Fundamentals of electronic materials, devices and fabrication

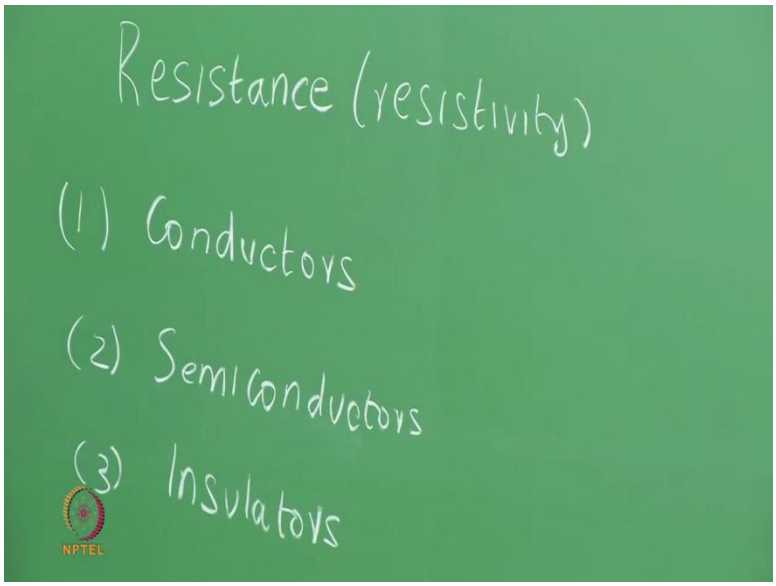
Dr. S. Parasuraman
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture – 01
Metals, Semiconductors and Insulators

Welcome to the first lecture of this course Electronic Materials Devices and fabrication. In this course, we will look at semiconductor materials, we will study the properties; mostly the electronic properties. We will then use the semiconductor materials to form devices. So, these devices could be made from two semiconductors; they could be made from a semiconductor and a metal or even a semiconductor and insulator and a metal. We will also look at devices for some optical applications like say, LEDs and solar cells. Finally, we will look at the current micro fabrication industry, where we will form integrated circuits made of these devices from semiconductors. Towards the end of the course we will also look at some alternate fabrication techniques where we use a bottom up approach to fabricate devices rather than the top down approach that is currently followed.

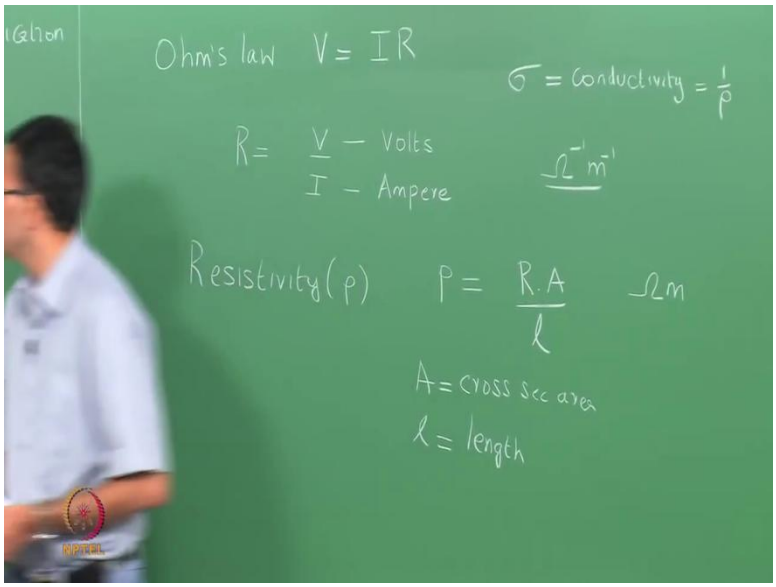
When we think of electronic materials, the first property that comes to mind is Resistance. Resistance or resistivity if you will can be used in order to separate materials into 3 categories. The first one is Conductors, then you have Semiconductors and then finally, you have Insulators.

(Refer Slide Time: 01:20)



Since we will be mostly dealing with metals as conductors, I will also write them as just metals. When we think of resistance the unit of resistance is ohm and the symbol is Ω. Resistance is related to both the voltage and the current by what is known as Ohm's law.

(Refer Slide Time: 02:30)



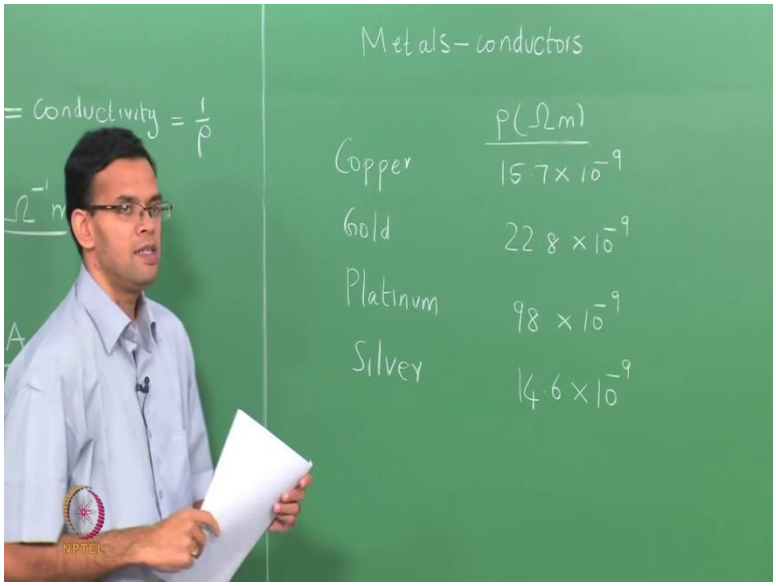
Ohm's law states the voltage is nothing but the current times the resistance another way of writing it is; Resistance is voltage over current unit of voltage is just volts, unit of current is Ampere. Now, resistance depends upon the dimensions of the sample, so if you

have a thinner material or if you have a wire with a smaller diameter, then the resistance is higher. So, we need to think of a parameter that does not depend upon the dimensions of the sample and this parameter is called Resistivity.

Resistivity is typically given as ρ and it is related to the resistance by; where R is the resistance, A is the cross-sectional area and l is the length of the sample. The unit of resistivity is Ω m, you can also have Ω cm. One over the resistivity is called conductivity. The unit of conductivity is nothing but Ω^{-1} m^{-1}.

So, we have introduced two concepts right, one is the resistivity, the other is the conductivity. We also said we have three types of materials, Conductors, Semiconductors and Insulators and the difference between them is because of the difference is the resistivity values. Let us look at some typical values for resistivity for all these three types.

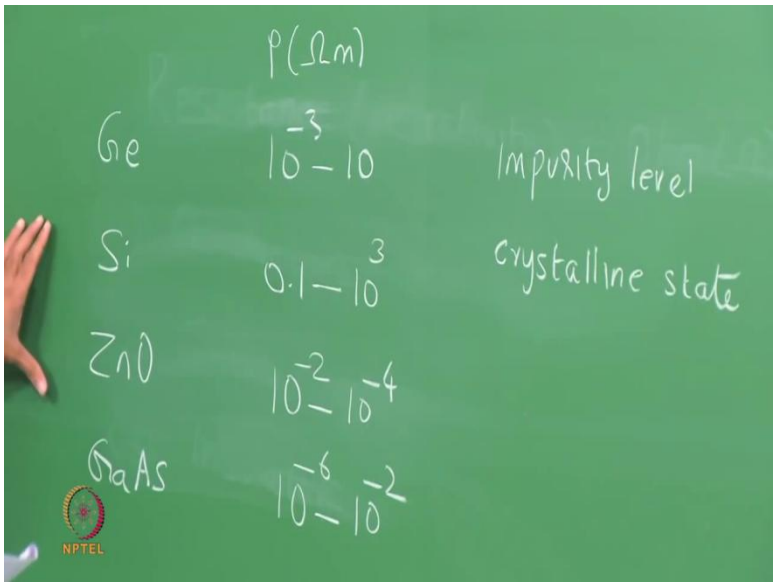
(Refer Slide Time: 04:55)



Let us start with metals or conductors. Some typical examples of metals are Copper, Gold, Platinum, Silver. What are some of the typical resistivities? so ρ unit is Ω m. In the case of copper, 15.7 x 10^{-9}, for Gold is 22.8 x 10^{-9}, 10^{-9} is common for all 4. Platinum is slightly higher its 98, Silver is actually a better conductor than Copper, but Sliver is also expensive. So, when we look at metals we have conductivity or we have resistivity of

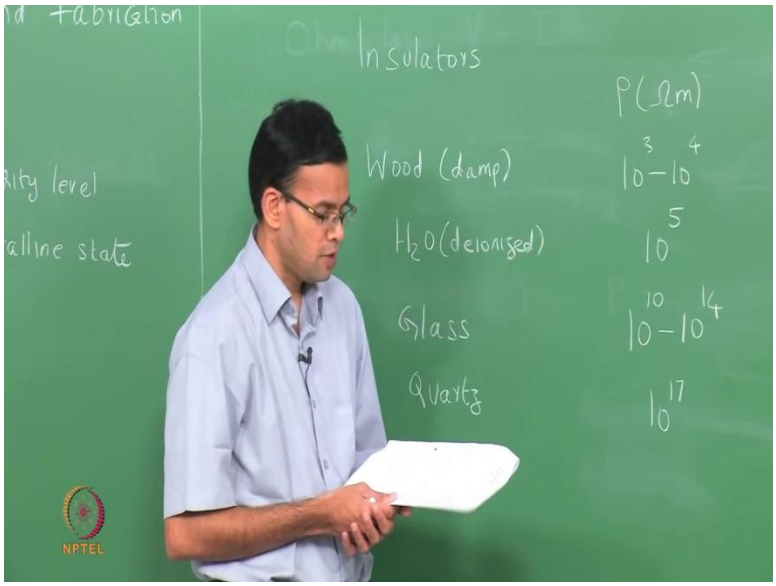
around 10^{-9} Ω m. Let us next look at semiconductors.

(Refer Slide Time: 06:20)



Some examples of semiconductors are Germanium, Silicon, Zinc Oxide, Gallium Arsenide. Some of the typical values of resistivity; Silicon is around $0.1 - 10^{3}$, Zinc oxide is 10^{-2} to 10^{-4} it is lower. Gallium Arsenide 10^{-6} to 10^{-2}. In all of these cases I have given a range of values. The actual resistivity or the conductivity depends upon the impurity level and also the crystalline state whether you have a single crystal or a poly crystal. These are some of the values for resistivity in the case of semiconductors. What about insulators?

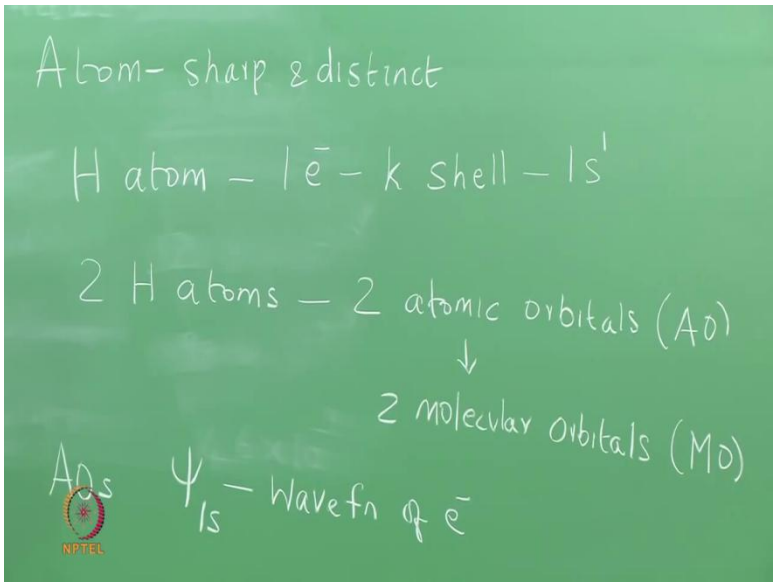
(Refer Slide Time: 07:32)



Examples of some typical insulators you could say Wood, Water we say its deionized water. So, there are no dissolved salts, Glass and Quartz. These are some typical values. So, 10^5 in the clays of glass where resistivity is around 10^{10} to 10^{14} depending upon if you have some doping agents in glass or not or some impurities, in case of Quartz its even higher. So, what we essentially see is a wide range of resistivity depending upon whether you are the metal or you have a semiconductor or you have an insulator.

So, the question is how to understand this difference in these values. In order to do that we need to look at the band gap of material and how the band gap evolves. Our focus will be mainly on metals and semiconductors, but whatever concepts we develop we can equally apply them to insulators. So, let us go ahead and look at how band gap evolves starting with a metal.

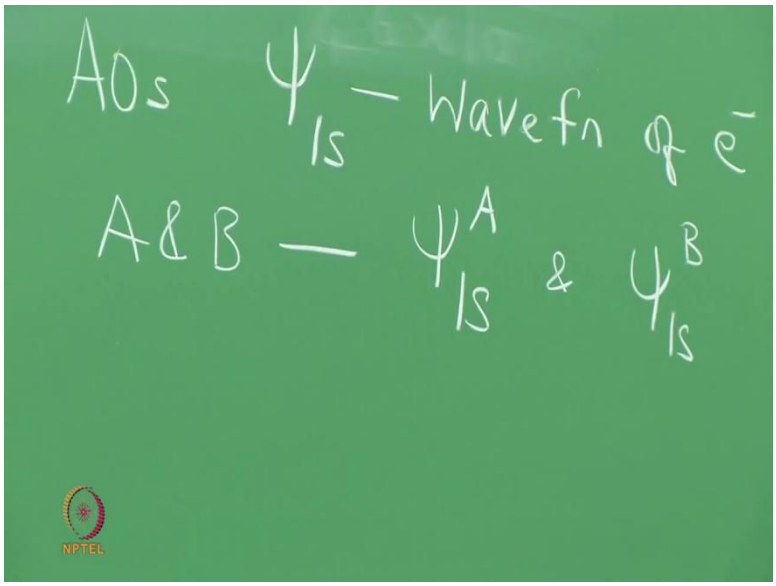
(Refer Slide Time: 09:16)



When you have an individual atom the energy levels are usually sharp and distinct. The question really is what happens when all these atoms come together to form a solid? Let us start with a simplest atom that we know that is the Hydrogen atom. Hydrogen atom has one electron and it has one proton in the nucleus. The one electron is in the k shell and the atomic configuration for Hydrogen is $1s^1$. What happens when we have 2 Hydrogen atoms come together? When we have two Hydrogen atoms you have 2 1s atomic orbitals that come together these interact and give you two molecular orbitals. So, a 2 Hydrogen atoms have 2 atomic orbitals which give you 2 molecular orbitals. For sake of gravity I will call atomic orbitals as AO and molecular orbitals as MO.

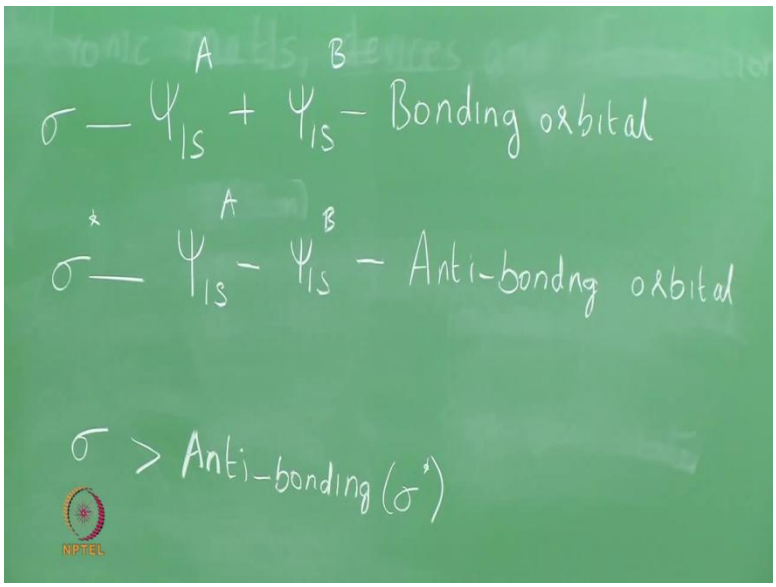
Let us denote this atomic orbitals by the symbol ψ_{1s}. 1s refers to the fact that you have the electron in the 1s shell. In quantum mechanics ψ represents the wave function of the electron. If you have 2 Hydrogen atoms A and B you will have 2 atomic orbitals, let us call them ψ_{1s}^{A} and ψ_{1s}^{B}.

(Refer Slide Time: 11:30)



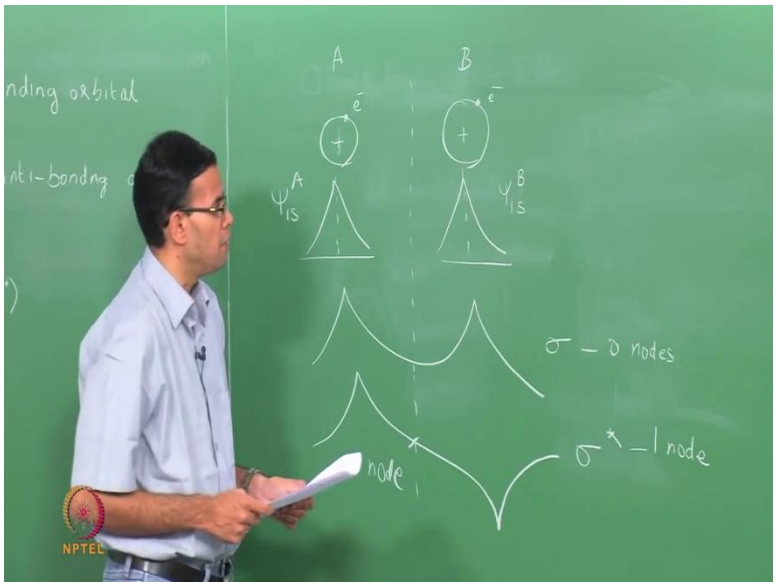
Now in order to form molecular orbitals, these 2-wave functions, ψ_{1s}^{A} and ψ_{1s}^{B} need to be put together and there are 2 ways of doing it.

(Refer Slide Time: 11:43)



You could add both of them, this is called a Bonding orbital and it is denoted by σ. You can subtract them and this is called the Anti-bonding orbital. In terms of energy the bonding orbital sigma has a higher energy than the anti-bonding orbital and I am going to denote this as σ^{*}. So, I will call this σ^{*}, we can also depict this pictorially.

(Refer Slide Time: 12:53)

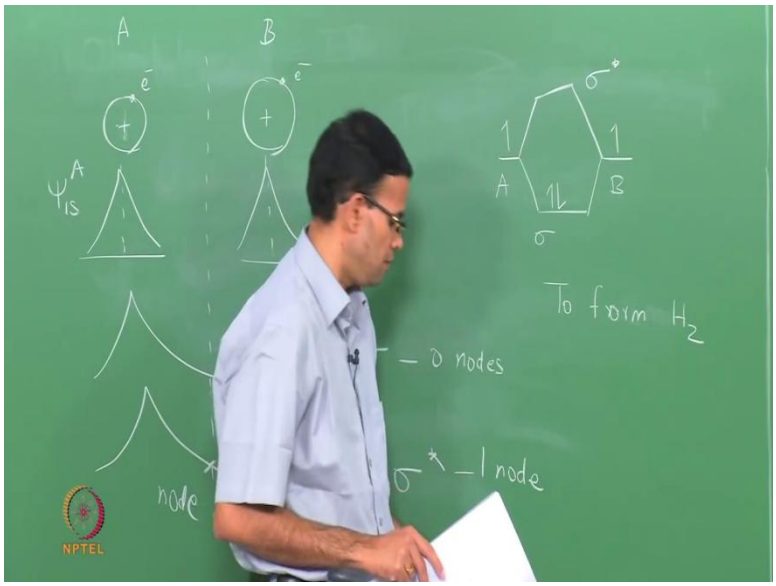


So, Let us take 2 Hydrogen atoms. So, at the center you have the nucleus and outside you have the electron A and B. Each of them has an atomic orbital so, an atomic wave function. So, This one is ψ_{1s}^{A}, which is the atomic orbital for A and ψ_{1s}^{B}. In both of these cases, I have chosen an exponential function for the atomic orbitals. There is a way of showing that it is actually an exponential function but, we won't go into it. As far as we are concerned, we have an orbital that is exponentially decreasing away from the nucleus and we will keep it that.

So, now we have 2 atomic orbitals; we can either add them or subtract them. If you add them the resultant wave function look something like this. So, you have a minimum between the 2 atoms and then you have a maximum at the 2 nucleus. So, this is your bonding orbital we will call it σ. You can also subtract them which case this is the anti bonding orbital that is σ^{*}. If you look at it σ does not go to zero at all. It goes to minimum between the 2 atoms on the other hand σ^{*} goes to a zero between the 2 atoms and this is called a node. So, the σ has zero nodes and the σ^{*} has 1 node.

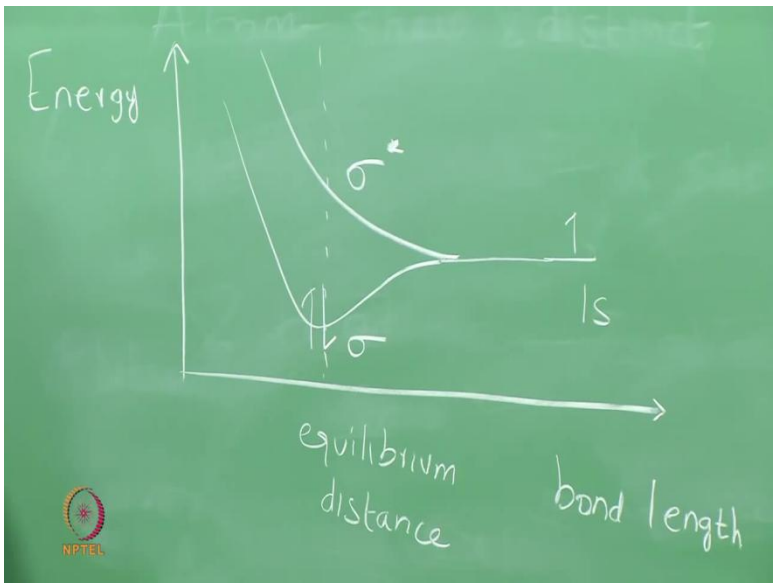
We say that the σ has a lower energy than σ^{*} right the bonding orbital is more stable than the anti-bonding. Another way to represent this compactly is to consider your 2 atomic orbitals A and B. Each has one electron; when these 2 merge they form both a bonding and an anti-bonding orbital.

(Refer Slide Time: 15:26)



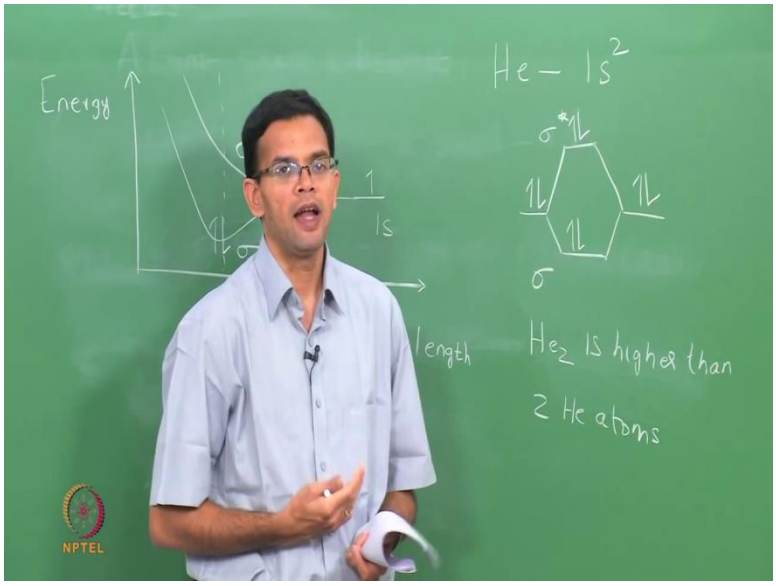
So, your bonding orbital has a lower energy that is your σ, anti-bonding orbital has a higher energy that is σ^*. Each orbital can take 2 electrons of opposite spin. So, both electrons go to the σ thus when you form a Hydrogen molecule from 2 Hydrogen atoms the overall energy of the system is lower. So, its favorable to form H_2. when 2 Hydrogen atoms come together you can also show this diagram by means of an energy versus bond length diagram. In that particular plot, we will have energy on the y-axis and we will have bond length on the x-axis. So, Energy this is bond length.

(Refer Slide Time: 16:14)



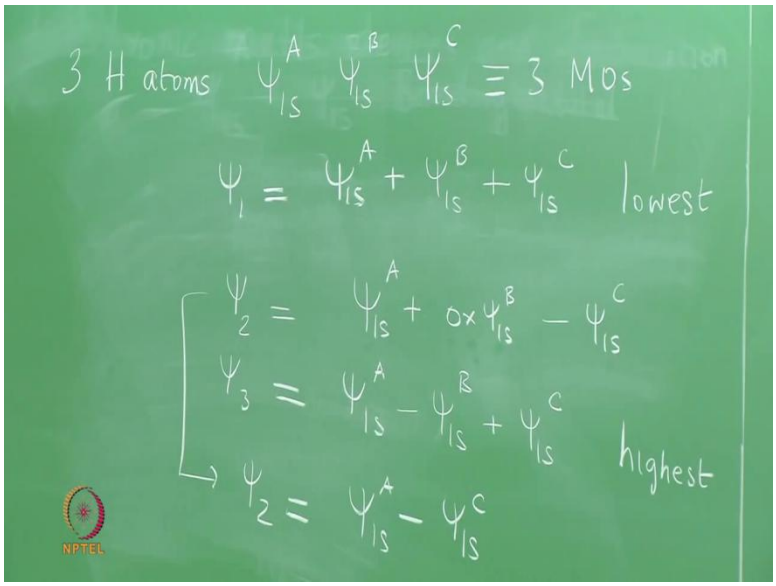
When the 2 Hydrogen atoms are far apart typically we say that the Hydrogen atoms are at infinity then what we have is simply the atomic orbitals. So, I will show them here which is the 1s orbital and it has 1 electron. Then you start to bring your Hydrogen atoms together. So, as I start to come together they will see the affect of each other ultimately the atomic orbitals will mix and give you your molecular orbitals σ and σ^*. So, for this we will have some equilibrium distance. Let me call this equilibrium distance. So, is the equilibrium distance for the 2 Hydrogen atoms in the molecule. So, You now have the atoms come together they form 2 our molecular orbitals 1 is σ the other is σ^*. So, σ has a lower energy which is the bonding σ^* has a higher energy that is anti bonding and both electrons go into σ. So, this is the picture as far as Hydrogen is concern right we can use the same diagram to explain while Helium 2 will not form.

(Refer Slide Time: 17:54)



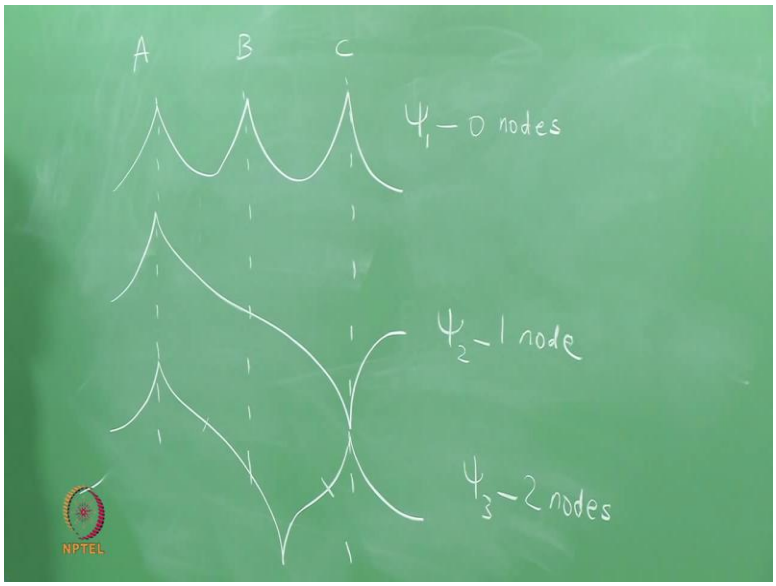
In the case of Helium its a noble gas it has 2 electrons in the 1s shell. If 2 Helium atoms come together, you have 2 electrons here, you have 2 electrons here. Once again both the 1s you can think of mixing and forming a bonding and an anti bonding. So, this is your σ this is your σ^*. Now, we have a total of 4 electrons 2 electrons will go into σ, but 2 electrons also go into the anti-bonding that is σ^*. So, the overall energy of He_2 is higher than just 2 He atoms. So, That is why you will not have Helium 2 this picture is good enough as long as we have 2 atoms now what if I had 3 Hydrogen atoms let us look at that.

(Refer Slide Time: 19:04)



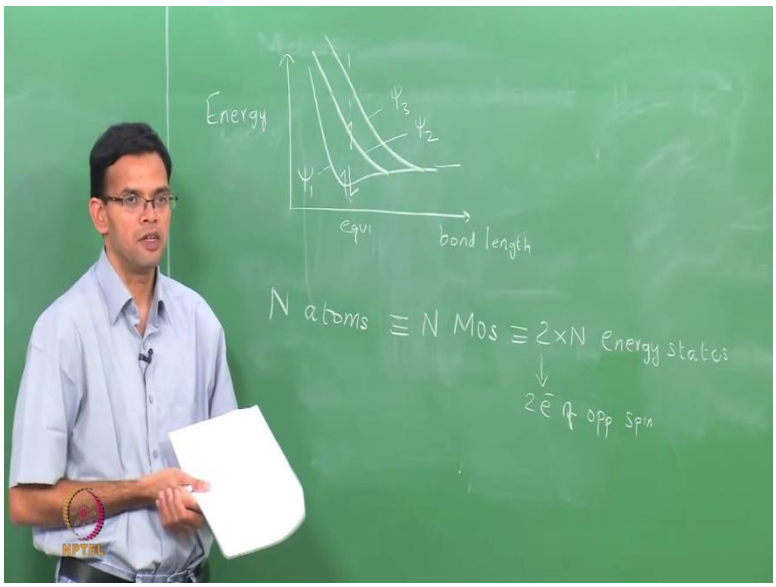
So, let us say we have 3 Hydrogen atoms A, B and C. Your atomic orbitals are ψ_{1s}^A, ψ_{1s}^B, ψ_{1s}^A when we have 2 atoms we said they form 2 orbitals, 2 molecular orbitals. Now, when we have 3 atoms we are going to get 3 molecular orbitals, there are 3 ways of obtaining this molecular orbitals. The first one is to just add all 3. This is the lowest energy you can also do one subtraction this is the lowest energy this has the highest energy and then you have one more in between them. So, in this particular case the contribution from the second Hydrogen atom is neglected because it is times 0. So, all you have is ψ_{1s}^A - ψ_{1s}^C. So, let me just write that down. So, ψ_2 is nothing but ψ_{1s}^A - ψ_{1s}^C. you can depict this pictorially again by taking 3 Hydrogen atoms.

(Refer Slide Time: 21:10)



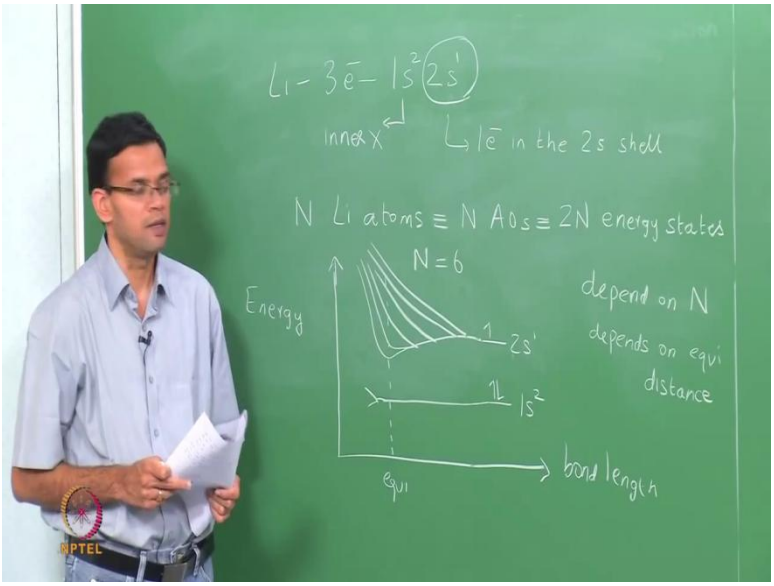
So, in the first case you are adding all 3 orbitals together. So, these are A, B and C this is ψ_1 now you are adding all 3. This one the function does not go to 0 anywhere. So, you have 0 nodes in the case of ψ_2 we said that the function goes to 0 at atom B that is why there was only contribution from A and C this is ψ_2. So, it has 1 node and in the case of ψ_3, we have 2 nodes. So, this is the lowest energy with 0 nodes then you have 1 node which is a higher energy finally, ψ_3 that has the highest energy for this case also we can draw an energy versus bond length diagram.

(Refer Slide Time: 22:34)



If we do the energy verses bond length for 3 Hydrogen atoms what we have our 3 orbitals ψ_1 with the lowest, ψ_3 with the highest and then ψ_2 in the middle. Now we have 3 electrons, 2 electrons will go to ψ_1 and 1 electron will go to ψ_2. So, this is what will happen if we have 3 Hydrogen atoms. Now if you have 4 Hydrogen atoms you will have 4 molecular orbitals you will have 4 lines here if we have 5 you will have 5 lines here. So, thus as a number of atoms increases you will have more lines on your energy versus bond length diagram. So, ultimately we can say if you have N atoms could be N Hydrogen atoms. Then you will have N molecular orbital's each molecular orbital can take 2 electrons of opposite spin. So, 2xN energy states and the number 2 comes because you can have 2 electrons of opposite spin. Ok, So, this is the picture you have developed using Hydrogen we also showed how Helium will not formed. What if we increase the complexity a bit further and then look at Lithium?

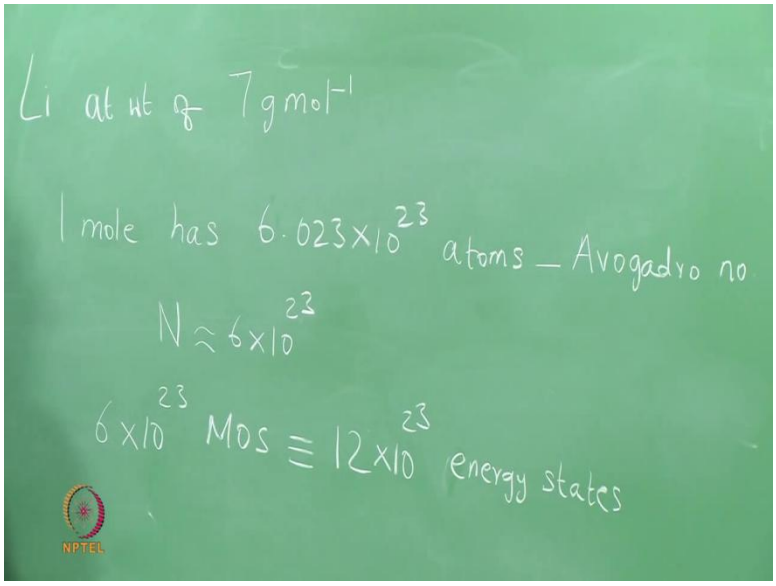
(Refer Slide Time: 24:40)



When we have Lithium, Lithium has 3 electrons. The electronic configuration is $1s^2$, $2s^1$ the 1s shell in Lithium is an inner shell. So, this is an inner shell. The inner shell is usually not involved in bonding. So, we would ignore the effect of the inner shell. So, what you are interested in is the $2s^1$ electron right. So, this again has 1 e^- in the 2s shell. So, This is similar to a Hydrogen atom. So, we can use the same argument for Lithium as in the case of Hydrogen. So, if you N Lithium atoms, taking only the 2s electron into a count you will have N atomic orbital's which will give you 2N energy states. Again why 2? because each energy state or each molecular orbital can have 2 electrons.

Once again we can draw an energy versus bond length diagram for Lithium. So, we have energy on the y-axis, bond length on the x-axis. So, energy, bond length then you have the equilibrium spacing here, this is the equilibrium spacing of the Lithium atoms when they come together to form a solid. So, you have the $1s^2$ which is a inner shell and as 2 electrons, as I said the inner shell does not take part in bonding. So, its remains a straight line, it does not form a band now you have the $2s^1$ if you have N Lithium atoms the $2s^1$ of all of those Lithium atoms comes together to form N molecular orbitals. Once again we can draw this picture, where we will have N lines here. In this particular case I have draw 1, 2, 3,…6 lines. In this particular case N is 6, the spacing between these lines depend upon N and it also depends on the equilibrium distance. So, what is a typical value of N?, N is usually a very large number.

(Refer Slide Time: 28:00)

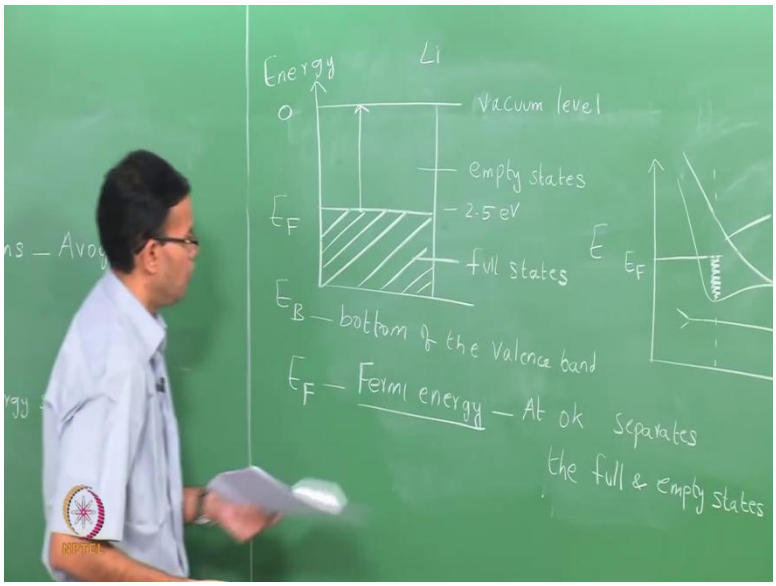


For example if we take Lithium, Lithium has an atomic weight of 7 g mol^{-1} right. So, if you have 7 grams of Lithium you have 1 mole and 1 mole has 6.023 x 10^{23} atoms, right this is nothing but the Avagadro number. So, your typical value of N, if you had seven grams of material is approximately 6 x 10^{23}. So, if you have 6 x 10^{23} Lithium atoms coming together to form a solid you have 6 x 10^{23} molecular orbitals. Each of them can take 2 electrons. So, you have 10 x or 12 x 10^{23} energy states and this is a really large number. So, what this means is the spacing between the individual energy states is really small if we go back to the diagram. The diagram where we drew here and had N equal to 6 and drew 6 lines if you have N equal to 23, 10^{23} you are essentially drawing 10^{23} of

these lines. What I am trying to say is for really large. N's these become continuous and what we have is an energy band.

So, we can redraw the energy band diagram for Lithium taking into fact that you no longer have individual molecular orbitals but you have an energy band.

(Refer Slide Time: 30:15)

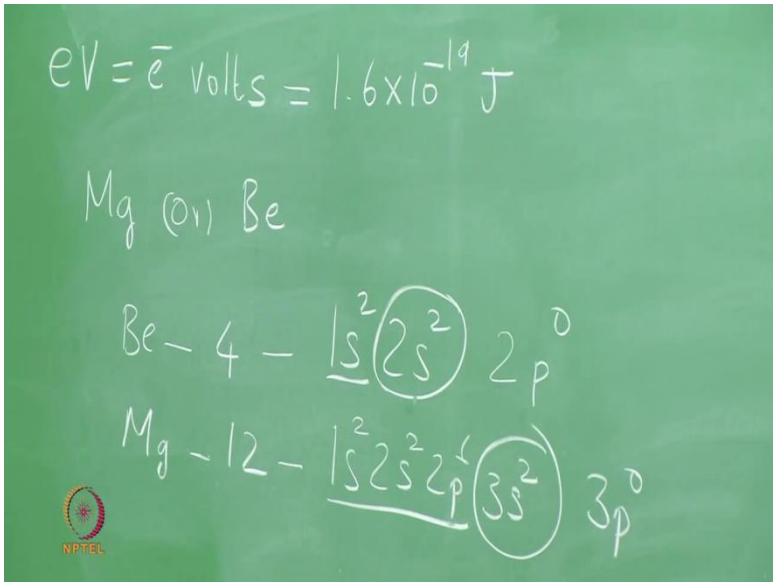


So, in this case the energy is on the y-axis, the reference an energy level called 0 which is the vacuum level. So, Let me call this the vacuum level and this has the value 0. So, everything can be reference to the vacuum level. So, You have an energy band that is half full. So, In this case, these are all the full states and these are all the empty states. So, how do we arrive the fact that the energy band is half-full? If you go back to the energy versus the bond length diagrams. Energy versus bond length, if you have Lithium which is $2s^1$. You have a 1s inner shell we have $2s^1$. So, this is the energy band here and there are a total of 2N states but each Lithium atom will only contribute one electron. So, you have only N electrons. So, hence only half of this band is full. So, We can erase the top half. So, You have a situation where you have half of the band, there is full, half of the band, there is empty.

This is the same thing I have shown here you have a half a band there is full and half a band, there is empty. This energy state that separates the full and the empty regions, I have labeled it as E_f. E_f is called the Fermi energy. Now this is a very important term the Fermi energy at 0 kelvin separates the full and empty states. So, Fermi energy separates

the full and empty states, this is the most often used working definition for Fermi energy. When we come to semiconductors we will try to modify this definition a little, but as far as we dealing with metals we will use this. So, let us just put some numbers here. So, in the case of Lithium this energy is 0, the Fermi energy is at minus 2.5 ev which means you need 2.5 ev of energy in order to excite an electron from the Fermi level to the vacuum level. E_B is the bottom of the valence band, in the case of Lithium. E_B has a value of -7.2 ev. The units of energy that are used here ev is called electron volts

(Refer Slide Time: 34:46)

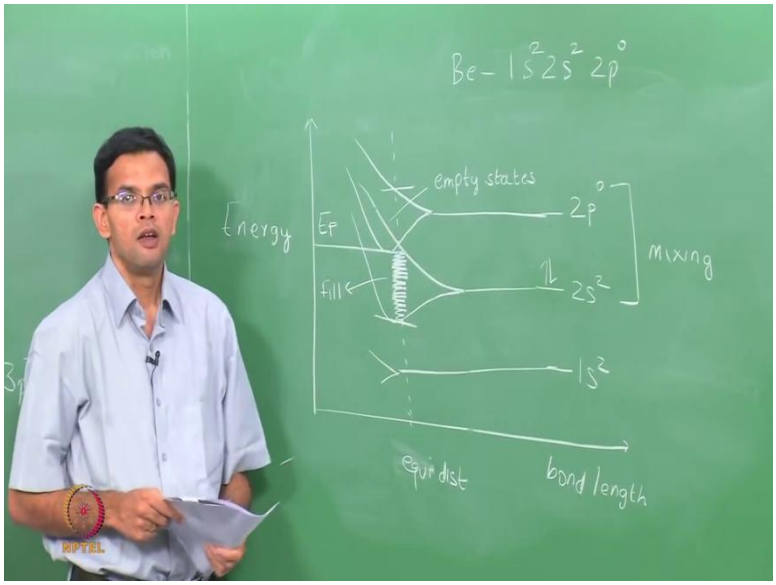


ev is called electron volts; is related to the energy in joules by the expression 1.6×10^{-19} joules. 1 ev approx is 1.6×10^{-19} joules, this is the picture as far as Lithium is concern. So, in the case of Lithium you have a 2s shell that is half full. So, you also have a band that is half full what about Magnesium or Beryllium? Beryllium has an atomic number of 4, it has an electron configuration $1s^2$, $2s^2$ the Magnesium is below Beryllium in the periodic table has an electronic configuration $1s^2$, $2s^2$, $2p^6$ and $3s^2$ once again for both of these elements these are the inner shell. So, your outer shell is essentially an s^2 configuration. This configuration is a same as in the case of Helium we saw that Helium has a $1s^2$ configuration.

The question is how will Beryllium or Magnesium form metals or form solid because we know they do and Helium does not. The reason is in the case of both Beryllium and Magnesium you also have the p shells and the p shells are empty. So, here you have a $2p^0$

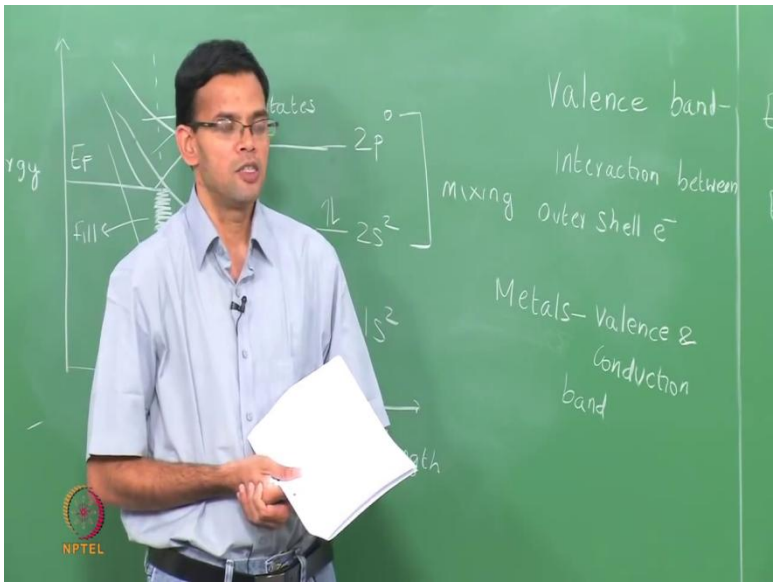
in the case of Magnesium you have a $3p^0$. So, what you have when you form a solid is the mixing between the empty $2p^0$ and the full $2s^2$, in the case of Magnesium you have mixing between the empty $3p^0$ in the full $3s^2$ and that is the reason why you have an unfilled state and why these are metals. So, this once again we can show this pictorially using the energy verses the bond distance diagram.

(Refer Slide Time: 37:12)



Let us use the example for Beryllium. You have energy on the y-axis and then bond length on the x-axis and we have some equilibrium distance the 1s shell is an inner shell that will not take part in bonding you have a $2s^2$ shell that is full and you have $2p^0$ that is empty. When you draw the bond diagram this is your 2s shell which you also have the $2p^0$ shell. So, what you have is the mixing of the 2s and the 2p. So, that this whole thing, which is the mixture of the 2s and the 2p forms a band. Then you can fill in the electrons in this band. So, that these are all the fill states and these are all the empty states and the energy separating the filled and the empty states is your Fermi energy. That is the reason where Beryllium or Magnesium even though they have a full $2s^2$ electronic configuration are still considered metals, because they have mixing between the s and the p. So, that now they have a band there is half full and half empty. This band which is caused by which is caused by interaction of the electrons in the outermost shell is called the Valence band.

(Refer Slide Time: 39:44)



It is caused by the interaction between the outer shell electrons, there is also a conduction band. In the case of metals the valence band and the conduction band are both the same. So, in case of metals you have both valence and a conduction band and they are both the same, in the case of semiconductors you will find that the valence and the conduction band are different and, there is a gap between them this is what we called the band gap. So, in today's class we have looked at how metals formed. How you can start with individual atoms and then these atoms come together to form molecular orbitals, the case of metals you find that these molecular orbitals ultimately form a band. And these bands are not completely full there are always some empty states are available and this is why metals are such good conductors because these electrons which are there in these bands can acquire energy and go to these empty states and thus can move freely within the metal and this makes metals very good conductors.

In next class, we will start to look at semiconductors and we will see how we have a band gap in semiconductors we will also look at different classifications of semiconductor.