Electronic Materials, Devices and Fabrication

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Lecture - 04
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.

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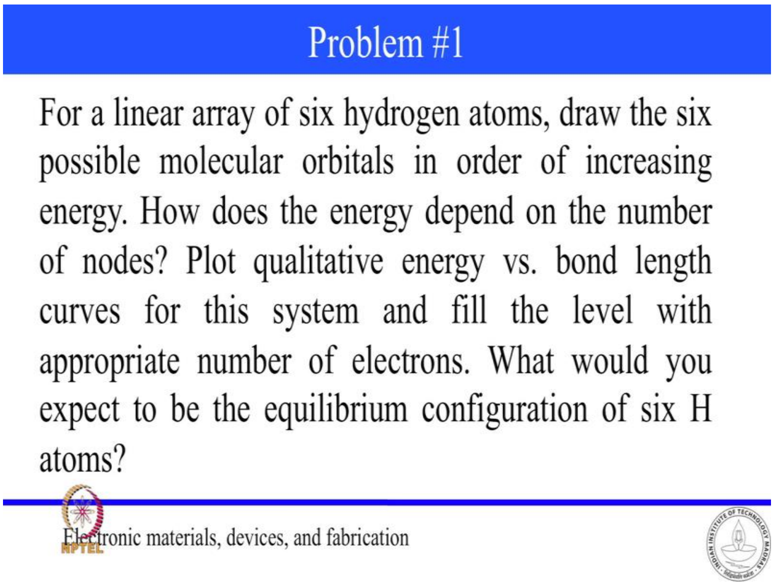

Problem #1

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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So, in today's assignments, 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 two lectures of this course. So, let us look at problem number 1. For a linear array of 6 hydrogen atoms, draw the 6 possible molecular orbitals in order of increasing energy. 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 2 n electrons, which can accommodate to an electrons.

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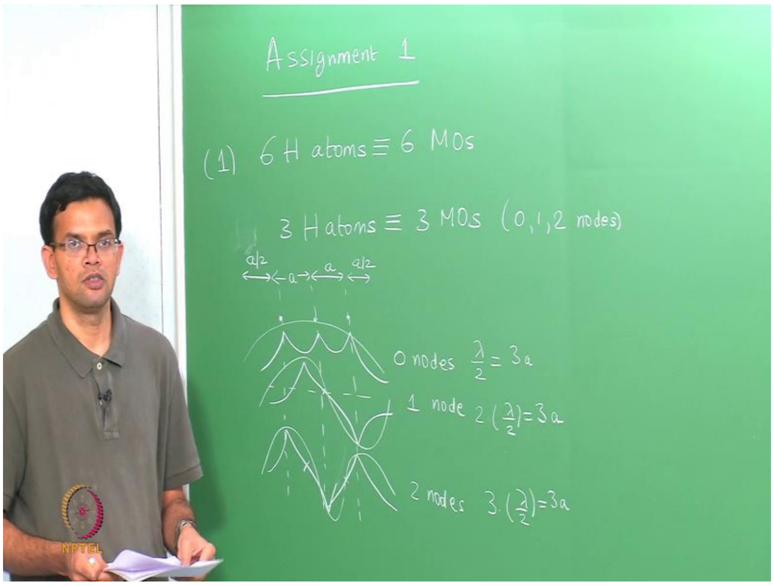

So, we have.6 hydrogen atoms and we know they are going to form 6 molecular orbitals. I will call them MOS and we need to draw those 6 possible configuration. So, we will start with this. But let me go back and start with the much simpler system that we looked at in class. So, during the lecture, we 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. So, these dots represent the centers of the 3 hydrogen atoms.

So, basically the nuclei, lets the distance between the hydrogen atoms be a, so this is also a. And just for the sake of symmetry, we consider a distance a over 2 from 1 side and a over 2 from the other side. So, the total length is 3 a. 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 this, so this has 0 nodes. Then, next 1 with increasing energy would be 1 node. So, in this particular case, the node goes through the centre, 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 the drawing the nodes, you can think of wave that essentially encompasses all the 3 hydrogen atoms. So, in this particular case, you have half of wave. Here you have 1 full wave, so you have both the up and the down. And here you have 1 and a half waves. So, if land up be the wave length of this wave, then the first case with 0 node, you had land up by 2, so half the wave equal to 3 a. In the case of 1 node, you have 2 times lambda by 2 equal to 3 a. In the case of 2 nodes, we have 3 times lambda by 2 equal to 3 a.

So, by knowing this value of lambda by 2 and lambda by 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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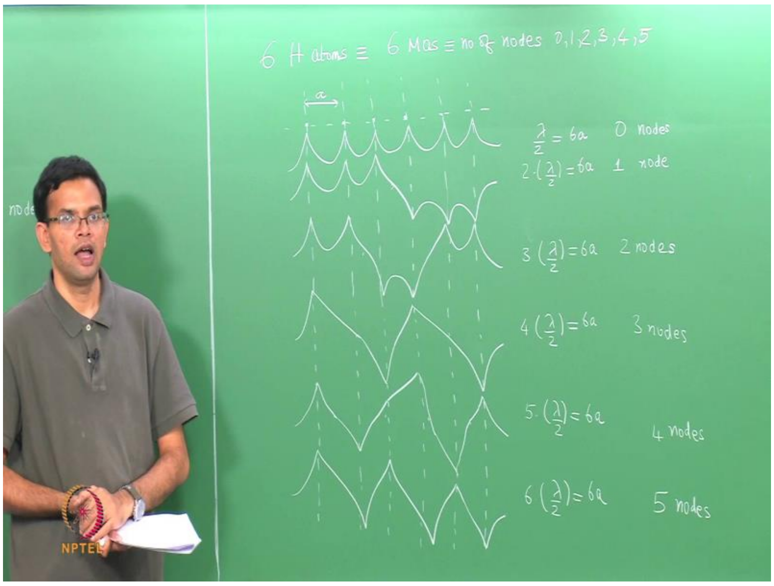

So, now, you have 6 hydrogen atoms 6 hydrogen atoms from 6 molecular orbitals 6 MOS. And the number of nodes will go from 0 1 2 3 4 and 5. So, you have 6 of these going from 0 to 5. So, once again let me mark the atoms. So, these are my 6 hydrogen atoms. This spacing between them is a and this spacing is uniformed throughout. We will also extend a over 2 on 1 side and a over 2 on the other side. So, the dotted line are just a guide to help me draw. So, these are the 6 hydrogen atoms. The first case is 0 nodes so that, lambda over 2 is 6 a. So, this is same as the 3 hydrogen atom situation, where lambda over 2 was 3 a.

So, this if you draw, so we have this 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 times lambda over 2 is 6 a. So, 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. So, if you were to draw the wave function; that is your 1 node. So, 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 3 times lambda over 2 its 6 a, so now, you have 2 nodes.

So, the nodes are located here and then here and 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. So, now, we are going to have 3 nodes so that, 4 times lambda over 2 this 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 we have 1 node here and the next node comes in between, next node here.

So, this is the case with 3 nodes 1 2 and 3. Then we have 4 nodes, so 5 times lambda over 2 is 6 a. So, the positions; so this is slightly 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, so 6 times lambda over 2 is 6 a. So, you have everything going up and down. So, the case of 6 hydrogen atoms, these are your 6 molecular orbitals and they go in the order of increasing energy.

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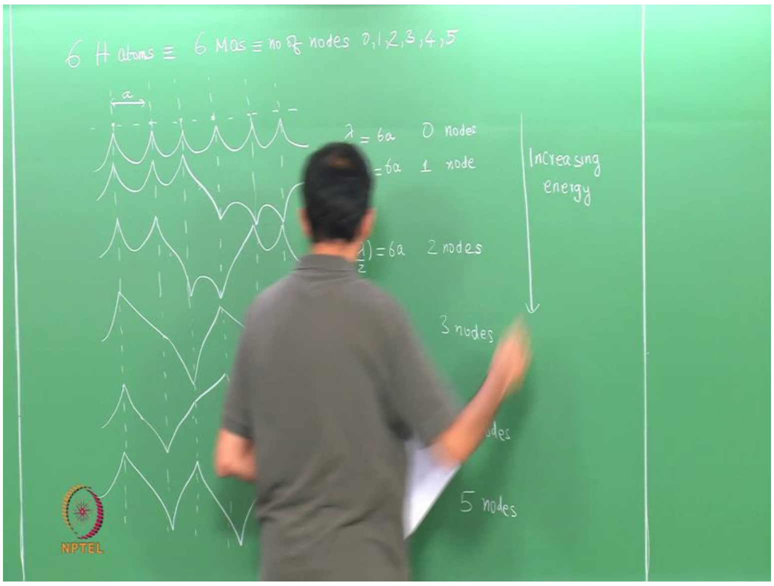

So, the 1 with the 0 nodes is the 1 that is more stable. And then as we go down we essentially increase in energy. So, this answers the first part of the question. So, draw the 6 possible molecular orbitals. And we also see that the energy increases with the number of nodes. So, when we ask the question how does the energy depend in 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 the system. So, that we have already seen in the class.

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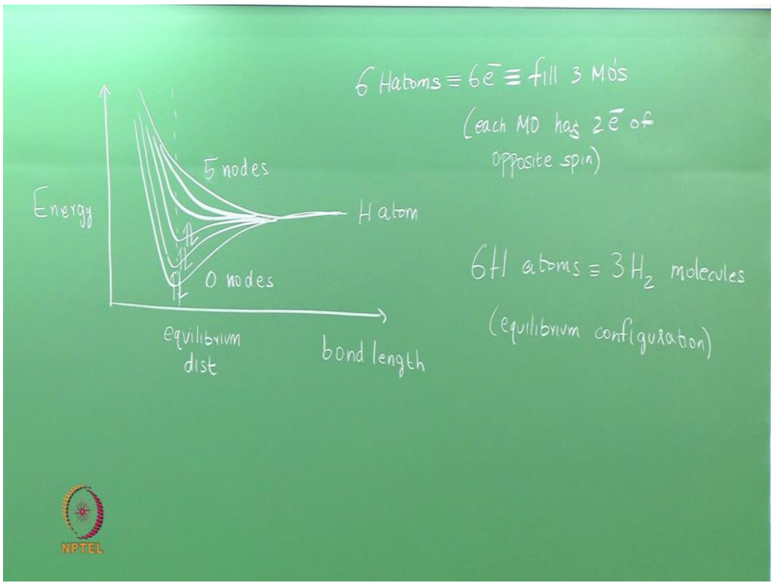

6 H atoms $\equiv 6\bar{e} \equiv$ fill 3 MO's

(each MO has $2\bar{e}$ of opposite spin)

$6H$ atoms $\equiv 3H_2$ molecules

(equilibrium configuration)

We can draw this energy verses bond length. If we had only 2 hydrogen atoms, you have 2 curves; 1 corresponding to bonding, 1 corresponding to anti bonding. We have 3 hydrogen atoms, you will have 3 curves and now we have 6 hydrogen atoms, we 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 1 with 0 nodes. So, this will be the 1 with 0 nodes. The highest energy will be the 1 with 6 nodes, so this 1 will be the 1 with 6 nodes, with 5 nodes so, 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 curve and they go again in order of increasing energy. So, we then need to fill this system with the appropriate level and the 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 orbitals can take 2 electrons of opposites spin. So, this means you will fill 3 molecular orbitals. So, each m o has 2 electrons of opposites spin. So, these electrons we can put, so first 2 electron go here, then the next 2 electron 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 expect the be the equilibrium configuration of 6 hydrogen atoms? So, if we have 6 hydrogen atoms, in reality 2 hydrogen atoms come together to form a hydrogen molecule. So, if you have a 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. So, question 2.

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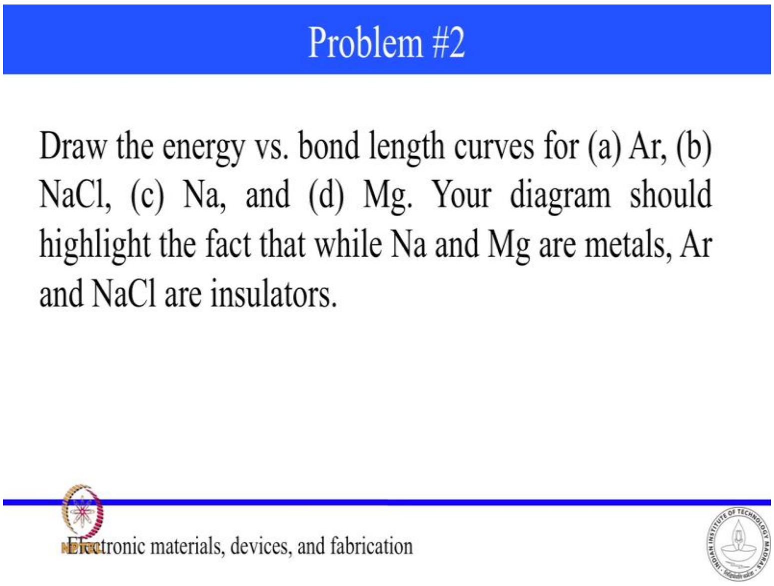

Problem #2

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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We want to draw energy verses bond length curves for various elements and components. So, we have organ, 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 convection band should overlap and organ and sodium chloride are insulated so that, we should show a band gap there.

So, let us draw the energy versus bond length curve.

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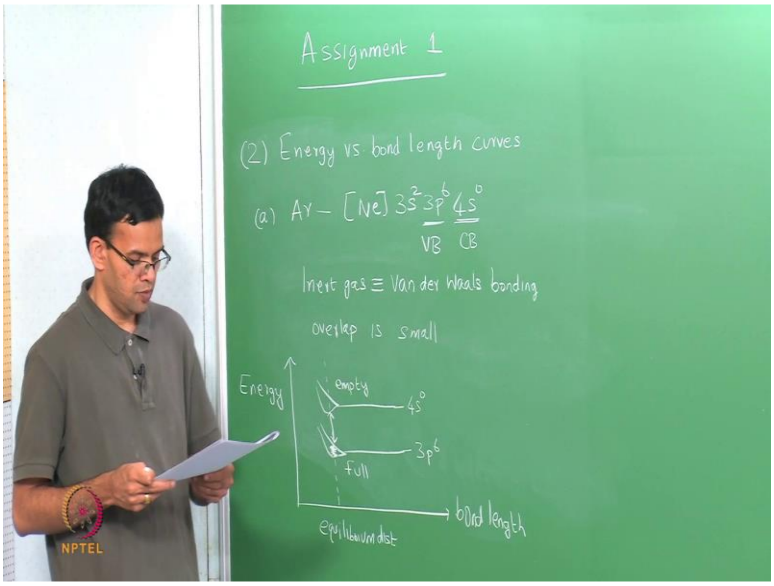

So, let us first start with argon. So, we can draw the electron or we can write the electronic configuration for argon. So, the previous inner gas is neon so we have helium, neon, argon. So, on neon followed by a 3 s 2, 3 p 6 and then the next higher level is empty, so 4 s 0. So, 3 p would form your valance band and 4 s would form your conduction band and there will be a gap between these 2. And the other 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 the class, but the important thing to note 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 a y access and then I have bond length on the x access. So, this is my 3 p 6 which is the full level and then I have 4 s 0, there is a certain equilibrant 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. So, this is a full level. So, I will just mark it full, but you can see that the overlap here is really small and then you have a 4 s level which is empty. So, this is full this is empty and there is a band gap making this a insulator. So, the next element, the next material we look at is sodium chloride.

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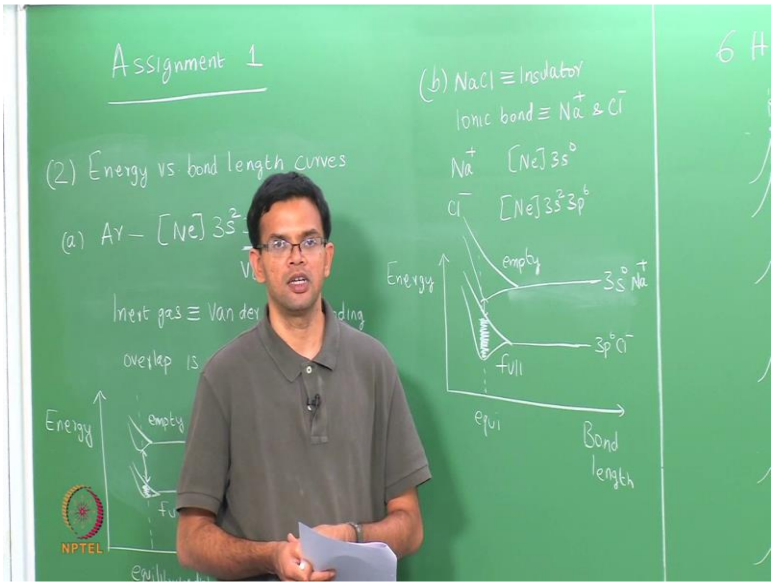

Sodium chloride is also an insulator, but it is an case of ironic bond. So, you have an ironic bond between Na plus and Cl minus. So, instead of writing the electronic configuration of the atoms, we need the electronic configurations of the irons. So, Na plus has the electronic configuration of neon 3 s 0, Cl minus has the electronic configuration of neon 3 s 2 and 3 p 6. So, this is your full level which is 3 p 6, this is the empty level and there is a gap between those 2 which forms your band gap.

So, we can draw again energy verses bond length use an equilibrium distance. So, I will just say equi to mean equilibrium distance. So, I have the 3 p 6 of chlorine, which is full and I have the 3 0 of sodium that is empty. So, once again this comes together to form a band. So, this is a band that is full because, the chlorine level is full. In the case of sodium, let me just read redraw this a bit. In the case of sodium, so this is my 3 s 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.

So, the next two are essentially metals, so you have sodium and magnesium. And we have to show an overlap between the valance and the conduction band. So, in c we will look at sodium.

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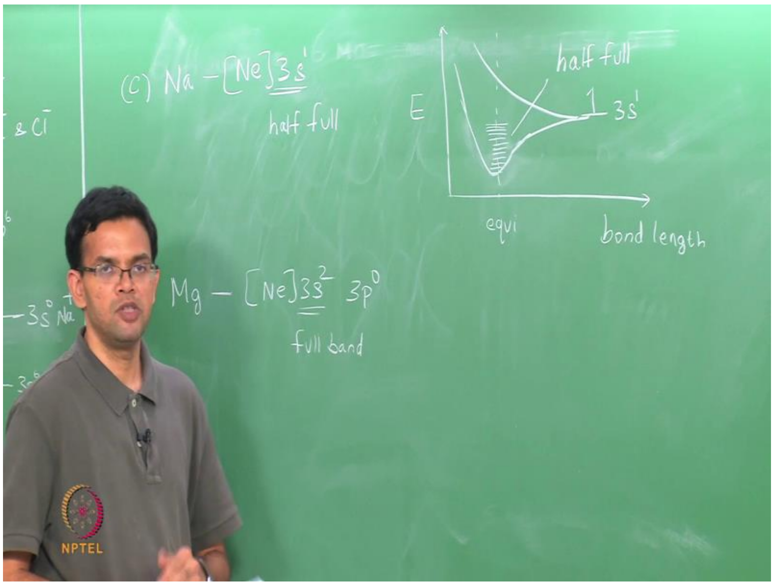

So, now we have sodium that is metal. So, its electronic configuration is neon 3 s 1. So, we have s 1. So, we have a band that is half full. So, the easiest way to depict this, just to have your energy e verses bond length. You have a 3 s 1 that has only 1 electron; there is your equilibrant distance. And when the atoms come together they form a band. So, let me just slightly modify this. The atom forms a band and the band is only half full. So, this makes sodium a metal because, we have a band that is half full. In the last 1, we are going to look at is magnesium. Magnesium is also a metal, but it has the configuration neon 3 s 2. So, s 2 is essentially full band. So, to make sure that, it is a metal to show the overlap between the valance and the conduction band, we consider the next level 3 p 0 and we say that, there is a mixing between the s and the p. So, this again we can show.

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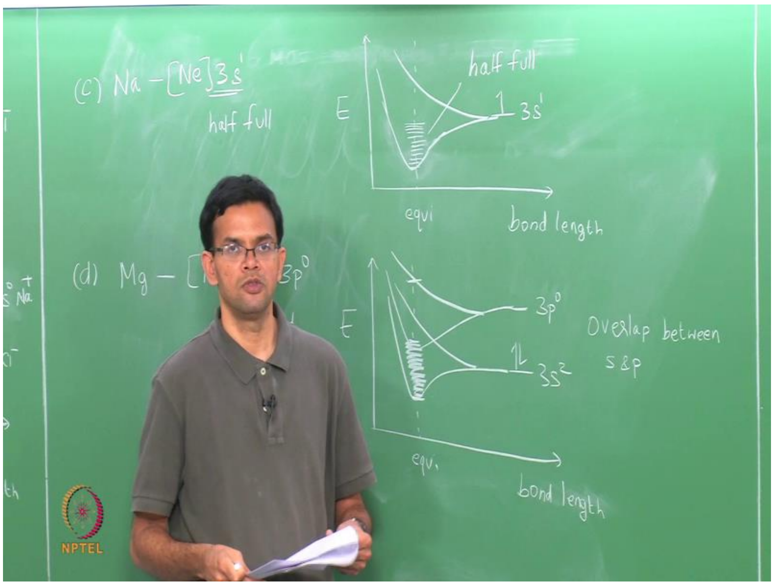

Energy verses bond length. So, this is the 3 s level, so that is full. Now you have a 3 p 0 that is empty and this overlaps with the 3 s. So, now, you have a full band and that is only half full. So, we have overlap between s and p. So, this way magnesium becomes a metal. So, let us now go to the next question.

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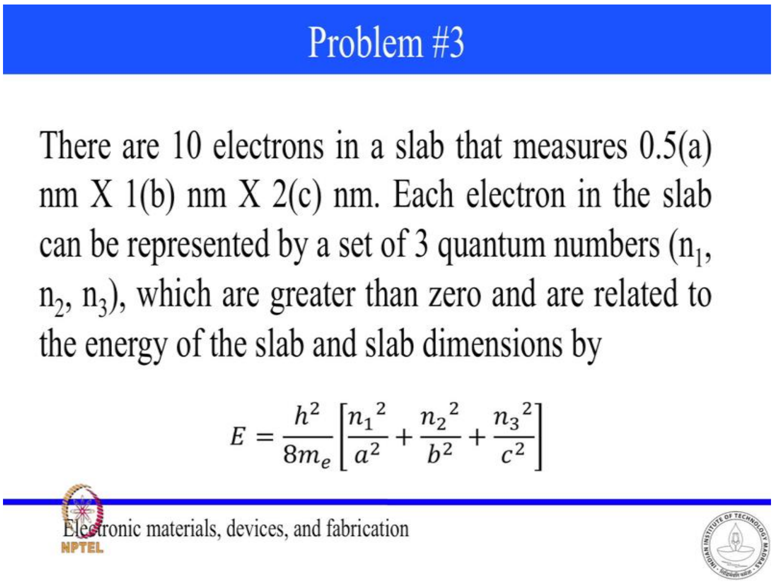

Problem #3

There are 10 electrons in a slab that measures 0.5(a) nm X 1(b) nm X 2(c) nm. Each electron in the slab can be represented by a set of 3 quantum numbers (n_1, n_2, n_3), which are greater than zero and are related to the energy of the slab and slab dimensions by

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

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So, question 3.

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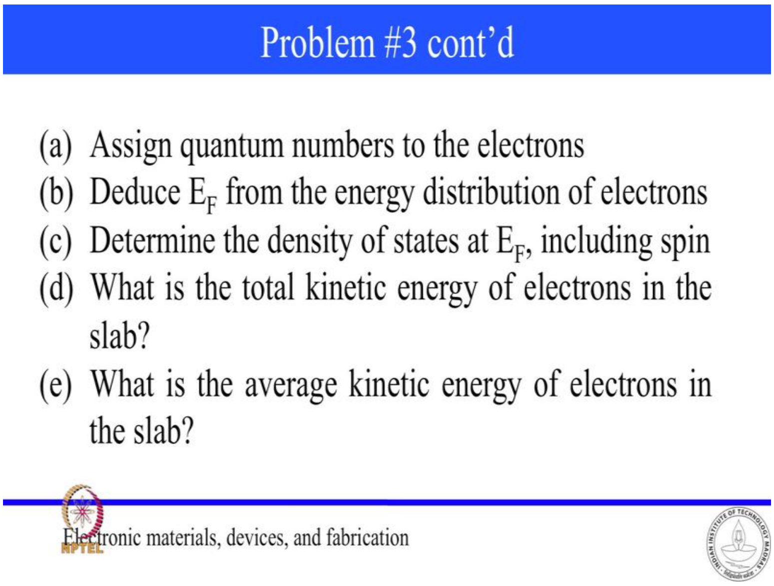

Problem #3 cont'd

(a) Assign quantum numbers to the electrons
(b) Deduce E_F from the energy distribution of electrons
(c) Determine the density of states at E_F, including spin
(d) What is the total kinetic energy of electrons in the slab?
(e) What is the average kinetic energy of electrons in the slab?

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There are 10electrons in a slap. So, we have 10 electrons.

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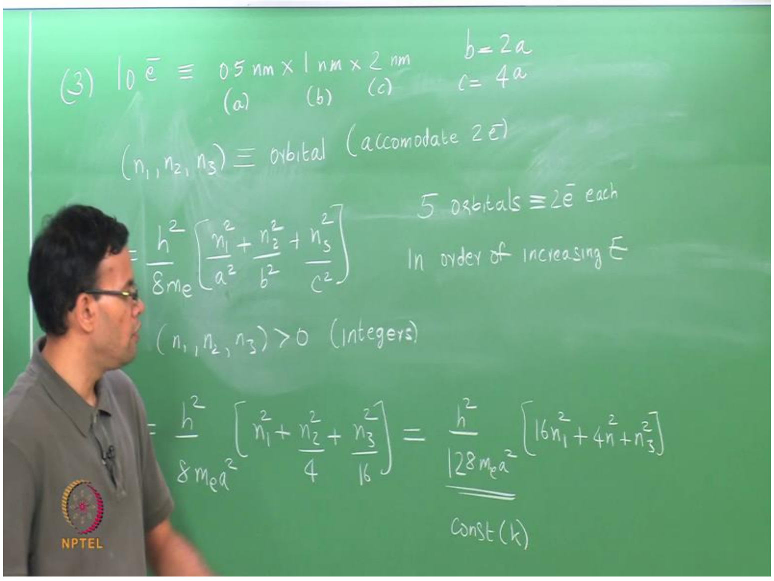

(3) $10\bar{e} \equiv \underset{(a)}{0.5\text{ nm}} \times \underset{(b)}{1\text{ nm}} \times \underset{(c)}{2\text{ nm}}$ $b = 2a$, $c = 4a$

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

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

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

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

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

And the dimensions of the slap are given. So, we have length of 0.5 nanometers and then width is 1 nanometer and height is 2 nanometer. So, for simplicity let us just call these a b and c. So, for an electron in a slap, 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 electrons. So, E in this case is nothing, but h square over 8 M e n 1 square over a square plus n 2 square over b square, n 3 square over c square. 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 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 odd n 1 n 2 and n 3, which will all go in the order of increasing energy. And 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 time a and c is nothing, but 4 times a, then energy E can be written as h square by 8 M e a square n 1 square plus n 2 square over 4 plus n 3 square over 16. 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 h square over 128 M e square 16 n 1 square plus 4 n 2 square plus n 3 square.

So, the first term here essentially a constant were just call it k. So, this is a constant time a variable that depends upon n 1 n 2 and n 3. So, we can plug in different values and then basically see that, lowest 5 energy levels and then we can put the electrons in them. So, let us let me write that in the form of a table.

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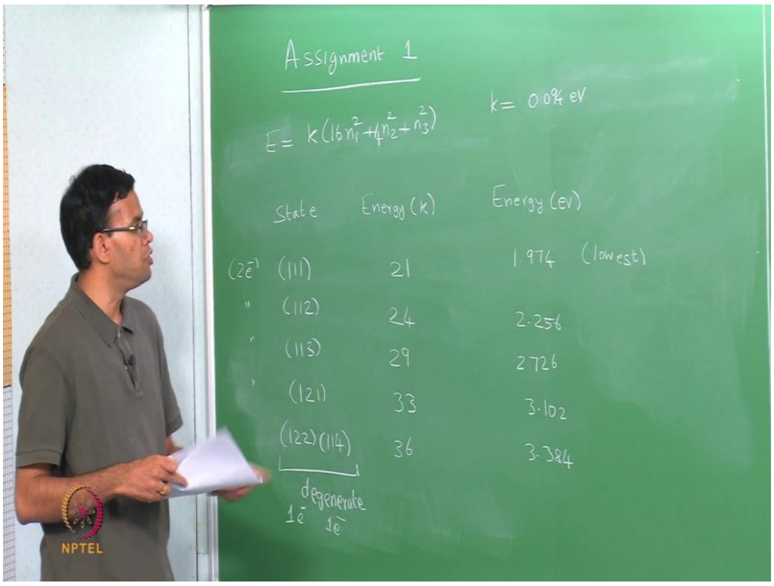

Assignment 1

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

$k = 0.094$ eV

	State	Energy (k)	Energy (eV)
($2\bar{e}$)	(111)	21	1.974 (lowest)
"	(112)	24	2.256
"	(113)	29	2726
"	(121)	33	3.102
	(122) (114)	36	3.384

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

$1\bar{e}$ $1\bar{e}$

So, we have the energy E is nothing, but a constant times 16 n 1 square plus n 2 square plus n 3 square, k we can evaluate and k come out to be 0.094 electron. So, let me write a table. The first state; next is energy in terms of k and then finally, energy in electron. So, we said that, n 1 n 2 and n 3 should all be integers and they should all be greater than 0. So, 0 is not an unacceptable number. So, the lowest energy state is typically 1 1 1. So, n 1 n 2 and n 3 are all once. In that particular case, this expression this should be 4 and 2 square 16 plus 4 plus n 3 square.

So, if it is all 1 1 1, this expression is essentially 21 and the energy is 1.974. So, this is your lowest energy level. The net energy level so 1 of these numbers must become 2, they can only be integer numbers. So, if you put 2 in the first case for n 1, we find that the energy is actually multiplied by 16. So, the next energy state would be 1 1 and 2. That gives you the 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 is 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 d generate states because, we have 2 sets of quantum numbers which have the same energy.

So, 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. So, we have 8 electrons and both of them have the same energy, so each gets 1 electron. So, if you 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. So, they have all be assigned. We want to deduce E F from this energy distribution. So, the next thing we want to find.

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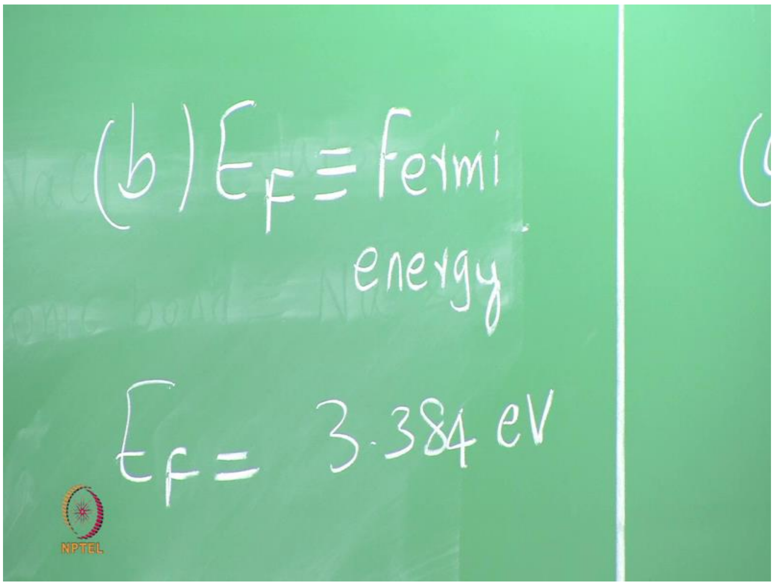

(b) $E_F \equiv$ Fermi energy

$E_F = 3.384$ eV

Is E F is the Fermi energy and if you 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 electrons.

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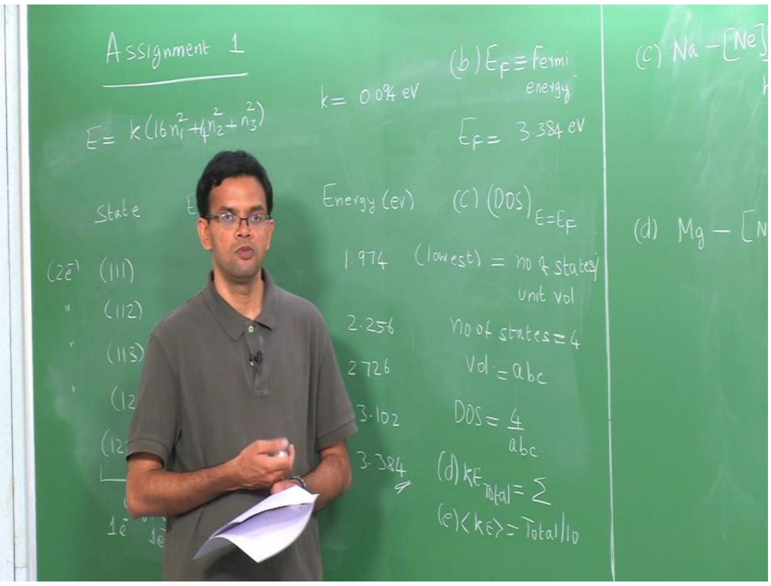

Part c; we want to determine the density of states at E F. So, density of state once again we will go back to the definition. So, density of states is the total number of states for unit volume. So, this is the number of states for unit volume. So, the question says; we want the density of states including spin. So, if you look at 3.384, we have essentially 2 states; each states 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, so the product of all 3. So, the density of state is nothing, but 4 over a b c.

So, we can express this either on electron vole or Newton meter cube or joules per meter cube. Part d; we want the total kinetic energy of all the electrons. So, 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 you have a discrete system with a specific number of electrons, instead of a solid where we have 10 to the 23 electrons, we can still define terms like Fermi energy or a density of states. Let us now go to problem 4.

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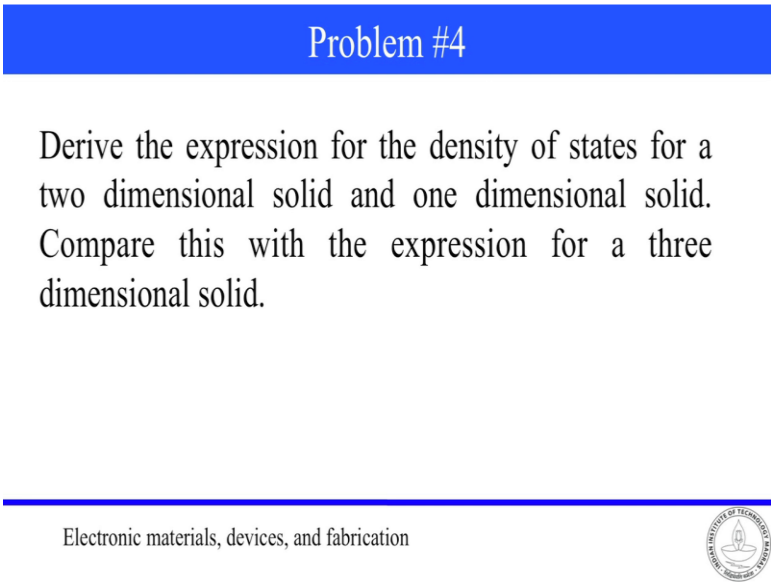

Problem #4

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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So, we want to derive an expression for the density of states for a 2 dimensional.

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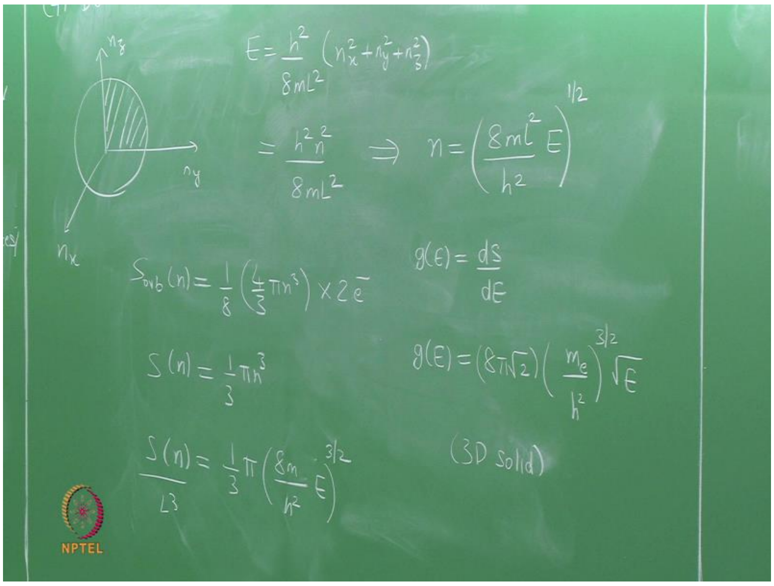

$$E = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

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

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

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

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

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

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

(3D solid)

And a 1 dimensional solid and we want to compare this with the derivation for a 3 D solid. So, we have looked at how to derive for a 3 dimensional solid in class. So, 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. So, 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 particle in the box, which we just saw in the previous problem, we were able to write an expression for the energy which is nothing, but h square over 8 m l square n x square plus n y square plus n z square. This is nothing, but h square n square over 8 m l square.

So, if you look at it, the total number of states for a given value of n is essentially a spear, but we only consider the first quadrant of this spear 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. So, the total number of states with energy less in n is nothing, but the volume of the spear and only considering the first quadrant so 1 over 8. If you also include spin, each state essentially take 2 electrons of opposite spin. So, S of n including spin is nothing, but 1 over 3 5 pi n cube.

So, we can write n in terms of energy. So, for to use this equation n is nothing, but 8 m l square over h square times e whole to the square root. So, S of n we can write in terms of energy by just substituting the value of n here, so S of n 3 pi 8 m l square over h square energy whole to the 3 over 2. So, this represents the total numbers of state in terms of the energy. If you want to know the total number of states for unit volume, you divide this by l cube, which will essentially cancel this expression l square. So, you left with this. If you want to find the density of states, then the density of states g of E is nothing, but d S over d E. So, we differentiate this with respect to energy.

The final expression which we write is 8 pi square root of 2 m E over h square whole power 3 over 2 square root of E. So, this is the derivation for 3 D solid. So, we can now modify this to apply to a 2 D and a 1 D solid for a 2 D solid.

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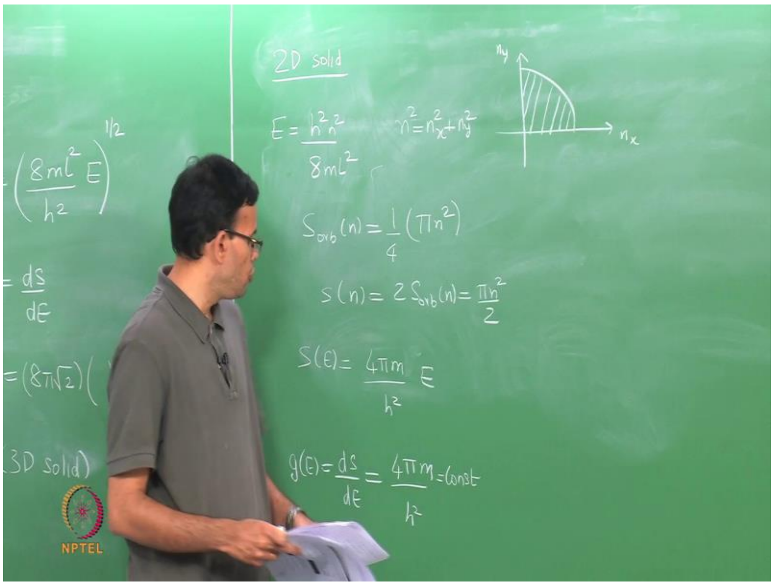

For a 2 D solid, we can once again write energy E has h square n square over 8 m l square, but now instead of 3 quantum numbers, you only have 2; n x square plus n y square. So, instead of spear, you will essentially have only a circle n x and n y and we will once again consider only the first quadrant of the circle. So, the total number of states whose energy is less than that of n is again the area of circle. So, in 3 D it was the volume of the spear, now it is the area of the circle pi n square and only the first quadrant so one-fourth. So, it is one-fourth pi n square.

If it takes spin so this is 2 times s orbitals of n. So, this is pi n square over 2, so n square, we can once again substitute in terms of energy. So, S of E we can write the expression is 4 pi m l square over h square times E. If you want to do this for unit volume, the l square term goes off and to find the density of states, we differentiate S with respect to E so that this is just a constant. So, 4 pi m over h square. So, for a 3 D solid, we found that the density of states increases with energy, it goes as a square root of E. For a 2 D solid, the density of states is essentially just a constant.

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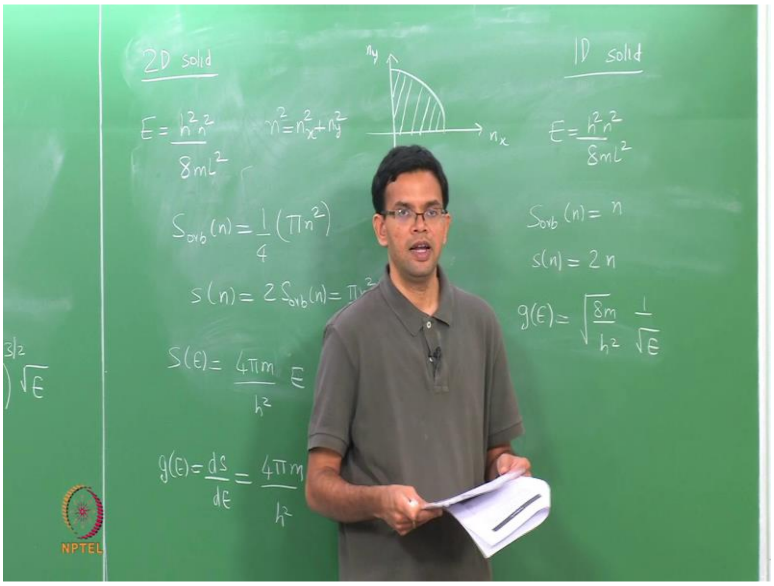

For a 1 D solid, we can once again write similar expression, but there is only 1 n, so it is only n x. In that particular case, S orbital is nothing but, n. If you take spin into account S of n is 2 n. We can substitute the value of n using this expression; we will go through the same math. The final answer in the density of states square root of 8 m over h square 1 over root E. So, for a 1 d solid, the density of states actually goes down with increase in energy. So, let us now look at the last problem.

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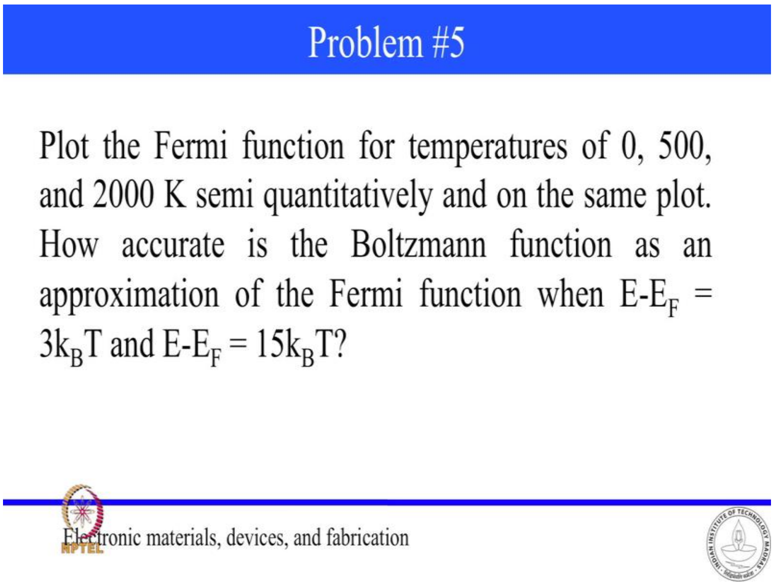

Problem #5

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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So, we want to plot the Fermi function for temperatures of 0 500 and 2000 Kelvin, it is a semi qualitative plot and we want to do this on the same plot. So, the Fermi function.

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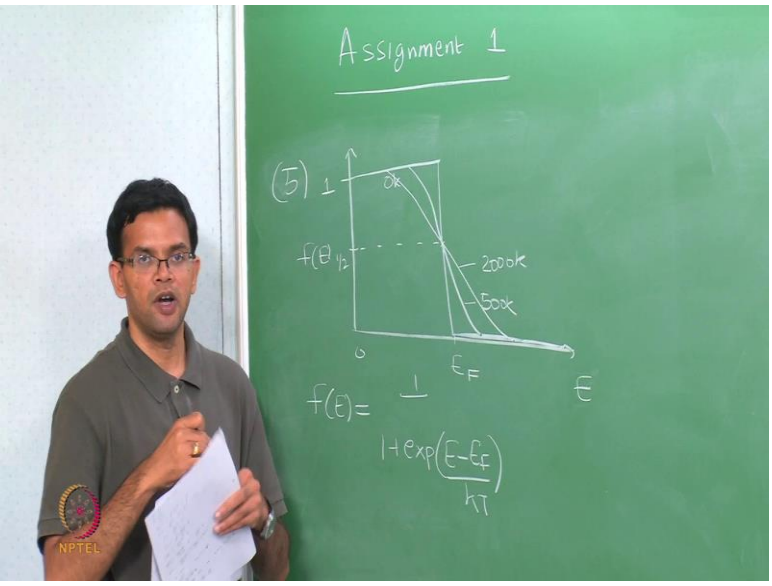

If you remember F of E is nothing, but 1 over 1 plus exponential E minus E F over k t. So, when the energy is less then E F, the probability is 1. When the energy is more than

E F at 0 Kelvin, probability 0and at E equal to E F probability is half. So, F of E was his temperature, F of E was his energy. So, we want to plot the Fermi function as function of energy. So, F of E verses energy let me mark E F and 0. And Fermi function goes from 0 to 1 and I will mark 1 half. So, if 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. So, we go to 500 Kelvin. So, now, you have a slight 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 I have 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 2000.

So, these spreads are essentially qualitative, they are 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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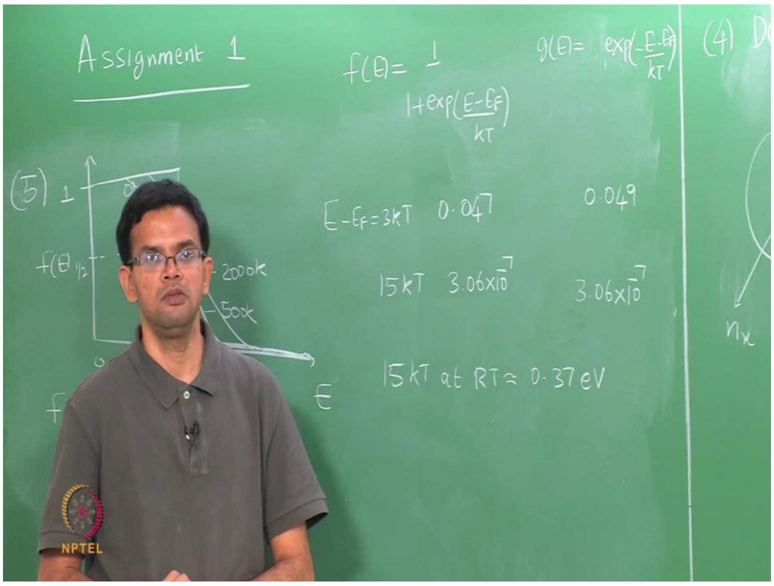

So, F of E, we have written E F over k t. The Boltzmann function is just exponential minus E over E F over k t. So, when e minus E F is 3 k t, we can substitute and the numbers are 3 minus 3 k t, the Fermi function 0.047, the Boltzmann function is 0.049. So, they are close, but there is a small deviation. For 15 k t, the Fermi function is 3.06 times 10 to the minus 7 and the Boltzmann function is also 3.06 times 10 to the minus 7. So, farther the deviation from the Fermi energy, so if you want to look at it 15 k t 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. So, in the case of solids, the Boltzmann function is a good enough approximation of the Fermi function.