# Fundamentals of electronic materials, devices and fabrication
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## Lecture – 03
## Density of States and Fermi – Dirac Statistics

Let us start with a brief review of last class. So, in last class we looked at semiconductors and how a bind gap evolves in them. We took the example of silicon as a material. Silicon in the outer shell has two electrons in the s orbital and two in the p. The s and p orbitals hybridize to give you 4 $sp^3$ orbitals. In the case the of a silicon atom, each silicon atom has 4 electrons in these $sp^3$ hybrid orbitals, so you can form 4 bonds. If you have 2 silicon atoms, they form a bond between them this forms the bonding orbitals which is the sigma and the anti bonding orbital that is the $\sigma^*$.

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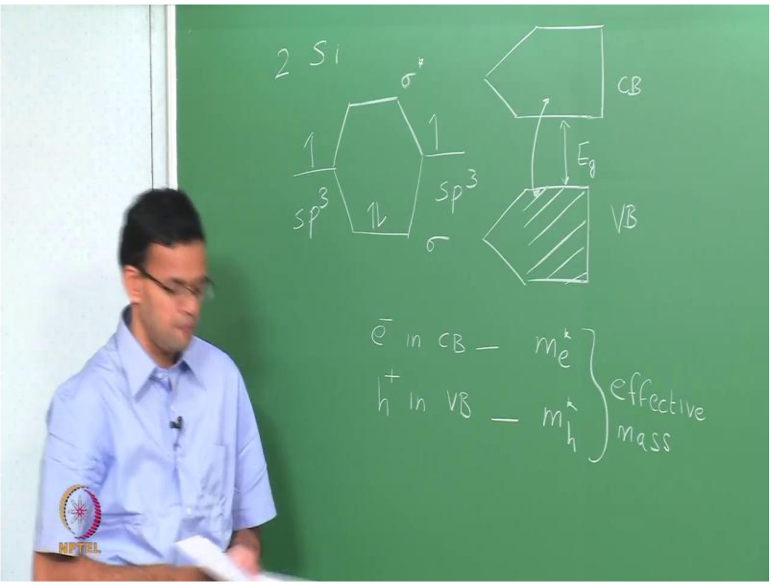

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So, in last class we saw that if you have a silicon atom with 1 $sp^3$ orbital you had another silicon atom with another $sp^3$ orbital, they form a bond and we called the bonding orbital $\sigma$ and the anti bonding orbital $\sigma^*$. Both these 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 Zero Kelvin, you would always have some electrons from the valence band going to the conduction band. You will have electrons in the conduction band the absence of an electron is called a hole. And we will have holes in the valence band. In the presence of an electric field these electrons and holes can move and there cause conduction. When these electrons and 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 $m_h^*$ and these take into account the effect of all the atoms in the lattice. Just a reminder 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 into this concept of the effective mass.

The difference between a semiconductor and a metal is that in a metal we do not have a band gap we have some fill 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 a semi conductor. But before we do that today we are going to talk about some concepts that we will use for these calculations.

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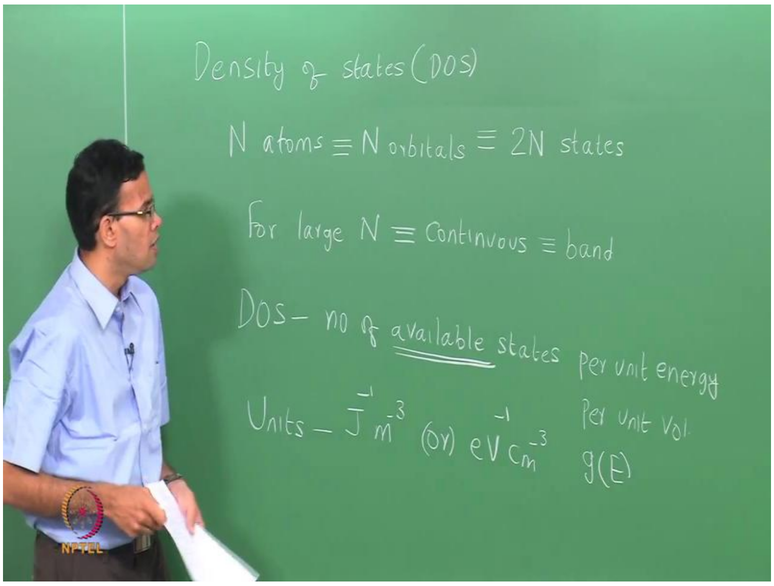

The first thing we are going to talk about today is called density of states. I will write this an abbreviation DOS. Briefly if you have a system where there are N atoms we saw that they give raise to N orbitals. So, these could be atomic orbitals which come together to form molecular orbitals and each orbital can have 2 electrons of opposite spin. So, you have a total of 2N states. So, these states are discrete, but for large values of N the spacing between the states are so close 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, theses are states that 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 electrons to occupy if you are 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 its either joule inverse and $m^3$ inverse or you can also write in terms of electron volts and $cm^3$.

Density of states, are typically written as $g(E)$ . Let us go ahead and calculate an expression for the density of states in terms of the energy.

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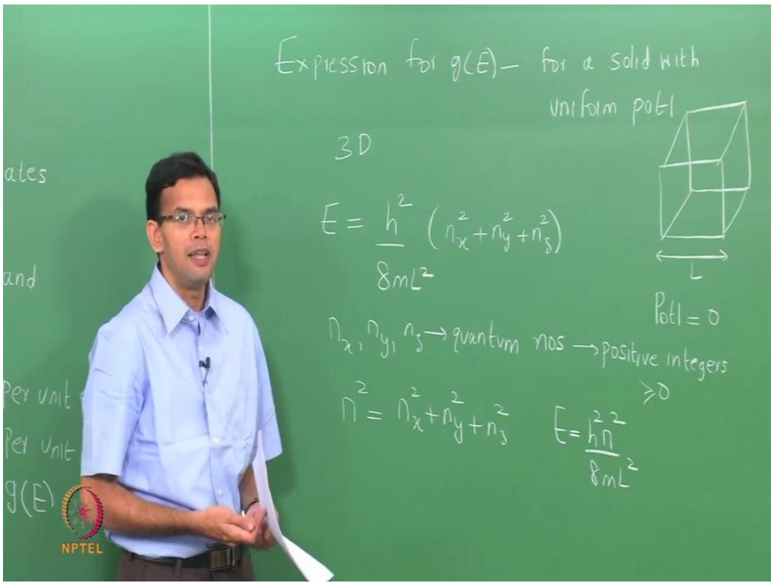

In the case of a real solid you can measure the local density of states by spectroscopic techniques as either a scanning tunnelling microscope or as using a photo electron spectroscopy. We can also do calculations for density of states taking into account the distribution of atoms and electrons. But what we will do is to derive a simple expression for g(E) for a solid with uniform potential. To simplify matters further we will take a solid to be a cube of length L and we will also take the potential inside the solid to be 0 uniforms. 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 and holes as we will see later. In the case of a solid in uniform potential and 3 dimensions, the energy E is given as

$$\frac{h^2}{8mL^2}\left(n_x^2+n_y^2+n_z^2\right)$$

$n_x^2,\ n_y^2\ and\ n_z^2$ are called Quantum numbers these are all positive integers. So, they have values greater than 0, so $n_x^2,\ n_y^2\ and\ n_z^2$ take values as 1, 2, 3 and so on.

You can write them as $n^2 = n_x^2 + n_y^2 + n_z^2$. So, that energy E can be just written as $h^2$ and $n^2$ which is the quantum number which includes both $n_x,\ n_y and\ n_z$. So, n is also a positive integer and it can 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 were essentially continuous.

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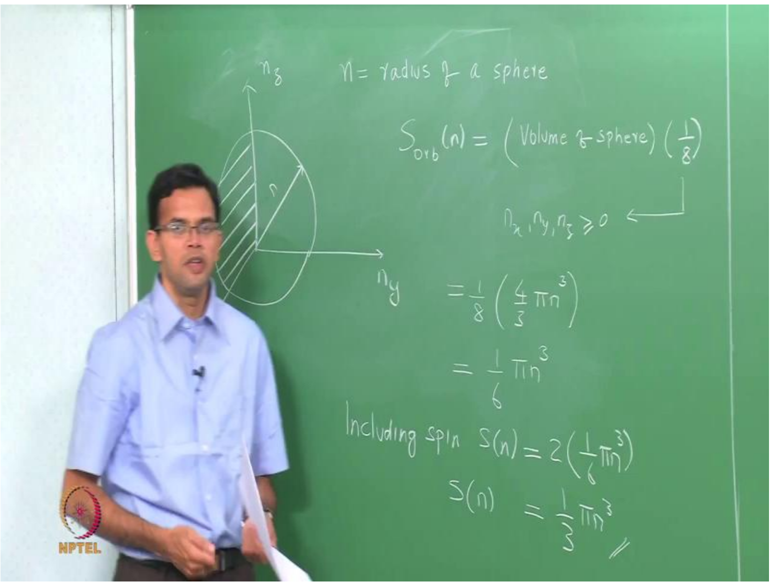

We can represent this by taking a 3D axis with the quantum numbers along all 3 axis. In this particular case, n represents the radius of a sphere, nothing but the radius of a sphere which is made up of $n_x,\ n_y and\ n_z$. If you want to find the total number of states whose energy is less than n then the total number of states is nothing but the volume of the sphere. But since a sphere can have both positive and negative values of these quantum numbers and since we said earlier that these quantum numbers are only positive we only take the part of the sphere lying the first quadrant. So, it is the volume of the sphere times $\left(\frac{1}{8}\right)^{th}$. So, the $\left(\frac{1}{8}\right)^{th}$ arises because $n_x,\ n_y and\ n_z$ are all greater than 0 volume of the sphere is nothing but $\frac{4}{3}\pi n^3$ since n is the radius of the sphere and you have the factor $\left(\frac{1}{8}\right)^{th}$. Now we also said that, each energy state can take 2 electrons right you can have a electron which spin up and spin down. So, including spin the total number of energy state s of n is 2 times, this expression is in terms of n. So, we need to convert it into energy. So, that we can calculate the density of states

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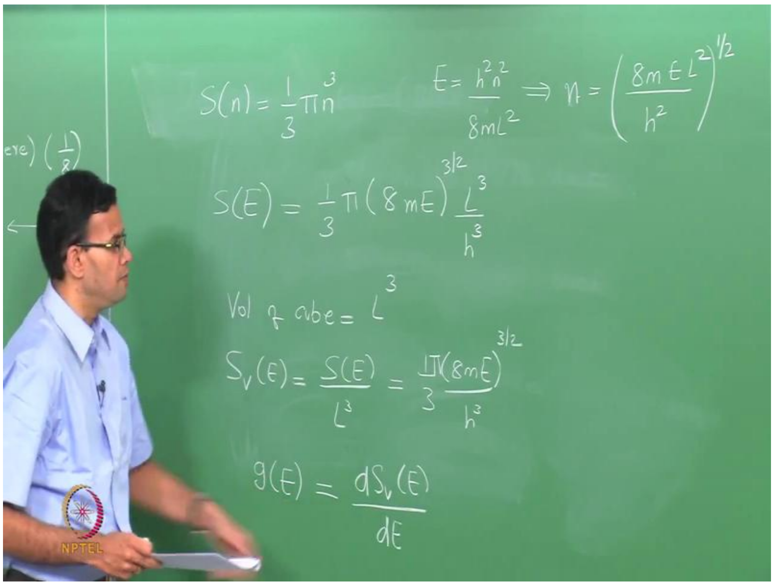

Let me rewrite the expression for s. We also wrote an expression earlier connecting energy and n. We can rearrange this; all you have done is to take L all the other terms this side and write n in terms of energy sorry this should be n write n terms of energy substituting for the n here we can write the total number of the states with energy less than e is nothing but now the density of states says is the number of states per unit volume per unit energy. The volume of the cube is nothing, but L cube. So, the number of states per unit volume which we denote as $S_v$ and energy is nothing, $S_v(E)$ but 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 is g(E) it is nothing but the deferential of the total number of states $\frac{Sv(E)}{dE}$ .

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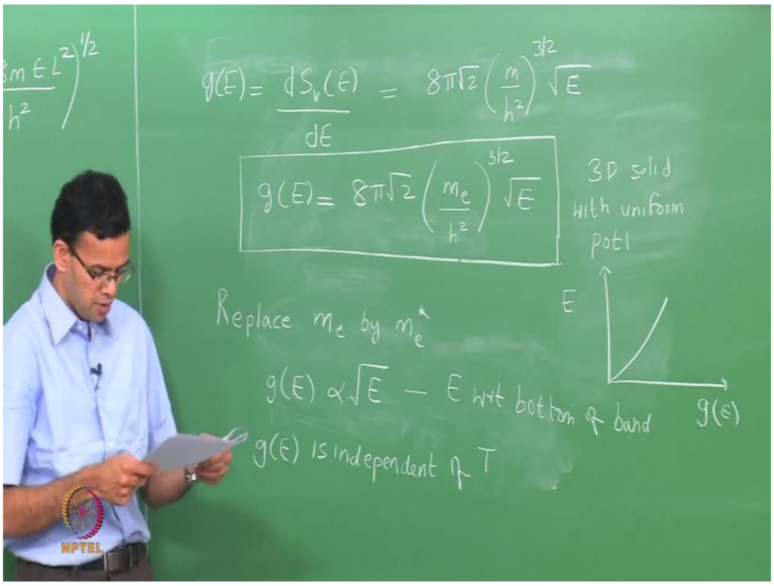

Let me rewrite the expression here g(E) is the differential of the total number of states with respect to energy if we do the differential, expression we get since we are talking about electrons I will replace the mass by the mass of the electrons to write the final expression is $8\pi\sqrt{2}$. So, this is the expression for the density of states for electrons in a 3D solid with a uniform potential typically in a solid. You can replace the mass of the electron by the effective mass, in the case of metals like copper, silver or gold. We saw earlier that the effective mass is very close to the real mass. This expression will stand if you are using the same expression for semiconductors like silicon or germanium or gallium arsenide then $m_e^*$ and $m_e$ are different. So, there will be a difference in the value of the density of the states depending upon of what effective mass you use. So, important conclusion from this is that the density of states depends on a constant time the square root of energy, other words $g(E)\alpha\sqrt{E}$.

Now, energy is taken with respect to the bottom of the band so E with respect to the bottom of the band. 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(E) also increases, we can plot g(E) on the x axis and E on the y axis and what we get is a parabolic expression. If you also look at this expression g(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 those 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. 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, has temperature increases. There are a number statistics for describing such a system the simplest statistics is called the Boltzmann statistic.

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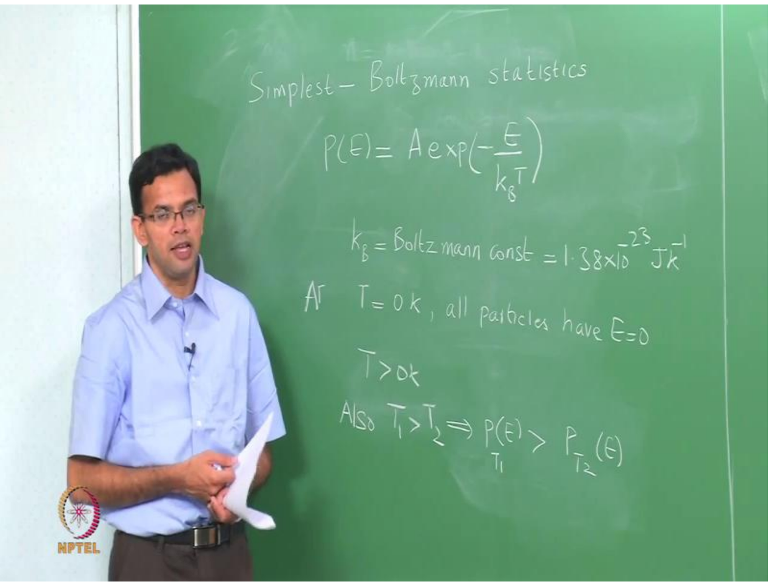

Simplest – Boltzmann statistics

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

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

At $T = 0k$, all particles have $E=0$

$T > 0k$

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

According to this the probability of occupation of an energy state E as a function of a temperature is given by the expression p(E) some constant times $exp\frac{-E}{k_B T}$ . So, E is the energy in joules, $k_B$ is called Boltzmann constant and is equal to 1.38 x $10^{-23}$ JK$^{-1}$. According to this at temperature T = 0 all the particles have 0 energy. As temperature increases above 0 Kelvin, there is a finite probability for occupation also for 2 temperatures $T_1$ and $T_2$ where $T_1 > T_2$. The probability of occupation $P_{T_1}(E) > P_{T_2}(E)$, 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 problem with using these electrons is that electrons have to obey Pauli's exclusion principle.

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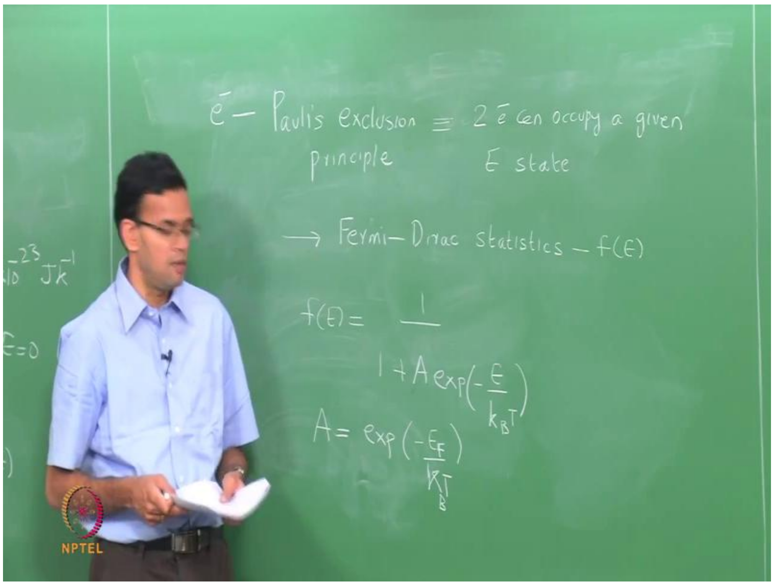

So, if you have electrons, electrons have to obey Pauli's exclusion principle which states that no 2 electrons can have the same set of all 4 quantum numbers this translate into the fact that only 2 electrons can occupy a given energy state this is the concept that we have used when we derive the density of states. Earlier as well now because of these electrons obey another set of statistics called Fermi Dirac Statistics.

Electrons obey the Fermi Dirac Statistics this is denoted by f(E) and the expression for $f(E) = \frac{1}{1+Aexp\left(\frac{-E}{k_B T}\right)}$. Now, A here is a constant and for a solid, A depends upon the Fermi energy. So, A is nothing but $\left(\frac{-E_f}{k_B T}\right)$ and we saw earlier the fermi energy represents the highest occupied energy state. So, if this is the gap between the occupied and the unoccupied states in the metal.

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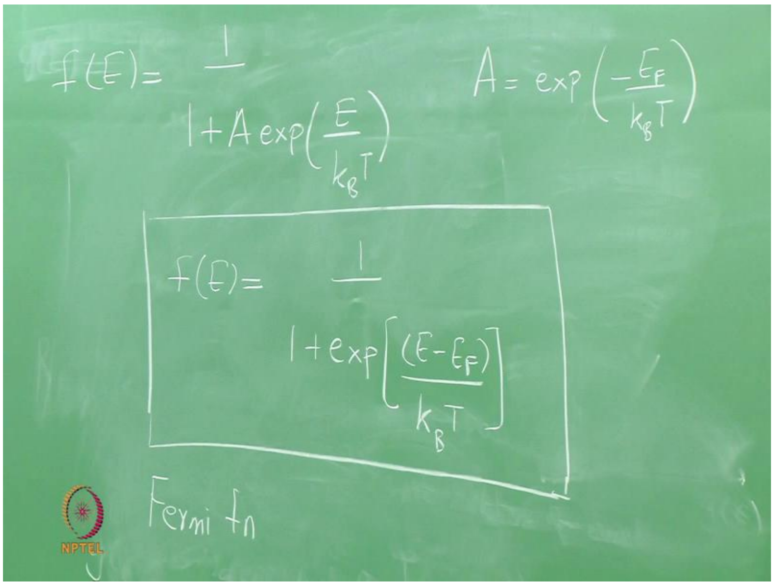

$$f(E) = \frac{1}{1 + A\exp\left(\frac{E}{k_B T}\right)} \qquad A = \exp\left(-\frac{E_F}{k_B T}\right)$$

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

Fermi fn

If we put those 2 terms together you have f(E), but $\frac{1}{1+A}$ and for a metal we said that a hence the expression for f(E). So, this is the Fermi Dirac Statistics and this tells you what is the probability of occupation of a given energy state as a function of a temperature.

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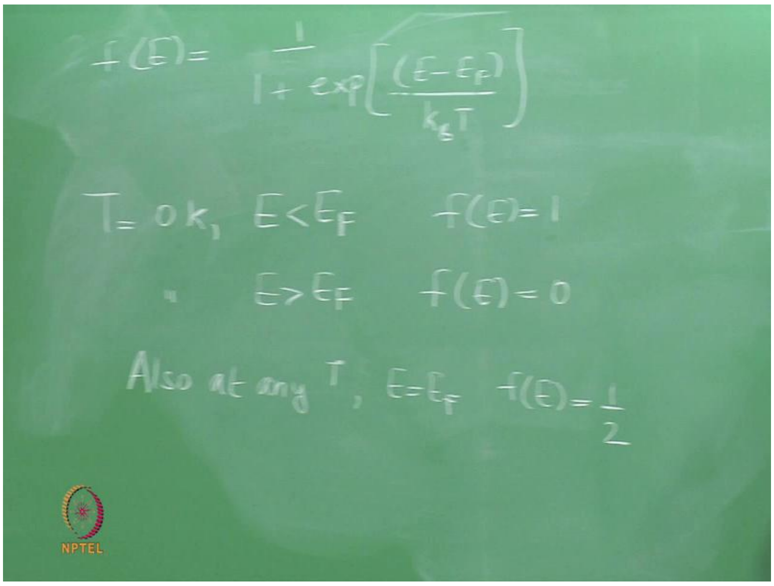

$$f(E) = \frac{1}{1 + \exp\left[\frac{(E - E_F)}{k_B T}\right]}$$

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

$E > E_F$ $\quad f(E) = 0$

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

Let me just rewrite the expression. So, at temperature T = 0 if you are energy E is less than the Fermi energy. So, energy 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. The Fermi function is nothing but 1 this make sense physically is well because at 0 kelvin all the energy states below the Fermi energy are occupied. Occupation probability is 1 or a 100 percent if the 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 the exponential of infinity which is again infinity and 1 over infinity is 0. So, all the states 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 $E = E_f$. So, this term is 0, f(E) is half we can put all these together and draw a pictorial representation of the fermi function as a function of a temperature.

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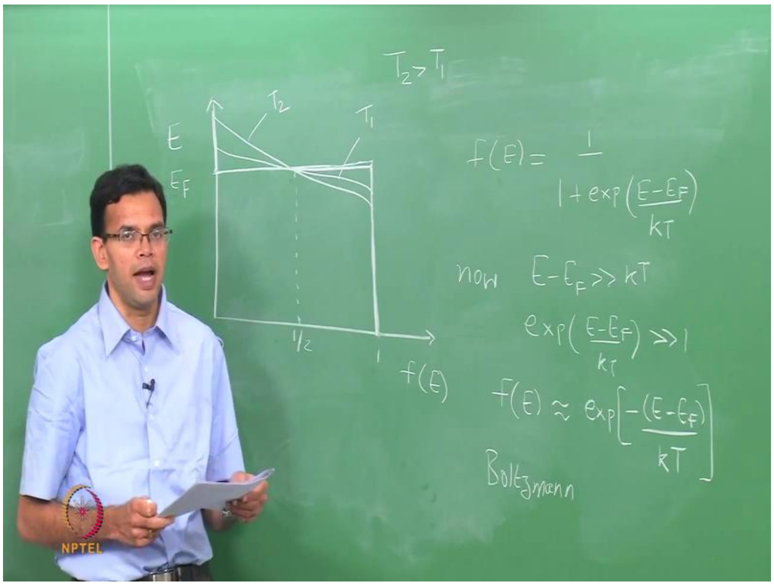

So in this I will have energy on the y axis, f(E) on the x axis and this is what we will be plotting. f(E) can go from 0 to 1 the immediate state is 1 half and then energy I will write $E_f$ here. At 0 kelvin f(E) is just a delta function.

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 $E_f$. Now, if you increase the temperature some of the states above $E_f$ will get populated. So, there will be the finite probability we draw this is at some temperature $T_1$ if you increase the temperature even more then once again f(E) will increase. If you 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 energy is always half. Now if $E - E_f$ is much larger than kT then the exponential term will be much larger than 1 in which case f(E) will simplify to this expression $exp\left(\frac{-(E-E_f)}{kT}\right)$ and this resembles the Boltzmann statistics. So, Thus, at high energies the Fermi functions become simplified to the Boltzmann function. So, this is the approximation which we will use later when we calculate the electron and hole concentrations in a conduction band and a valence band. So, today we have talked about 2 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 other words what is the probability of these states being occupied if you put these 2 together you can get the total number of electrons or holes in a band.

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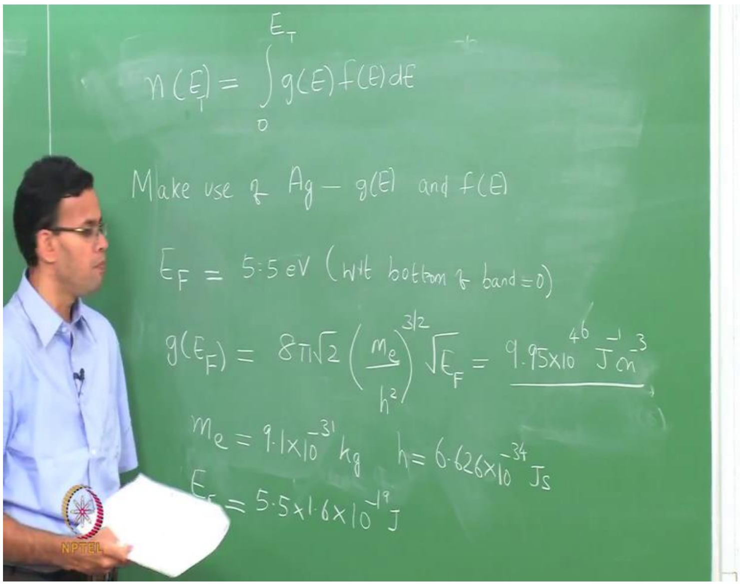

$$n(E_T) = \int_0^{E_T} g(E)\, f(E)\, dE$$

Make use of Ag – g(E) and f(E)

$E_F = 5.5$ eV (wrt bottom of band = 0)

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

$m_e = 9.1\times10^{-31}$ 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 Fermi function and the density of states times the Fermi function dE 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, will take the example of silver and you will calculate the density of the 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 and it is also metal. So, you have a band that is half full. 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 expressions that we derived earlier for a solid with a uniform potential. That expression we saw earlier is proportional to square root of the energy also depends up on the mass of the electron in the case of the silver the effective mass is very close actual mass of an electron. So, I have just left it as $m_e$ and $E_f$ is the Fermi energy you can plug in the numbers in SI units and $m_e$. $m_e$ as the value of the $9.1 \times 10^{-31}$, h which is Plancks constant and $E_f$ is 5.5 electron volts which we can convert into 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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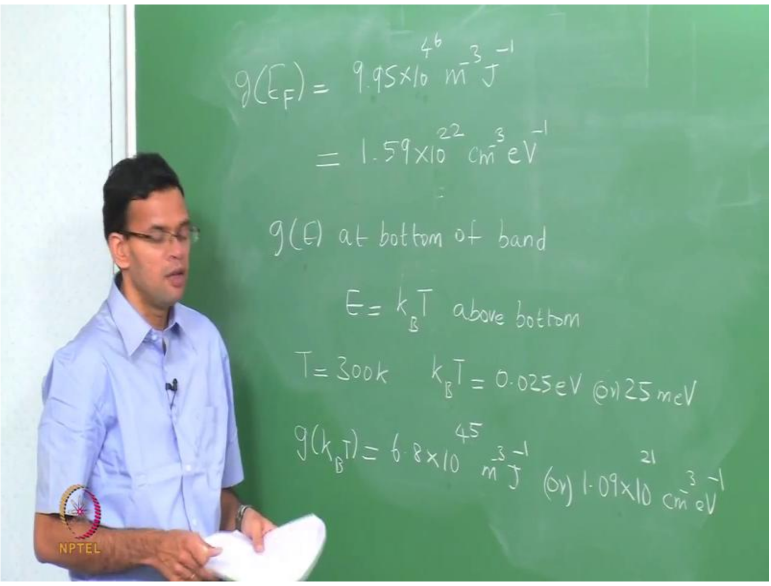

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Let me write the value again we can convert this number into electron volts and centimetre cube. We will just make use of the conversion factor and if we do the math these comes down now $E_f$ represents the top of the band we said at the bottom of the band the density of states nearly close to 0. So, if you want to calculate g(E) at the bottom of the band. So, E is equal to 0 then g(E) is 0. Let us look at E equal to kT above the bottom at room temperature T is nothing but 300 kelvin. So, kT is 0.025 ev or 25 mev 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 mev above the band is still a large number, $6.8 \times 10^{45}$. So, these are the values at the top of the band. So, $10^{46}$

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. 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 to do that.

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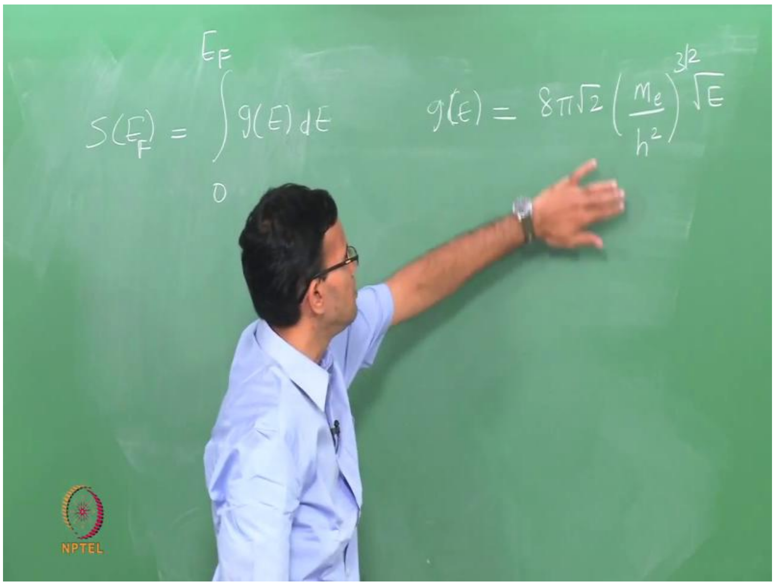

$$S(E_F) = \int_0^{E_F} g(E)\,dE \qquad g(E) = 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{3/2}\sqrt{E}$$

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The number of states from the bottom of the band to the top of the band is nothing but an integration of the density of states. So, we will use the expression for g(E) all these terms are constant. The only terms that is function energy is E.

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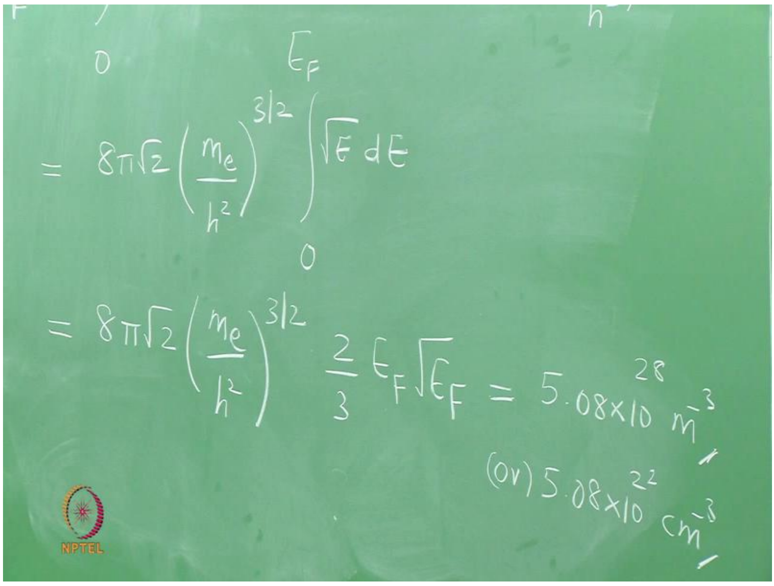

$$= 8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{3/2}\int_0^{E_F}\sqrt{E}\,dE$$

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

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

.

So, in this expression you can take the constants outside you can do the integration and then substitute the limits 0 and $E_f$ we do that which if you calculate is $5\ \mathrm{x}10^{28}\ \mathrm{m}^3$ or $5\ \mathrm{x}\ 10^{22}$, if you write it $\mathrm{cm}^3$. 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 number of atoms in silver per unit volume depends upon the density Avogadro's number and the atomic weight.

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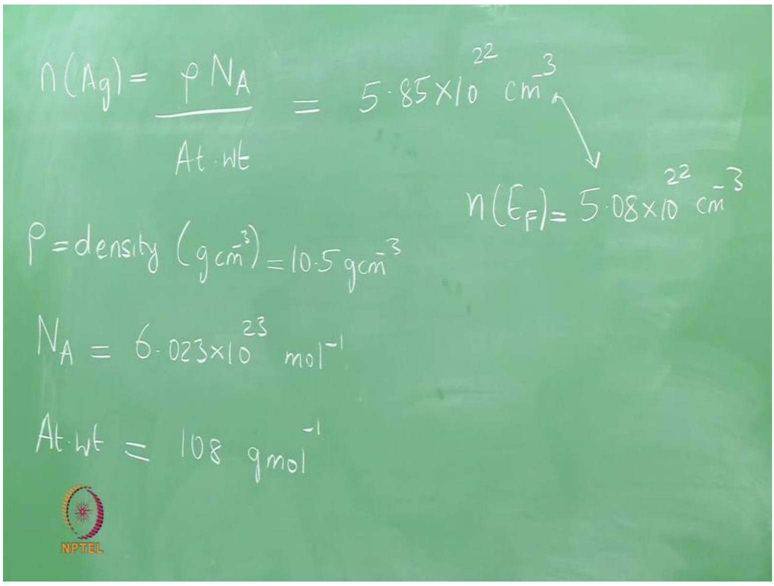

$$n(Ag) = \frac{\rho N_A}{At \cdot wt} = 5 \cdot 85 \times 10^{22}\ cm^{-3}$$

$$n(E_F) = 5 \cdot 08 \times 10^{22}\ cm^{-3}$$

$$\rho = \text{density}\ (g\,cm^{-3}) = 10 \cdot 5\ g\,cm^{-3}$$

$$N_A = 6 \cdot 023 \times 10^{23}\ mol^{-1}$$

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

$\rho$ is the density you can write it in $\mathrm{g\ cm}^{-3}$ for silver the value 10.5, $N_A$ is Avogadro's number which is the number atoms per mole is $6.023\ \mathrm{x}\ 10^{23}$ point naught 2 3 and atomic weight for silver is 108 $\mathrm{g\ mol}^{-1}$ . You 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 3D solid with uniform potential which we have written before in we fine that these 2 numbers are very close to each other. So, each atom will donate 1 electron and each of these electrons can occupy the states. You have a whole bunch of fill states from the bottom of the band up to $E_f$. All the 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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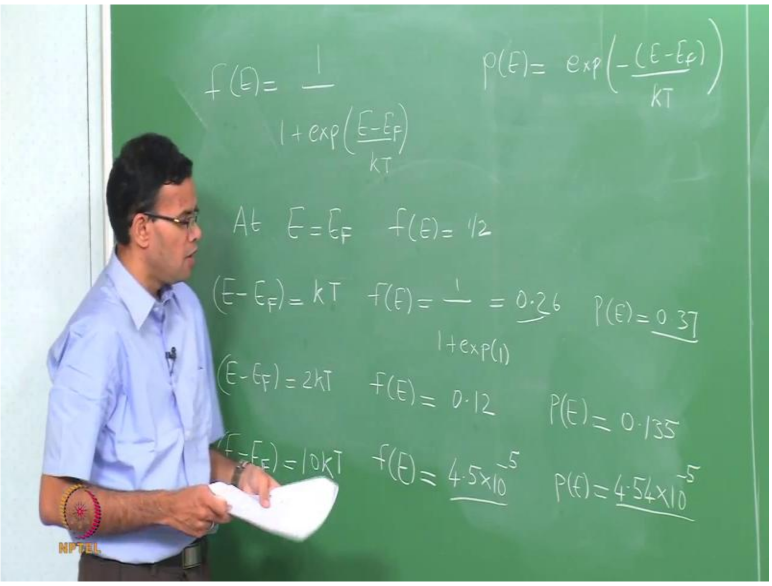

So, let me write the expression for f(E). We also said that when $E - E_f$ is much larger than kT this can be approximated by a Boltzmann function p(E) . Now at the Fermi level $E = E_f$, f(E) is always one half; does not matter what the temperature is the probability of occupation is always half. Let us say, we are kT above the Fermi energy. So, $E - E_f$ is nothing but kT. In this case f(E) can substitute kT there $\frac{1}{1+e}$ ,if we 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 kT or 25 mev at room temperature above the Fermi energy.

p(E) for the same value is 0.37. So, trying to approximate the Boltzmann function for the Fermi function is not good here. What happens if $E - E_f$ is 2 kT? So, again we can substitute you get f(E) is 0.12 and p(E) is 0.135. Once again the values are closer but they are still not the same.

What if $E - E_f$ is 10 kT? At room temperature, this is 0.25 electron volts above the Fermi energy. In this case f(E) is $4 \times 10^{-5}$ and if you look at the Boltzmann approximation it is very close. So, already 0.25 electron volts above the Fermi function at the Fermi energy we can easily use the Boltzmann approximation instead of f(E).

So, we will stop here for today. In the next class, we will use these concept of density of states and the fermi functions in order to calculate the electron in hole concentration. We will first start with an intrinsic semiconductor, which is a semiconductor which is pure and no dopends and we will calculate the carrier concentration in that and after we are done with intrinsic we will move on to extrinsic semiconductors.