Physics of Materials

Prof. Dr. Prathap Haridoss
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture No. # 34

Bands; Free Electron Approximation, Tight Binding Approximation

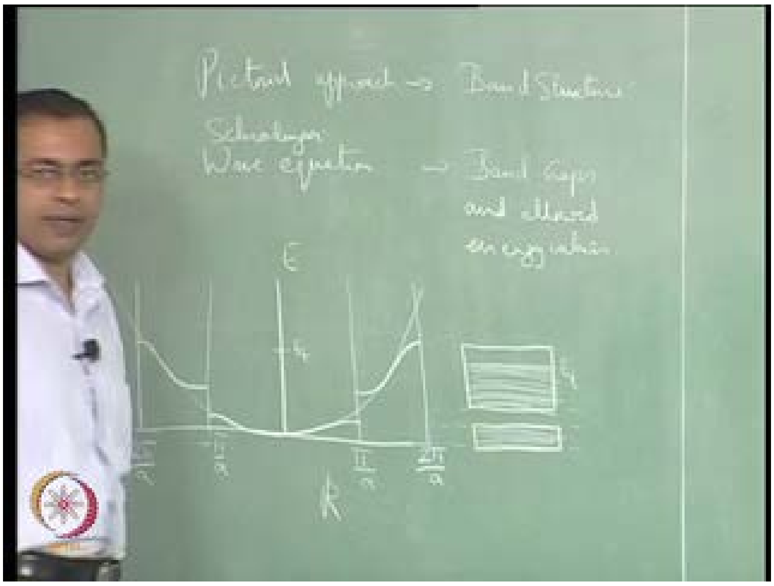
Hello, welcome to the thirty fourth class in this course the physics of materials. In the last class we when through the detail calculation, series of equations which saw in the form of slides where in we try to look at what would happen to the wave vectors of the and the energy values that the nearly free electrons have as a result of the their interaction with the periodic potential of the crystal lattice. So, we did this with the series of equations that you saw and as I mentioned it is something that you can yourself do as an exercise. However, you have them in the form of those slides where you can refer to them and see for yourself if your procedures are correct. At the end of it, we found that we had an equation where we had on one side the cos of some angle and on the other side an expression and what we what I indicated to you at stage is that if evaluate the expression you can find that we will have a series of values which do not have to stay within the plus or minus 1 boundary.

So, as long as that expression stays within the plus or minus 1 boundary the energy values corresponding to those expressions are allowed energy values. In fact, the only thing we will be changing those expression is the energy because everything else fixed by the system and so as you change energy you will find that for some values of energy the expression will evaluate to between plus or minus 1. And so, then that then that equation makes sense because you have cos of some angle which has to evaluate between plus or minus 1 and then expression which is also evaluating to plus or minus 1.

So, those are all energy values that are now allowed for the system. At specific sets of energy values you will find that the expression evaluates to quantities which are more than this window. So, they are either greater than plus 1 or less than minus 1 and those values then or not allowed for the system and the and I mean they do not makes sense for the equation because you have something on 1 side of the equation which requires you to stay within the plus or minus 1 window. And the interpretation as the said is that then those energy values or not allowed for the system. So, that is how we see that you know we can use the start stringer wave equation and look at the behavior of the electrons in structure that has the periodic potential window, potential wells and in that process by using start stringer wave equation on the electrons both under conditions where the potential is 0 and the potential is v naught we are able to then look at 2 situations and we said that you know those equation have to reasonable therefore, at the boundaries the values from either side whether you coming from the potential equal to 0 or potential equal to v naught, the value should become equal and also the slope should be equal.

So, it is on this basis that we created all those equations and the solved them. So, so you have now become familiar with the procedure for such a process and you have also become familiar with how we would in interpret this work and of course, this is all work that was done a long time ago, we are going over it to understand for our own understanding to see how such process is done and what we can interpret from it.

(Refer Slide Time: 03:35)



So, we finished off by realizing that we now have both based on are last 2 classes, A pictorial wave to understand approach which gave us the band structure and we also did the we did the calculation using the wave equation, start stringer wave equation and that give us also the bands structure, the band gaps at least and.

I also pointed out to you that you know we have actually done this in a much more detail way than you have perhaps the way used you have been exposed to before and in principle we have and diagram the utility of it we have not yet touched we completely see, we will do that they will understand the utility of it little later may be in the next class in fact we will look at it. So, this was E, this was k and we have the guideline which is the free electron parabola and we said that you now add the Brillouin zone boundaries pie by a minus pie by a minus 2 pie by a and 2 pie by a, at all these boundaries this nearly free electron parabola which itself is the set of discrete points, this near free electron parabola is distorted and the specifically we drew the distorted the structure as something like this, something like that.

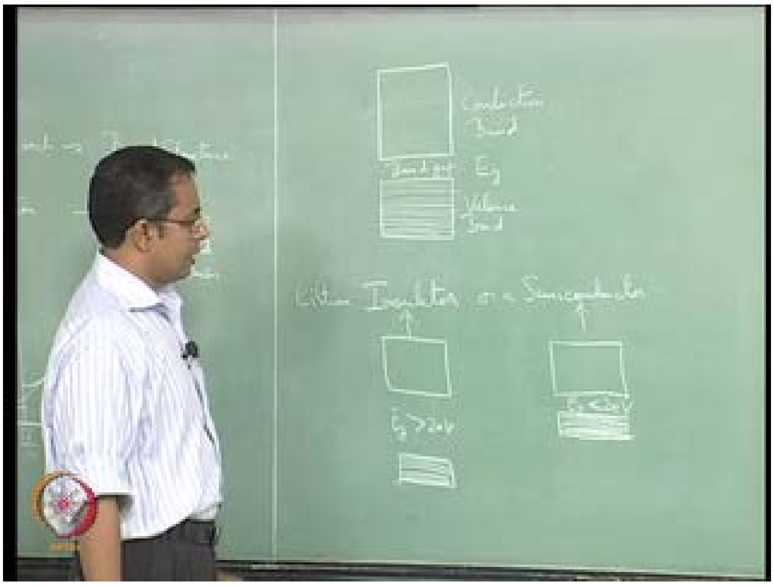
So, if you draw in to scale this how you see. Basically, they all have they will all finish up with the same values if you are looking at the same direction and this then become the band. So, this is the band and this lower end is also a band. So, I am just going into a drop 2 band here for the moment and that will illustrate our purpose. So, we have representation for the band structure in the E verses k space which has some detail here. The utility of the detail we have not really examined and will hold (( )) for one more class. Next class you will see the utility of this detail which is what value of energy is permitted at which value of k. So, this is E verses k diagram.

We have actually also this same information or an aspect of the same information being represented to us here in the form of the flat band diagram. So, here also we have a similarly you can have other bands I have just drawn 2 bands here. Obviously, you can have bands above it. So, to speak and so, we just have you know energy levels here, series of energy levels here and a series of energy levels here and exactly and these are based on what is allowed in the system. I have throughout this course at various point I pointed out that there is something there is this concept of what is allowed in the system and there is also this concept of what is actually being used in the system. So, those are 2 separate things. So, that is why we have the density of allowed states and the density of occupied states.

So, the of those that are allowed some up to some level is occupied. So, this is all allowed in the system. these are all allowed values in the system, based on where the Fermi energy is which is the highest value of electron energy in the system which let say arbitrarily I am setting here. If I set this is E f there up to here everything is occupied, all this energy values are occupied. So, all this discrete energy values are occupied up to this Fermi energy E f above this you have a vacant space.

So, even with respect to the today we will focus little more on this flat band structure then we will come back to this structure here in the next class. In the flat band does structure we can see that you know you can identify the allowed energy values and you can also identify the level up to which those energy value are being used.

(Refer Slide Time: 08:42)



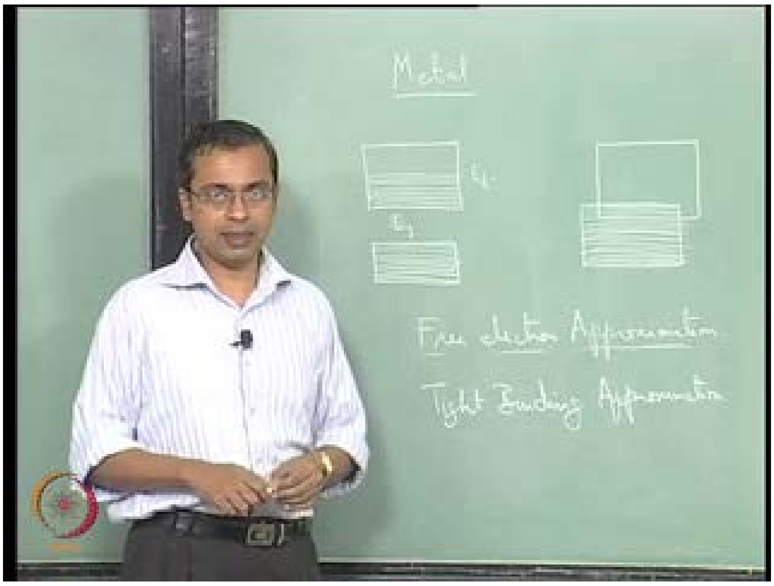
So, on just this basis we can of course, says something about the system and what we conventionally say is that you know we can have, if you look at the last 2 bands as you go up an energy some 2 bands whichever are the highest energy level bands. So, then we have the following situation. We have something in the middle which is the band gap. These are the energy values that are not allowed, this is typically if it is if it is the last occupied by band fully occupied band, this is called the valance band.

So, they should be the valance band and this empty band here will be the conduction band. So, between based on the layout of all this bands and what is being filled up we have materials with different properties. So, for example, if you have this structure here where you have a empty conduction band and a filled valance band then you either have and insulator or a semi conductor . So, it is either an instant insulator or it is the semi conductor. If you have a structure that look something like this whether or not it actually insulator or as semi conductor simply depends on the extend of its band gap.

So, if you have this band gap is typically denoted with the with E subscript g. So, this is what we have there. So, if you have E g greater than 2 electron volts, if the band gap is greater than 2 electron volts then it is an insulator. If on the other hand these are all filled states, if you have E g less than 2 electron volts are this is called semiconductor. So, so greater than 2 electron volt is an insulator, less than 2 electron volts is the semiconductor. So, in that sense what you see for semi conductor insulator at least you concept is the same, it is it is the matter of the value that you see here and in principle the reason they are what they are called the names that they are given is simply is based on the fact that if you have band gap greater than this band gap represents effectively the amount of energy you have to provide to get electrons off of this well is bands in to the conduction band and. So, therefore, the larger the band gap more is the energy that you have to provide for the transition to work out and only after that you going to see any kind of conductivity.

And in generally if it crosses this threshold for our purposes that we typically use materials for, this tends to be very insulative and if this is the kind of value involved less than 2 electron volts then the properties that shows you falls more and in line with what we are utilizing and calling as semi conductors. So, that is how this nomenclature comes.

(Refer Slide Time: 12:24)



So, this is what is there for these 2. For metallic system we have actually couple of 2 different of possibilities that can occur if it is a metal. We can have 1 situation where you are the last filled band, it is actually half filled. So, here also in a sense there is the band gap here, but it is not the band gap that if you want to call just we can call this the band gap, but it is not the band gap between in what we would call the in the in the sense of a (( )) band versus a conduction band. So, it is not the band gap in that sense, further down there are gaps. I mean further down in energy there are gaps, but we are more interested as I always mentioned at what is happening at the Fermi energy level. So, this is the Fermi energy level E f is the Fermi energy level.

So, this is the Fermi energy level. It is the last occupied ah energy level for the electrons at 0 Kelvin. This is the Fermi energy level we are interested in what is going to happen here, that is what often dictates what is the property of the material. So, if you look at that for as a mention for electrons to move, for a electrons to move through the system, the ease of moment depends on how easily they can locate energy levels immediately above that. So, here there are energy values immediately above the Fermi energy which are all vacant. So, if you give its slight amount of energy the electron can get on to those energy levels and then it is free to random up. So, that is how conduction occurs and therefore, this is the this becomes metallic. Metallic simply conveys the sense that you know amongst its various properties is the fact that it conducts electricity very well and also as a mention 1 of the defining characteristic is of course, the coefficient of thermal coefficient of resistivity which is negative.

So, you raise the temperature. The, I am sorry is positive. So, as you raise the temperature the resistances goes up. So, that is what we see in this system. So, for resistance. The other way in which metals could also have a band structure is if they have overlapping bands. I just display the bands so, that you can see them clearly.

So, these are filled levels and this is the vacant band. Only thing is that the bottom most energy of that vacant band is less than the top most energy of the filled band therefore, electrons are able to easily get on to the other band and keep moving around. So, therefore, this kind of a structure where there is overlapping bands also enables that material to be a to show you metallic behavior which is very good conduction with the very little amount of energy. So, this is the general layout of how these materials are incidentally I will also point out 1 other concept here, the Fermi energy for metallic system has been defined the way we have seen it and we have discussed this in considerable detail. However, there is the difference when you talk of semi conductors for insulator.

So, I just briefly show you in this schematic that we have shown, by convention for insulator or semi conducting material this kind of a material where you have a filled band and then band gap and then vacant band. When you have this kind of situation by convention half way between the bands is where E f s, by convention that is what the Fermi energy is. So, half way between the bands is what the Fermi energy is. So, this is 1 case where you know the Fermi energy is actually at the location where there is the band gap.

So. In fact, when you say this is the Fermi energy an electron can actually not sit at that energy, it is actually it is the forbidden energy for the system, but the convention that is what is chosen as the Fermi energy for semi conducting system and also the Fermi energy of course, as I mentioned conveys queue what can or cannot be done in the system. So, therefore, when you dope these are all intrinsic semi conductor we will see that in are next class, but basically when you dope this system we Fermi energy effectively you are raising or lowering the Fermi energy of the system. So, that is effective of what you are doing. So, so this is the way in which it occurs. So, we now see that you know there all that lot of different properties of materials that we can associate with this bands and we have seen in the last few classes how bands arise. It is now of interest to look at a couple of things, we have tended to approach this problem this entire problem of the band structure of materials from the from certain perspective and the perspective was that we had this set of atomic cores and this cloud of so called free electrons running across the material. So, this is what we did. Our approach the way we have done is in fact, called the free electron approximation.

So, everything that we have done so far effectively all the theory that we have developed so far represents this general approach refers to as the free electron approximation. So, the free electron approximation starts off with the position that you have free electrons in the system and then gradually introduces all the details of the system, especially the periodic potential of the system a into the picture. So, that is how you get the free electron approximation. Now, effectively the same result can be obtained if you actually started the other end of the picture which is the opposite of the free electron approximation wherein you are in your actually starting from a condition that the electrons are bound. Let me just explain here little bit in greater detail. Here we have already said that we have created a solid.

So, in this free electron approximation we already have a solid to start with. So, all the atoms are already in position, they have already released that 1 electron or 2 electrons or 1.5 electron on average per atom whatever it is that they are doing. They have already released that into that free electron gas. That system at that stage is where we are analyzing the system. Can we take it at that moment where you already have solid and we do our analysis on the basis of what currently exist in that solid. The opposite approach is 1 where you do not actually have the solid to begin with. So, you say that you have actually only independent atoms to begin with, you bring the atoms together and the process of bringing the atoms together you build the solid.

So, when you build the solid whatever is happening that is how you try to understand how the property of the solid has come about. You sort of know what the properties of each of the individual atoms are and then you bring those atoms together, create the solid and then try and understand what is the why is the solid showing us certain property.

So, in that case the electrons in that situation are originally all belonging to specific individual atoms. In other words they are bound to those atoms. So, that approach which is the opposite of this free electron approximation starts from, its starting position is that you have an individual atom though that individual atom has electron at specific energy levels and those are specific discrete energy levels and those electrons are bound exclusively to that atom, you take such atoms and those electrons associated with each of those atoms, bring them together and create solid. So, the starting point there is that the though the electrons are bound tightly to each of those into individual atoms and therefore, it is called the tight binding approximation.

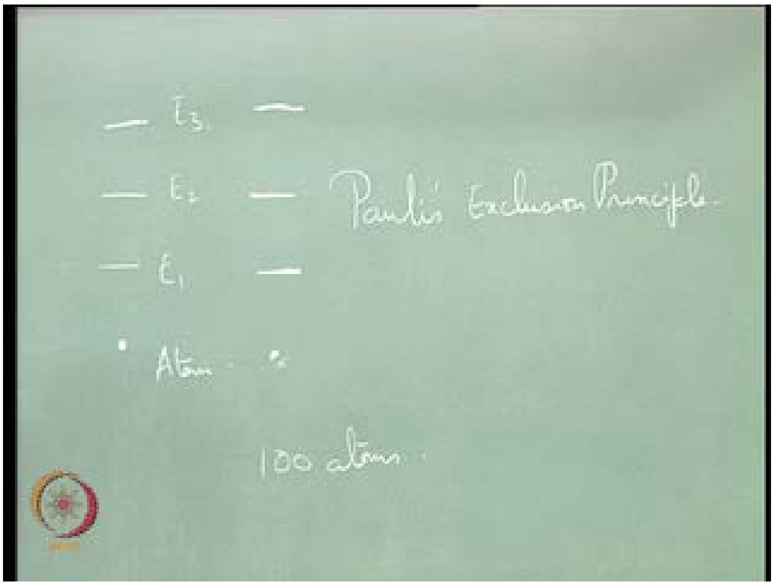
So, you start from the individual atoms where the electrons are tightly bound. The names can be slightly confusing because when you say tight binding approximation you are actually starting with atoms that are not tightly bound, they are free, free atoms. The point is the electrons are tightly bound that is the difference. So, in this case the starting position is that atoms are free, but the electrons are tightly bound to each of those atoms that is why we called tight binding approximation. In this case of course, the electron itself shows up in the name therefore it is very clear, it is free electron approximation.

However, you will note that here the atoms are tightly bound in the sense that they are stuck to those lattice side.

So, the for the atoms situations as the opposite as it is for the electrons with respect to the electrons. Here the electrons are free the atoms are stuck, here the atoms are free the electron are stuck that is the starting position.

So, and that is how you build a solid. So, we will briefly look at what this type binding approximation says.

(Refer Slide Time: 21:16)



So, what it basically says is that if you take a given atom you have electrons at specific energy levels. So, you have electrons at specific energy level associated with this atom. Now, if you take a solid you have a huge number of these atoms. All right. So, basically these are all atoms that were let us assume they are all atoms of the same kind that we are not really changing the type of atom that we are looking at here. Therefore, if you take the same atom if you take you know a million such atoms or each 1 of those million atom have a exactly the same energy levels for the electrons when they are separate, when you have separately you have laid out all the select atoms the energy level of those atoms will be exactly the same. So, that is how.

In fact, that is the characteristic of the atom that, is how we know that it is that atom. It shows you all those property. So, that is how these values are. Now, as you start bringing them together. So, we also have some kind of a sense of you know the inertial atom electrons are closer to the core of the atom, the outer shell electrons are little further away from the core of the atom and so on. So, when you bring the individual atoms which are initially separated you start bringing them together then the as you get them closer and closer and closer the electrons at the outer shell begins to overlap, the electron clouds begin to overlap if you if you if based on the description we tend to use, electron clouds overlap. So, the outer shell electron begin to overlap and then if you push them even further closer then slowly shells which are below the outer shell also begin to overlap.

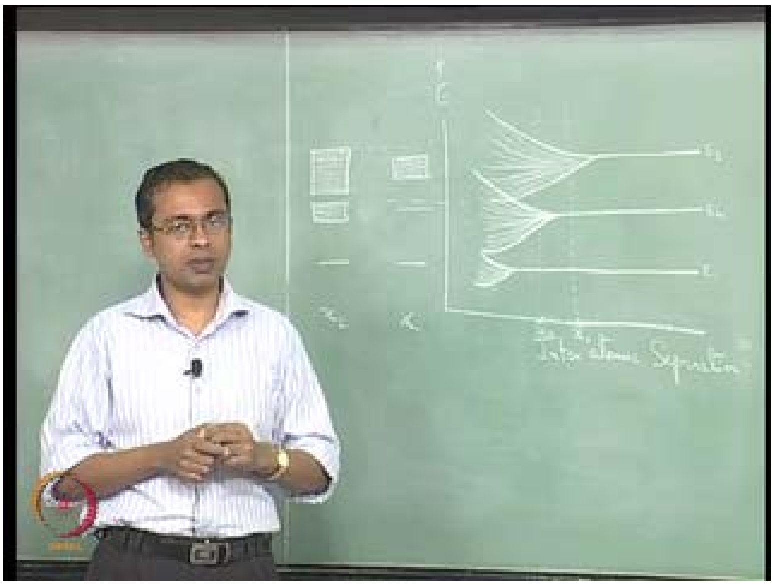
So, this kind of a system occurs. However, regardless of whether you start from independent atoms and bring them together, all will start with a solid where the electrons are already running around in the solid regardless of these 2 given the nature of electrons we are forced to accept the fact that they are subject to the Paulis exclusion principle. In the free electron approximation we implemented the Paulis exclusion principle using the Fermi Dirac statistic. Here, what we are basically saying that is that as the energy levels in the tight banding approximation as the atom get closer and closer and closer when the when a given energy level of and therefore, that shell of electrons begins to overlap they are forced to split in energy.

In other words what was originally a single energy level, a single energy level will now split into enough number of energy levels above and below this original energy level such that it can still accommodate all the electrons. For example, let us say I take 100 atoms, we have 100 atoms and I start moving them closer and closer and closer together. What will happen is as they begin to overlap as the out shell electrons begins to overlap, this energy value here whatever is this I just called E 1, E 2, E 3. Let us say we have brought the atoms close enough that only the E 3 energy value and therefore, that corresponding shell of electrons are beginning to overlap, that E 3 energy value will now split into 100 different energy values. Let us assume that for the moment it is the single state it may be has it 2 electrons per state whatever.

We will assume it is the single state there and it will now split into 100 states because you have got 100 atoms together, there are 100 electrons that need to be accommodated. All of those original 100 electrons where at E 3. Now, then split up here and slowly split into wide range of energy values as they get closer and closer and closer. So, that they can still accommodate all of those 100 electrons. So, or if you are assuming 1 electron per state or whatever. So, therefore, this what is originally 1 state will now become 100 states, 100 energy levels it become around this around this value it will become set of energy values around that energy values.

So, this process is then called as tight binding approximation. We will just draw this we will draw the energy was as the function of. So, clearly it really depends on how a close you bring the atoms. If you take another atom here and the same energy values here. So, what we actually see occurring will depend on the exact inter atomic separation, as you bring the inter atomic separation closer and closer you will see the appropriate kind of splitting, that is what the type binding approximation describes. So, we will just pictorially at least look at it at the type binding approximation as see what we what we can except.

(Refer Slide Time: 25:53)



So, we will make a plot now of inter atomic distance, inter atomic separation. So, this is the average inter atomic separation spread across all of those atoms, if you are looking at a 100 atoms ,100 atoms that kind of what that is what we are looking at and energy. So, let us say initially the atoms are very far away, very far from each other. So, when they very far from each other they are not really interacting with the each other. So, every atom has the energy levels corresponding to the original energy level of that atom. So, whatever is the energy levels of that individual atom that is the energy level that they have when you keep them widely separated.

So, at that point they are not really interacting with each other. So, we just say that you know the same E 1, E 2, E 3 I just put something there. So, we just assume the same thing E 1, E 2, E 3, E 1, E 2 and E 3. So, as you bring them closer what you will see is I just draw it here then I will describe it. As you bring them closer at some point the outer most shell electrons begin to the clouds begin to overlap and at that point the energy levels are forced to split to accommodate all those electric electrons within with in a in energy value with energy values very close to that original energy value that they had, but it cannot keep them at the same energy value because that could then violate the Paulis exclusion principle. So, therefore, this begins to split.

So, I will just draw it here like this. So, it splits like this, you actually have huge number of energy values here. Exactly, how many energy values you have here will depend on the number of atoms that you are pulling together. So, because that many electrons have to be accommodated. So, that is how you get this. If you. So, this is what is happening to be outer most shell. If you take the next shell of electrons which is the lower next lower energy they don’t overlap at this point, because at this point only outter most shells have shell electrons overlap.

You have to bring the atoms much closer before the next shell of electrons begin to overlap. So, but then the general trend of the behavior looks similar. You bring it much closer and you start seeing a similar kind of behavior. So, you see the behavior looks like that again that consist of the series of energy values. So, you see something like this and for the third the lowest energy value that we are looking at the same concept will hold true, you have to go to even much deeper you have to bring the atoms much closer before they begin to overlap and so, you start seeing a behavior that look like that. So, this is what we can expect, if you take set of atoms and you start moving them together and we have now drawn what we can expect of from this situation based on all possible inter atomic separation that we can think of which we can perhaps experimentally create or enforce on the system.

Now, what is it that we actually have in the system. So, this is this is the general picture of what is possible. What is possible is this. This is the general system. Now, we could have different inter atomic separations. So, we can create a solid with the certain inter atomic separation, we may be able to create the solid with the different inter atomic separation, you may be able to manipulate the inter atomic separation. So, so these are all things that we have at our disposal. So, what we see is the band structure of the material, the band structure that eventually exists in a material that we probe, that we that we are able to experience in the form of the property of the material that band structure depends on whatever is the equilibrium spacing of the atoms in that material. So, whatever happens to be equilibrium spacing?

So, let us assume that you know 1 possible equilibrium spacing is here. So, corresponding to that we can draw line vertical line. So, if I just call this x 1. So, when equilibrium spacing is x 1 we will see a we will basically see. So, I just draw it here at x 1, we can draw it this side may be. So, it be clearer to see. So, at x 1 this is the E. We will see a single energy value corresponding to this E 1.

We would also see a single energy value corresponding to E 2 and you will see this band, this band here. So, this is now how the flat band structure will evolve in when you use the tight binding approximation, in this is this picture comes from the tight binding approximation and when you bring this picture together with the actual inter atomic separation that exist in the material, you can you can understand how it’s band structure will evolve. So, at this inter atomic separation, this energy level remains undisturbed at the original energy level, this energy level remains undisturbed and the original energy level, this energy level has split into band which is this width because further corresponds to this x and that width if you just draw again you get this. So, you have flat band structure of flat band representation of the band structure in a material where you see this tight binding approximation of this form.

This picture actually is much more it gives us further insight because you can consider changing the inter atomic spacing, we can change the inter atomic spacing. So, for example, I will say that you now have an new inter atomic spacing which is here. So, this is x 2. So, what do we have at x 2? We can again draw the line vertically up here. So, we have x 2, at x 2 we will draw the band structure, at x 2 this energy value here is undisturbed E 1 remains undisturbed . So, it remains single energy value as before. So, that is what we have. At x 2 even this energy level E 2 has split into a band, it is a relatively narrow band here. So, that is the band we have here. So, if you look at the band here it is roughly something like this, that is what roughly it is going to be that 1 and that 1. So, that is the band.

So, that is already a band that is split and the band that is above it has actually become wider. So, based on the inter atomic spacing we have different band structure, now that this material can have. So, we have a material which based on inter atomic spacing simply based on the atoms you can come up with this diagram regardless of the actual inter atomic spacing you can come up with this diagram and you can select the particular inter atomic spacing and you can see what will be the what will be its band structure given that inter atomic spacing.

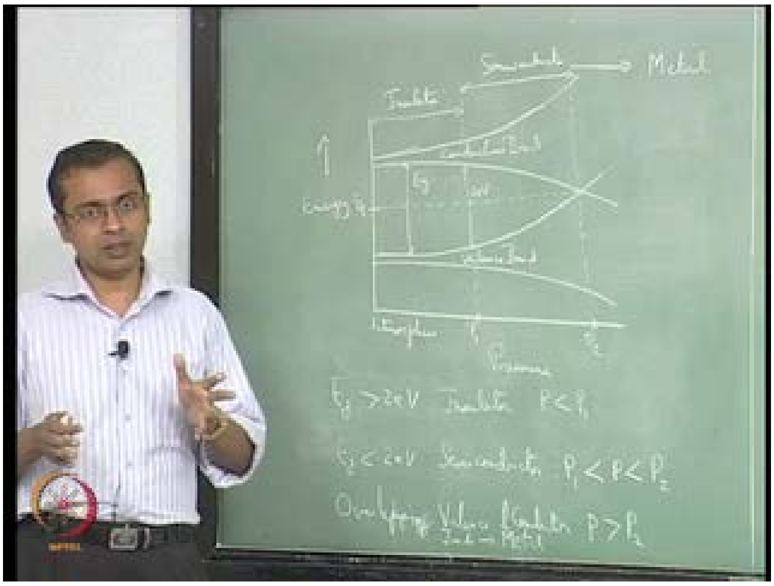
So, whatever. So, when it forms certain crystal, some kind of a crystal structure it forms based on the inter atomic spacing you can now predict you can you can understand how its band structure would have come about. So, you can see how 1 band would show up and another band would show up in this material and so that is how the structure would show up and of course, we are assuming now these are all these are all only the available states, this are all available states. We have not indicated how much is filled and what is filled. As supposing for instance there is another band and top which is filled, which is let us say it is empty. So, we could of thought of another energy level E 4 and that would have given a set of that would have overlapped even faster, we would have had a set of empty energy levels here and then based on the separation between that band and this band and similar the same band their and this band here. So, clearly the separations are going to be different, it going to be closer here, it is going to further apart here.

So, this gap is going to be larger here, going to smaller here based on the separation we could either have this material being insulator or being a semi conductor. So, therefore, we see that you know as the function of inter atomic separation we can use this tight binding approximation and we can understand what might be happening the material? How it could be changing its property? In fact, people essentially use this idea you can actually change a semiconductors semi conducting behavior because in many semi conductors in semi conductors manipulating the band gap is a very important thing and so, you this is a tool that you have available to you to manipulate the band gap if it chooses to do so. So, this is 1 way in which you can do it.

Now, the same idea we can actually look at in a slightly different angle. So, we are talking of inter atomic separation here. So, we can look at inter atomic separation also as the function of pressure for example. So, that is see when you strain a material, when you stretch a material you are raising the inter atomic separation. So, when you pull a material you are as long as you know you are doing it elastically. Elastically you are doing it.

You are you are marginally increasing the inter atomic separation. Once, you start plastically deforming it your that is different, that is a different situation. Then entire set of sets of atoms are moving, but as long as you doing it elastically then you are marginally changing the inter atomic separation. When you put you are raising the inter atomic separation when you stress the material. When you put pressure on the material you are actually compressing the material which means you are trying to force the atoms to take a smaller space therefore, you are reducing the inter atomic separation. So, we will just see what could happen if you put you increase the pressure that a material experiences as you put I mean subject it to high pressures.

(Refer Slide Time: 36:33)



So, we will again look at energy and this is pressure, this energy here. So, we just say the this is conduction band energy value. These are some energy value. I will just draw it then will I will explain it you. So, us let say this is the conduction band, it has a certain energy band at some at some pressure let us say this is the atmosphere pressure, I will just say this is at 1 atmosphere. So, at 1 atmosphere atoms pressure. So, we you form this material at room temperature and atmospheric pressure let say we do that and at those conditions it has the certain bands structure.

So, we can say that you know the valence band has this is the set of range energy values over which the valence band exists, that is the range of values over which conduction band exist and half way between them somewhere here is the Fermi Fermi energy E f. Now, as you raise the pressure you are forcing the atoms to come closer and closer. So, if you look at are picture here if you comeback to this picture here as you force this atoms to get closer and closer and closer, the bands wider, the bands begin to widen you get wider and wider bands and this is true for any band that you are looking at, any band structure that any band that you are looking at is essentially widening.

So, if you come back here we will say that this is the conduction band and this is the range of energy values over which it exists at atmosphere pressure, as you raise the pressure slowly the conduction band biggest to widen. So, it this widens very significantly then similarly valence band you can assume that originally at 1 atmosphere the source the width of that band and as you raise the pressure as you bring the atoms closer and closer the valence band begins to expand in energy values. So, what is actually happening is that see this value here. So, you now have the conduction band of the valence band, the difference in energy between the highest energy of the valence band and the lowest energy of the conduction band, that is your band gap.

So, this is here is the band gap. So, we have a band gap here. So, on this picture we see that as you change the pressure as you raise the pressure you are changing the band gap, band gap is actually whatever it is the initial value it is steadily decreasing. The band gap is decreasing as you raise the pressure. So, what will happen is. So, we it is assume this is the Fermi energy. Our original definition still holds. If it is if E g is greater than 2 electron volts it is an insulator and E g is less than 2 electron volt it is the semi conductor. So, assuming like you know we start with something that was a insulating material.

So, what will see is up to some point let say that let say that here the E g becomes 2 electron volts, So, that is an arbitrary designation, let me just say that this is 2 electron volts. So, that is 2 electron volt. So, we can now consider 3 situations, for pressure up to here as you raise the pressure of this material as you raise the pressure that this material is subject to up to this point this material behavior like an insulator. The same material as you raise the pressure further and further and further the band gap of the material now has decreased the less than 2 electron volts.

So, the material now begins to behave like a semi conductor. If you now both in pressure pass this point also if you have raised the pressure past this point here. So, this is p 1, p 2. So, when you go past p 2 in pressure what you see is that the bands now begin to overlap, the valence band now begins with overlap with the conduction band therefore, at pressure past this point the material now begins to display, behave like a metal. So, we now see. So, this is E g is greater than 2 electron volts is an insulator at for p less than p 1, E g is great less than 2 electron volts it becomes the semi conductor. So, that is pressure between p 1 and p 2 and overlapping bands you can imply it has become a metal that is for p greater than p 2.

So, when you go and pressure past p 2 this same material, exact same material, the atoms are all exactly the same and we can assume even the crystal structure we have not really the at least the symmetry we have not changed, we have changed the dimension of shell, but you are not changing that symmetry. So, as you simply raise the pressure in the system everything else being the same. The material moves from being insulator to being a semi conductor to being a metal. So, what? So, what you what wish to convey to you is that you know there is a lot of interesting information here. It means first of all that you know when we test materials we at always keep in mind that you know we are testing materials at often we are testing materials at room temperature and atmosphere pressure. So, that is often the case.

We can always test them under special condition, there is no doubt about it, but some time we forget the fact that we are conducting a test at room temperature and atmosphere pressure we are taking it is for granted. Often the end use of the material may be under condition where the temperature and pressure are very different from room temperature and atmosphere pressure. Therefore, at that point many things of about that material might change, some of the properties we are more what should I say sensitive to we are more aware that you know based on our understanding of things certainly for example, temperature affects we take into account often we often know that you know as you raise the temperature materials often materials meld, materials can boil.

So, lot of things can occur. So, this is something that we are more intuitively aware of because we tend to see it more often in day to day life. Pressure on the other hand is something that we do not experience a lot in terms of change. 1 atmospheric pressure is something that we assume. Changing pressure is not something that is often convenient in experimental sense especially when you are dealing with metallic system and such.

So, that is something that we tent to ignore, but on the other hand if you have to send space craft in to space, you are now going from 1 atmospheric pressure to something that is virtually 0 atmosphere in to (( )) basically. So, to (( )) you send it to some other planet, you send into some other planet which has whatever atmosphere it may not be a breathable atmosphere, it may be it may consist of methane, but the important thing is the pressure might be different. So, the pressure experienced by components might be different.

So, in addition to other chemical reaction that might occur in the atmosphere the fact is that even if you are insulated everything you will find that the pressure being experience by a component if you not accommodated for you know if you have not sealed it so, that pressure is not experienced to the system. If you are not mainly pressure tight so to speak, then pressure experience by the system can be different. If you go to you know other planets where the pressure is very high then these things can change, material properties can change. So, the and therefore, something that you know you have you have you may have made a circuit assuming something is going to be a semi conductor, if you send it to some location where the pressure is very high it may actually become metallic and therefore, you circuit might free. So, so it is something that you have to be more aware of, you have to be aware of the fact that the property can change very dramatically even as a result of pressure. That said I also what to point out that you know the in general the sensitivity to pressure is rather poor even though this pictures shows you what can happen with pressure, what is not really conveyed to you is even that this is 1 atmosphere what is the p 1 and what is the p 2. So, the actual values are not really indicated here. So, for example, just give you an example.

So, that you understand is scale of what we are looking at hydrogen which we think of traditionally as a gas. So, it is only something that we are conventionally we are conventionally used to thinking of it is the gas may be it to some degree as liquid hydrogen if you can be liquefy it and for storage purposes, but this is conventionally all that we looking at, but if you actually put enough pressure on it, it can become a solid and if you keep raising the pressure on the on this hydrogen solid you can reach a pressure at which point the bands I mean you create the situation where hydrogen becomes metallic. So, this is possible. So, for at least theoretically predicted expected that it can happen. So, this is possibility, but the kind of pressure that you are talking of is in the millions of bars. So, it is of the order of a mega bar. So, bar the bar is 1 atmosphere pressure.

So, this is 1 bar here. So, if you talking of a mega bar, you are talking of a million atmospheres. So, that is not something that you have going to generate that easily. So, it is not something that. So, that is what I mean by saying you know the sensitivity to pressure is rather low. Many materials are much more sensitive to a temperature, many material properties are much more sensitivity to temperature than they have to pressure typically. So, as a result and certainly this is true with solid systems for gases that is different.

For solid system when you take a solid system and you analyze it typically you will find that it sensitivity to temperature, the sensitivity of its properties to temperature is much higher than it's the sensitivity of its properties to pressure. So, therefore, but at the same time we I think it is worth notice keeping in mind that properties can change with pressure. So, that and that is what is the convey here. In particular the electronic properties are being shown here and so you understand that you can go from an insulator to a semiconductor to a metal simply by changing the pressure being experienced to component. So, this is what we have. So, what we have looked at today is we have kept in mind that fact much of the discussion we have done so far has been based on the free electron approximation and which basically has started with the assumption that you already have free electrons in the system. So, the electrons are already there. You are only explaining what the behavior of those electron is, the electron is already there in that atmosphere and so, we looking at those free electrons, we are looking what is the impact of first we ignore the impact of the periodic potential of the lattice and later we will introduce the periodic potential of the lattice in to the system and then we understand the properties.

Today, what we have looked at is the fact that if you takes separate atoms and you understand the description of the separate atoms independently and you move those atoms together in that process also you can try and understand, you can try and predict what are the properties of the solid going to be when you start from independent atoms and push them together. So, in this process also you can create the same kind of understanding of the material and that is for the tight binding approximation. Now, in principle in terms of predictions both these properties both these approaches whether you talking of a free electron approximation or a tight binding approximation. In principle given that you know they are all essentially trying to explain the same things to you, at the end of the day if you take a given material both these approaches should actually give a reasonably good prediction of the property of the material.

So, that is 1 thing to be said about both approaches. However, given the fact that a metal actually has this general structure that you have this ionic core and free electron gas that picture fits the metal pretty well, given this situation what we find is the free electron approximation is much more relevant if you look at this free electron approximation both I mean this free electron approximation is much more relevant, much more likely to give a good prediction for metallic system. Simply because the situation it is examining or its starting point is very close to what a metal is already. So, that is the good starting point for metals. So, therefore, the free electron approximation is generally what is looked at greater detail when you talk of metallic system which is the very large part of the periodic table and that is why we have spent so, much of time on the free electron approximation. Generally, for a semi conductor and insulators the tight binding approximation tends to give you at least considered as more likely to give you the right kind of analysis in an easier sense.

So, for semi conductors and insulators be this is the perhaps the slightly better approach or a more appropriate approach is the way I would say, more appropriate approach is tight binding approximation for metallic system. So, free electron approximation is the better approach. So, this is how this system this approaches compare with each other. I would just conclude by just pointing out 1 more aspect that we have not really touched upon which is the fact that regardless of this which approach you are taking we have we have already seen now that the you know the bands structure if you talking of free electron approximation we have see that there are Brillouin zone and such and then the band structure evolves based on the interaction of k vectors with the Brillouin zones. The important thing in to note is that the location of the Brillouin zone is at different places based on the based on the direction in which we are looking at. So, we already saw that you know you have some polygonal shape of some sort, some sort which appears based on what system you are looking at.

So, the Brillouin zone appears zones can appear at different distances from the origin based on the direction in which you are looking at the material. Therefore, the k vector and its interaction with the Brillouin zone can occur at different locations which simply means that based on the direction in which we are looking at in the material the property can be change because based on the direction you are looking at the definition of which is the allowed energy level, which is the next allowed energy level, is there an overlap, is there no overlap, all those things are changing based on the direction in which are looking at the lattice because the Brillouin zone appears at various locations, at different position within the structure.

Similarly, in the tight binding approximation it only talks of inter atomic spacing, it is not telling you in which direction. So, depending on the direction you go again you can start seeing variation of properties. So, therefore, both this approaches can also predict to you, can also convey to you the fact that anisotropy can exist in a material. So, what we had in our earlier models we were unable to show you anisotropy because we assumed a uniform number of free electron by unit volume. These approaches can actually show you the anisotropy, certainly the free electron approach when you taken into account to fact that you know the Brillouin zone is at a different position based on this structure at various location it can be a different positions. The its interaction with the Fermi surface can therefore, occur at different location and therefore, the properties can check.

So, I conclude by saying now we have seen the various approaches, we have seen where 1 is better, where one is the other is better and we see that you know at regardless of the approach ultimately it is the same material that you are discussing. So, therefore, to the extent that they are valid they should predict the properties appropriately. So, with this we will halt. In our next class we will look at semi conductors and in detail and see a what we can say about semi conductors based on the approaches we have to it. Thank you. .