Concepts of Chemistry for Engineering
Indian Institute of Technology, Bombay
Professor Arnab Dutta
Lecture 39
Band structures of solid material

Hello, my name is Arnab Dutta and I am an assistant professor in Chemistry Department. Today in this particular segment, we are going to talk about the electron and its arrangement in a solid state, where we will discuss in details about the band structure and about the doping in those semiconductors. So, let us begin. So, first we start with the solid material, solid material is different from gaseous or liquid, because in those states, electrons and the atoms are free to move. Wherever in solid state, the positions of the atoms are quite stable quite stoic.

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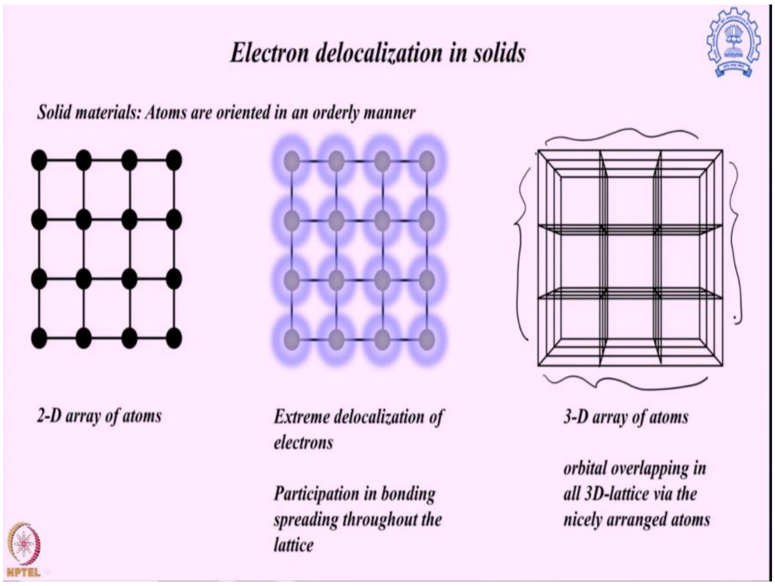

Electron delocalization in solids

Solid materials: Atoms are oriented in an orderly manner

2-D array of atoms

Extreme delocalization of electrons

Participation in bonding spreading throughout the lattice

3-D array of atoms

orbital overlapping in all 3D-lattice via the nicely arranged atoms

So, over there, I am showing you the structure of a two-dimensional material. Over here, each of these dots represents one of the atoms present over here and over here, we are also showing what happens to the electrons around it. So, the electrons shown in these blue spheres is actually showing that it is actually spread over beyond the atom. So, when this interaction among those atoms are taking place, the electrons are also interacting and through this interaction, electrons are getting delocalized all over this two-dimensional array.

And this is nothing but showing a picture how the bonding is happening, because bonding is nothing but sharing of the electrons and electrons are shared within the neighbouring atoms through the space. Over here, I am showing you the two-dimensional structure you can see the electrons are affecting each other in the neighbouring centre. And through this, they are having a huge delocalization and for that, this system can be explained also that the atoms are sitting inside the sea of electrons or the electrons are all interconnected through the bonding to the space. This is the structure what we are seeing in the two-dimensional.

Now, what happens when we talk about the three dimensional structure, so, the two dimensional structure what we found that the atoms are all interconnected and they can interact, the same is true also for this three-dimensional structure. Through these particular spaces, all the electrons are actually connected to each other. And through this and over here, we are looking into the three dimensional structure. This is nothing but an extension of the two dimensional structure just we discussed.

Over here, atoms present each of these connections and over there the electrons are shared all throughout the three dimensional sphere. So, now that electron sea is not in only two dimension, but in three dimensional space. And they are interacting with each other with each of the atoms which are connected through the bonding all over the three dimensional orderly structure, which is known as the lattice structure.

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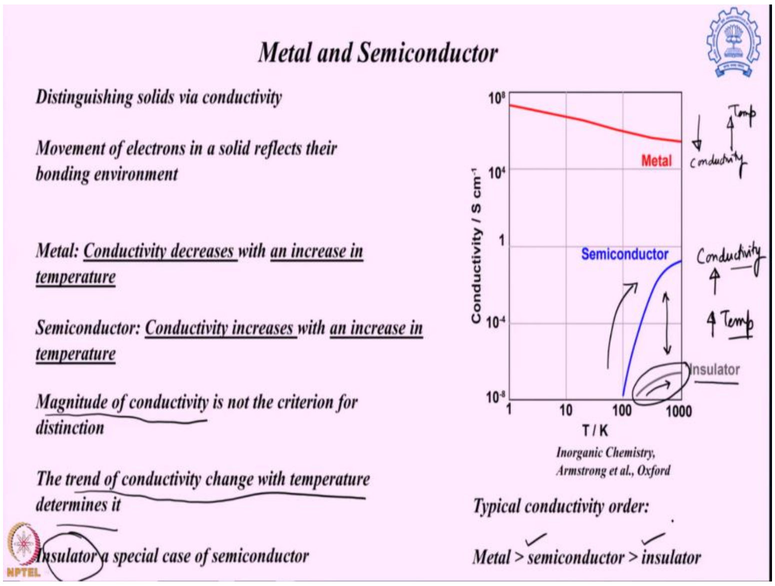

Metal and Semiconductor

Distinguishing solids via conductivity

Movement of electrons in a solid reflects their bonding environment

Metal: Conductivity decreases with an increase in temperature

Semiconductor: Conductivity increases with an increase in temperature

Magnitude of conductivity is not the criterion for distinction

The trend of conductivity change with temperature determines it

Insulator a special case of semiconductor

Inorganic Chemistry, Armstrong et al., Oxford

Typical conductivity order:

Metal > semiconductor > insulator

Now, we know how the electrons are behaving in a solid state, but can we understand it properly so that we can understand how the electrons movement can control the behaviour of a solid material. And for that, we are going to discuss about two different systems, metal and semiconductor, which we can distinguish by the conductivity, the electrical conductivity.

So, what is an electrical conductivity? Electrical conductivity is the movement of the electron through the solid and over there, the conductivity shows that how the electrons are moving through the system. So, it is nothing but a reflection of the electrons' movement through the surface of the solid. And at the same time, it is distinguishing or providing us the information about the bonding environment inside the material.

So over here, I am showing you two different systems which are connected to each other. One is the metal, a metal is a system which has a conductivity and which the conductivity actually decreases as we increase the temperature. So, metal is defined with respect to not about the absolute conductivity value, but how that conductivity changes with respect to temperature. So, what we said a metal is such a system whose conductivity decreases as we increase the temperature which is shown over here you can see the metal system the conductivity value which is shown in the y axis as we increase the temperature in the x axis you can see it is slowly decreasing.

So, that is why this kind of behaviour we will say it is actually a metallic behaviour. On the other hand, semiconductor is showing exactly the opposite behaviour where the conductivity actually increases with an increase in the temperature. Previously, it was a decrease in conductivity for metal, but now, in semiconductor the conductivity actually increases.

And over here I am showing you the figure and you can see for the semiconductor the conductivity actually increases as I am increasing the temperature. So, that is the basic distinguishing sorry, so, that is the basic distinction between a metal and a semiconductor. So, as you just said, the magnitude of the conductivity is actually not the criterion not the important factor about this distinction, it is a train of conductivity change with temperature.

Again, a metal is a system whose conductivity decreases with an increase in temperature and this is the conductivity that actually decreases whereas, a semiconductor is a system whose conductivity increases with an increase in temperature. So, they vary in the same direction. So, that is the main distinction between a metal and semiconductor.

Now, the absolute value comes to in the picture when we discuss about a special kind of semiconductor known as insulator. Insulator is a system which is nothing but a semiconductor, but where the absolute value of the conductivity is way too low you can see this is the insulator whose actual value is way too low compared to the semiconductor. However, the important factor is over there even in the insulator if I increase the temperature the conductive value actually increases.

So, that actually shows that insulator is nothing but a special kind of semiconductor. However, its absolute conductivity is way too low compared to a semiconductor and typically we found the conductivity of the metal is generally higher than the semiconductor and semiconductor is higher than the insulator. So, if we want to order the different materials with respect to their conductivity, we generally found this particular trend.

Again, we want to emphasize that how we distinguish between metal and semiconductor, that is with respect to how the conductivity changes with respect to the temperature. If the conductivity increases with respect to the temperature increase that is a semiconductor and if the conductivity decreases with respect to the temperature, it is a metal.

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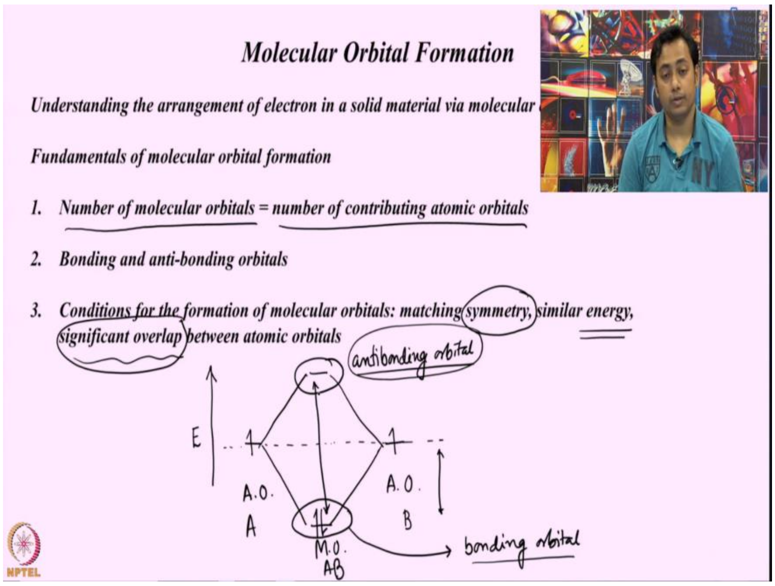

Molecular Orbital Formation

Understanding the arrangement of electron in a solid material via molecular

Fundamentals of molecular orbital formation

1. Number of molecular orbitals = number of contributing atomic orbitals
2. Bonding and anti-bonding orbitals
3. Conditions for the formation of molecular orbitals: matching symmetry, similar energy, significant overlap between atomic orbitals

Now, coming to the next picture. We generally talk about the electronic arrangement through the molecular orbital theory. This molecular orbital theory has been discussed in detail in the previous section, where we discuss about the structure of small molecules and that can be extended even for the solid form. But before going to the details of the solid, let us have a quick look back the fundamentals of the molecular orbital formation. So, molecular orbital theory generally comes as following. So, generally we have two atoms say atom a and atom b coming together and giving us each of them one set of atomic orbitals.

And these two atomic orbitals interact between themselves and gives us two sets of molecular orbitals, this is the molecular orbital of the molecule AB and if there is one electron over here, one electron on the B they actually combined to come in the orbital over here. So, over here you can see with respect to the energy of A and B atomic orbital, this molecular orbital is actually stabilized with respect to the energy scale. So that is why this orbital will be called the bonding orbital.

On the other hand, this particular molecular orbital which actually comes in the opposite symmetry during the interaction, that is called as the anti-bonding orbital. And this is actually higher in energy, higher energy with respect to the atomic orbitals that is constituting this molecular orbital. So, that is a difference between anti-bonding and bonding orbital and how many molecular orbital I am going to produce that will be exactly the equal number to the contributing atomic orbitals.

So, we cannot produce extra molecular orbital or destroy some molecular orbital with respect to the atomic orbitals, if I am combining, n number of atomic orbitals, I am going to produce n number of molecular orbitals. So that is the important factor and we are always going to produce some molecular orbital which is lower than the energy of the constituting atomic orbitals, that will be called the bonding orbital, some of them will be higher in energy that we will be calling the anti-bonding orbital.

And if with respect to symmetry, such thing happens where an atomic orbital was unable to contribute in the bonding and remains at the same energy as its atomic orbital that is known as non-bonding orbital. So, when two atomic orbital can come and produce a molecular orbital, the important factors are three. One, they have to match the symmetry.

They have to have similar energy, they do not always need to have exact same energy, but in the similar energy. So, the orbitals in respect to the energy scale are close enough so that they can start interaction and during that interaction, they are actually overlapping, the orbitals actually overlap and there should be a significant overlap to be there so that this molecular orbital can produce and more the overlap more will be the stability of the bonding and more will be the destabilization of the anti-bonding orbital.

So, this difference between the bonding and antibonding orbital energy is dependent on the overlap and also on the symmetry and with respect to the energy difference between the two atomic orbitals. So, that is the basic of the molecular orbital theory.

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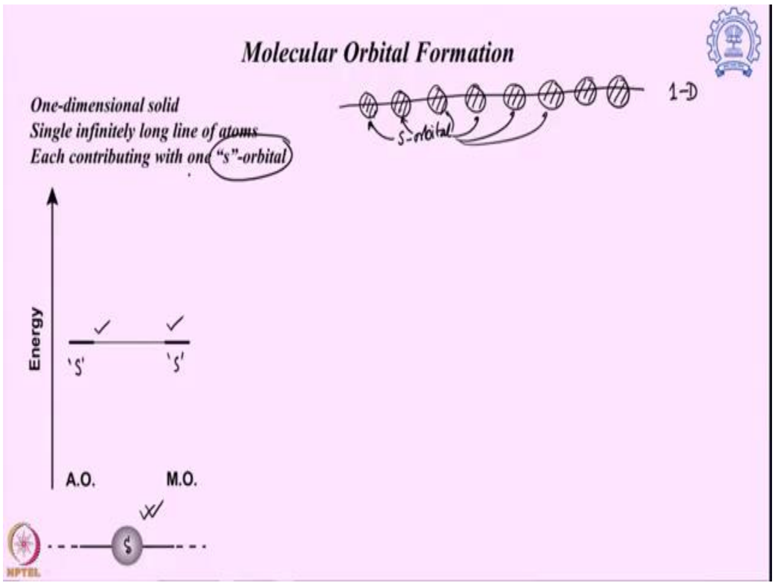
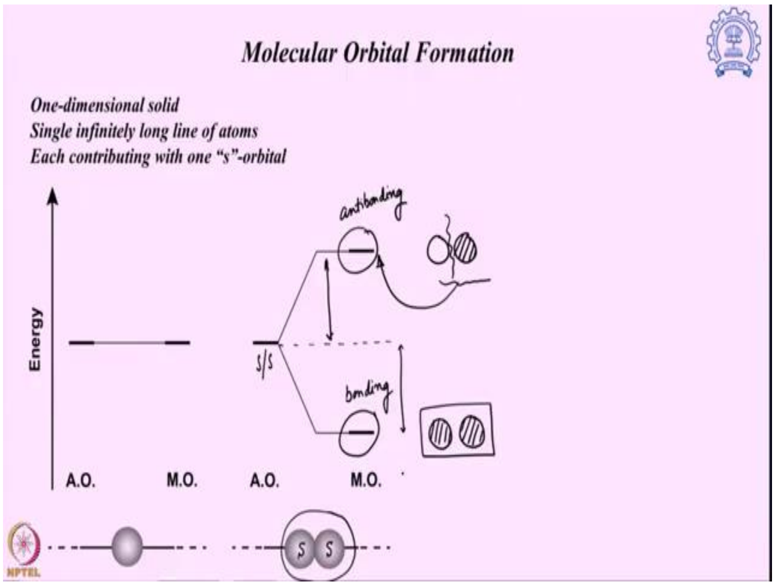


Molecular Orbital Formation

One-dimensional solid
Single infinitely long line of atoms
Each contributing with one "s"-orbital



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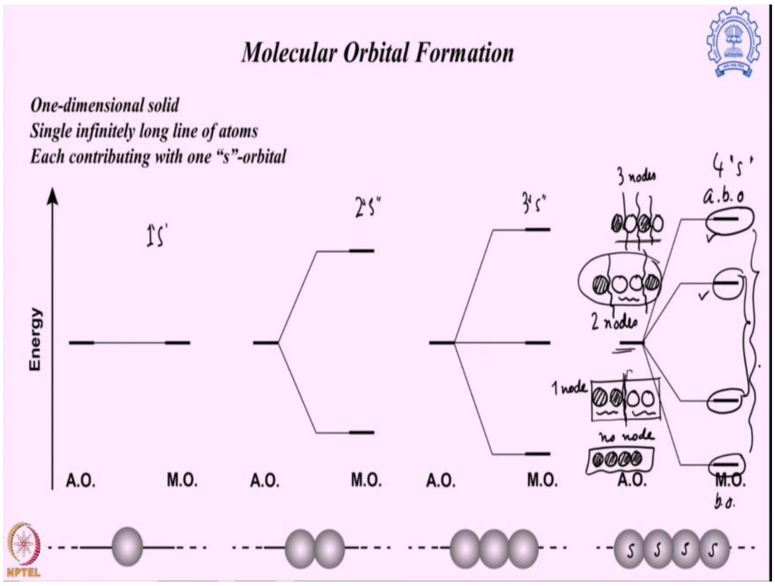

Molecular Orbital Formation

One-dimensional solid
Single infinitely long line of atoms
Each contributing with one "s"-orbital

Now, we go and discuss the molecular orbital formation in form of a solid. Now in solid, we have atoms present in three-dimensional array, all in a perfectly position in the lattice. So, to make the situation easier, what we actually assume that we have a solid, but all the atoms are present in only one dimension. So, we are trying to understand the molecular orbital formation in one dimension, and then we can expand that to the three dimensions.

So, what is our assumption that with this particular line, we have different atoms present and these atoms are combining with the electrons to have this interaction. So, all of them are present in this one particular line. So, that is why it is a one-dimensional system. And the other assumption I am assuming that each of them are contributing with one S-orbital because a S-orbital is the first one with respect to the energy and that is one of the easiest system to understand.

So, we consider not only the atoms that present in this line, but also at the same time, they are also contributing with S-orbitals for each of them. So, each of them are contributing one S-orbital at a time. So, how that is going to help me to understand how they are going to form the molecular orbital theory. So, again, we start from the beginning. First, we assume there is only one atom present over here and this one atom is not interacting with anything else, but it has this S-orbital present over there.

And this is S-orbital is not interacting with anything, so this S-orbital that I start with will remain at the same energy, if it is not interacting with any other atom and that is created the molecular orbital where only one atom is present in that solid in one dimension, but only one atom. So, here the energy you can see is same for both the atomic orbital and molecular orbital.

Now, we go to the next part where now we have two atoms and both of them are contributing with S-orbitals. And these two S-orbitals are now interacting over here. And during their interaction what happens as we just discussed, two atomic orbitals are participating now and they are going to contribute to one bonding and one anti-bonding molecular orbital.

So, this is the bonding one, this is the anti-bonding one and why there is one bonding on anti-bonding, because these two S-orbitals present over there they can combine in two different ways. In one particular sector, both the S-orbitals can have same symmetry. So, this is going to be the bonding interaction.

On the other hand, these two orbitals can have opposite symmetry. So, over there, there is a node present over there where there is no electron density possible over there. So, that is why this interaction make sure that this energy is higher compared to the original energy of the atomic orbital, whereas, this favourable interaction of bonding that actually stabilize the system with respect to the atomic orbital. So, that is why it is the bonding interaction.

So, that is happening when I bring two atoms. Now, let us bring the third one. So, over here, we have now bought the third S-orbital and over here all these three S-orbitals combined, it is still giving one bonding, one anti-bonding and very interestingly one remains as non-bonding orbital that is because in the bonding interaction, all the S-orbitals can come in the same phase and interact. So, that will be the bonding interaction and during the anti-bonding interaction, there can we have maximum number of two nodes present.

So, this is anti-bonding to either side of the orbitals. So, this set of three a S-orbital interaction is going to give me the antibonding interaction. There is a maximum antibody interaction we can find. So, over here there is no node at all and there are two nodes. Nodes means against a space where I cannot have electron density because they are opposites symmetry. So, I cannot have anything in between. In that non-bonding, I should have something come with only one node and how it is possible.

So, it is going to be nothing but we have orbital something like that, where there is actually it is not interacting with the other atomic orbitals or in that other way, we can write it like that there is no electron present over there. Now, you can see, these systems are actually showing that energy of the orbital will be exactly same as the orbital we begin with. So, that is why it is giving a non-bonding set of orbitals. So, it generally happens when we have an odd number of orbitals present during the interaction with the similar symmetry.

Now, we go to the next section where I have four atoms coming to the picture. Now, we have again one molecular orbital, which is bonding in nature. One is anti-bonding in nature, and there are two sets of other orbitals and even then, one is bonding, one is anti-bonding. So, how it is coming? So, for the bonding section, it is easier to understand that all of them are in the same symmetry and for the anti-bonding one, we have this particular system where I have one, two and three anti-bonding interaction.

So, over here there is no node. Over here I have three nodes. So, I can have other system where I have only one and two nodes and that comes over here. So, it is possible to have this kind of interaction. These two in the same face, the other two is in the opposite. So, there is bonding over here bonding over here, but in between them there is anti- bonding introduction and there is this one single node coming and the other way, we can have this interaction, where there is one anti-bonding interaction over here one anti-bonding interaction over here.

So, total two nodes and the middle two orbitals are in the same place. So, these are the four different orientations are possible and over there this interaction is stabilized compared to the S-orbital we start with, but it is less stable less compared to the fully symmetrically connected bonding system. Similar to that over here also there is two nodes, which is less destabilized compared to the three nodes bound, fully anti-bonding orbital.

So, these two are different sets of antibonding orbital and their energy depends on how many different nodes they have, how many different antibody interactions they have. So, this is as you are seeing that as I am going from one S-orbital to two S-orbitals to three S-orbitals, now, we actually have four different S-orbitals. So, these are not exactly one S, two S set of it, but one single S-orbital, two different S-orbitals, three different S-orbitals and four different S-orbitals, when they come together, as you can see, we are increasing the number of different molecular orbitals over there. And this will continue if I go to n number of a S-orbitals.

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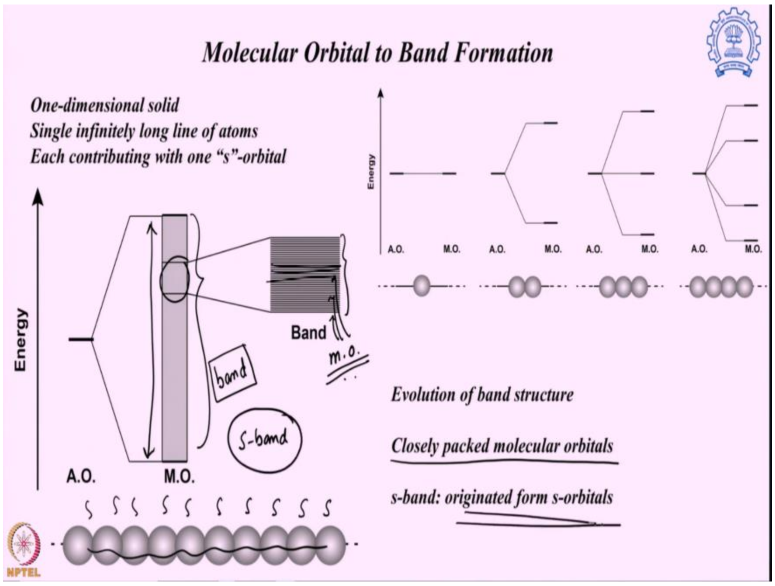

Molecular Orbital to Band Formation

One-dimensional solid
Single infinitely long line of atoms
Each contributing with one "s"-orbital

Evolution of band structure

Closely packed molecular orbitals

s-band: originated form s-orbitals

And that is shown over here, there are a number of S-orbitals now over here, all of them are contributing one S-atomic orbital, and those are going to give me a huge range of energy, where I will have all the atomic orbitals and those are actually so many numbers because I actually have put so, many of the n number of S-orbitals, that they will be very closely lying to each other. So close that it may look like they are almost continuous. And this particular system where all the S-orbitals are kind of combining and coming close together, this is known as band where they are actually nothing but closely packed molecular orbitals. So, over here, if we try to see it, and you can see all these particular lines is denoting each of them, each of these particular lines over there, you are seeing it is nothing but denoting one set of molecular orbital that is formed during the interaction between this S-orbitals in this one-dimension. So, that is what we are actually seeing from here, and this particular band, we will call it as it S-band because it is constituted from the S-orbitals to begin with.

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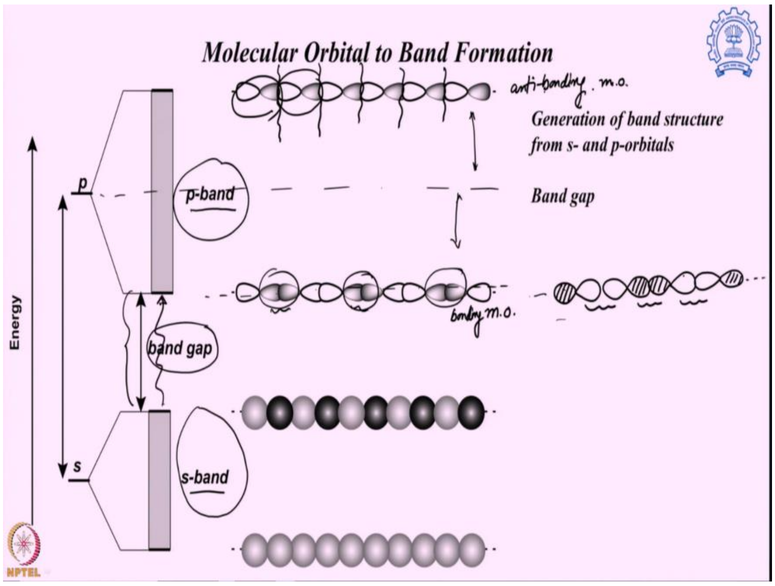

Molecular Orbital to Band Formation

Generation of band structure from s- and p-orbitals

Band gap

Then, we can have the same thing happening with the p-orbitals also, which will give me a p-band. So, over here as I shown over here, there are p-orbitals coming from each of these atoms can come and interact. And over there, I am showing the most stable bonding orbital what is actually happening there. So, say this is the interaction. So, the p-orbitals are lying such a way that they are only having bonding interaction between them so on and so forth. So, over there you can see the two different sets of p-orbitals are having bonding interaction. And the same thing happens when it is opposite symmetry over there as it is shown you can see this is one set of the p-orbital, this is another set of p-orbital and they are in opposite symmetry.

So, that is going to show a node over there same over here, same over here. So, this is the maximum number of nodes I can have. So, all the p-orbitals are exactly in the opposite symmetry, such a way that they are facing an anti-bonding interaction and over here, they are only showing bonding interactions. So, that actually shows how it is happening. So, this is going to be the most stable bonding molecular orbital and this is going to be the most unstable anti-bonding molecular orbital.

And there will be other combinations in between where not all of them are in bonding, not all of them are in anti-bonding, but different combinations of it, when there are more bonding the energy will be lower than the p-orbital I start with and when there will be less number of interactions and when there will be more anti-bonding interactions and bonding, we will see a huge number of anti-bonding orbitals which will have higher energy compared to the starting p-orbital.

And over there very interesting we find there is this S-band system there is the p-band system and they are actually situated a little bit differently. And this gap between this S and P-band of the system is known as the band gap. So, if we can cover up the energy and electron from s-band can travel to the p-band and that will be very important while we are discussing the conductivity of the system.

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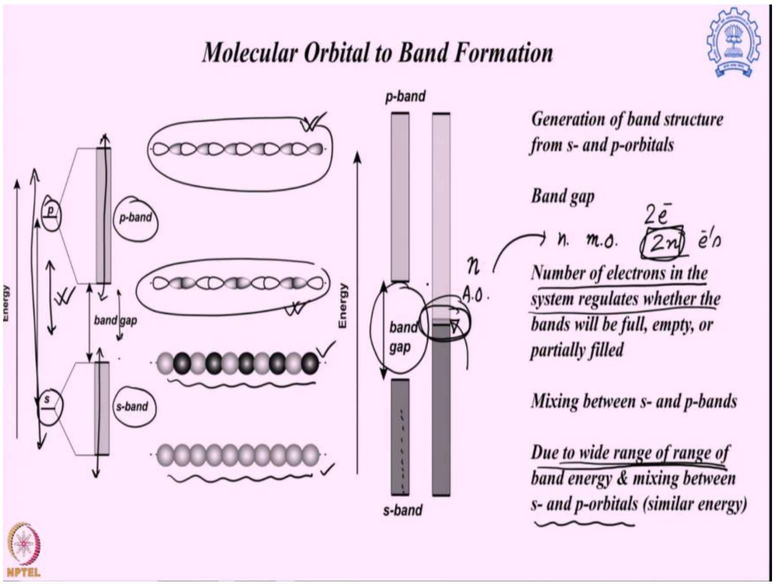

Molecular Orbital to Band Formation

Generation of band structure from s- and p-orbitals

Band gap

Number of electrons in the system regulates whether the bands will be full, empty, or partially filled

Mixing between s- and p-bands

Due to wide range of range of band energy & mixing between s- and p-orbitals (similar energy)

So, now over here, what we are showing is that S and P band sets of the orbitals are shown over here, they can combine and over here you can see that is the best bonding is the best anti-bonding. So, these are the ages of the bands. Similar happening with the p-band of systems is the most stabilized in a bonding most destabilised in the anti-bonding, and they actually shows this band gap. However, in certain system, if we have a huge number of atoms present, the number of atoms present is going to affect the width of this bands in the energy scale, more number of orbitals present, better will be the width.

So, if you have a huge number, they are going to expand further and they can come closer that they can close up the band gap. And it can also happen that they actually cross over. So, it will happen when you have a large number of electrons coming into the picture when it is coming through the huge number of atoms. And how many of these bands will be filled up with electrons and how many of them will be empty that depends on how many electrons they started with.

So, if I give n orbitals to start with of atomic orbital, I will end up with n number of molecular orbitals. Now, each orbital can hold two electrons altogether, I can have 2n number of electrons out of this 2n how many electrons I have, and that will start filling from the bottom stage. And with respect to that, I can feel some of them will be filled, some of them will remain empty depending on how many electrons I can have, if I have total 2n electrons, everything will be filled up. And over there, as we just discussed, there is a possibility of mixing of s and p bands that depends on the number of atoms actually participating in this bond formation.

So, that is going to affect the range of the band energy and also the S and P orbitals, when we start with their original energy gap in the atom that also differs. If they actually come close, I have better chance of mixing this and if they go around much larger gap, I will have less chance and I should see an increase in the band gap.

So, that energy gap between the P and S orbital of the atoms they are participating and how many of them participating will control the band gap and whether there is a possibility of mixing in the bands or not. So, we will stop the first segment of the band theory over here, where we discuss the band theory is nothing but an extension of a molecular orbital theory for solid materials, where n number of atomic orbitals can come together and give me n number of molecular orbitals.

And depending on the symmetry, they are showing a width where they all combined and give us different kinds of molecular orbitals, starting from the very stable bonding molecular orbital, to very unstable anti-bonding orbital. And in the middle, they have different combinations of bondings to anti-bondings and they will lie very close to each other. And that is why they look like more of a band rather than distinct energy state and that is known as the band structure of molecular solids. Now, the effect of it will come into the next segment. Thank you.