Properties of Materials (Nature and Properties of Materials: III)
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Lecture 35 - Free Electron Theory

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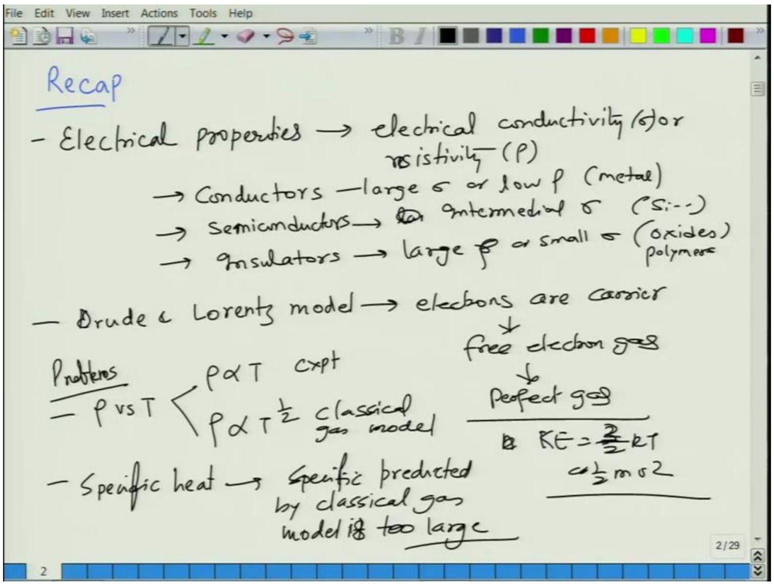

Recap

- Electrical properties → electrical conductivity (σ) or resistivity (ρ)
  - → Conductors — large σ or low ρ (metal)
  - → semiconductors → ~~for~~ intermedial σ (Si - -)
  - → insulators → large ρ or small σ (oxides) polymers
- Drude & Lorentz model → electrons are carrier ↓ free electron gas ↓ Perfect gas

Problems

- ρ vs T $\begin{cases} \rho \propto T & \text{expt} \\ \rho \propto T^{\frac{1}{2}} & \text{classical gas model} \end{cases}$

$KE = \frac{3}{2} kT$
$= \frac{1}{2} m v^2$

- Specific heat → Specific predicted by classical gas model is too large

So, welcome again to the new lecture of the course, Properties of Materials. Let us again recap what we did in the last lecture. So, in the last lecture, we began our discussion on electrical properties and here we are mainly interested in talking about electronic, electrical conductivity or resistivity. There are other properties as well that we can discuss, but our main concern here is only the electrical conductivity or resistivity, which is basically the ability of a material to conduct electricity.

So, materials which conduct electricity good, excellently they are called as conductors with large sigma or low rho which are generally metals. Then we have semiconductors which have intermediate sigma and these are generally things like silicon and then we have insulators which have large rho, sorry rho or small sigma such as you know oxides generally, such as quartz, polymers and so on and so forth they have. And that is the reason we use things like copper for conducting electricity whereas, oxides and ceramics or plastics for plugged option etcetera, so that they do not conduct electricity and gave us shocks.

So, different materials have different purposes whereas, semiconductors with lower with intermediate conductivity are used for semiconducting devices such as P-N junctions, etcetera. And then we looked at the Drude and Lorentz model on electronic conductivity assuming that electrons are the ones which conduct electricity in metals or in materials. So, we assume that electrons are carriers and these electrons make what we call as free electron gas which we assume to be a perfect gas.

But if you assume, which means a perfect gas will mean, each electron will have energy, kinetic energy of 3 by 2 k T or half m v square. What it suggest is that, then every electron occupies the same energy level and conducts and takes part in electronic conduction. But the problems arise. The problems which arise is that, one, the first problem is the behaviour of rho versus temperature. Experiment says that rho should be proportional to T, but the classical model says that, rho is proportional to T to power half. This is classical gas model.

And then we have this is experiment behaviour. Second is the specific heat, the specific heat, predicted by classical gas model is too large whereas, the experimental values are nearly 100 times lower. So, what are the reasons? And the reasons in summary is that, not all valence electrons take part in conduction. There is only a certain number of electrons which takes part in conduction and we are going to do that by invoking quantum mechanics which will explain that why is that these number of electrons lower which are actually taking part in electronic phenomenon.

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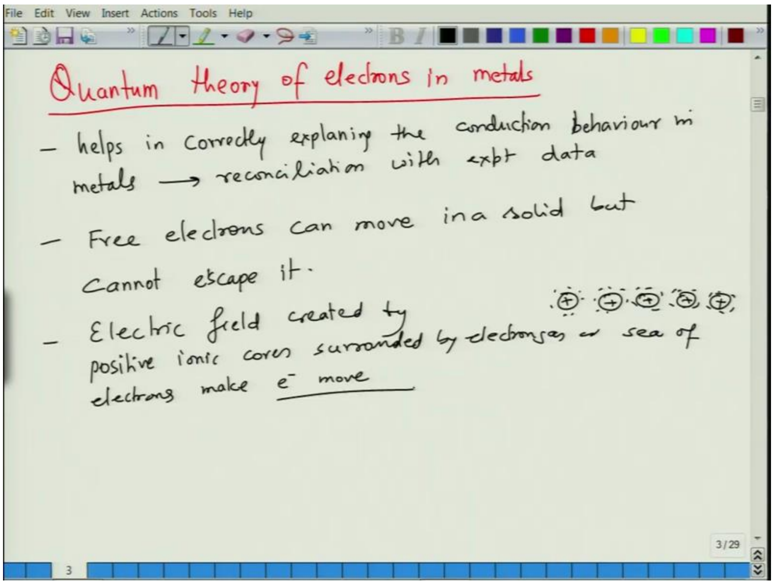

Quantum theory of electrons in metals

- helps in correctly explaning the conduction behaviour in metals → reconciliation with expt data
- Free electrons can move in a solid but cannot escape it.
- Electric field created by positive ionic cores surrounded by electrongas or sea of electrons make e^- move

So, this is where we invoke what we say is quantum theory of electron in metals. So, one way to go about quantum theory is to take the help of Schrodinger equation and do the wave mechanics. But we do not, I mean that is very that is more elaborate and beyond the scope of this course. So, here we will take a little bit of short cut and talk little bit more qualitatively about it. So, the first thing what quantum theory does is, it helps in correctly explaining the conduction behaviour in metals, reconciliation with the experimental data.

The problem with free classical gas model is the experimental data, you might you may have some match with experimental data provided if you happen to be at the same temperature where things match. But if they do not, then you have no match. And then another thing that it does is, it assumes free electrons are there, so, we still assume that free electrons are there, they are non-interacting. Free electrons can move in a solid but cannot escape it. So, if you have electrons in a solid bar, they are there in the bar but they cannot escape it.

An electric field is created by so, free electrons can move in a solid but cannot escape it. And the other thing is that electric field, so we have these, in a solid you will have these ions so, these ions are positively charged. And these are surrounded by these electrons. Electrons are negatively charged and the electric field which is created by positive ionic cores which are surrounded by let us say, this electron gas or you can say sea of electrons will make electron move.

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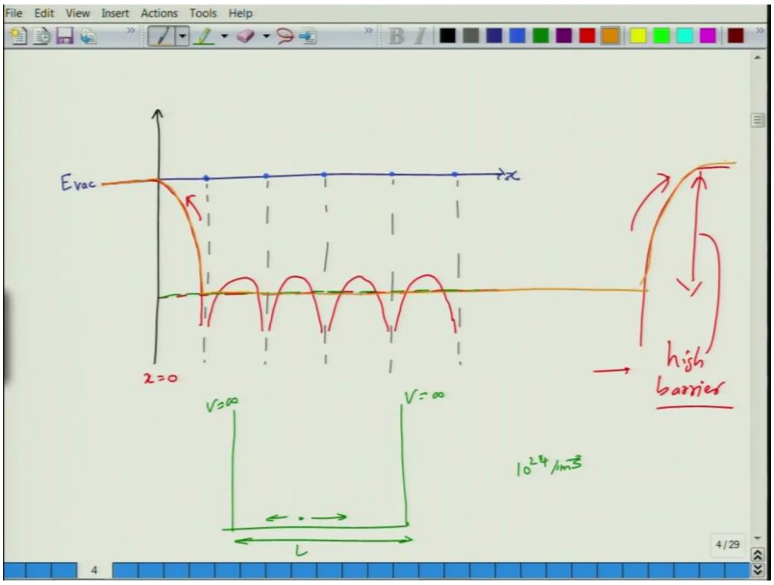

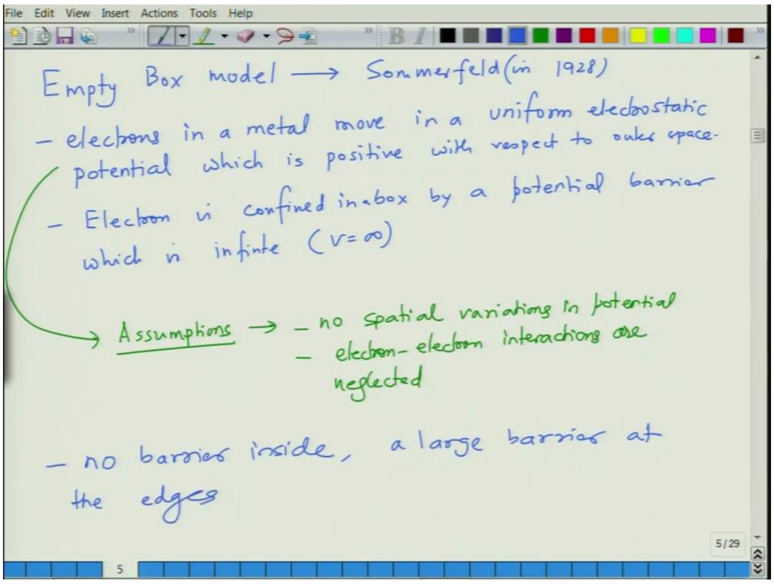

Empty Box model → Sommerfeld (in 1928)

- electrons in a metal move in a uniform electrostatic potential which is positive with respect to outer space.
- Electron is confined in a box by a potential barrier which is infinte ($V = \infty$)

Assumptions → - no spatial variations in potential
- electron-electron interactions are neglected

- no barrier inside, a large barrier at the edges

So, the situation is something like this, we have if you plot this potential as a function of distance, then let us say, this is the vacuum level so, this is the E vac and the atoms are somewhere here. This is first, this is second, this is third, fourth, fifth and so on and so forth and this is let us say the distance x. If you now plot the potential energy, if you now plot energy as a function of distance, the energy will go, it is very high at the edges.

So, this it cannot escape this part but it goes steeply near the iron core like this. And then it varies periodically within the solid. So, this is how it is going to vary and the other side at the other edge as well. So, this is the edge which is let us say, x is equal to 0. So, at x is equal to 0, that potential barrier is very high. Electron is going to move within this plane. So, this plane is something like, it is going to move within the solid but it cannot escape.

Similarly, on the other side as well you will again have high potential energy barrier on the other side if you go. So, electron basically on this and on this side the barrier is too high. This is very high barrier. You can say, high barrier, and electron cannot move this overcome this barrier. So, this model basically is a situation like this. So, you have this box of length L. this L is the length of the box.

This box may contain millions of atoms. I mean that the atomic density in a solid is 10 to power 24 per metre cube, something like that. So, it may contain several hundreds of thousands of atoms, but at the edge of this solid, the potential is very high. So, this is, v is equal to infinity nearly. So, electron can move within this but it cannot leave the solid. It cannot leave the edges. And this model is called as empty box model which is proposed by Somerfield in 1928.

So, electrons basically what it says that, electrons in a metal move in a uniform electrostatic potential. Realistically speaking, this potential is not uniform because you have ionic cores, you have (electronic) electron electron interactions. So, ignoring those effect of ionic ion to ion variations, ignoring the effect of electron to electron configuration, we assume that electron in a metal move in a uniform electrostatic potential.

So, what we see here, the variations which are these humps are there. So, instead of having these humps, what you are saying that there is a line like this. This is the uniform potential. So, the potential landscape is going to look something like this. So, you have something like this, then this and then you will have this. So, basically, you have averaged it out to a uniform potential. And so, electrons move in a metal or in a solid in a uniform electrostatic potential which is positive with respect to outer space, in terms of energy it is lower.

So, and you can say that electron is confined in a box by a potential barrier which is infinite, v is equal to infinity. So, what we have assumed here in this case is, one first assumption is, no special variations in potential which is not true but we have assumed because you have ions, you know that there is a variation of potential energy which is not true but we have assumed that it is true. And then electron electron interactions because electrons also repel each other. So, electron electron interactions are neglected.

So, basically, what we are saying in this empty box model in summary, there is no barrier inside and a large barrier at the edges. And so far we are taking only about one electron. So, let us describe first the situation for single electron.

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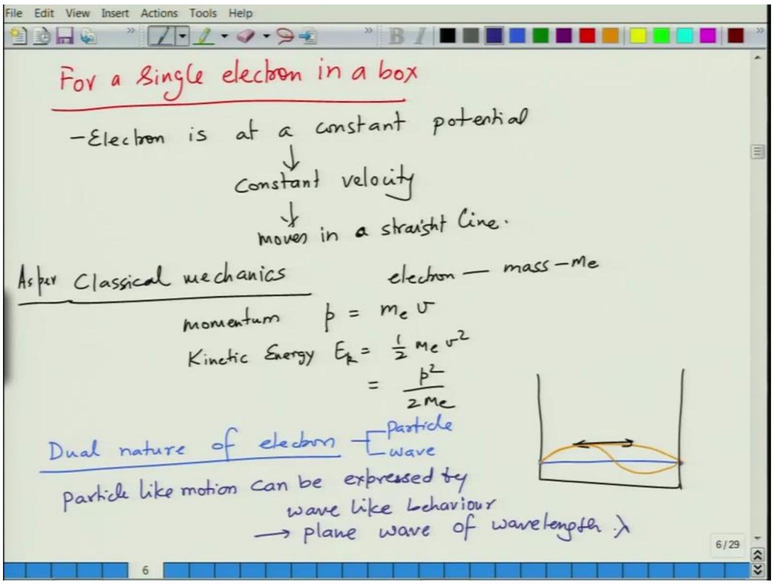

For a single electron in a box

- Electron is at a constant potential

$\downarrow$

Constant velocity

$\downarrow$

moves in a straight line.

As per Classical mechanics

electron — mass — me

momentum $p = m_e v$

Kinetic Energy $E_k = \frac{1}{2} m_e v^2$

$= \frac{p^2}{2 m_e}$

Dual nature of electron — particle / wave

particle like motion can be expressed by wave like behaviour

→ plane wave of wavelength λ

So, first the situation is for a single electron in a box. So, essentially, when you have electron in this single electron, it has it is in, let us say, it is infinite space at some constant potential. So, electron is at a constant potential, which means it has a constant velocity. And if it has a constant velocity, it also moves in a straight line. We just assume that it is a 1 D box. So, as per now, this is where we first bring classical physics in picture, classical mechanics. So, as per classical mechanics, let us say, electron mass is m e, the momentum of electron p can be given as m e into v and its kinetic energy E k can be given as half m e v square or we can write this as p square divided by m, sorry p square divided by 2 m e.

Now, this is where classical mechanics ends. Now, this is where we bring quantum mechanics into picture because if you have now situation like this, you have a box and you have electron moving back and forth. If it is, if you just take part particle like behaviour, it goes here there bounces back it goes there, go to other side and bounces back. This situation if you consider at dual nature of electron, considering now the dual nature of electron, which means that electron is a particle and a wave and this was proven and this was proven by diffraction patterns.

Because if it was a wave, then electron will diffract and it did show diffraction through lattices. So, there was a famous experiment that was Davidson experiment that was done. So, electron diffraction was proven by this time so, electron had this wave and particle duality, which means it is a particle but it is also a wave. If it is a wave, then this motion of electron within this box can be considered as if you have a rope tied on two ends, which means there is no freedom to rope on this.

But rope can undergo vibrations. The rope can go like this. It can have a wavelength like this. Rope can have a wavelength like this and so on and so forth. It can adopt many configurations. Essentially, if you consider this dual nature of electron then this particle like motion can be represented by the wave like nature of electron. So, we can say that particle like nature, particle like motion can be expressed by wave like behaviour. In this case, we take a plane wave of wavelength lambda.

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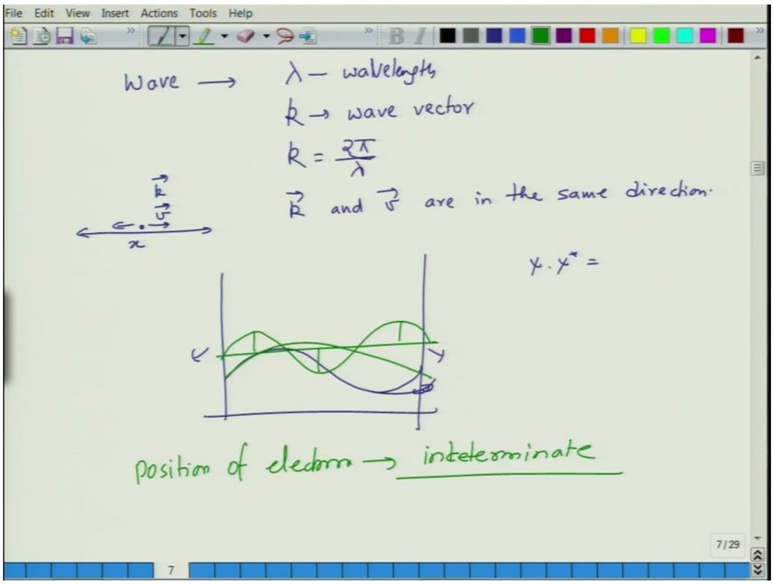

Wave $\longrightarrow$ λ — wavelength

$k \rightarrow$ wave vector

$k = \frac{2\pi}{\lambda}$

$\vec{k}$ and $\vec{v}$ are in the same direction.

$\psi . \psi^* =$

position of electron $\rightarrow$ indeterminate

For a wave, we know that lambda is the wavelength, which is also related to another quantity called as k, which is which is called as wave vector, where k is equal to 2 pi divided by magnitude of this wave vector is and since we are saying that electron is moving in this direction only, this is x. So, electron is moving in this direction only, which means, if it has a velocity v in this direction, the k is also in the same direction, which means k and v are in the same direction. So, k and v are in the same direction.

And this of course, this wave like duality can be expressed by what we call as de Broglie's relation. So, the problem with this, there is a problem however, we are saying that, in this case, the electron shows a wave like behaviour and you can have multiple configurations of the wave. The wave fills the whole space. As a result, you cannot find out the exact position of electron.

So, you do not know. You consider this as a wave. But if you want to determine where the electron is, it is not possible to determine the position. Because it shows the same wave line. If you so, it has a finite probability of finding everywhere, which means the product of so, size the wave function. If you product chi size star, chi size star is same everywhere, which means you cannot, the position the probability of finding electron is same everywhere.

So, you cannot find electron here, you cannot find electron here, so probability is 0 outside the box, but within the box, the probability is the same because this wave packet or wave fills the whole box and you can have this kind of configuration, you can have this kind of configuration, you can have this kind of configuration, and so on and so forth. And this and the amplitude of this is just this. This is the amplitude.

If you plot this chi sized star, you will get the same number everywhere. And chi is proportional to A and then chi star will be A square. So, as a result, the amplitude will remain the same. It will not be possible for you, we say indeterminate. What we so, basically we can say, the position is position of electron is indeterminate because of electron wave filling this space. Now, this is where we bring in now de Broglie relation.

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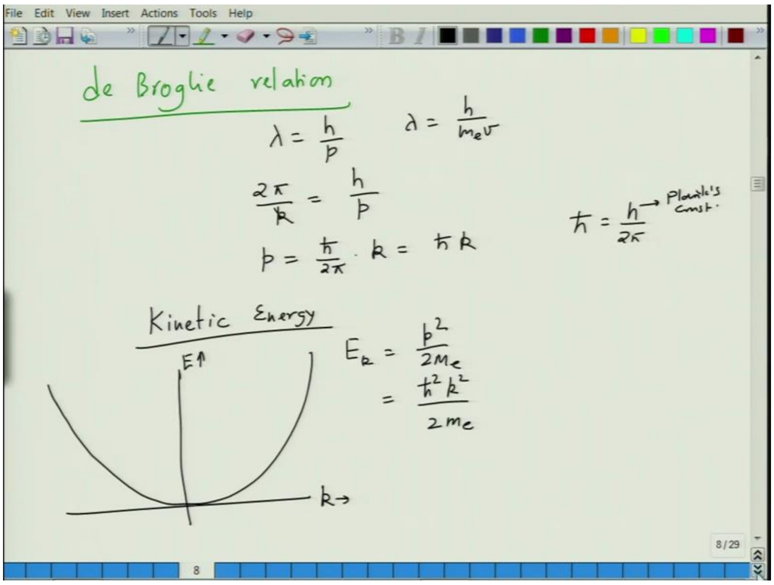

de Broglie relation

$$\lambda = \frac{h}{p} \qquad \lambda = \frac{h}{m_e v}$$

$$\frac{2\pi}{k} = \frac{h}{p}$$

$$p = \frac{\hbar}{2\pi} \cdot k = \hbar k$$

$$\hbar = \frac{h}{2\pi}$$ → Plank's const.

Kinetic Energy

$$E_k = \frac{p^2}{2m_e}$$
$$= \frac{\hbar^2 k^2}{2m_e}$$

The de Broglie relation says that, lambda is equal to h divided by p, which means lambda is equal to h divided by m e into v. But lambda is also equal to 2 pi divided by k and this is equal to h divided by p. So, we can say that, p is equal to h divided by 2 pi into k or you can say this is equal to h cross k, where h cross is equal to h divided by 2 pi, where h is nothing but Plank’s constant. So, kinetic energy now for electron, we wrote that E k was equal to p square divided by 2 m e.

So, this will be h cross square k square divided by 2 m e. So, if you plot the kinetic energy of electron as a function of k, it will go like this.

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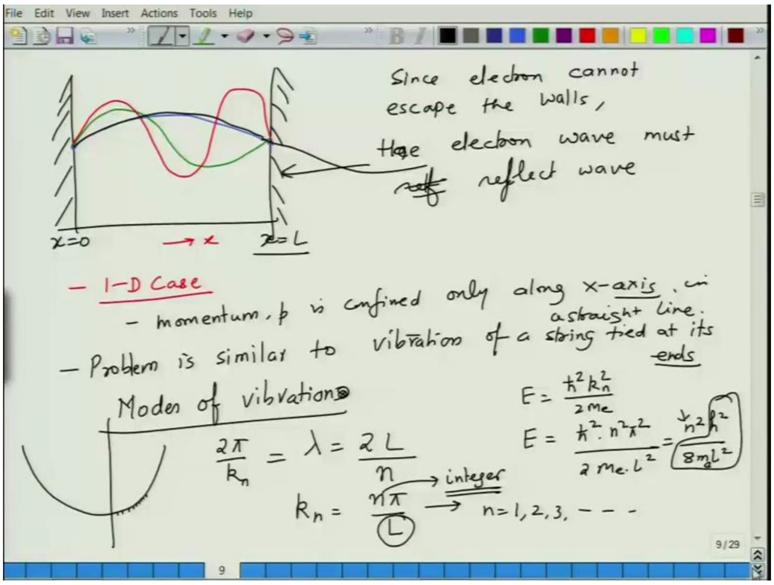

Since electron cannot escape the walls, the electron wave must ~~ref~~ reflect wave

- 1-D Case
  - momentum, p is confined only along x-axis in a straight line.
- Problem is similar to vibration of a string tied at its ends

Modes of vibrations

$$\frac{2\pi}{k_n} = \lambda = \frac{2L}{n} \xrightarrow{} \text{integer}$$

$$k_n = \frac{n\pi}{\textcircled{L}} \longrightarrow n = 1, 2, 3, ---$$

$$E = \frac{\hbar^2 k_n^2}{2m_e}$$

$$E = \frac{\hbar^2 \cdot n^2 \pi^2}{2m_e \cdot L^2} = \boxed{\frac{n^2 h^2}{8m_e L^2}}$$

Now, since electron cannot escape the box, since electron cannot escape the box so, this is the box which has rigid walls here, which means the wave must reflect back from the walls. So, since electron cannot escape the walls, the electron wave. Just like you know, if you have a big big jar, and you have some water there and you just shake it up, since water cannot go out, the waves which strike the wall they will come back.

So, it is like electron being a wave will also reflect back from the wall. And this leads to situation like this. So, now this is like having this string and this is string is, and you do not you do not allow the length of the string to change but you change the amplitude of the vibrations. As a result, the string may obtain a situation like it may have situation like this. It may have a situation like, it can have these various modes of vibration or it can have something, sorry, this is not very nicely drawn. Something like these.

So, these are the modes. So, if you take this, so we are taking first the 1 D case. We take this 1 D case, this is only along x direction. So, first we are saying it is 1 D case, which is momentum p is confined only along x axis in a straight line. And if it oscillates between the two points, so at x is equal to 0 and at x is equal to L, then there is a reflection of wave at the walls. So, this leads to reflection of wave at the walls. Now, this problem is similar to vibration of a string which is tied at its ends.

So, such strings shows various modes of vibration. So, as a result, you have now various modes of vibrations. And what you remember from your 12th physics for such a case, if you have various modes of vibration, which means the wavelength is integer fraction of the length. So, this wavelength lambda so, the maximum lambda that you can have is you can have, this is the case, then this will go to the other side. This lambda could be equal to 2 L for the first case.

And for the other successive cases for the first harmonic, for the second harmonic, for the third harmonic, or the first Eigen stage, second Eigen state, third Eigen state, this will become lambda divided by, lambda is equal to 2L divided by n. So, basically wavelength is the integral fraction of the length. What it means is that, now lambda is equal to 2 pi divided by k and just a small subscript n for different values of n. This k n will become equal to n pi divided by L.

And this means, so now you look at it. We say that h cross e is equal to h cross square k divided by 2 m e. We did not know that k is quantised or k is continuous. Now, we are saying that for a given length of the box, this L could be anything. It would be 1 metre, 2 metre, 4 metre, does not matter. For a given length, the values of n which it can, values of k which are permissible are the values defined by n which is a integer.

So, basically k value could only be n is equal to 1, 2, 3 and so on and so forth. What it tells us is that that this e now becomes h cross square into n square pi square divided by 2 m e into L square. Or this becomes n square h square divided by 8 m L square. So, this is constant, for a given material this is constant. m is m e basically. This is what it says is that, now this energies of electron is quantised. So, you have this multiple energy level for different values of n.

So, basically, there are multiple electron states which are discrete or quantised states of energy. There is no continuous energy. So, even when we say this e is equal to h cross square k square, all of these is basically quantised. They are different quantum values of L. There is one value, second value, third value, fourth value, they may be very close to each other. They may be very close to each other because remember the value of k is very small as compared to L.

So, they may be very closely spaced, but what it says is that, the energy is not continuous, it is energy levels are discrete, they are quantised. And this is what is an important outcome of quantum mechanics.

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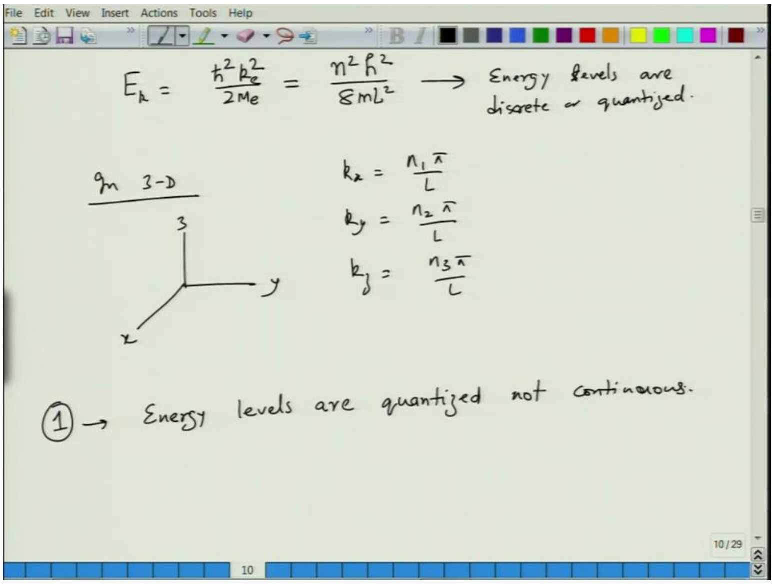

$E_k = \frac{\hbar^2 k_e^2}{2M_e} = \frac{n^2 h^2}{8mL^2} \longrightarrow$ Energy levels are discrete or quantized.

In 3-D

$k_x = \frac{n_1 \pi}{L}$

$k_y = \frac{n_2 \pi}{L}$

$k_z = \frac{n_3 \pi}{L}$

① → Energy levels are quantized not continuous.

So, what it says is that, energy E k is equal to h cross square k square divided by 2 m e, which for a box when electron cannot escape the solid is, n square h square divided by 8 m L square. So, basically, what it says that, energy levels are discrete or quantised.

This is the first observation that we observed. So, now if you want to do this in the 3 D, so in the 3 D, in 3 D basically the three directions so, you have x, you have y, you have z. Along the three directions now if you say, then the k x will be equal to n 1 pi divided by L. k y could be equal to n 2 pi divided by L. And k z will be equal to n 3 divided by into pi divided by L along the 3 directions of the assuming that it is a cube, where n 1, n 2, n 3 are the integers.

Another thing so, this is first thing is so, the first lesson that we have learnt is, number 1 is energy levels are quantised not continuous. Now let us say you have these n number of electrons. So, this is for 1 electron.

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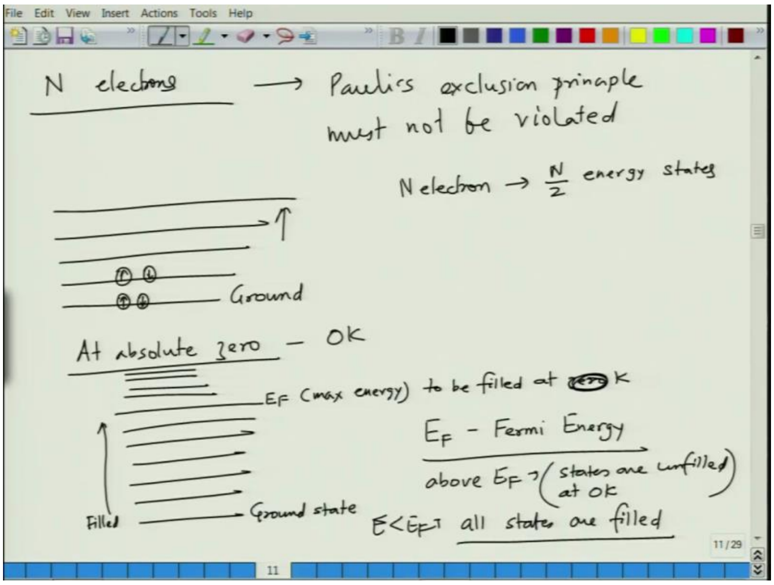

N electrons → Pauli's exclusion principle must not be violated

N electron → $\frac{N}{2}$ energy states

At absolute zero – 0K

E_F (max energy) to be filled at ~~zero~~ K

E_F – Fermi Energy

above E_F → (states are unfilled at 0K)

$E < E_F$ → all states are filled

Now, let us say we have n electrons. So, we start from the ground state. This is the ground state. So, if you have n electrons, for complete filling, how many energy levels will you need?

You need to obey what we call as Pauli's exclusion principle. This must be, must not be violated. Which means, no two electron of same quantum state can occupy the same energy level. So, which means, electrons will occupy in this fashion. So, you have 1 electron of up spin, 1 electron of down spin, that is it. Then you have here, you have here and so on and so forth. You keep filling these energy levels. So, if you have n electrons, you are going to require minimum of n by 2 energy states for complete filling.

You are going to require minimum of n by 2 energy states for complete filling in the space. So, as you so at absolute 0, it turns out. At absolute 0, it turns out, that is 0 kelvin. As you keep filling the electrons, as you keep filling, there is a maximum energy up to which you can fill. And this energy is called as this is ground state, minimum energy and this is the maximum energy that can be filled. Above this nothing is filled.

So, every state is filled so, this is filled, filled up to this point and this is the maximum energy state to be filled at 0 k. This is E F is called as Fermi Energy. So, you have quantised states, you have n number of electrons. As you keep filling them, those as you keep filling these discrete states of energy, you would require at least energy states up to E F for complete filling. Because every electron lies at certain energy level.

So, these are the minimum, these are the so, this is what is at 0 k. Energy states are also available above E F by the way, but nothing is filled at 0 k above E F. So, above E F states are unfilled at 0 k, they are empty. And E less than E F all states are filled. So, this is what it is. We have learned about the energy discretisation and how many energy levels can be filled at equilibrium up to 0 kelvin. Another thing that we did not talk about is density of the states.

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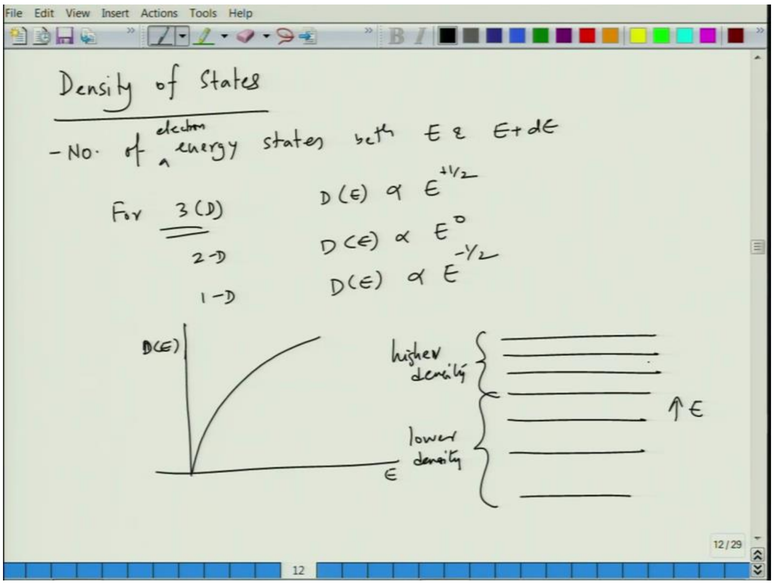

Density of States

- No. of electron energy states betw E & E+dE

For 3(D) $D(E) \propto E^{+1/2}$

2-D $D(E) \propto E^{0}$

1-D $D(E) \propto E^{-1/2}$

Density of the states is basically you can say, number of energy states which occur between an interval E and E plus d E of course, per unit. Number of electrons states with energy, number of electron states, electronic energy states we can say. So, this is electron energy states between E and d E. So, this density of the states n E for 3D, this we define this as D Eth. For 3D it is proportional to E to the power minus 1 by 2. For 2D, D E is proportional to E to power 0. And for 1D, it turns out to be, sorry, for 3D it is plus half, is this half. And if you plot this 3D, the density of the states will as a function of energy, so this is D E as a function of energy.

What it tells you is that, you are going to have more states available at higher energies than at lower energies. That is what it tells. So, basically you are looking at this thing is something like this. So, if this is E, at lower energy level, the density is lower. So, lower density you can say. And this is basically higher density. In the same interval delta E, you have more states available in this region than in other region. And this is what it means that, in a 3D solid, this is what happens.

So, we will not invoke density of solids here right now. We probably want to take much simpler route. What we have introduced is the concept of firm energy until now.

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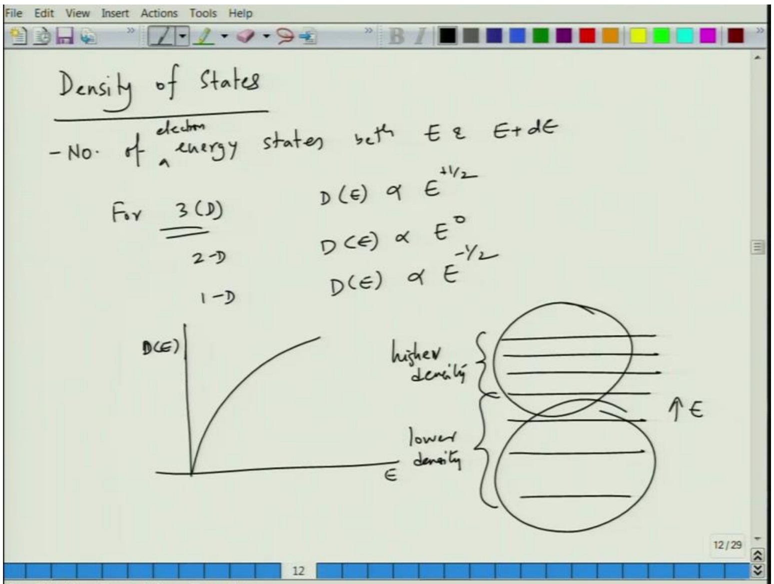


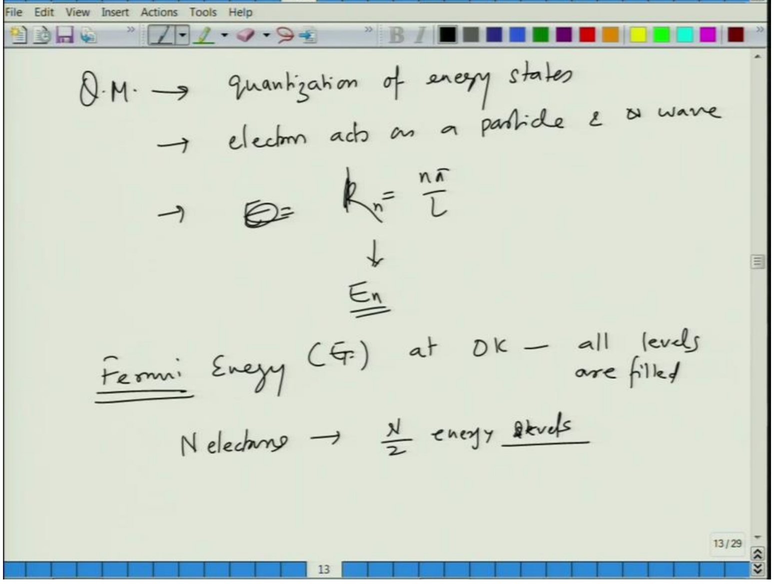
Density of States

- No. of electron energy states betn E & $E+dE$

For 3(D) $D(E) \propto E^{1/2}$

2-D $D(E) \propto E^{0}$

1-D $D(E) \propto E^{-1/2}$



Q.M. → quantization of energy states

→ electron acts as a particle & as wave

→ $k_n = \frac{n\pi}{L}$

$\downarrow$

E_n

Fermi Energy (E_F) at 0K — all levels are filled

N electrons → $\frac{N}{2}$ energy levels

And by introducing quantum mechanics, we talked about quantization of energy. They are not continuous, they are discrete electron and this was done by assuming that electron acts as a particle as well as the and as a wave. And it is only by assuming this wave like nature, because wave when it is in a confined box, it has to reflect back from the walls. You can further analyse its behaviour. If it was only particle, you could not go any further. So, that is where this wave like nature comes into picture and when you consider this wave like nature, then we come up this expression of various values of k. The wave vectors which are basically which represents various nodes of the waves, so the normal modes of the waves which are the Eigen states.

So, k basically is n pi divided by L. So, there are quantised value of k which gives rise to quantised value of energy. And then we said that, there is a Fermi energy up to which all the levels are filled at 0 k, all levels are filled. So, if you have n electrons, you are going to require minimum of n by 2 energy levels, energy states, energy levels because each level can occupy 2 electrons because of its spin up and down.

So, if you have n electrons below E F at 0 k, you are going to have n by 2 energy levels. And of course, you have free you have empty energy levels above E F also which gets, which get occupied as you increase the temperate and which is the point of discussion in the next lecture. So, with this we have sort of moved a little bit forward into the free electron theory of electrons, moving on from the Drude model which considers everything as classical gas where we assumed that every electron takes part in conduction.

Now, what we have done is, we have quantised these energy states, so one thing you can see is that, in this thing you are going to have some electrons with lower energy and some electros with higher energy. So, all the electrons will not be of same energy 3 by 2 k T. This sort of gives you an idea that if electrons are distributed all across these energy levels, as you increase the temperate, not every electron is going to go and conduct.

Only those electrons which are going to conduct are which are lined closer to E F. And this is what makes a fundamental difference between classical way of conductivity and quantum way of conductivity. Thank you.