are very large too. They are very dense. So, it makes sense to talk about the density of states rather than sum over every state. Suppose you want to do an integral or a sum, you can go over every k value, but then the k values are 10 to the power 22 - 23 order. So, instead, you convert it into an integral and then you are required to know what is the density in a region of k space or in an energy interval between E and E+dE.

That is what we are after now.