Electronic Materials, Devices and Fabrication

Prof. Dr. S. Parasuraman
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture - 3
Density of States and Fermi - Dirac Statistics

Let us start with a brief review of last class. So, in last class we looked at semi conductors and how a band gap evolves in them. We took the example of silicon as a material. Silicon in the outer shell has 2 electrons in the S orbital and 2 in the P. The S and P orbitals hybridized to give you 4 S P 3 orbitals. In the case of a silicon atom, each silicon atom has 4 electrons in this S P 3 hybrid orbitals. So, you can form 4 bonds. So, if we have 2 silicon atoms, they form a bond between them. This forms the bonding orbital, which is the sigma and the anti bonding orbital that is the sigma star.

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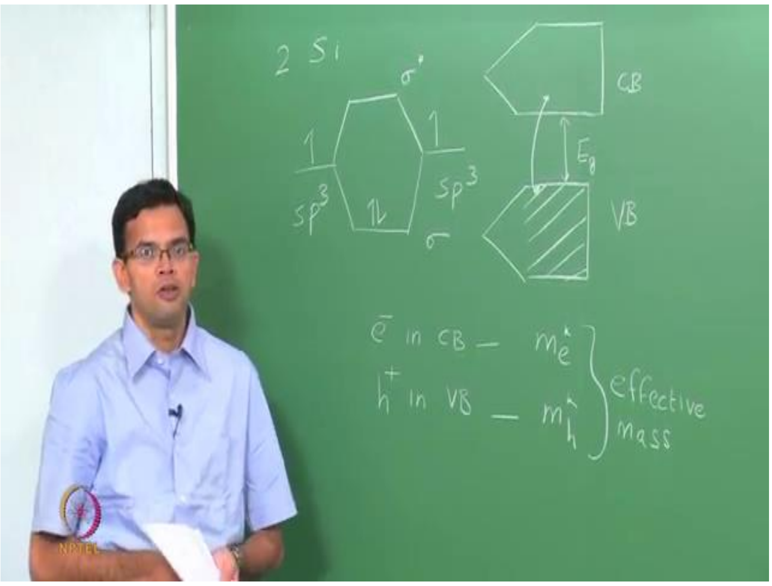

So, in last class we saw that, if we have a silicon atom with 1 S P 3 orbital. You had another silicon atom with another S P 3 orbital. They form a bond and we called the bonding orbital sigma and the anti bonding orbital sigma star. Both these electrons will go to the sigma. So, the bonding orbital is full and the anti bonding is empty. So, this is in the case of 2 silicon atoms. If you had a silicon solid, you had a lot of these bonding and anti bonding orbitals.

And these came together to form the valence band and the conduction band. So, the bonding forms the valence band, which is completely full and the anti bonding forms the conduction band that is empty. So, the valence band is completely full. The conduction band is empty. And there is a band gap between them. Last class, we also saw that at any temperature above 0 Kelvin, you would always some electrons from the valence band going to the conduction band.

So, you will have electrons in the conduction band. The absence of an electron is called hole. And we will have holes in the valence band. In the presence of an electric field, these electrons in holes can move and they cause conduction. When these electrons in holes move, we also saw that they also see the effect of all the other atoms in the lattice. So, we introduced the concept of the effective mass, m e star and m h star.

And these take in to account, the effect of all the atoms in the lattice. Just remind that, we do not mean that, the mass of the electron is actually changed. The mass still remains the same. But, we just club the effect of the atoms in to this concept of effective mass. The difference between a semi conductor and a metal is that, in a metal we do not have a band gap. We have some full states and we have some empty states.

So, electrons are always available for conduction. And the number of electrons is typically equal to the number of atoms which means, metals have high conductivity. So, the next thing we are going to do is to try and calculate the number of electrons in holes that are available for conduction in the semi conductor. But, before we do that, today we going to talk about some concepts that we will use for this calculations.

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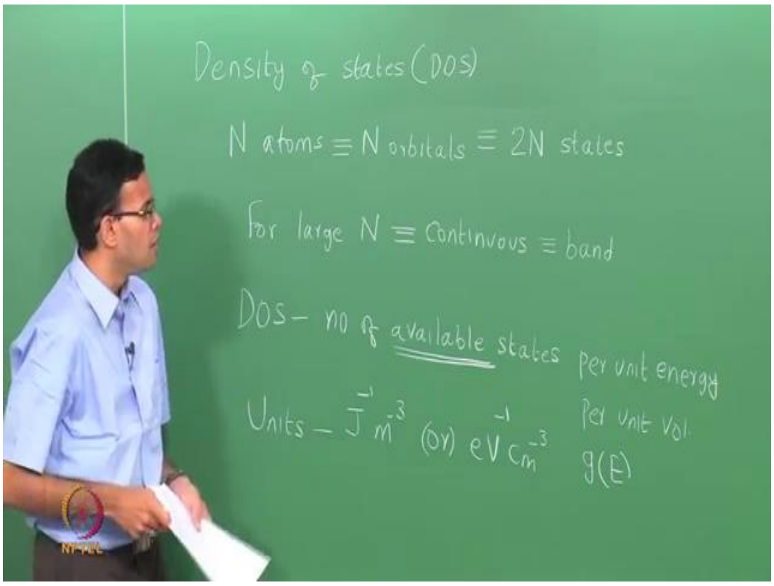

The first thing we are going to talk about today is called density of states. I will write this as an abbreviation DOS. Briefly, if you have a system where there are N atoms, we saw that they give raise to N orbitals. So, these could be atomic orbitals, which come together to form molecular orbitals. And each orbital can have 2 electrons of opposite spin. So, you have a total of 2 N states. So, these states are discrete but for large values of N, this spacing between the states are so closed, that we can take it to be a continuous change in N.

So, we have a band. The Density of States, DOS is defined as the total number of available states per unit energy and per unit volume. The operative word here, that it is the available states. So, these are the states that are available for the electrons to occupy. So, if you looking at the conduction band, the density of states in the conduction band tells you, how many states are there for the electrons to occupy?

To looking at the valence band, then you look at the density of states of holes. The units for this, since it is per unit energy and unit volume. It is either joule inverse and meter cube inverse or we can also write it, in terms of electron volts and centimeter cube. Density of states are typically written as g of E. So, let us go ahead and calculate an expression for the density of states, in terms of the energy.

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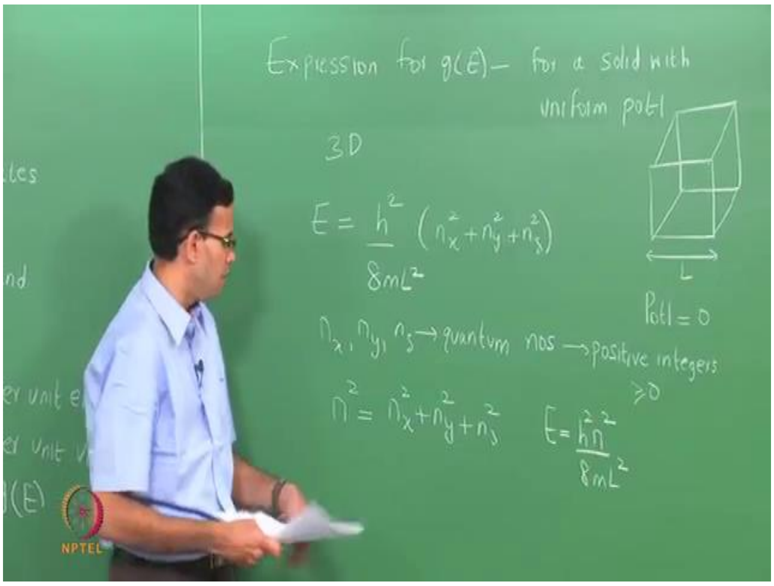

In the case of a real solid, you can measure the local density of states by spectroscopic techniques, as either a scanning tunneling microscope or as using a photo electrons spectroscopy. We can also do calculations for density of states, taking into account the distribution of atoms and electrons. But, what we will do is, to derive a simple expression for g of E for a solid with uniform potential.

To simplify matters further, we will take our solid to be a cube of length L. And we will also take the potential inside this solid to be 0, uniform. So, this is a simplification of an actual solid. But, the values we will get are good enough in order to make calculations for electrons in holes, as we will see later. In the case of a solid in a uniform potential and three dimensions, the energy E is given as x square and y square plus n z square.

And next, n y and n z are call quantum numbers. These are all positive integers. So, they have values greater than 0. So, n x n y and n z can take values of 1 2 3 and so on. We can write them as n square is equal to n x square plus n y square n z square. So, that energy E can be just written as h square and n square, which is the quantum number, which includes both n x n y and n z. So, n is also a positive integer and it take all possible values depending on the values of n x, n y and n z.

For small values of n x, n y and n z, the energy levels are discrete. But, for large values they are essentially continuous.

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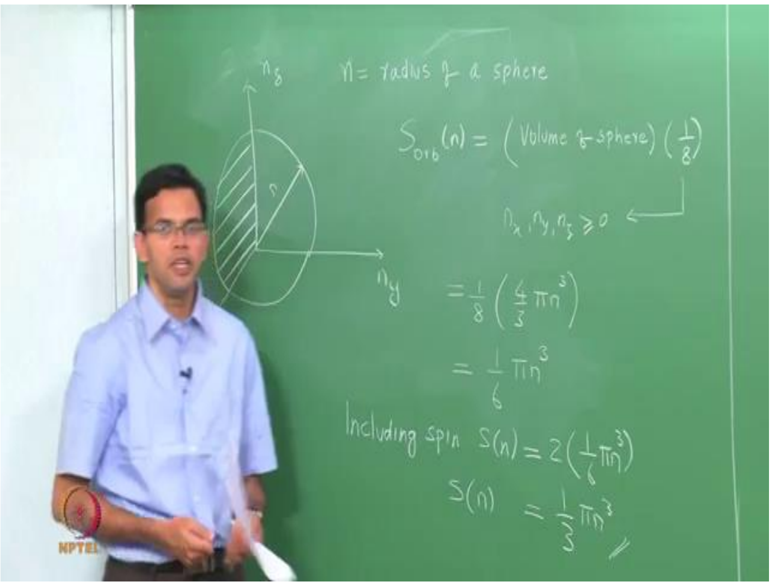

n = radius of a sphere

$$S_{orb}(n) = (\text{Volume of sphere})\left(\frac{1}{8}\right)$$

$n_x, n_y, n_z \geq 0$

$$= \frac{1}{8}\left(\frac{4}{3}\pi n^3\right)$$

$$= \frac{1}{6}\pi n^3$$

Including spin $S(n) = 2\left(\frac{1}{6}\pi n^3\right)$

$$S(n) = \frac{1}{3}\pi n^3$$

We can represent this by taking a 3 D axis, with the quantum numbers along all three axis. In this particular case, n represents the radius of a sphere nothing but the radius of a sphere, which is made up of n x, n y and n z. If you want to find the total number of states, whose energy is less than n. Then the total number of states is nothing but the volume of the sphere. But, since as sphere can have both positive and negative values of this quantum numbers.

And since, we said earlier that these quantum numbers are only positive. We only take the part of this sphere, lying in the first quadrant. So, it is the volume of the sphere times one eighth. So, the one eighth arises, because n x, n y and n z are all greater than 0. The volume of the sphere is nothing but 4 by 3 pi n cube, since n is the radius of the sphere. And you have the factor one eighth. Now, we also said that, each energy state can take 2 electrons.

You can have an electron with spin up and spin down. So, including spin, the total number of energy states S of n is 2 times. This expression is in terms of n. So, we need to convert it in to energy, so that we can calculate the density of states.

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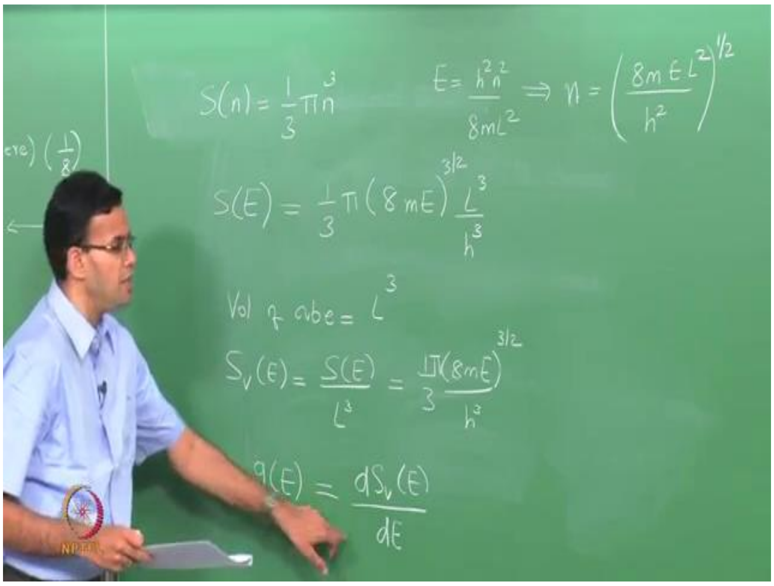

Let me rewrite the expression for S. We also wrote an expression earlier, connecting energy and n. We can rearrange this. So, all if done is to take L and all the other term this side and then write n, in terms of energy. This should be n, write n in terms of energy. Substituting for the n here, we can write the total number of states with energy less than E. It is nothing but now the density of states says is the number of states per unit volume per unit energy.

So, the volume of the cube is nothing but L cube. So, the number of state per unit volume, which we denote as S subscripts v in energy E is nothing but S of E over L cube, which will take this expression out. So, this gives the total number of states per unit volume having energy less than E. If you want to find the density of states, so it is g of E. It is nothing but the differential of the total number of states, d S v over d E.

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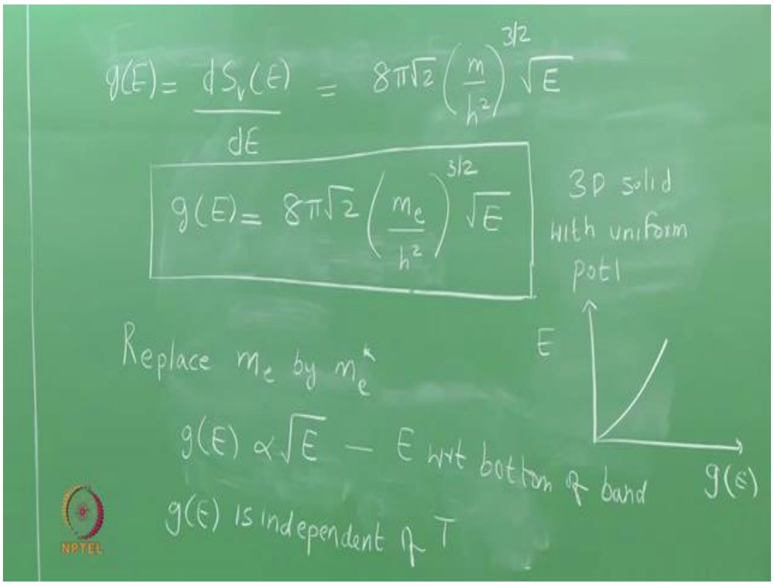

$$g(E) = \frac{dS_v(E)}{dE} = 8\pi\sqrt{2}\left(\frac{m}{h^2}\right)^{3/2}\sqrt{E}$$

$$\boxed{g(E) = 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{3/2}\sqrt{E}}$$

3D solid with uniform potl

Replace m_e by m_e^*

$g(E) \propto \sqrt{E}$ — E wrt bottom of band

$g(E)$ is independent of T

So, let me rewrite the expression here, g of E. So, differential of the total number of states with respect to energy, if we do the differential, the expression we get. Since, we are talking about electrons, I will replace the mass. By the mass of the electrons to write the final expression, 8 pi root 2. So, this is the expression for the density of states, for electrons in a 3 D solid with a uniform potential.

Typically, in a solid we can replace the mass of the electrons by the effective mass. In the case of metals like cooper, silver or gold, we saw earlier that the effective mass is very close to the real mass. So, this expression will stand. If you using the same expression for semi conductors like silicon or germanium or gallium arsenide, then m e star and m e are different. So, there will be a difference in the value of the density of states depending upon, what effective mass you use.

So, important conclusion from this is that, the density of states depends on a constant times this square root of the energy. On other words, g of E is proportional to the square root of the energy. Now, energy is taken with respect to the bottom of the band. So, E is with respect to the bottom of the band. So, the bottom of the band when E is very close to 0, the density of states is close to 0. And as the energy increases, g of E also increases.

We can plot g of E on the x axis and E on the y axis and what we get is a parabolic expression. If you also looked at this expression, g of E is independent of temperature. It only tells you, what are the states that are available for the electrons to occupy? It does not tell you, whether the electrons occupy the states or not. In order to do that, we need to look at the occupation probability of electrons and that is what, we will do next.

So, consider a system that is at 0 kelvin. In such a system, all the electrons or all the particles are at the lowest energy. So, what we want to know is, what happens to the system as temperature increases? So, there are number of statistics for describing such a system.

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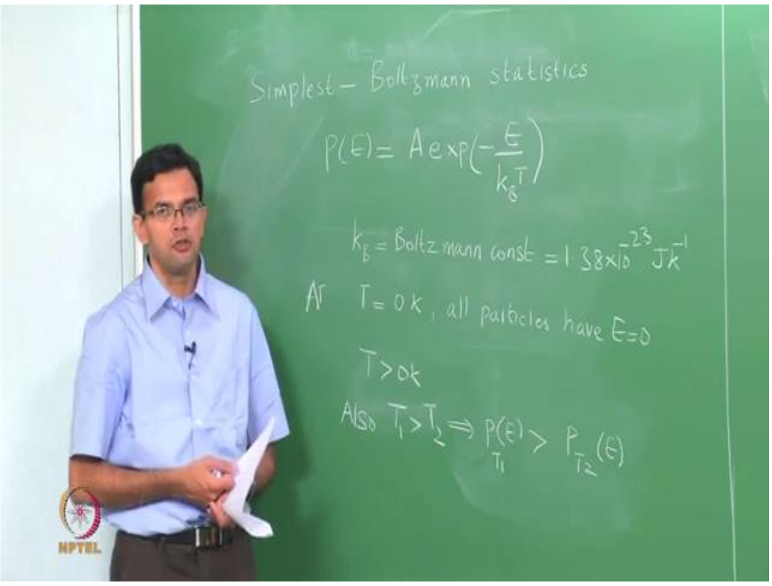

Simplest – Boltzmann statistics

$$P(E) = A\exp\left(-\frac{E}{k_B T}\right)$$

k_B = Boltzmann const = $1.38\times10^{-23}\ JK^{-1}$

At $T = 0\,K$, all particles have $E = 0$

$T > 0K$

Also $T_1 > T_2 \Rightarrow P_{T_1}(E) > P_{T_2}(E)$

The simplest statistic is called the Boltzmann statistics. According to this, the probability of occupation of an energy state E, as a function of temperature is given by the expression P of E, some constant times exponential minus E over K B T. So, E is the energy in joules. K B is called Boltzmann constant and it is equal to 1.38 times 10 to the minus 23 joules per kelvin. According to this, at temperature T equal to 0, all the particles have zero energy.

As temperature increases above 0 kelvin, there is a finite probability for occupation. Also for 2 temperatures T 1 and T 2, where T 1 is greater than T 2 to probability of occupation P of E at T 1 is greater than T 2, which means higher the temperature, higher the probability of occupation. Now, a Boltzmann statistics is good enough to describe a set of non interacting particles. The problem with using this for electrons is that, electrons have to obey paulis exclusion principle.

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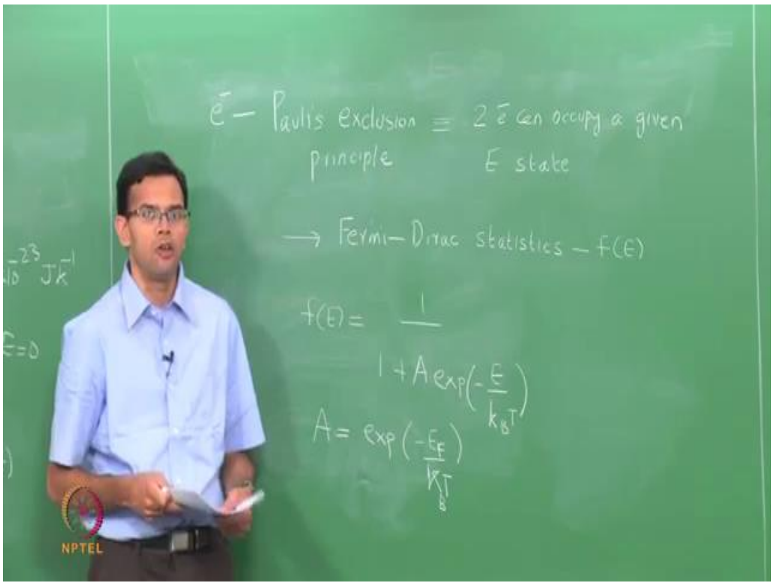

So, if we have electrons, electrons have to obey paulis exclusion principle, which states that, no 2 electrons can have the same set of all 4 quantum numbers. This translates in to the fact that, only 2 electrons can occupy a given energy state. This is the concept that we used, when we derive the density of states earlier as well. Now, because of this electrons obey another set of statistics called Fermi - Dirac statistics. This is denoted by F of E.

And the expression for F of E is 1 over 1 plus some constant time exponential minus E over K B T. Now, A here is a constant and for a solid, A depends upon the Fermi energy. So, A is nothing but minus E F over K B T. And we saw earlier that the Fermi energy represents the highest occupied energy state. So, it is the gap between the occupied and the unoccupied states, in a metal.

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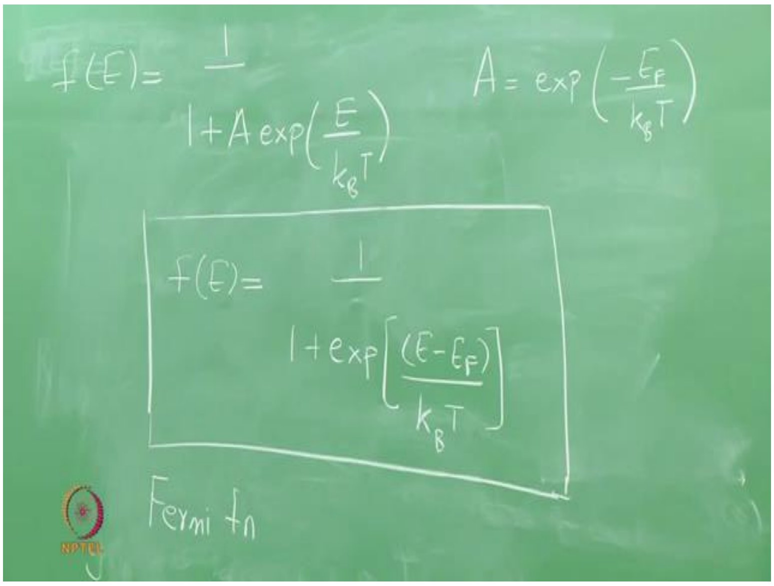

$$f(E) = \frac{1}{1 + A\exp\left(\frac{E}{k_B T}\right)} \qquad A = \exp\left(-\frac{E_F}{k_B T}\right)$$

$$\boxed{f(E) = \frac{1}{1 + \exp\left[\frac{(E - E_F)}{k_B T}\right]}}$$

Fermi fn

So, if you put those two terms together, you have F of E 1 over 1 plus A. And for a metal, we said that A, hence the expression for F of E. So, this is the Fermi Dirac statistics. And this tells you, what is the probability of occupation of a given energy state has a function of temperature?

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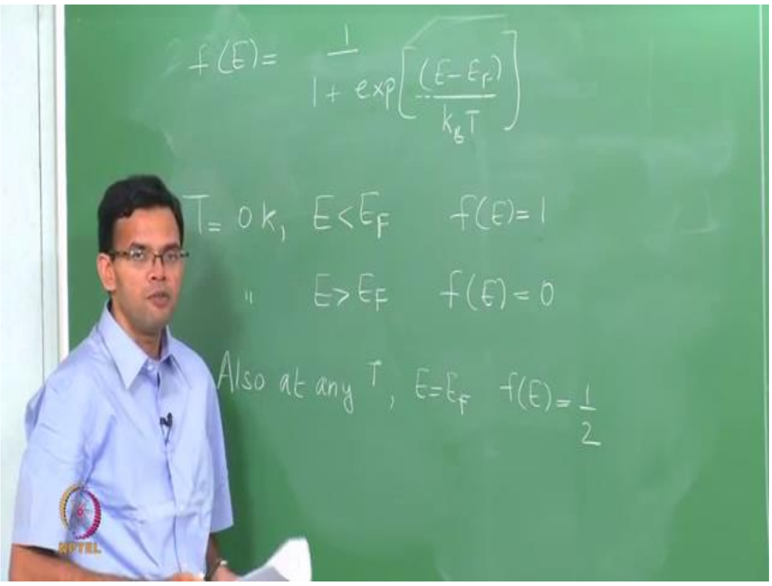

$$f(E) = \frac{1}{1 + \exp\left[\frac{(E - E_F)}{k_B T}\right]}$$

$T = 0\,K$, $E < E_F$ $f(E) = 1$

" $E > E_F$ $f(E) = 0$

Also at any T, $E = E_F$ $f(E) = \frac{1}{2}$

So, let me just rewrite the expression. So, at temperature T equal to 0, if your energy E is less than the Fermi energy. So, energy is below the Fermi energy. This term is negative. So, exponential of a negative number divided by 0, is exponential of minus infinity which is 0. So, the Fermi function is nothing but 1. This makes sense physically as well, because at 0 kelvin all the energy states below the Fermi energy are occupied.

So, your occupation probability is 1 or a 100 percent. If your energy is greater than the Fermi energy E F, again your temperature is 0 kelvin. So, this is a positive number divided by 0, which is exponential of infinity. So, it is again infinity and 1 over infinity is 0. So, all these takes above the Fermi energy are unoccupied. So, the occupation probability is 0. Also at any temperature, when E is equal to E F, so at the Fermi level E is equal to E F. So, this term is 0. F of E is half. We can put all these together and draw a pictorial representation of the Fermi function, as a function of temperature.

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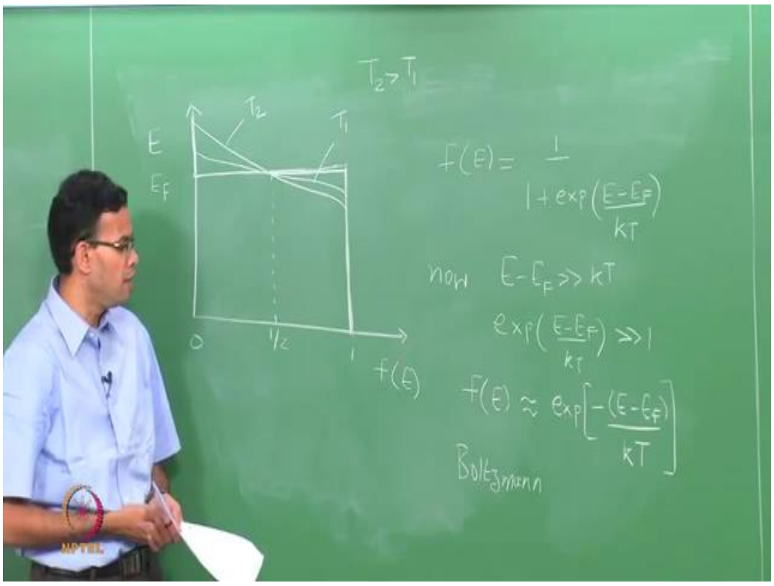

So, in this I will have energy on the y axis. F of E on the x axis and this is what, we will plotting. F of E, in go from 0 to 1 to immediate state is one half. And then energy I will write E F here. At 0 kelvin, F of E is just a delta function. So, as long as the energy E is less than E F, the value is 1. The energy goes above E F, the value is 0. So, this is F of E at 0 kelvin. I will just mark half at E F. So, now if you increase the temperature, some of the states above E F will get populated.

So, there will be a finite probability. You draw this. This is at some temperature T 1. If you increase the temperature even more, and once again F of E will increase, so if we have some other temperature T 2, this is the occupation probability at T 2, where T 2 is more than T 1. Whatever be the temperature, the probability at the Fermi energies always half. Now, if E minus E F is much larger than K T, then the exponential term should be much larger than 1.

In which case, F of E will simplify to this expression, exponential minus E minus E F over K T. And this resembles the Boltzmann statistic. So, thus at high energies, the Fermi function becomes simplified to the Boltzmann function. So, this is an approximation, which we will use later, when we calculate the electron and whole concentrations in a conduction band and a valence band.

So, today we have talked about two terms. One is the density of states, which tells you the number of available states that are to be occupied. And then the Fermi function that tells you, whether these states will be occupied or not or in other words, what is the probability of these states being occupied? If you put these two together, you can get the total number of electrons or holes in a band.

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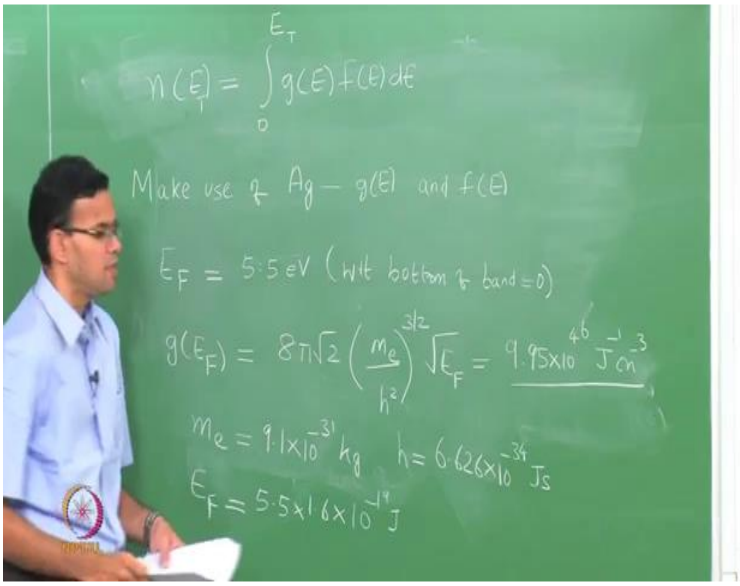

$$n(E_T) = \int_0^{E_T} g(E) f(E)\, dE$$

Make use of Ag – g(E) and f(E)

$E_F = 5.5\ \text{eV}$ (wrt bottom of band = 0)

$$g(E_F) = 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{3/2}\sqrt{E_F} = \underline{9.95\times10^{46}\ J^{-1}\,cm^{-3}}$$

$m_e = 9.1\times10^{-31}\ kg$ $h = 6.626\times10^{-34}\ Js$

$E_F = 5.5\times1.6\times10^{-19}\ J$

So, this expression for the number of electrons or holes is nothing but the Femi function or the density of states times the Fermi function D E. The bottom of the band, we set as 0 and we say E T is the top of the band. So, this is a total number of electrons with energy less than E T or the total number of electrons in a band. So, let us do an example to get a sense of some of these numbers and we will make use of a metal.

So, we will take the example of silver. And we will calculate the density of states. And also some values of the Fermi function. So, silver is a metal which obeys nearly free electron model. So, each silver atom will contribute 1 electron. So, it is also a metal. So, you have a band that is half full. So, these electrons are available for conduction. The Fermi energy of silver is 5.5 electron volts. This Fermi energy is with reference to the bottom of the band.

So, the bottom is taken as 0. If you want to find the density of states at the Fermi energy, we will make use of the expression that we derived earlier, for a solid with uniform potential. The expression, we saw earlier is proportional to square root of the energy also depends upon the mass of the electrons. In the case of silver, the effective mass is very close to the actual mass of an electron. So, I have just lefted as m e and E F is the Fermi energy.

We can plug in the numbers. In SI units, m e has the value of 9.1 is 10 to the minus 31, h which is the plains constant and E F is 5.5 electron volts, which we can convert it in to joules. If we do the numbers, we get the density of states to be equal. So, these many states are available per joule and per meter cube, in the case of silver at the Fermi energy.

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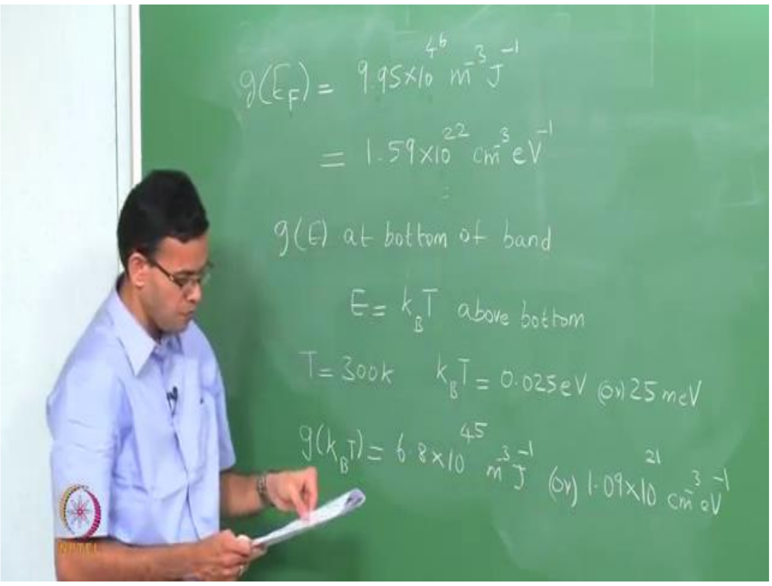

So, let me write the value again. We can convert this number into electron volts and centimeter cube. So, we will just make use of the conversion factor. And if you do the math, this comes down. Now, E F represents the top of the band. We said at the bottom of the band, the density of states is nearly close to 0. So, if we want to calculate g of E at the bottom of the band. So, if E is equal to 0, then g of E is 0. Let us look at E equal to K T, above the bottom. At room temperature T is nothing but 300 kelvin. So, K T is 0.025 e v or 25 milli e v, above the bottom of the band. So, we can do the same calculation that, we did earlier.

Except, replace E F by K B T. And if you do that, the density of states 25 milli electron volts above the bottom of the band is still a large number, 6.8 times 10 to the 45. So, these are the values at the top of the band. So, 10 to the 46 but even at the bottom of the band, the difference is only 10 orders of magnitude. This is 46, this is 45. Or if you want in terms of electron volts, this is 22, this is 21. So, now we need to know, how many available states are there from the bottom of the band up to E F, which is the top of the band.

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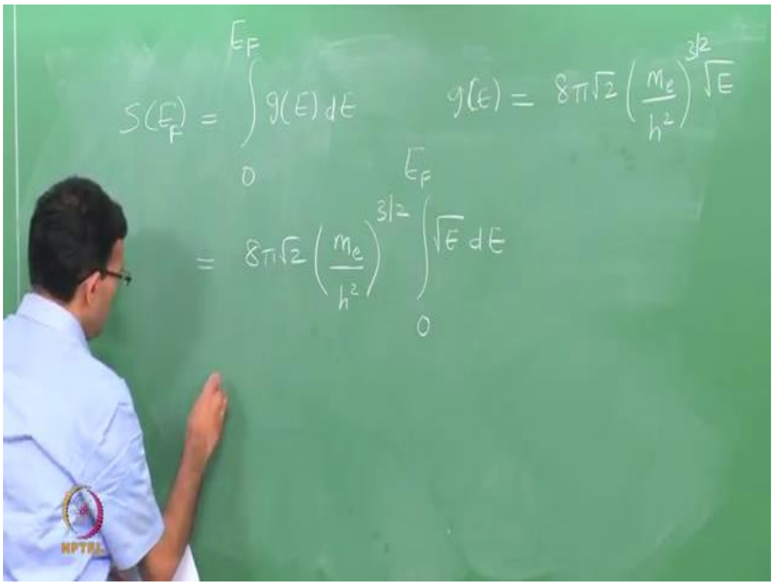

$$S(E_F) = \int_0^{E_F} g(E)\,dE \qquad g(E) = 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{3/2}\sqrt{E}$$

$$= 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{3/2}\int_0^{E_F}\sqrt{E}\,dE$$

To do that the number of the steps from the bottom of the band to the top of band is nothing but an integration of the density of states. So, we will use expression for g of E. All these terms are constant. The only term that is the function of energy is E. So, in this expression you take the constant outside. We can do the integration and then substitute the limits 0 and E F.

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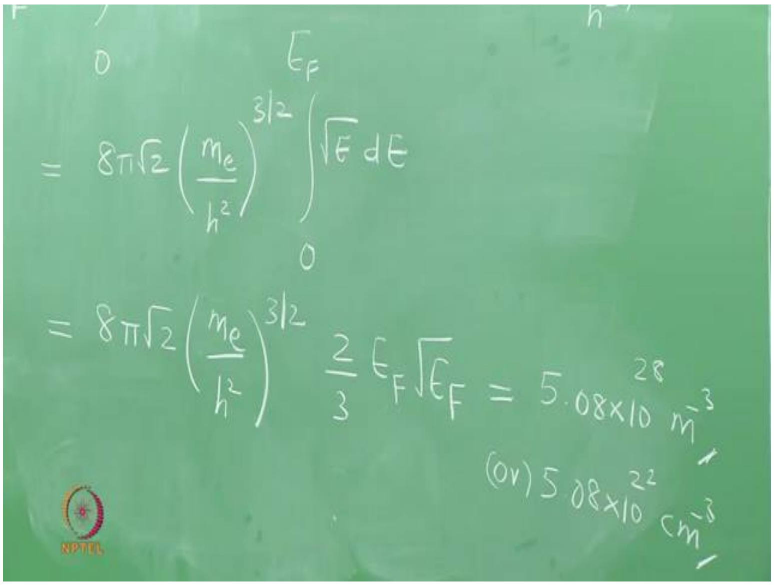

$$= 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{3/2}\int_0^{E_F}\sqrt{E}\,dE$$

$$= 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{3/2}\frac{2}{3}E_F\sqrt{E_F} = 5.08\times10^{28}\ m^{-3}$$

$$(or)\ 5.08\times10^{22}\ cm^{-3}$$

If we do that, which if you calculate is 5 times 10 to the 28 states per unit volume per meter cube or 5 times 10 to the 22 centimeter cube. So, these are the total number of states that are available in silver, from the bottom of the band up to the Fermi function E F. We can also calculate the total number of atoms that are there in silver.

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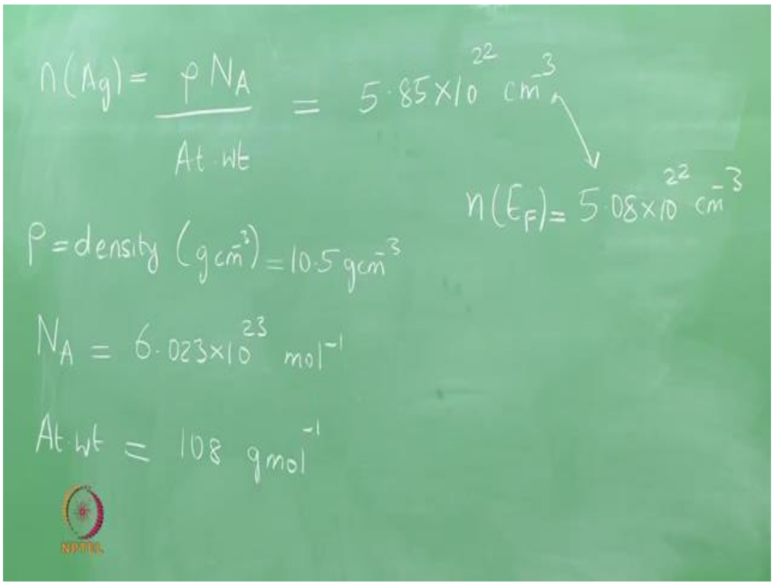

$$n(Ag) = \frac{\rho N_A}{At.wt} = 5.85\times10^{22}\ cm^{-3}$$

$$n(E_F) = 5.08\times10^{22}\ cm^{-3}$$

$$\rho = density\ (g\,cm^{-3}) = 10.5\ g\,cm^{-3}$$

$$N_A = 6.023\times10^{23}\ mol^{-1}$$

$$At.wt = 108\ g\,mol^{-1}$$

Number of atoms in silver per unit volume depends upon the density Avogadro's number and the atomic weight. So, rho is the density. We can write it as gram per centimeter cube. For silver, the value is 10.5, n is Avogadro's number. Choose the number of atoms per mole, 6.023. An atomic weight for silver is 108 grams per mole. We can substitute these values in this expression. So, the number of silver atoms is 5.85.

So, these are the number of silver atoms. Each silver atom can donate 1 electron. So, these are the number of electrons. The number of states, which we calculated using a very simple model of a 3 D solid with a uniform potential, which we have written before. Then, we find that these two numbers are very close to each other. So, each atom will donate 1 electron. And each of this electron can occupy this states.

So, you have a whole bunch of full states, from the bottom of the band up to E F. In all these states, above it are empty. These calculations are done at temperature equal to 0 kelvin. So, we do not take into account. What is the probability of occupation? In order to do that, we need to look at the Fermi function.

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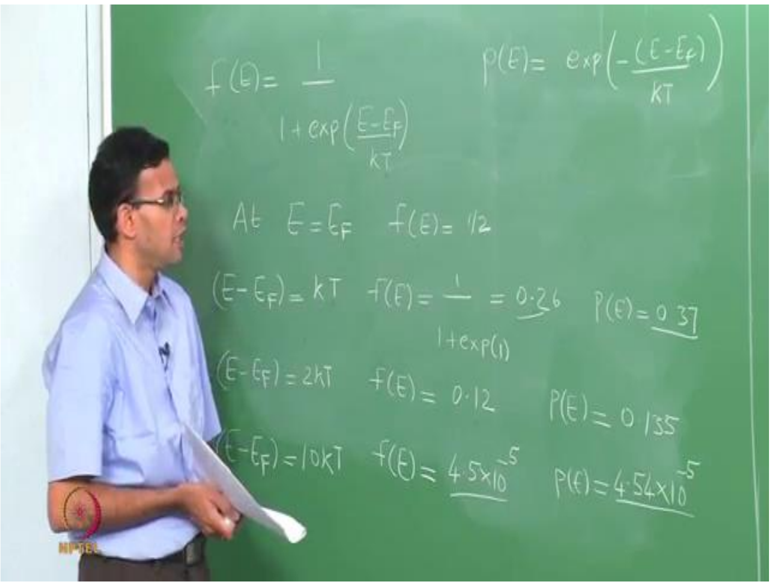

So, let me write the expression for F of E. We also said that, when E minus E F is much larger than K T, this can be approximated by the Boltzmann function P of E. Now, at the

Fermi level E equal to E F, F of E is always one half. It does not matter, what the temperature is? The probability of occupation is always half. Let us say, we have K T above the Fermi energy. So, E minus E F is nothing but K T.

In this case F of E, we can substitute K T there, 1 over 1 plus exponential of 1. If you do the calculations, that is 0.26. What this number means is that, there is a 26 percent chance for an electron to occupy an energy state K T or 25 milli electron volts at room temperature, above the Fermi energy. P of E for the same value is 0.37. So, you are trying to approximate the Boltzmann function for the Fermi function. It is not good here.

What happens, if E minus E F is 2 K T. So, again we can substitute, you get F of E is 0.12 and P of E is 0.135. So, once again the values are closer. But, they are still not the same. What if E minus E F is 10 K T? At room temperature, this is 0.25 electron volts above the Fermi energy. In this case, F of E is 4 times 10 to the minus 5. And if you look at the Boltzmann approximation, it is very close. So, already 0.25 electron volts above the Fermi function or the Fermi energy, we can easily use the Boltzmann approximation instead of F of E.

So, we will stop here for today. In the next class, we will use this concept of density of states and the Fermi function, in order to calculate the electron and holes concentration. We will first start with an intrinsic semi conductor, which is a semi conductor that is pure and node opens. And we will calculate the carrier concentration in that. And after we are done with intrinsic, we will move on to extrinsic semi conductors.