Introduction to Solid State Physics

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Lecture – 12
Introduction to Sommerfeld's Theory of Electrons in a Metal Part- II

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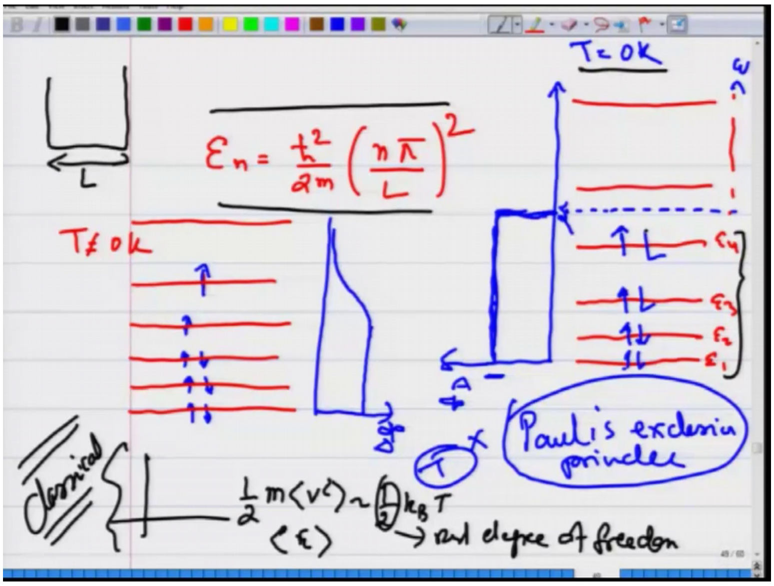

We were looking at a particle confined in a one dimensional box and in that one dimensional box, if you consider the quantum mechanical nature of the particle, you get the energy eigenstates which are available inside that box which is this E 1 E 2 E 3 and these are the energy eigenstates which we had derived for the particle in this box. One dimensional box, these are the energy eigenstates and now you start putting in many particles. As you start putting in particles more than 1, then they will start distributing amongst the energy states available and that distribution is going to be given by the Fermi Dirac distribution and each state is going to be occupied by 2 particles.

So, the Fermi Dirac distribution will be governed by that all the states below a chemical potential will be completely occupied and the above ones will be unoccupied and this is the situation at temperature T equal to 0. The situation changes a little bit when you apply a temperature of finite temperature to the system and then, the particles which are near the higher energy state they start distributing around the chemical potential, there is this distribution that some of the higher states also start getting occupied because the thermal energy excites these particles to the higher unoccupied states and there is a distribution which develops there. And so, this is how you have energy states inside the system and how the particles are distributed amongst these available energy states. This is as far as this 1 D box is concerned. And so, the particle can get a significant higher energy these are the particles which are sitting at E 4 they have significant higher energy compared to these particles.

But these particles have reached this just because of Pauli's exclusion principle. You cannot put more particles here. So, they have to go to the next state and the next state. So, the average energy of the particles in the system increases because of Pauli's exclusion principle. Just the Pauli's exclusion principle increases the average energy of the particles which is governed by this particular statistics and these principles. Whereas, if you recall in the Maxwell distribution, the Maxwell's distribution has given us a relationship that average energy square would be like half kBT per degree of freedom. The average energy was governed by the temperature, the average energy of the system is very much a function of temperature this was the classical situation.

And which was there in the drudes picture which we have to avoid and this is what was realized by Sommerfeld and he came up with the Somerfelds model of a particle in a metal. And what is the nature of distribution of energies which the particle in a metal undergoes. Now before I go further I have been telling you about this concept of a chemical potential, which is very close to the maximum energy which the particles have inside the system which is this chemical potential mu.

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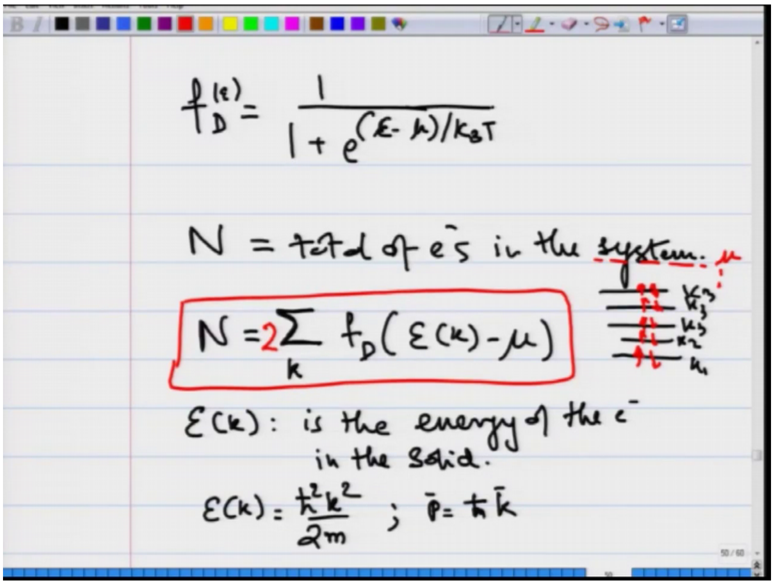

$$f_D^{(\epsilon)} = \frac{1}{1+e^{(\epsilon-\mu)/k_BT}}$$

N = total of e^-s in the system.

$$\boxed{N = 2\sum_k f_D(\epsilon(k)-\mu)}$$

$\epsilon(k)$: is the energy of the e^- in the solid.

$\epsilon(k) = \frac{\hbar^2 k^2}{2m}$; $\bar{p} = \hbar \bar{k}$

And this chemical potential is there in the Fermi Dirac distribution as 1 plus e raised to E minus mu by kBT. This is in the Fermi Dirac distribution. And this mu how do we define it? We define it through again the total number of particles.

The total number of particles if you count the total number of particles which are filling up to the maximum energy in the system up to mu if you count the total number of particles, then these should be equal to the total number of electrons which are present inside the system. If you count how many are present in this energy state plus the number which are present in this state plus this state plus this state, the total has to be equal to the total number of particles inside the system.

So, if N is the total number of electrons in the system, then mu is the chemical potential mu is such that N is equal to summation over all the states which are present inside the system f D where E k is the energy of the electron in the solid. You know that for a free electron what is E? The energy of the particle the energy of the particle is a function of the wave vector k it is h cross square k square by 2 m, where the momentum p of the particle is h cross k this is the momentum of the particle and I will be often calling momentum with k.

In the course of the next few lectures, because k and momentum are just related by a constant. So, instead of saying k as a wave vector I will just call it as momentum often. So, the energy of this free particle is very much related to k and if I So, I have summed it if I look at this expression, the energy of each particle in a state k if I sum up all those particles where k is the label of the state and the occupancy if I sum up all this then, so, there are states which are occupied; this is k 1 k 2 k 3 k 4 these are momentum states inside the system which are occupied by particles whose occupancy is given by the Fermi Dirac distribution.

So, these are certainly occupied. So, there will be 2 particles. So, you will have 2 out here. So, 2 particles per state and these have probability 1. So, if I take a sum of all this then if I continue like this then up to mu, because above mu it will be 0 then the total number of particles this should be equal to the total number of particles. And that is the way we define the chemical potential mu. Through this counting expression that if you take the total of the number of particles which are occupying a given state through this expression, then you will get the total number of particles inside the system.

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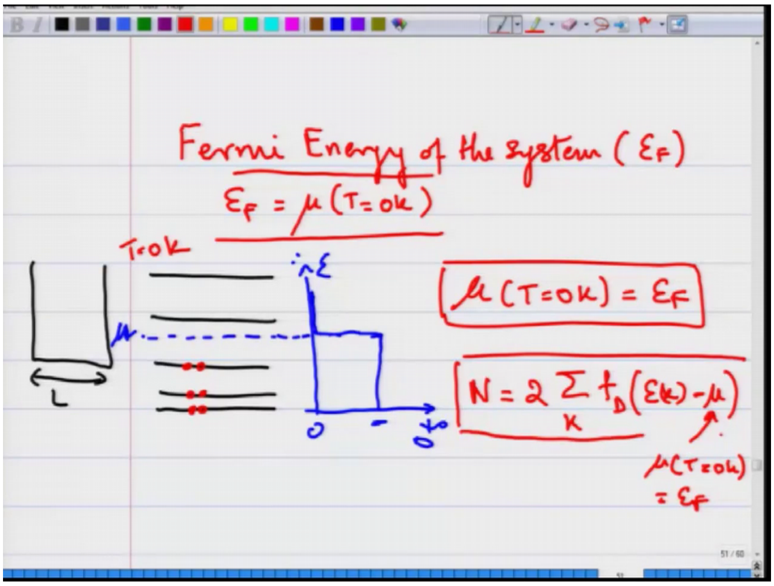

Fermi Energy of the system (ε_F)

$\varepsilon_F = \mu(T = 0K)$

$$\boxed{\mu(T=0K) = \varepsilon_F}$$

$$\boxed{N = 2\sum_{k} f_D(\varepsilon(k) - \mu)}$$

$\mu(T=0K) = \varepsilon_F$

Now, we define an important term which is the Fermi Energy of the system. It is denoted by E F. E F is equal to the chemical potential of the system at T equal to 0 Kelvin. If you recall that for a particle in a one dimensional box of length L, we had these different energy states and we had the that if you put in this is your Fermi Dirac distribution this is your energies and then they are going higher.

So, the distribution is going to be 1 up to a certain energy which is mu, the distribution is going to be 1 up to a certain energy which is mu out here up to this energy mu it is distribution and then it will be 0 this I have already shown here. So, when you start filling up there are two particles per state at this is at T equal to 0 Kelvin, then above mu it is empty and up to mu it is full. So, this was your chemical potential at temperature T equal to 0 and this chemical potential is close to the maximum energy of the particles which are present inside the system. So, this chemical potential at T equal to 0 Kelvin is defined as the Fermi energy of the system.

Namely what is an energy scale in the system which is close to the maximum energy of the particles present and we have an expression for the chemical potential, which for T equal to 0 we will write this expression for all states K the Fermi Dirac distribution Ek minus mu. Where mu is the chemical potential at T equal to 0 which is equal to the Fermi energy. You can of course, write this also for at other temperatures, but for the moment we will restrict ourselves to calculating it for mu equal to 0. So, now, let us try and find out what are the energy states which are available inside a 3 dimensional metal.

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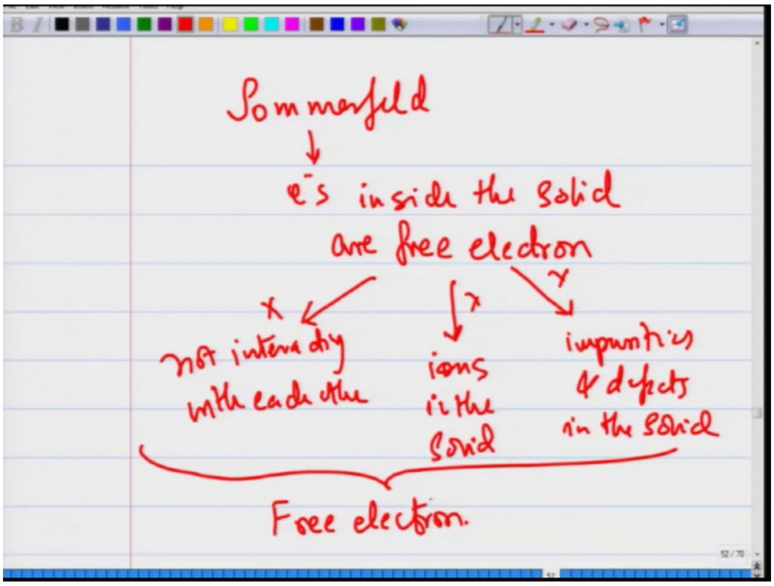

And this was the model proposed by Sommerfeld. So, Sommerfeld also proposed that the electrons inside the solid are free electrons namely they are not interacting with each other. So, they are not interacting with each other, they are not interacting with ions in the solid and neither are they interacting with impurities and defects in the solid. So, for all practical purposes the electron inside a solid is a free electron.

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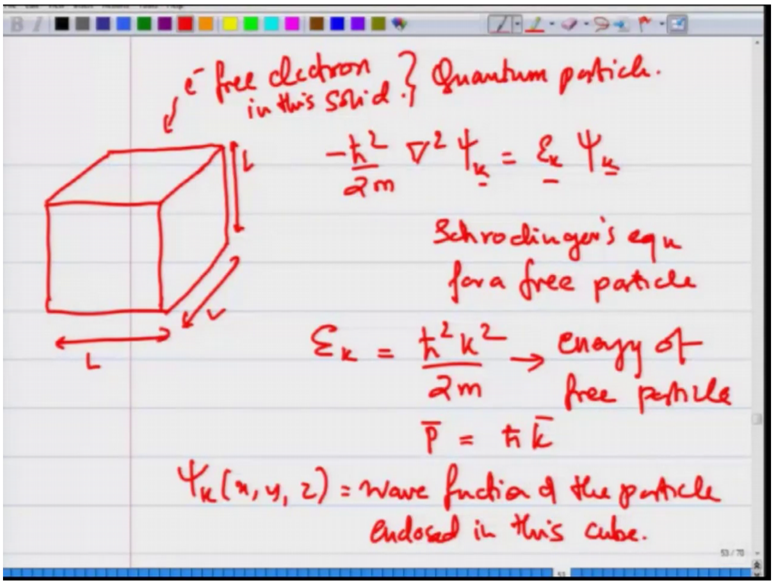

e^- free electron in this solid ? Quantum particle.

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\underline{k}} = \mathcal{E}_{\underline{k}}\psi_{\underline{k}}$$

Schrodinger's equ for a free particle

$$\mathcal{E}_k = \frac{\hbar^2 k^2}{2m} \rightarrow \text{energy of free particle}$$

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

$\psi_k(x, y, z)$ = wave fuction of the particle enclosed in this cube.

So, consider the solid as a 3 dimensional cube and for simplicity, we consider it as a cube with sides of length L, the electron is a free electron in this solid. It is a quantum particle. So, its energy states will be governed by the Schrodinger's equation which is minus h cross square by 2 m del square psi k is equal to E k psi k.

Where this is the wave function of the electron with carrying a momentum k and with an energy eigenstate E k. As you can see this is the Schrodinger's equation for a free particle, it does not experience any potential. So, there is only a kinetic energy term which is minus h cross square by 2 m del square psi and this is the energy eigenstates psi. The energy of the particle is a function of the momentum and it is h cross square k square by 2 m this is the energy of a free particle, where the momentum is equal to h cross k and psi is the wave function of the particle xyz is the wave function of the particle enclosed in this cube.

So, let us calculate what are the energy states which are available for the electron inside this solid. Are they a continue of states or are they discrete states which are available for the electron inside the solid.

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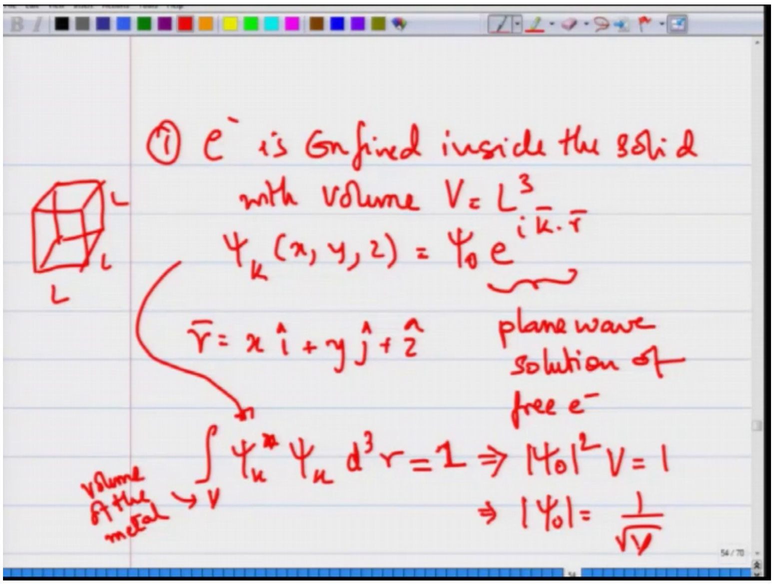

① e^- is confined inside the solid with volume $V = L^3$

$$\psi_k(x,y,z) = \psi_0 \underbrace{e^{i\bar{k}\cdot\bar{r}}}$$

plane wave solution of free e^-

$$\bar{r} = x\hat{i} + y\hat{j} + \hat{z}$$

$$\int \psi_k^* \psi_k \, d^3r = 1 \Rightarrow |\psi_0|^2 V = 1$$

Volume of the metal → V

$$\Rightarrow |\psi_0| = \frac{1}{\sqrt{V}}$$

So, one very important thing is that the electron is confined inside the solid with volume V equal to L cube. So, the electron you have this cube which is shown here.

And the electron is confined within this cube. It is not free to move outside the cube it is present only inside the cube. So, the ions actually pull the electron back before it can escape out from the solid. So, in that sense the electron is stuck within the cube, but at the same time the electron is free inside the solid, it does not experience any interactions with other ions inside the solid. So, the first thing is that the wave function is confined within this cube and the wave function that we will write for the solid is sum psi naught e raised to i k bar dot r bar this is the plane wave.

This is the plane wave solution the obvious solution for the Schrodinger's equation is this plane wave form where k is the momentum of the particle and this is the form of the and r is nothing else, but the position vector x i cap plus yj cap plus zk cap. Now because it is confined within the metal, the first thing that you can do is that you can normalize the wave function within this volume ok. So, if you normalize this wave function psi k star psi k d cube bar you normalize it within this volume of the metal v is the volume of the metal then this is equal to 1 which implies that psi naught if you put in this out here.

You will get psi naught square into the volume of the sample is equal to 1 which implies that psi naught is equal to 1 by square root v.

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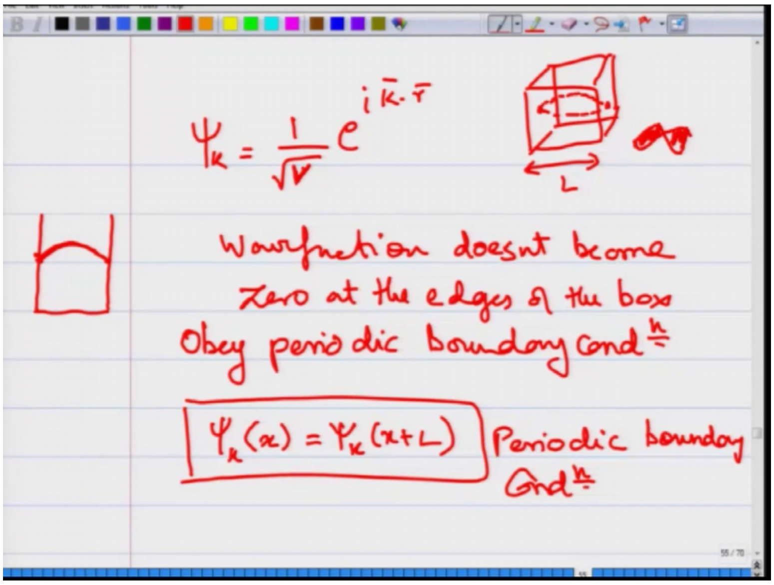

$\psi_k = \frac{1}{\sqrt{V}} e^{i\bar{k}\cdot\bar{r}}$

Wavefunction doesnt become zero at the edges of the box

Obey periodic boundary Cond$^{\underline{n}}$

$\boxed{\psi_k(x) = \psi_k(x+L)}$ Periodic boundary Cond$^{\underline{n}}$

So, I can immediately write down my free electron wave function inside the metal as 1 by square root of v; v is the volume of the sample e raise to i k bar dot r bar. Now, is there any conditions on the momentum of the particle or does the particle can take any value of momentum? If you recall that in a box we had actually stated that the wave function has to become 0 at the corners of the box.

This was explicitly imposed in the solution of the particle in a box problem, that the wave function becomes 0 at the corners of the box. What Sommerfeld considered was that, the wave function need not become 0 at the edges of the box; the wave function does not become 0 at the edges of the box or the cube rather the allowed wave functions are those which obey periodic boundary conditions.

So, in this cube of a solid at the edges of the cube the wave function need not become 0. The condition that was explicitly imposed for a particle in a box we need not impose that Schrodinger's equation that the wave function has to have nodes at the edges of the box rather if the box is of length L what he suggested was, to use a condition that suppose we are looking at a one dimensional situation then, the wave function at x should be periodic with a period equal to the length of the box. That psi k x should be equal to psi k x plus L. Now one of the reasons to avoid this sort of a condition namely the wave function becomes 0 at the boundaries would mean that you can have if the wave function became

0 at the boundaries, then it means that the electron would get reflected from the edges and the only solutions which are possible are standing wave solutions.

Namely you have waves which are standing waves energy is confined and there are no propagating modes inside the solid, you do not have propagating electrons or propagating waves inside the solid. So, if you impose the boundary conditions that the wave becomes 0 at the corners or the edges of the sample, then you will get standing solution standing wave solutions inside the solid which are to be avoided.

These are not good because then you do not have electrons propagating inside the solid, you know standing waves the energy is static the particles are just vibrating around those positions and you do not have a plane wave traveling through the solid.

So, rather than imposing a boundary condition that the wave function becomes 0 at x equal to L, he imposed the condition of a periodic boundary condition that the wave function at x is equal to the wave function at x plus L.

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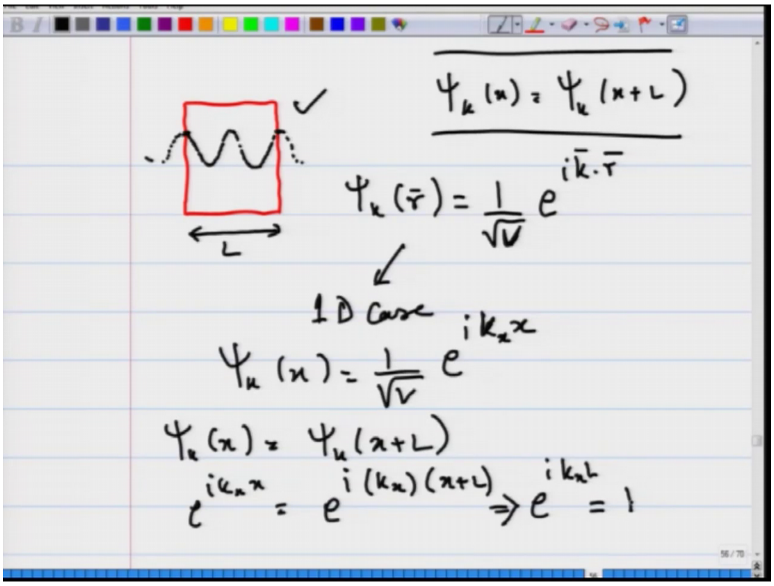

$$\psi_k(x) = \psi_k(x+L)$$

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

1D Case

$$\psi_k(x) = \frac{1}{\sqrt{V}} e^{ik_x x}$$

$$\psi_k(x) = \psi_k(x+L)$$

$$e^{ik_x x} = e^{i(k_x)(x+L)} \Rightarrow e^{ik_x L} = 1$$

And this if you would like considers that the wave function need not be 0 at, suppose this is a box of length L, then with this condition that psi k x equal to psi k x plus L what the states is that, the types of solutions which are possible is that you need not have x equal to 0 at the boundary.

You can have a solution of this form where this is a propagating plane wave, but at x equal to 0 and x equal to L, the wave is exactly identical or if you look at any x and if you go x at a distance L away the wave function is going to be exactly identical. So, as you can see that the wave function is not zero at the edges, but it is a propagating wave inside the solid and this is the solution that he introduced. So, this is an allowed solution and this imposes the periodic boundary conditions now impose conditions on the wave function. So, as I had said that the 3 dimensional form of the wave function, the 3 dimensional form of the wave function is psi k is equal to 1 by square root of v.

Where v is the volume of the sample E raised to i k bar dot r bar. Now if I make it into a 1 D case one dimensional case the wave function psi k x is 1 by square root of v e raised to i k x where x is the x component of the momentum along the x direction this is anyway the 1 D case. So, I did in give a subscript, but now if I introduce the condition that psi k x should be equal to psi k x plus L, what it implies is that e raised to i k x x is equal to e raised to i kx x plus L which tells me that e raised to i kx n should be equal to 1 or that k x should be 2 pi n over L.

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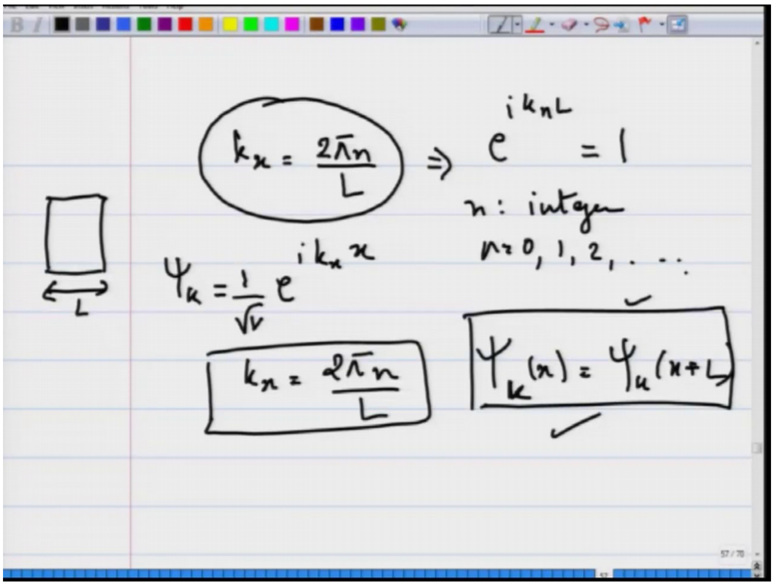

$k_x = \frac{2\pi n}{L} \Rightarrow e^{i k_n L} = 1$

n : integer

$n = 0, 1, 2, \ldots$

$\psi_k = \frac{1}{\sqrt{v}} e^{i k_x x}$

$\boxed{k_x = \frac{2\pi n}{L}}$

$\boxed{\psi_k(x) = \psi_k(x+L)}$ ✓

This will ensure that e raised to i kn L is equal to 1 because if you put in 2 pi over L you will get 1 and also for any integral multiples of where n is some integer n could be 0 1 2 and so on. So, these are the allowed momentum states which you can fit into this one dimensional metal of length L of length L if you want to fit waves, the waves have to satisfy psi k is equal to 1 by square root of v e raised to i kx into x where the momentous are 2 pi n by L.

These are the specific momentum states which can be fitted inside this box. Because they satisfy the condition that psi k x is equal to psi k x plus L and this is a very important boundary condition to be satisfied.