# Fundamentals of electronic materials, devices and fabrication
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## Assignment 1
## Bonding, DOS, and Fermi statistics

In today's class, we are going to look at some numerical problems which basically help us understand some of the concepts that we have covered in class. So, in today's assignment we are going to look at problems related to bond formation, we are going to look at problems related to density of states and other related aspects. So, these will essentially cover the first 2 lectures of this course.

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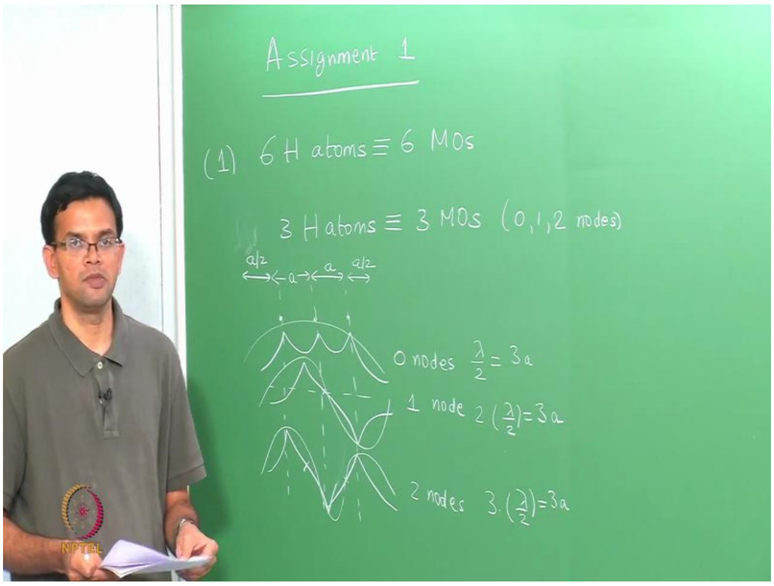

Let us look at problem number 1.

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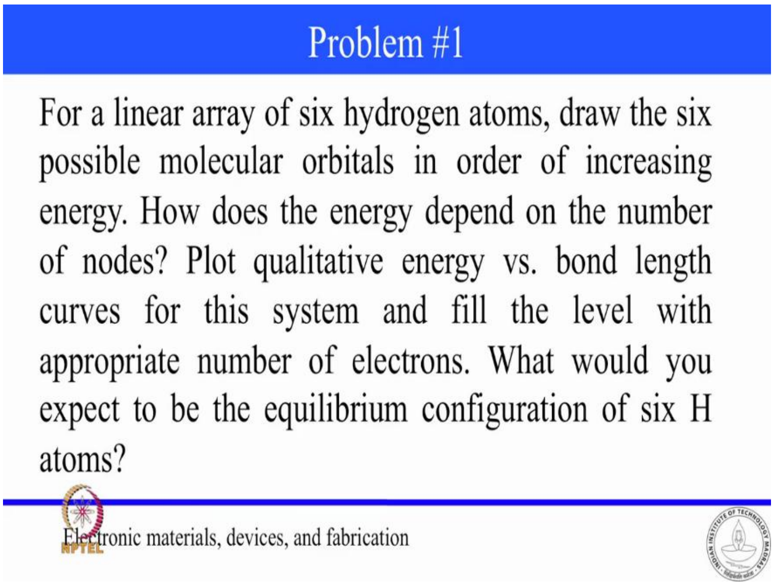

## Problem #1

For a linear array of six hydrogen atoms, draw the six possible molecular orbitals in order of increasing energy. How does the energy depend on the number of nodes? Plot qualitative energy vs. bond length curves for this system and fill the level with appropriate number of electrons. What would you expect to be the equilibrium configuration of six H atoms?

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For a linear array of 6 hydrogen atoms draw the 6 possible molecular orbitals in order of increasing energy.

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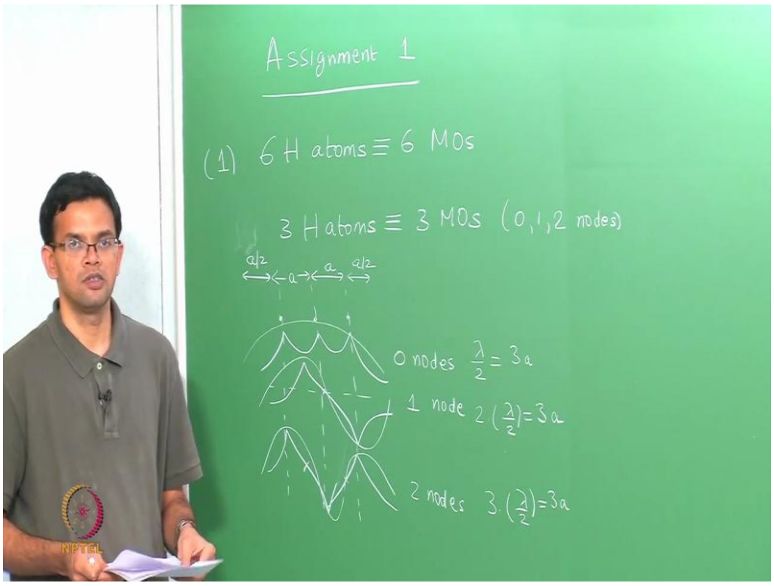

So, we have 6 hydrogen atoms and we know that when 6 atoms come together or when n atoms come together they form n orbitals which have 2n electrons which can accommodate 2n electrons. We have 6 hydrogen atoms and we know they going to form 6 molecular orbitals, I will call them MOs and we need to draw those 6 possible configurations. So, we will start with this but let me go back and start with the much simplest system that we looked at in class.

During a lecture, we considered 3 hydrogen atoms. For 3 hydrogen atoms, you have essentially 3 molecular orbitals. We saw that they have 0, 1 and 2 nodes and we are able to draw them in this fashion. These dots represent the centers of the 3 hydrogen atoms, so basically the nuclei. Let the distance between the hydrogen atoms be a. So, this also a and just for the sake of symmetry we consider a distance $\frac{a}{2}$ from one side and $\frac{a}{2}$ from the other side. So, the total length is 3a. So, we can draw 3 molecular orbitals for this particular case. In the first case with 0 nodes, we were able to draw something like, So, this has 0 nodes. Then the next one with increasing energy would be 1 node. So, In this particular case the node goes through the center so this has 1 node. And we can draw something similar with 2 nodes. So, here you have 2 nodes and these are the 3 molecular orbitals with increasing energy.

So, if you look at the concept behind drawing the nodes you can think of a wave that essentially encompasses all the 3 hydrogen atoms. In this particular case, you have half a wave. Here you have one full wave; so you have both the up and the down and here you have one and half waves. So, if $\lambda$ be the wave length of this wave then the first case with 0 node you had $\frac{\lambda}{2}$, half the wave equal to 3a. In the case of 1 node you have 2 times $\frac{\lambda}{2}$ equal to 3a. The case of 2 nodes we have 3 times $3\left(\frac{\lambda}{2}\right) = 3\text{ a}$. By knowing this value of $\frac{\lambda}{2}$ and $\frac{\lambda}{2}$ defines the position of the node you can go ahead and construct the molecular orbitals. So, this is the case of 3 hydrogen atoms we can go ahead and extend the same concept to 6 hydrogen atoms. So, let me just draw that.

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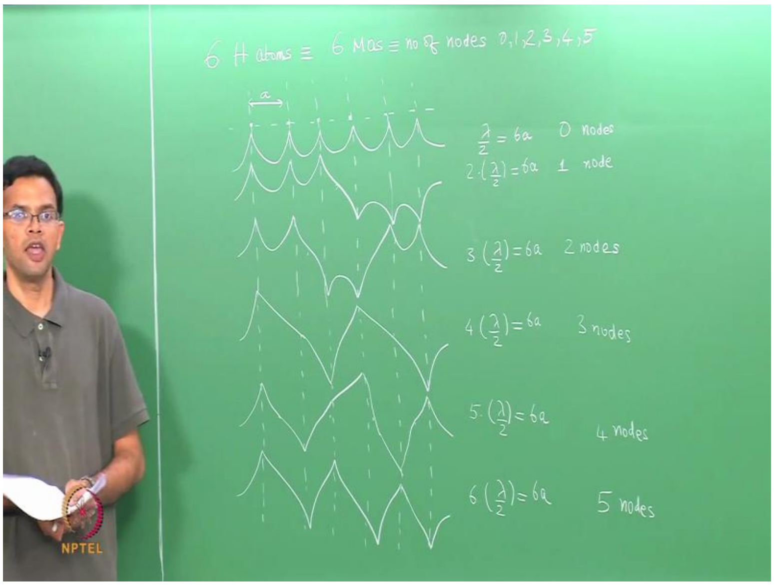

So, now you have 6 hydrogen atoms. 6 hydrogen atoms from 6 molecular orbitals 6 MOS and the number of nodes we will go from 0, 1, 2, 3, 4 and 5. So, you have 6 of these going from 0 to 5. Once again let me mark the atoms. These are my 6 hydrogen atoms the spacing between them is a and the spacing is uniform throughout we will also extend $\frac{a}{2}$ on 1 side and $\frac{a}{2}$ on the other side. The dotted lines are just a guide to help me draw. So, these are the 6 hydrogen atoms. The first case is 0 nodes. So that $\frac{\lambda}{2}$ is 6a. So, it is a same as the 3 hydrogen atom situation where $\frac{\lambda}{2}$ was 3 a. This if you draw So, we have the 6 atomic orbitals mixing to form 1 molecular orbital which has 0 nodes the next 1 is the 1 with 1 node. So, that $2\left(\frac{\lambda}{2}\right) = 6\ a$. now, we have 3 up and 3 down and the function goes to 0 at essentially the middle of this. So, here is where it goes to 0. If you were to draw the wave functions that is your 1 node. We have 1 node 3 of the atomic orbitals are up and 3 are down next you have 2 nodes. So, let me draw write this is 0 nodes, 1 node, 2 nodes so now, it is $2\left(\frac{\lambda}{2}\right) = 6a$. Now, you have 2 nodes.

So, the nodes are located here and then here. Then we can draw the wave functions. So, we have 2 up, 2 down and 2 up. So, that overall we have 2 nodes. So, let me just extend this down. So, then we can keep going on. Now, we have going to have 3 nodes,So, the $4\left(\frac{\lambda}{2}\right) = 6\ a$. So, we use this formula to find out the position of the nodes and once we know the position of the nodes we can go back and draw the molecular orbitals. So, here you have 1 node here in the next node comes in between next node here. This is the case with 3 nodes 1, 2 and 3 then we have 4 nodes. So, it is $5\left(\frac{\lambda}{2}\right) = 6\ a$. So the positions, this is lightly more complicated to draw, but once you have the nodal positions you can draw it and then the last with 5 nodes that is the trivial. That is $6\left(\frac{\lambda}{2}\right) = 6\ a$. So you have everything going up and down. So, In the case of 6 hydrogen atoms, these are your 6 molecular orbitals and they go in the order of increasing energy. So, the one with 0 nodes is the one that is more stable and then as we go down we essentially increase in energy. So, this answers the first part of the question. So, draw the 6 possible molecular orbitals and we also see that the energy increases with the number of nodes. So, when we ask the question, how does the energy depend on the number of nodes the more the number of nodes greater is the energy.

We also want to plot a qualitative energy verses bond length curve for this system. So, that we have already seen in class.

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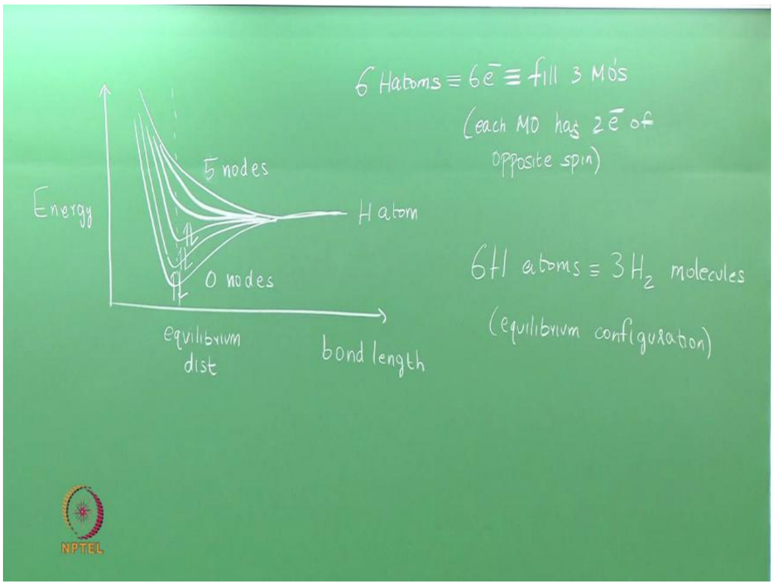

6 H atoms ≡ $6\bar{e}$ ≡ fill 3 MO's
(each MO has $2\bar{e}$ of opposite spin)

6H atoms ≡ 3 $H_2$ molecules
(equilibrium configuration)

We can draw these energy verses bond length if we had only 2 hydrogen atoms you will have 2 curves 1 corresponding to bonding 1 corresponding to anti bonding if we have 3 hydrogen atoms you will have 3 curves and now we have 6 hydrogen atoms we will essentially have 6 curves. So, at infinity you have the energy level corresponding to the hydrogen atom. There is a particular position at which the energy is minimum this is the equilibrium distance. So, we can plot energy verses bond length. So, the lowest energy is the one with 0 nodes. This will be the one with 0 nodes the highest energy will be the 1 with 6 nodes. So, this one will be the 1 with 6 nodes sorry with 5 nodes. So, the 1 with the last 1 and everything else will come in between, so, 1 node and then 2 nodes 3, 4 and 5. So, we essentially have 6 curves and they go again in order of increasing energy. So, we then need to fill this system with the appropriate level and position of the electrons. So, if we have 6 hydrogen atoms. Each hydrogen atom can provide 1 electron. So, we have 6 electrons and each molecular orbital can take 2 electrons of opposite spin. So, this means you will fill 3 molecular orbitals. So, each MO has 2 electrons of opposite spin.

These electrons we can put. So, first 2 electrons go here then the next 2 electrons go here and then the final 2. So, the lowest 3 molecular orbitals are full and the highest 3 are empty. So, the last part of the question, what would you except to be the equilibrium configuration of 6 hydrogen atoms? So, if you have 6 hydrogen atoms in reality 2 hydrogen atoms come together to form a hydrogen molecule. If you have 6 hydrogen atoms the equilibrium configuration is essentially 3 hydrogen molecules. So, rather than form this linear chain of 6 hydrogen atoms the actual configuration would just be 3 hydrogen molecules. So, let us now go to the next question.

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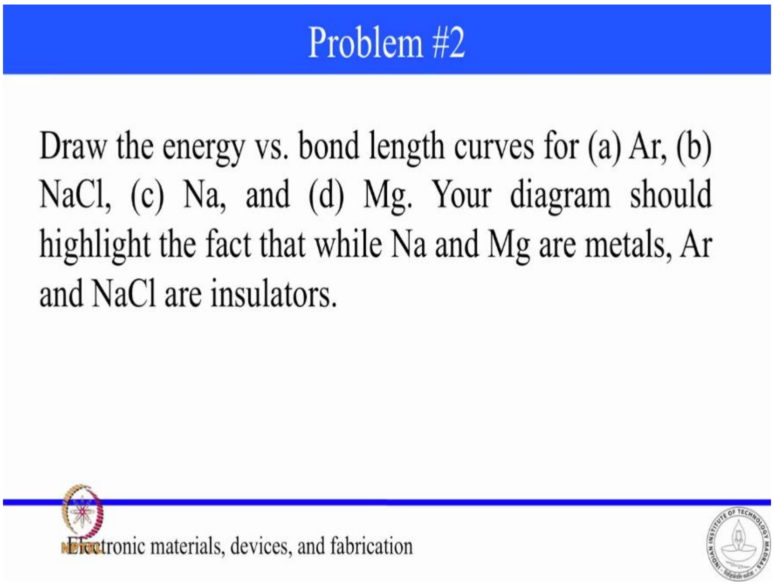

Problem #2

Draw the energy vs. bond length curves for (a) Ar, (b) NaCl, (c) Na, and (d) Mg. Your diagram should highlight the fact that while Na and Mg are metals, Ar and NaCl are insulators.

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So, question 2 we want to draw energy verses bond length curves for various elements and compounds. So, we have argon, sodium, sodium chloride and magnesium. So, The important thing to note here is that sodium and magnesium are metals and we know in the case of metals the valance band and the conduction band should overlap and argon and sodium chloride are insulators so that we should show a band gap there.

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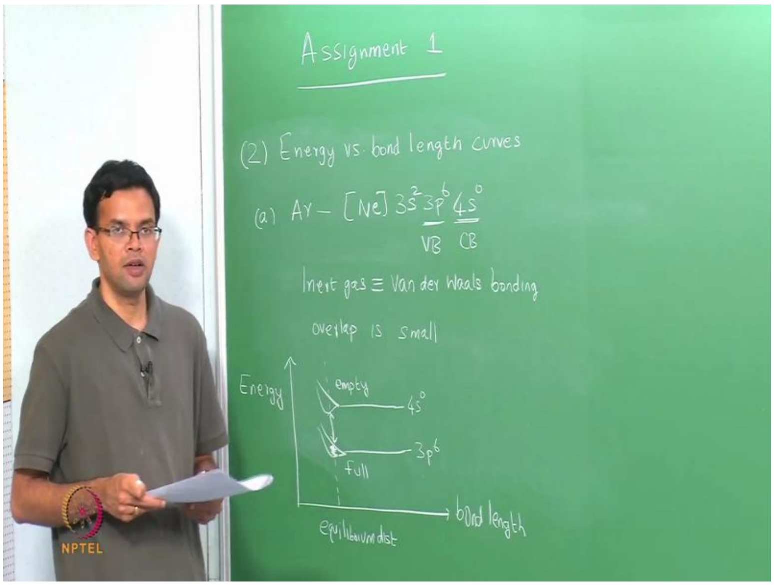

So, Let us draw the energy verses bond length curves. So, let us first start with argon. So, We can write the electronic configuration for argon. So, the previous inner gas is neon. So, we have helium, neon argon and so on.

Neon followed by a $3s^2$, $3p^6$ and then the next higher level is empty so $4s^0$. 3p would form your valence band and 4s would form your conduction band and there will be a gap between these 2. Another important thing to note is that argon is an inner gas which has something called a Van Der Waals bonding. We did not talk too much about Van Der Waals bonding in class, but the important thing to know here is that the overlap is very small. Which means the energy bonds or the energy bands are all very small. So, let us draw the energy verses bond length. So, I have energy on my y-axis and then I have bond length on the x-axis. This is my $3p^6$ which is the full level and then I have $4s^0$ there is a certain equilibrium distance which we will keep so, I am going to call this equilibrium. So, we again have to show that there is some overlap, but the overlap is very small. This is a full level I will have just mark it full. But you can see that the overlap here is really small and then you have a 4s level which is empty. So, this is full this is empty and there is a band gap making this an insulator.

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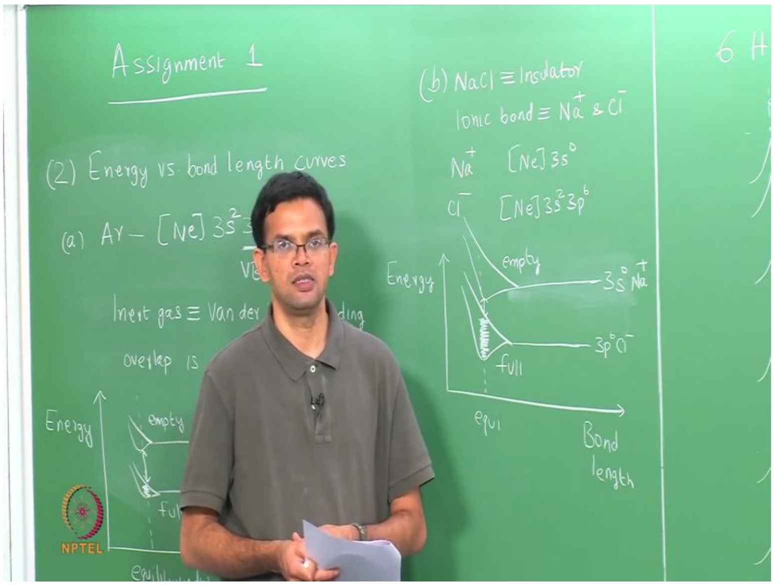

The next material we will look at sodium chloride. Sodium chloride is also an insulator but it is a case of an ionic bond. So, you have an ionic bond between $Na^+$ and $Cl^-$. Instead of writing the electronic configuration of the atoms we need the electronic configuration of the ions. So, $Na^+$ has the electronic configuration of $[Ne]3s^0$, $Cl^-$ has the electronic configuration of neon $3s^2$ and $3p^6$. So, this is your full level which is $3p^6$ this is the empty level and there is a gap between those 2 which forms your band gap. We can draw again energy verses bond length this is an equilibrium distance. I will just say equi to mean equilibrium distance. So, I have the $3p^6$ of chlorine which is full and I have the $3s^0$ of sodium that is empty. So, once again these come together to form a band. This is a band that is full because the chlorine level is full the case of sodium. Let me just re draw this a bit the case of sodium. So, this is my $3s^0$ of sodium you have a band that is empty and once again you have a band gap. So, both sodium chloride and argon are essentially insulators and the way we depict them in your energy verses bond length diagram is to show a gap between a full state and an empty state.

The next 2 are essentially metals. So, you have sodium and magnesium and we have to show an overlap between the valence and the conduction band.

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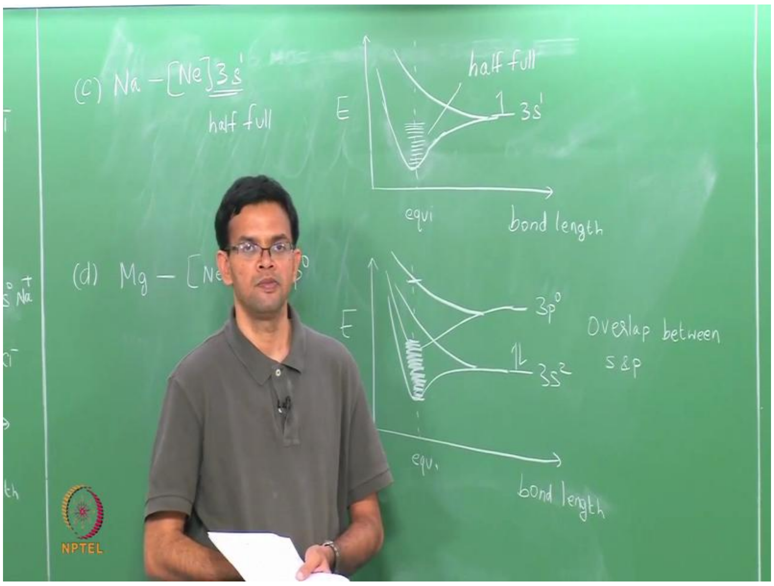

So in c we will look at sodium. Now we have sodium that is a metal. So, it is electronic configuration is neon $3s^1$. We have $s^1$; we have a band that is half full. So, The easiest way to depict this is to have your energy E verses bond length you have a $3s^1$ that has only 1 electron there is your equilibrium distance and when the atoms come together they form a band. Let me just slightly modify this atoms, form a band and the band is only half full. This makes sodium a metal because we have a band that is half full the last 1 we are going to look at is magnesium. Magnesium is also a metal, but it has the configuration $[Ne]3s^2$. So, $s^2$ is essentially a full band.

So, to make sure that it is a metal to show the overlap between the valence and the conduction band we consider the next level $3p^0$ and we say that there is a mixing between the s and the p. So, this again we can show energy verses bond length this is the 3s level so that is full. Now you have a $3p^0$ that is empty and this overlaps with the 3s. Now, you have a full band and that is only half full. We have overlap between s and p so, this way magnesium becomes a metal. Let us now go to the next question.

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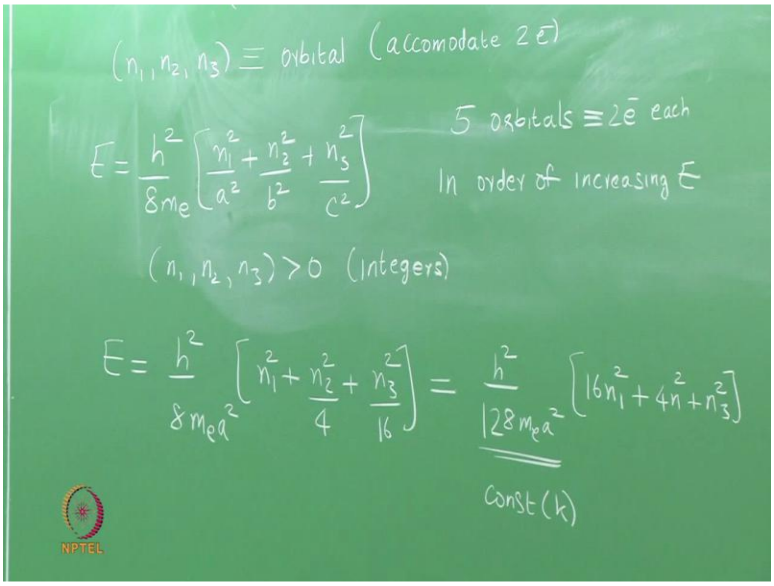

$(n_1, n_2, n_3) \equiv$ orbital (accomodate 2 $\bar{e}$)

$$E = \frac{h^2}{8m_e}\left[\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right]$$

5 orbitals $\equiv 2\bar{e}$ each

In order of increasing E

$(n_1, n_2, n_3) > 0$ (integers)

$$E = \frac{h^2}{8m_ea^2}\left[n_1^2 + \frac{n_2^2}{4} + \frac{n_3^2}{16}\right] = \underbrace{\frac{h^2}{128m_ea^2}}_{\text{Const }(k)}\left[16n_1^2 + 4n_2^2 + n_3^2\right]$$

So, question 3. There are 10 electrons in a slab. We have 10 electrons and the dimensions of the slab are given. So, we have length of point 5 nanometers and then width is 1 nanometer and height is 2 nanometers. For simplicity let us just call these a, b and c. So, for an electron in a slab there are essentially 3 quantum numbers $n_1$, $n_2$ and $n_3$. So, we have a set of quantum numbers $n_1$, $n_2$ and $n_3$ and they are used to define the energy of the electron. So, e in this case is nothing but $\frac{h^2}{8m_e}\left[\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right]$. So, these represent the energy of the electron as a function of $n_1$, $n_2$ and $n_3$ and each of these we can think or each set of these we can think of as an orbital which can accommodate 2 electrons.

So, If we have 10 electrons in a slab, we essentially have 5 orbitals which can each take 2 electrons. So, that all the 10 electrons are filled and these orbitals go in order of increasing energy. So, We have 5 orbitals with 2 electrons each in order of increasing e. So, we need to find 5 sets of $n_1$, $n_2$ and $n_3$ which are all go in the order of increasing energy and the important thing is $n_1$, $n_2$ and $n_3$ are all integers and they all should be greater than 0. So, we can simplify this expression which we have here when we realize that b is nothing but, 2 x a and c is nothing but, 4 x a the energy e can be written as h square by $\frac{h^2}{8m_ea^2}\left[n_1^2 + \frac{n_2^2}{4} + \frac{n_3^2}{16}\right]$ this is just by substituting b and c in terms of a and taking a out, by writing by taking a common factor out this can be written as $\frac{h^2}{128m_ea^2}\left[16n_1^2 + 4n_2^2 + n_3^2\right]$. So, the first term here is essentially a constant where is called it k, so this is a constant times a variable that depends upon $n_1$, $n_2$ and $n_3$. So, we can plug in different values and then basically see the lowest 5 energy levels and then we can put the electrons in them.

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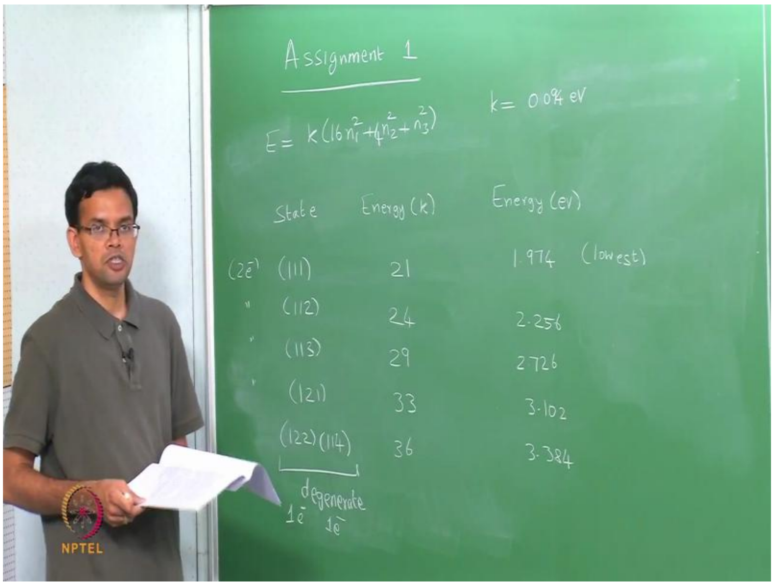

Assignment 1

$E = k(16n_1^2 + 4n_2^2 + n_3^2)$ $k = 0.094$ eV

| | State | Energy (k) | Energy (eV) |
|---|---|---|---|
| $(2e^-)$ | (111) | 21 | 1.974 (lowest) |
| " | (112) | 24 | 2.256 |
| " | (113) | 29 | 2.726 |
| " | (121) | 33 | 3.102 |
| | (122) (114) | 36 | 3.384 |

$\underbrace{(122)\,(114)}_{\text{degenerate}}$

$1e^-$ $1e^-$

Let us let me write that in the form of a table. We have the energy E is nothing, but a constant times $[16n_1^2 + 4n_2^2 + n_3^2]$ k we can evaluate and k comes out to be 0.094 electron volts. So, Let me write a table the first is state, next is energy in terms of k and then finally energy in electron volts. So, we said that $n_1$, $n_2$ and $n_3$.should all be integers and there should all be greater than 0. So, 0 is not an acceptable number. So, the lowest energy state is typically 1, 1, 1. So $n_1$, $n_2$ and $n_3$.are all 1s in that particular case this expression, this should be 4 $n^2$ sorry, 16 + 4 + $n_3^2$. So, if it is all 1, 1, 1 this expression is essentially 21 and the energy is 1.974. This is your lowest energy level. The next energy level, 1 of these numbers must become 2 because they can only be integer numbers. So, if you put 2 in the first case for n 1 you find that the energy is actually multiplied by 16. So, the next energy state would be 1, 1 and 2 that gives you a number 24 and the energy is 2.256 then we have 1, 1, 3 again it is just a question of plugging the numbers and checking the math 7, 2, 6 then we have 1, 2, 1 that is 33, 3.102. And then, actually we find that we have 2 states 1, 2, 2 and 1, 1, 4 both have the same energy. So, the number is 36 and the energy is 3.384. So, these states are called the Degenerate States. Because you have 2 sets of quantum numbers which have the same energy.

Now, we have our 5 orbitals. So, if we fill in this gets 2 electrons, this gets 2, this gets 2 and this gets 2. We have 8 electrons and both of them have the same energy so each gets 1 electron. So, if we look at the first part of the question we have to assign the quantum numbers to the electrons. Quantum numbers are the numbers $n_1$, $n_2$ and $n_3$. They have all be assigned we want to deduce $E_F$ from this energy distribution

So, the next thing you want to find is $E_F$.

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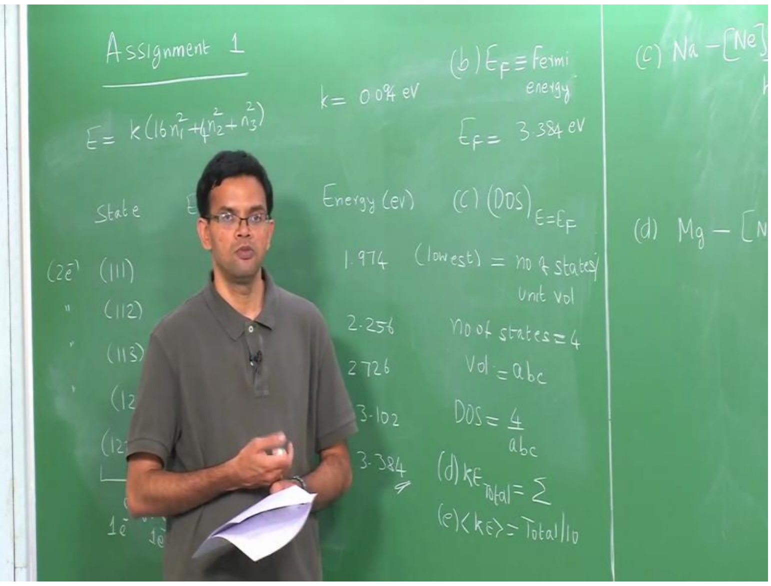

$E_F$ is the fermi energy and if we go back to the definition of $E_F$ the fermi energy is the highest energy state. So, in this particular example the highest energy state is this so $E_F$ is just 3.384 electron volts part c we want to determine the density of states at $E_F$. So, density of states once again we will go back to the definition. So, Density of states is the total number of states per unit volume. So, this is the number of states per unit volume. So, the question says we want the density of states including spin. So, If you look at 3.384 we have essentially 2 states each state can take 2 electrons. So, we have a total of 4 available states. So, the number of states is 4. The volume of the slab is nothing but a, b, c the product of all 3. So, the density of states is nothing 4 over a, b, c. So, we can express this either in ev N $m^3$ or J $m^{-3}$ part d we want the total kinetic energy of all the electrons.

The total kinetic energy is nothing, but the sum of all these energy values. So, you just add all these numbers the average kinetic energy is nothing but the total divided by 10.

So, the idea is even if we have a discrete system with a specific number of electrons instead of a solid where we have $10^{23}$ electrons we can still define terms like a fermi energy or a density of states.

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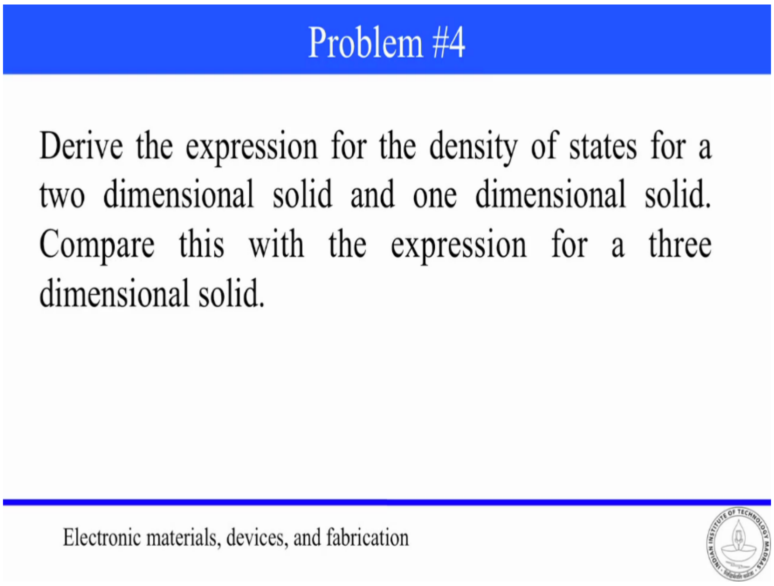

## Problem #4

Derive the expression for the density of states for a two dimensional solid and one dimensional solid. Compare this with the expression for a three dimensional solid.

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Let us now go to problem 4. So, We want to derive an expression for the density of states for a 2 dimensional and a 1 dimensional solid and you want to compare this with the derivation for a 3 d solid.

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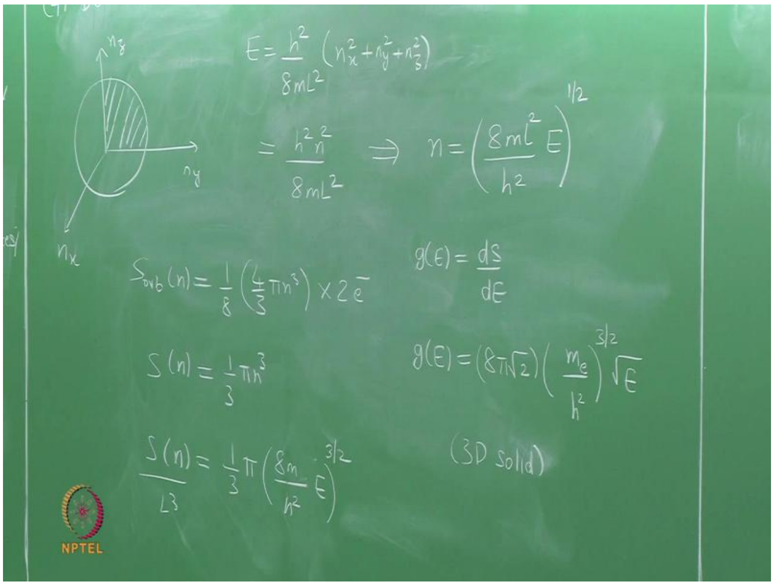

$$E = \frac{h^2}{8mL^2}(n_x^2+n_y^2+n_z^2)$$

$$= \frac{h^2 n^2}{8mL^2} \Rightarrow n = \left(\frac{8mL^2}{h^2}E\right)^{1/2}$$

$$S_{orb}(n) = \frac{1}{8}\left(\frac{4}{3}\pi n^3\right) \times 2e^-$$

$$g(E) = \frac{dS}{dE}$$

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

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

$$\frac{S(n)}{L^3} = \frac{1}{3}\pi\left(\frac{8m}{h^2}E\right)^{3/2}$$

(3D solid)

We have looked at how to derive for a 3 dimensional solid in class. Let me refresh that briefly and then we will come back to how we do this for a 2 D and a 1 D solid. In the case of a 3 dimensional solid we once again define 3 quantum numbers $n_x$, $n_y$ and $n_z$ and just like a particle in a box which we just saw in the previous problem we were able to write an expression for the energy which is nothing $\frac{h^2}{8m_eL^2}\left[n_x^2+n_y^2+n_z^2\right]$ this is nothing but $\frac{h^2n^2}{8mL^2}$ . So, if we look at it the total number of states for a given value of n is essentially a sphere, but we only consider the first quadrant of this sphere because all the values of n should be positive that is there should be greater than 0.

So, if you want to write the total number of states, so s orbital of n. The total number of states with energy less than n is nothing but the volume of the sphere and only considering the first quadrant. So, 1 over 8 if we also include spin each state can essentially take 2 electrons of opposite spin. So, s(n) including spin is nothing but 1 over 3 by $n^3$. We can write n in terms of energy. If we use this equation n is nothing but $\sqrt{\frac{8mL^2E}{h^2}}$ so, s(n) we can write in terms of energy by just substituting the value of n here. So, s(n) 3 π, $\left(\frac{8mL^2E}{h^2}\right)^{3/2}$. So, this represents the total number of states in terms of the energy if you want to know the total number of states per unit volume you divide this by $L^3$ which will essentially cancel this expression $L^2$. So, you left with this if you want to find the density of states, then the density of states g(E) is nothing but $\frac{ds}{de}$. So, we differentiate this with respect to energy and the final expression which we write is $8\pi\sqrt{2}\left(\frac{m_e}{h^2}\right)^{3/2}\sqrt{E}$. So, this is the derivation for a 3 D solid. So, We can now modify this to apply to a 2 D and a 1 D solid.

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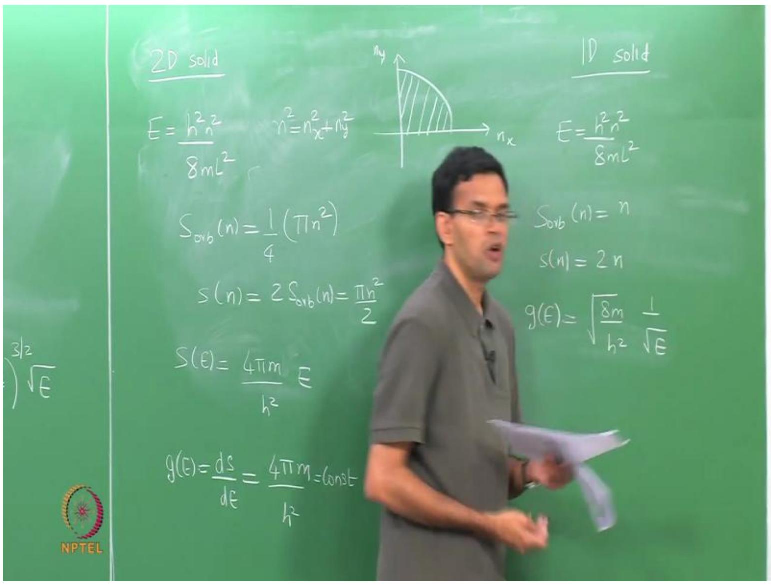

For a 2 D solid, you can once again write energy e has $\frac{h^2n^2}{8mL^2}$, but now instead of 3 quantum numbers you only have $2n_x^2 + n_x^2$. So, instead of a sphere you will essentially have only a circle $n_x$ and $n_y$ and we will once again consider only the first quadrant of the circle. So, the total number of states whose energy is less than that of n is again the area of the circle. So, in 3 d it was the volume of the sphere now it is the area of the circle $\pi n^2$ and only the first quadrant one-fourth so, it is one-fourth (¼) $\pi n^2$ if we take (Refer Slide Time: 43:02) spin. So, this is 2 x s orbital of n. This is $\pi n^2/2$, So, $n^2$ we can once again substitute in terms of energy. So, s(E) we can write the expression is $\frac{4\pi mL^2}{h^2E}$ 4 phi m l square over h square times e if you want to do this per unit volume the $L^2$ term goes off and to find the density of states we differentiate s respect to e. So, that this is just a constant, so $\frac{4\pi m}{h^2}$. So, for a 3 d solid we found that the density of states increases with energy it goes as a$\sqrt{E}$ for a 2 D solid the density of states is essentially just a constant for a 1 D solid. We can once again write a similar expression but there is only 1 n so, it is only $n_x$ in that particular case s orbital is nothing, but n if you take spin into a count s(n) is 2 n we can substitute the value of n using this expression we will go through the same math the final answer is the density of states a $\sqrt{\frac{8m}{h^2}\frac{1}{\sqrt{E}}}$. So, for a 1 D solid the density of states actually goes down with increase in energy.

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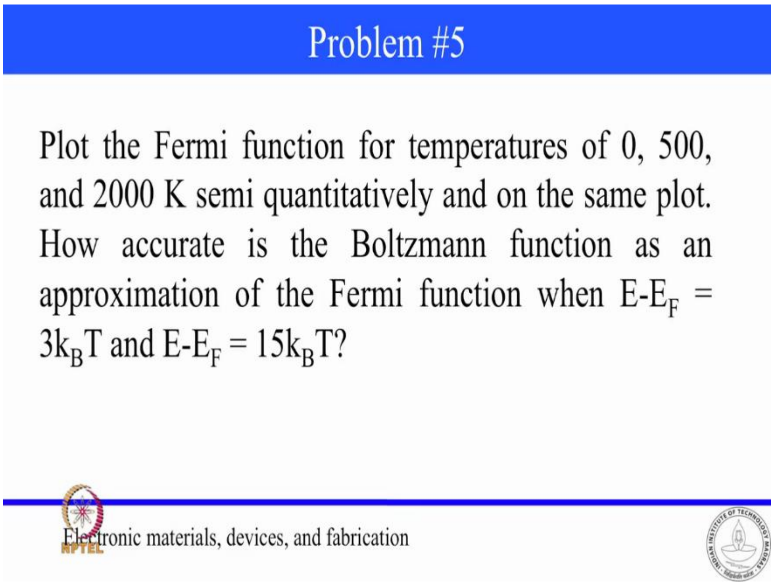

## Problem #5

Plot the Fermi function for temperatures of 0, 500, and 2000 K semi quantitatively and on the same plot. How accurate is the Boltzmann function as an approximation of the Fermi function when $E-E_F = 3k_BT$ and $E-E_F = 15k_BT$?

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Let us now look at the last problem. We want to plot the fermi function for temperatures of 0, 500 and 2,000 Kelvin is a semi qualitative plot and we want do this on the same plot.

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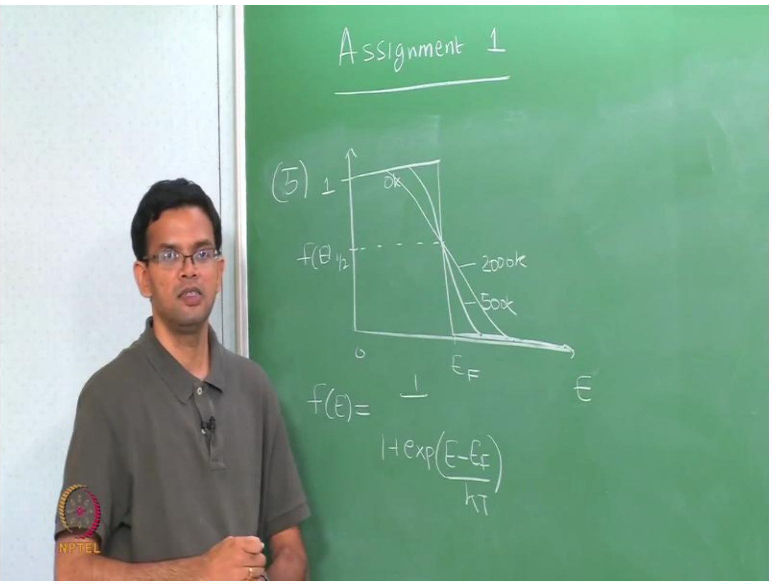

So, the fermi function if you remember $f(E)$ is nothing, but $\frac{1}{1+exp\left(\frac{E-E_F}{kT}\right)}$. So, when the energy is less than $E_F$ the probability is 1 when the energy is more than $E_F$ at 0 Kelvin probability is 0 and at $E = E_F$ probability is half, so $f(E)$ versus $T$ sorry $f(E)$ versus $E$. So, we want to plot the fermi function is function of energy, so f(E) versus E. Let me mark $E_F$ and 0 and fermi function goes from 0 to 1 and I will mark 1 and half. So, at 0 Kelvin it has a value of 1 and then it has a value of 0. So, it is a delta function. So, this is 0 kelvin we now increase the temperature slightly. We go to 500 kelvin. So, now, you have a slide broadening. So, you have some states that can get excited. So, here you have a certain occupation probability above the fermi energy and you have some electrons that are lost below the fermi energy. So, this is 500 kelvin we can do the same if we increase the temperature further this deviation is even more, but all cases it passes through half. So, whatever be the temperature the occupation probability is always half at the fermi energy. So, this 1 is 2,000.

So, these spreads are essentially qualitative they just to show that with increase in temperature more and more higher energy states are being occupied. So, the next part we want to compare the fermi function and the Boltzmann function.

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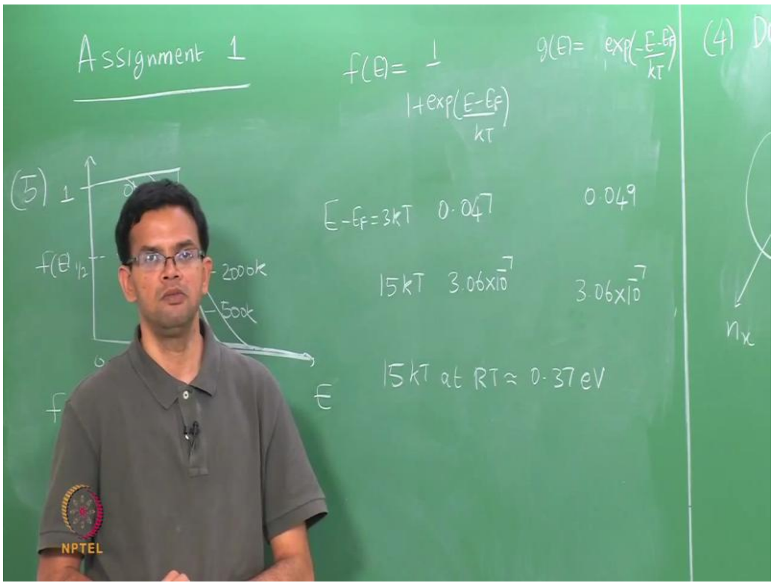

So, f(E) we have written $E_F/kT$ the Boltzmann function is just $exp\left(\frac{E-E_F}{kT}\right)$. So, when $E-E_F$ is 3 kT we can substitute and the numbers are 3 - 3 kT the fermi function is 0.047 the Boltzmann function is 0.049. So, they are close, but there is a small deviation for 15 kT the fermi function is 3.06 x $10^{-7}$ and the Boltzmann function is also 3.06 x $10^{-7}$. So, further the deviation from the fermi energy. So, if you want to look at it 15 kT at room temperature is approximately 0.37 electron volts, which is smaller than the band gap of silicon or half the band gap of silicon. In the case of solids the Boltzmann function is a good enough approximation of the fermi function.