

**Physics of Renewable Energy Systems**  
**Professor Amreesh Chandra**  
**Department of Physics**  
**Indian Institute of Technology Kharagpur**  
**Lecture 05**  
**Origin of Band Structure and Energy Band Gap**

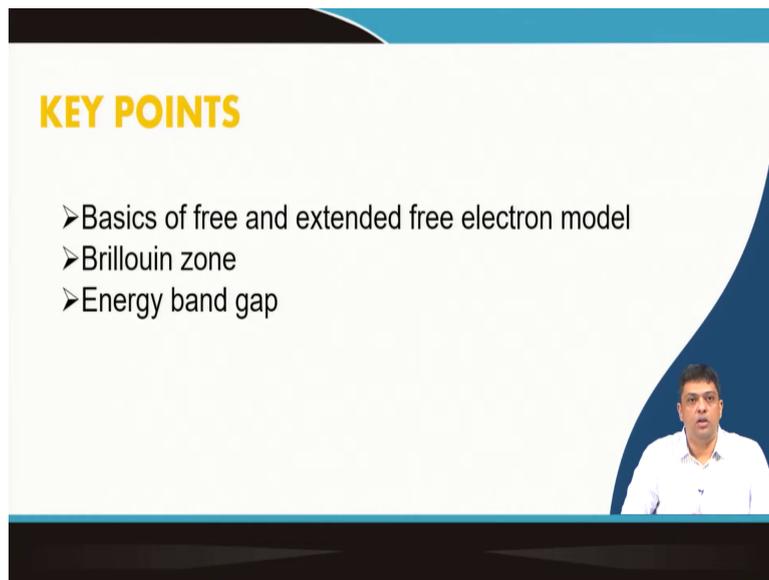
Welcome back to this course on physics of renewable energy systems. In today's lecture, we will be focusing on energy band structure and the origin of band gap in materials.

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And, these are the concepts which would be covered what leads to the origin of energy band gap in materials and based on the energy band gap, how do we classified these solid materials and the materials which we will be talking about would be metals, semiconductor and insulators.

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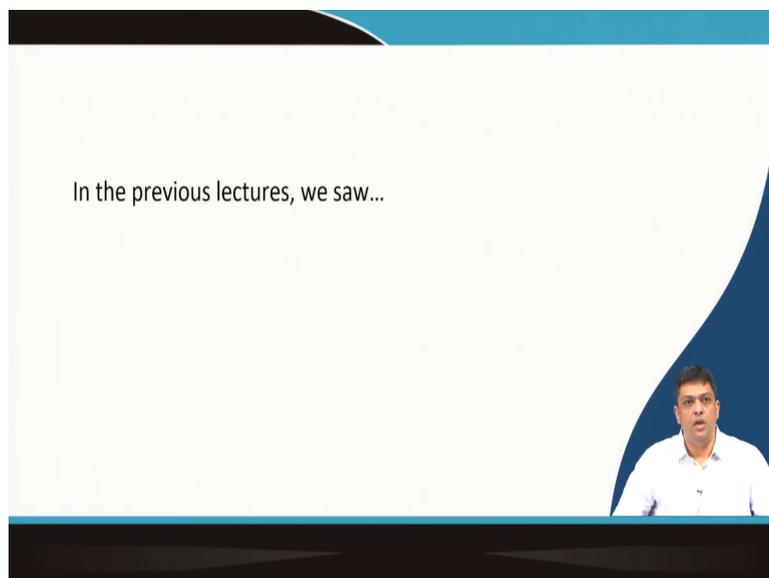
**KEY POINTS**

- Basics of free and extended free electron model
- Brillouin zone
- Energy band gap

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By the time you finish the lecture, hopefully, these are the main points, which you will be able to understand the basics of free and extended free electron model, the concept of Brillouin zone and the energy band gap.

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In the previous lectures, we saw...

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**Edmond Becquerel discovered the photovoltaic effect in 1839.**

In **1875**, *William Grylls Adam and Richard Evans Day*, using selenide as a solid material, showed that light can be used to generate electricity.

In **1894**, probably, the first true solar cell was reported by Charles Fritts. Efficiency (~ 1%)

A major increment in the performance came in **1950s**, by the studies in Bell laboratories, where *G. Pearson, D. Chapin and C. Fuller*, using doped silicon reported a solar cell with 5.7% efficiency Efficiency (~ 1%)

**We are now in 2021!**

*Lot of work still needs to be done and are being done*

In the previous lectures, we have seen that the effect of photovoltaic was discovered in 1839 and if I say okay, it was only in 1875 that we actually saw that material can be used to generate electricity when light was used as the source and we are now in 2021, so it is already more than 170 years and we have still not reached to the point where the technology is available of the shelf and a lot of work is still going on and a lot needs to be done before it becomes available to everybody without any government subsidy and that is why this portion of the course becomes extremely important for all of us.

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### Photovoltaic effect

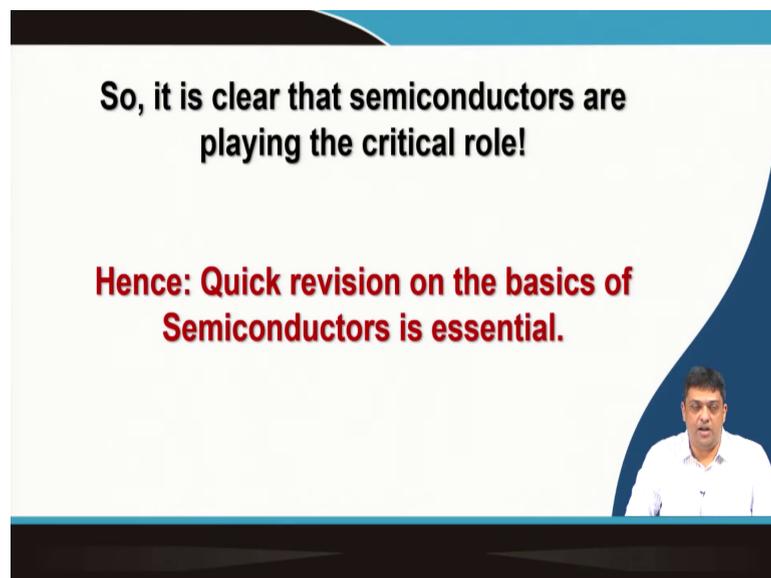
The process occurs in or close to the depletion layer

- The resulting electron is not ejected from the surface, but is promoted to a higher-lying energy level in the semiconductor, which enables it to move freely through the semiconductor material.
- A metallic grid forms one of the electrodes of the cell, and a metallic layer on the back of the solar cell forms the other electrode.
- An incident photon must have sufficient energy to generate an electron-hole pair, i.e.  $h\nu > E_g$
- The band gap of a semiconductor is ~1 eV, e.g.  $E_g=1.1$  eV for silicon.

Labels in diagram: Grid electrode,  $h\nu$ , n-type region, Depletion layer, electron-hole pair, Back electrode, p-type region, Load

We had also shown to you that the photoelectric effect is based on p-n junction when you form a p-n junction, then you have the region where the holes and electrons recombine and you get a region which is devoid of charges and free moving charges and you get those that is called depletion layer and if you have proper connection through an external load and electrodes, which are connecting the two ends of this p-n junction and if you are able to shine light on this depletion layer, then you can generate electricity, which is a result of the flow of free electron from the n-type region to the p-type region from the external load.

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It is clear that I am many times emphasizing on the role of p-type semiconductor n-type semiconductor and the depletion layer. Therefore, it is clear that semiconductors are playing the critical role in the particular device which we are discussing and that warrants a quick revision on the basics of semiconductor and that is what I have planned to discuss with you in today's lecture.

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**Conductor, semiconductor and insulator**

**If we analyze the materials, we see every solid contains electrons.**

According to the nature of band occupation by electrons, all solids can be broadly classified into two groups viz.;

- 1) The ones which have completely filled valence band overlapping with partially filled conduction band (Metals) and
- 2) The ones which have empty conduction band lying over completely filled valence band

Depending on the width of forbidden band, the second group can be divided into:

Insulator (band gap  $E_g > 3 \text{ eV}$ )      Semiconductor (band gap  $0.1 < E_g \leq 3 \text{ eV}$ )

The diagram illustrates the energy band structure for three types of materials: Metal, Insulator, and Semiconductor. In the Metal case, the valence band and conduction band overlap, allowing for easy electron movement. In the Insulator case, there is a large band gap ( $E_g > 3 \text{ eV}$ ) between a completely filled valence band and an empty conduction band. In the Semiconductor case, there is a smaller band gap ( $0.1 < E_g \leq 3 \text{ eV}$ ) between a completely filled valence band and an empty conduction band. A small inset shows a person speaking.

And if you pick up a book all of you have read these definitions and we find that conductors, semiconductors or insulators are classified according to the nature of band occupation by electrons and the solids which have their valence band overlapping with partially filled conduction bands are called as metals, the ones which have empty conduction band lying over completely filled valence band can be classified into two sub classifications the first insulator and second as semiconductor.

Now, as I say, there is a forbidden gap that is called energy band gap and if you see, if the energy band gap is more than three electron volts, then those are called as insulators and typically and conventionally we have been saying that semiconductors are the ones which have band gap in the range of 0.1 to 3 electron volts, but these definitions slightly vary some people give different values, but these are the conventional definitions which have been followed and you all have seen it.

If I ask you the question, what do I mean by band occupation, what do you mean by valence band or conduction band and if there are two bands, what happens and from where does this energy band gap actually come in, why should there be two different bands where energy levels are present and between two levels you have a gap also? I ask you this question and let us try to answer this question today and if we are able to do that will form the basis of semiconductors and the knowledge we will use to fabricate solar based systems.



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From Metal → Semiconductor to Insulators  
*[Mostly explained in terms of electrical conductivities and energy band]*

We will have to understand the concepts of energy bands, band gaps and interaction of the conduction electron waves with the ion cores of the crystal.

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So, we already know that metals semiconductors or insulators are explained in terms of electrical conductivities, but today, we would also like to understand the concept of energy band and this concept of energy band and band gap is also closely associated by the understanding of interaction which occurs in the conduction electron waves with the ion cores of the crystal.

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Brief revision and understanding of the origin of energy bands in solids

We will use the understanding to:

- Distinguish between metals, semimetals, semiconductors and insulators
- To explain relation between conduction and valance electrons

*This can be developed using Extended free electron model or nearly free electron model*

**Assumptions:**

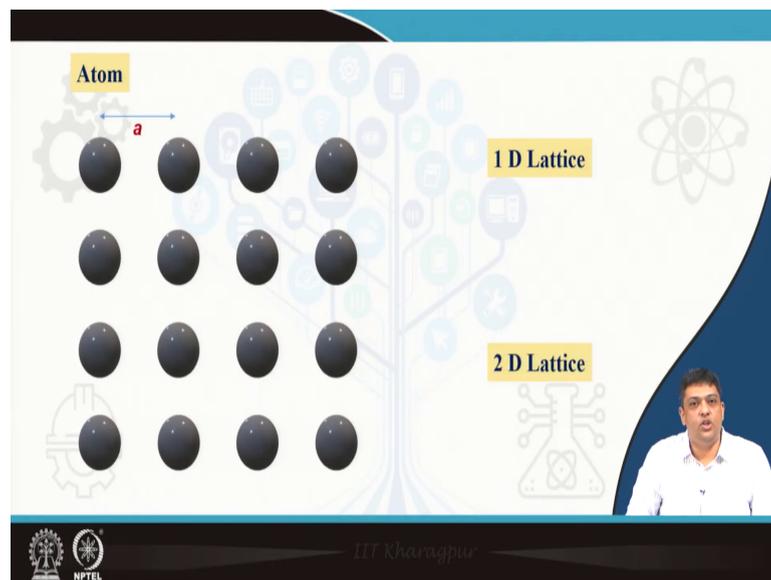
- Subjected to periodic lattice
- Potential energy of electron is not constant
- Varying potential has periodicity similar to crystal lattice.

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So, what we will be doing? We will use the understanding to distinguish between metals, semi metals, semiconductors and insulators and we will also explain the relation between

conduction and valence electrons and to develop this understanding, we will be using the extended free electron model or nearly free electron model, so this is what we will be using to explain the concept, we will also be using certain assumptions to prove the hypothesis which we will propose.

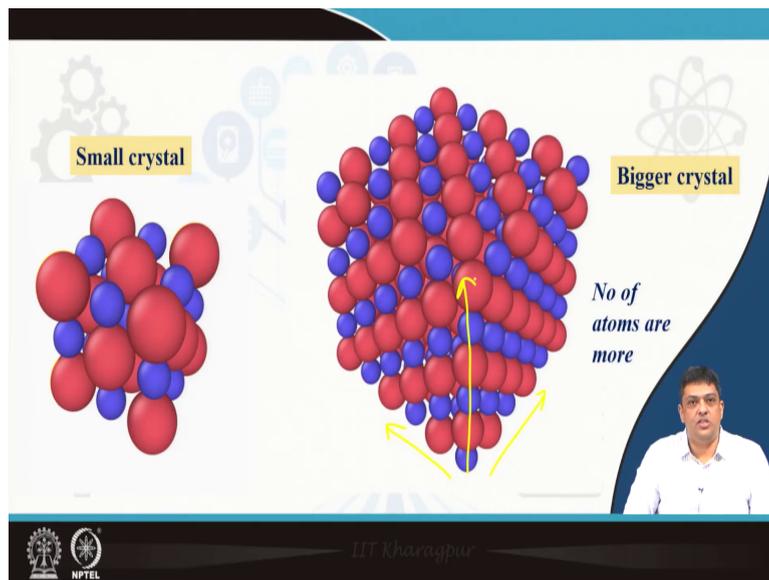
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So, let us first understand what is this structure or metal or semiconductor or insulator which we are talking about these are solid materials that we are talking about, and they are formed of atoms. Now, based on the arrangement of these atoms, you can have linear structures, you can have two dimensional structures or you can have three dimensional structures.

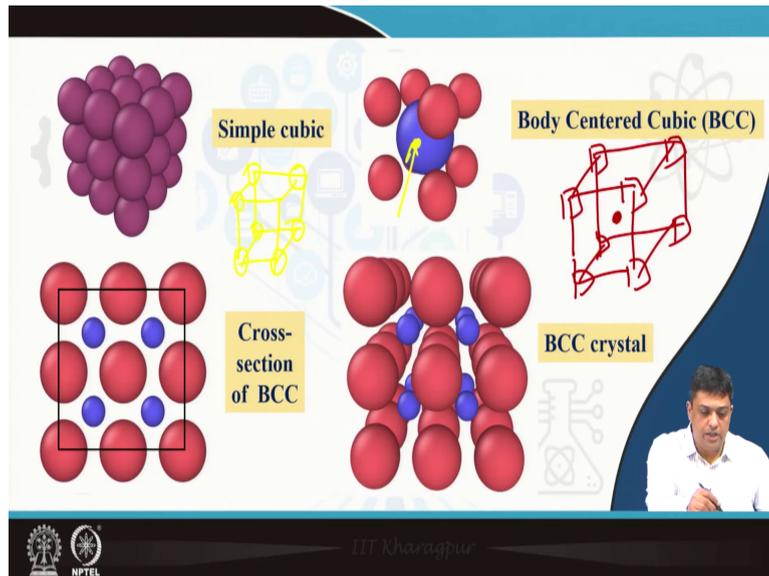
So, let us consider an atom if they are linearly arranged only in one direction and you have these atoms on one line, those are called as the atoms which are arranged in 1D lattice. Now, you have the arrangement such that these atoms are also arranged in the other direction, so you have the let us say x direction and the y direction, and they are arranged if those kind of arrangements are present, then you give the condition of 2D lattice.

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But now, we not only have it one direction, two direction but we also have the third direction where the atoms are arranged. So, if you have these kind of arrangements, you actually need to 3D structures. So typically, if you have, these are small crystals, I am just calling them a small crystals, because the number of atoms which are used to show this animation is quite limited, so we call it as small crystals, so the number of atoms in these crystals are less, if I have to explain a 3D crystal, which is much bigger than, the number of atoms in this 3D crystal would be much larger, so you have arrangement in this direction in this direction as well as in the third direction, so you have a three dimensional crystal.

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Now, each of these atoms can if you see these crystals, they can arrange themselves in a particular manner, so if they are arranging in certain ordered manner, which can be described using crystallographic rules, then you have different crystal systems this all of us understand.

So, you have different Bravais lattices, you have different kinds of crystals and then these atoms relate to each other in a crystal using point group or space group symmetries, this is what we have understood from crystallography, so just to give a feel what do I mean, so this is a simple cubic structure that the atoms are at the corners of a cube, so if I draw a cube and then I say that it is a simple cubic structure, then you have atoms, which are only at the cube edges and the number of molecules unit, per unit per unit cell is 1. If I go to a body centred cubic, then you have atoms at the cube edges and also at the centre of the body you have another atom.

So, you have this atom which is the body centered of the cell, so if I draw again this let us say a cube and I want to explain the body centered cubic then you have another atom, so you have an atom which is at the body centered along with atoms at the edges of the cube, this is the cross sectional view of a BCC lattice and if I have a BCC crystal, you see this unit cell is repeated  $n$  times and you get a BCC crystal

So, this is what do we understand with various arrangements and what happens when you have different kinds of crystallographic lattices and then, what is the significance of the space group and point group symmetries. One thing should be clear everything is based on the

arrangement of the atoms again arrangement of the atoms and that is where we will start our discussion on free electron model

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**Assumptions of free electron model**

- A metal crystal consists of positive metal ions whose valence electrons are free to move between the ions.
- The crystal is held together by electrostatic forces of attraction between the positively charged ions and negatively charged **electron gas**.
- The mutual repulsion between the electrons is ignored.
- The potential field due to positive ions is completely uniform ✓
- At any given temperature, the velocity of electrons could be determined according to Maxwell-Boltzmann distribution law.

Free Electron Model *Successfully explained* →

- Electrical conductivity ✓
- Thermal conductivity ✓
- Thermionic emission ✓
- Thermoelectric effect ✓
- Galvanomagnetic effect ✓

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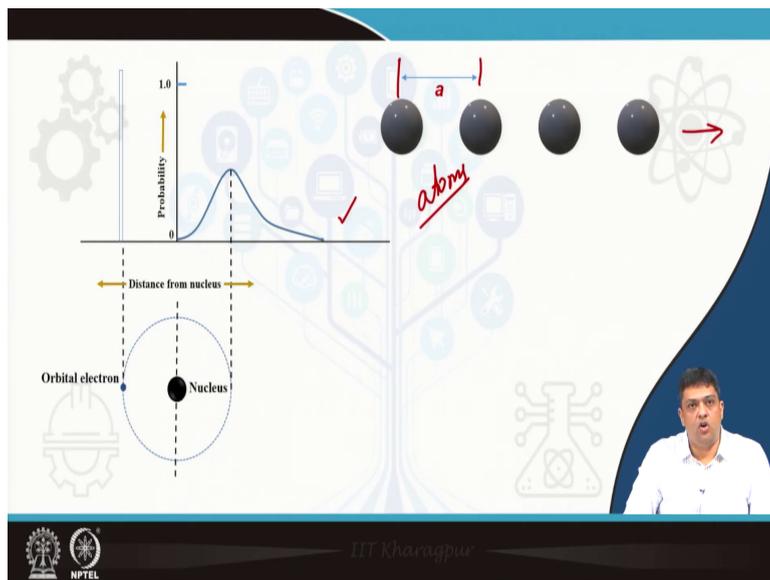
The free electron model means that an electron is free to move in the lattice and in the such lattice which is a metal crystal it consists of positive metal ion, whose valence electrons are free to move between the ions, the crystal is held together by electrostatic forces of attraction between positively charged ion and negatively charged electron gas, so what do we mean by this so, if you have the nucleus, the electrons are revolving round the nucleus and because large number of electrons are revolving round the nucleus, you call this as an electron gas.

The mutual repulsions between two electrons in which may be coming near to each other in various orbits or while they are revolving in orbit is ignored. And the potential field due to the positive ions is completely uniform, this will become clear to you in subsequent slides and at any given temperature, the velocity of electrons could be determined by the Maxwell-Boltzmann distribution law.

So, these are the basic assumptions of free electron model and using these model we can explain electrical conductivity, thermal conductivity, thermionic emission, thermoelectric effect or Galvanomagnetic effect, so it is a very powerful model to explain many of the physical phenomena which we observe in solids, so most of you may have learned about this in solid state physics and if you have not learned it well, you will have participants from different backgrounds, let me give a slightly more detailed explanation to what I said just now.



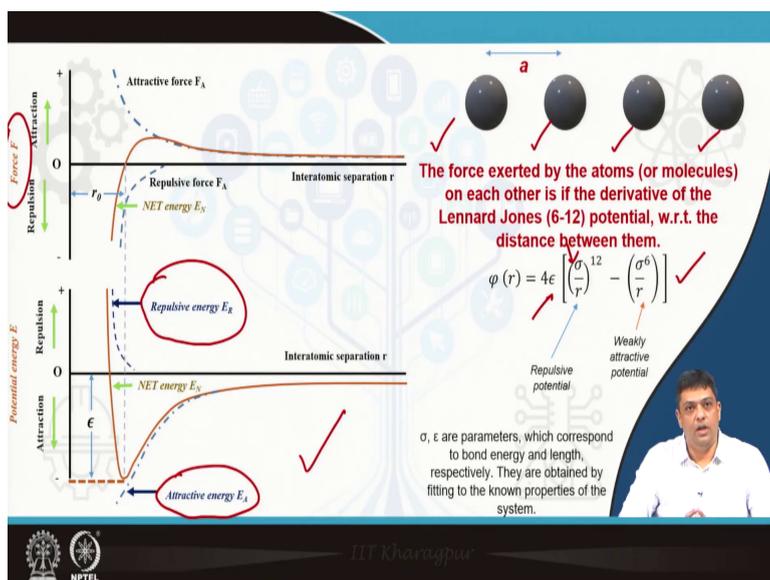
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So, let us consider a linear, so we have considered a linear lattice to and where the atoms are separated by a distance  $a$  and so we have a positive centre and around this the electron is revolving and if you plot the potential as a function from the distance of nucleus, you get a curve which is given in this top most figure.

So, this is what we mean that the probability of finding the electron in a particular orbit is maximum and then on either side of this orbit it falls significantly, so this is what we know from our basic physics.

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Now, let us try to understand what is happening you have one atom and then the other atom they are coming together to form a lattice, when they are coming together to form a lattice what is happening this can be believed as an attractive force acting, so this can be considered as the action which is forced by the attractive force.

But, if two similar charges come very near to each other, then there is repulsion, so if they come near, very near then there will be repulsion, so there are two components which act during the arrangement of atoms in a lattice and at equilibrium there is a balance between the attractive and repulsive forces and if this force exerted by the atoms on each other is actually a derivative of the Lennard Jones potential, which is also called Lennard Jones 612 potential.

Because of the powers which you see in the potential which is given by Lennard Jones, so if you plot a potential energy function, for an atom, you have two components, one of them comes in as the repulsive energy component, which is given by  $\sigma$  by  $r$  raise to the power of 12 and the other is the attractive force which is given by  $\sigma$  raise to the power of 6 by  $r$  and these parameters  $\sigma$  and  $\epsilon$  actually correspond to bond energy and bond length and they are obtained by fitting to known properties of a given system.

So, now you have an atom and around this atom you have its potential energy function, which is there and the force can be obtained by taking the derivative of this potential energy, so now if I want to draw a potential energy curve associated with each atom then I will take separate atoms and then I will try to draw this potential energy curve and then what will be the force which is exerted on each other will be given by the derivative of the Lennard Jones potential, this is what should be clear to you now.

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**Energy bands in solids**

**One-dimensional case:**

- In the one-dimensional case, the Schrödinger equation can be written as:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m^*}{\hbar^2} [E - E_{pot}(x)] \psi = 0$$

- Kronig and Penney suggested a simple model of periodically varying potential energy.
- They assumed that the potential energy of an electron had the shape of a periodic array of square wells.
- The distance between successive wells was assumed to be  $a+b$ , where  $b$  is the width of the well.

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So, let us take a one dimensional case that means, you have atoms arranged in linear lattice, so we have atoms these if you plot the potential energy functions that around the atom you will have the fields will be strong and then they will have slightly away from the atom the fields will be weaker and then it will go on repeating this is what is shown in this figure.

So, in the one dimensional case, the Schrodinger equation can be written as  $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m^*}{\hbar^2} [E - E_{pot}(x)] \psi = 0$ . Now, this is a potential function which is going to be used to solve the Schrodinger wave equation.

So let us see what we mean by the potential energy function for each atom and how does it affect the arrangement in a linear lattice, so each atom has its own potential energy function and then they are interacting, so what happens this is what we should try to understand now. And to understand this case, that is one dimensional case because the atoms are linearly arranged in 1D, the Schrodinger equation can be written as  $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m^*}{\hbar^2} [E - E_{pot}(x)] \psi = 0$ .

To solve this equation, it became very easy when Kronig and Penney suggested a simple model of periodically varying potential and such that, the shape of the periodic array was similar to that of a square well. And the distance between the two square wells was assumed to be  $a+b$ , where  $b$  is the width of the well. So, this is similar to what is shown here, so

rather than using the curve nature, Kronig and Penney came in and suggested that let us consider a square well type periodic array.

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**Energy bands in solids**

**One-dimensional case:**

- The Schrödinger equation for the two regions can be written as:
  - ✓  $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m^*}{\hbar^2} [E - 0] \psi = 0$  For,  $0 < x < a$  Region-I
  - ✓  $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m^*}{\hbar^2} [E - E_0] \psi = 0$  For,  $a < x < a + b$  Region-II
- In the case of a linear lattice with the spacing  $a$ ,  $b$  is small. The solution of the Schrödinger equation, i.e. the eigenfunction for a given  $k$  value, can be written as:
 
$$\psi(x) = e^{ikx} U_k(x) \quad \text{where } U_k \text{ is the periodic Bloch function}$$

$$U_k(x) = U_k(x + a)$$
- The corresponding eigenvalue in terms of  $k$  depends on the lattice constant.
- Both the eigenvalues and the wavevectors are quantized for a free electron.

The diagram shows a periodic potential well structure with wells of width  $a$  and spacing  $b$ . The x-axis is marked at  $0, a, 2a, 3a$ . A red curve represents the energy bands above the potential wells.

Then, you can solve the Schrodinger equation in two regions, one of the regions is from 0 to a and then in the region which is b, so one very near to the atoms and one where the separation between the two potential energy functions was being observed, so you solve the Schrodinger wave equations in these two regions.

Now, in the case of a linear lattice with spacing  $a$ ,  $b$  is generally small. Therefore, the solution of the Schrodinger equation, what does it give, it gives you the Eigen function for a given  $k$  value and it can be written as  $\psi(x) = e^{ikx} U_k(x)$ , where  $U_k$  is a periodic block function which says that you will have  $U_k(x) = U_k(x + a)$  that means, the value which you have at  $x$  if you move a distance by  $a$  you get the same value, why does it come in to picture because, if you move from one atom to the other the function should be same because you cannot differentiate between the two atoms which are arranged in a linear lattice, here you are considering the arrangement of a similar atoms.

So, the corresponding Eigen value in terms of  $k$  depends on the lattice constant this is a very important observation because, if you make a lattice where the atoms are far apart, then you will have different kinds of consequence to the case where you place atoms very near to each other, this is also quite easy to imagine. And the second thing which became clear that both

the eigenvalues and the wave vectors are quantized for a free electron, quantized that may they will have discrete values.

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**Energy bands in solids** (One-dimensional case)

➤ For the values of  $k$ , which are given by the conditions:

$$k = p \frac{\pi}{a} \quad \text{for: } p = \pm 1, \pm 2, \dots$$

*the Schrödinger equation has no unique solutions. For each of these  $k$  values there are two eigenvalues, separated by an **energy gap**.*

- The above condition is analogous to Bragg's law, applied to X-ray diffraction in crystals.
- The Kronig-Penney energy curve shows bands of allowed energy values separated by energy gaps i.e. regions of forbidden energy values.
- The eigenvalues and the  $k$  numbers are quantized.
- The broken curve is not continuous but consists of closely spaced points.

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And for the values of  $k$  which are given by the conditions  $k$  equal to  $P \pi$  by  $a$  where  $P$  can take values plus minus 1, plus minus 2 and so on so forth the Schrodinger equation has no unique solutions, it actually happens that for each case of  $k$  there are two Eigen values which become possible and now, that comes the concept of quantized, what is happening if I move from one value to the other, I jumped to the next value there is no continuity which is there when I go from one value to the other.

So, for each value of these  $k$  there are two Eigen values and because you are having a condition of quantized state these two values are separated by a energy gap and you will see that this gap actually is also called as energy band gap and above condition is analogous to Bragg's law, which is applied to X-ray diffraction in crystals and Kronig-Penney model was used to draw an energy curve which very clearly then shows the formation of energy gaps.

And the eigenvalues and  $k$  numbers are quantized are the fundamental concepts, which lead to the formation of these energy band gaps and this again be said in another way that the broken curve is not continuous, but consists of close v spaced points.

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**Energy bands in solids**

**E vs k relationship:**

- The  $k$  zones of allowed energies are called Brillouin zones.
- The widths of the energy bands increase with increasing energy.
- The stronger the electron is bound to the lattice ions, the narrower will be the widths of the energy bands.
- The band theory of solids is able to explain properties of solids where the Sommerfeld model fails.

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So, if you plot the E versus k curve, you will find that the k zones of the allowed energies form the Brillouin zone the width of these energy bands increase with increasing energy and the stronger the electron is bound to the lattice ions the narrower will be the widths of the energy bands and this band theory of solid is able to explain the properties of solid where this Sommerfeld model actually filled and the gap between the two energy bands is called as band gap that is energy band gap.

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**E vs k relationship**

For finite crystal of length  $L$ ,

$$\psi(x+L) = \psi(x)$$

$$U_k(x+L)e^{ik(x+L)} = U_k(x)e^{ikx}$$

$$e^{ikL} = 1 = e^{i2n\pi}$$

$$k = \frac{2n\pi}{L}$$

$$k = \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \dots, \pm \frac{N\pi}{L}$$

**Energy vs wave vector for one dimensional lattice**

**Major inferences:**

- The motion of electron in a periodic lattice is characterize by the bands of allowed energy separated by forbidden regions.
- The width of allowed energy band increases with the increasing energy.

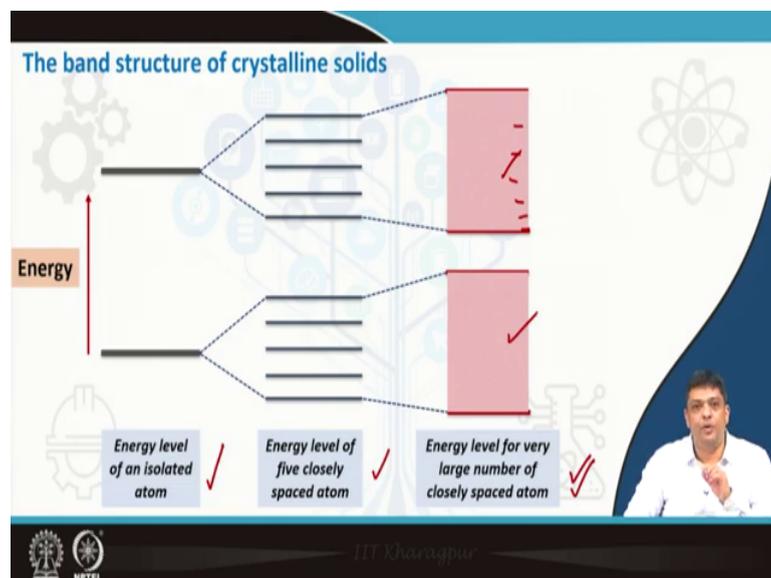
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And if you want to understand further you can refer to the various books which are there on solid state physics this is call the reduce zone scheme this is just the scheme which is derived from the original E versus k curve and this comes in and it tells, why is it called reduced zone scheme?

Because, if you plot the first Brillouin zone, you will find that the first Brillouin zone contains the complete information about the lattice. So, it is the reduced zone scheme because, if you have the information about the first Brillouin zone then everything about the lattice is known, why because you can shift the origin from one atom to the other and somebody can shift from let us say atom 3 to atom 5 or atom 5 to atom 7, because all atoms are identical and therefore, the first Brillouin zone carries all the information about the lattice and this is the kind of curve which you may have seen or encountered in many books and this is your band gap.

So, the major inferences which we have obtained till now are that the motion of electron in a periodic lattice is characterized by the bands of allowed energy separated by forbidden regions and the width of the allowed energy band increases with the increasing energy.

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So, let us see when we go from let us say 1 atom 2 atom 4 atom 10 atom 100 atom 1000s of atoms, how does this band structure actually change and we have been saying that energy

levels change and the separation between two consecutive energy levels change, schematically let me try to explain it further.

So, if you look into the energy level of an isolated atom, these are the two energy levels which are possible for this atom. Let us take energy level of 5 closely spaced atom then you see that the number of energy levels increase and if you take a large number of closely spaced atom, you will find that there are large number of energy levels which are present. But, please see that we are still actually showing that there is a gap between the two consecutive energy bands which are available.

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**Conductor, semiconductor and insulator**

**If we analyze the materials, we see every solid contains electrons.**

According to the nature of band occupation by electrons, all solids can be broadly classified into two groups viz.;

- 1) The ones which have completely filled valance band overlapping with partially filled conduction band (Metals) and
- 2) The ones which have empty conduction band lying over completely filled valance band

Depending on the width of forbidden band, the second group can be divided into:

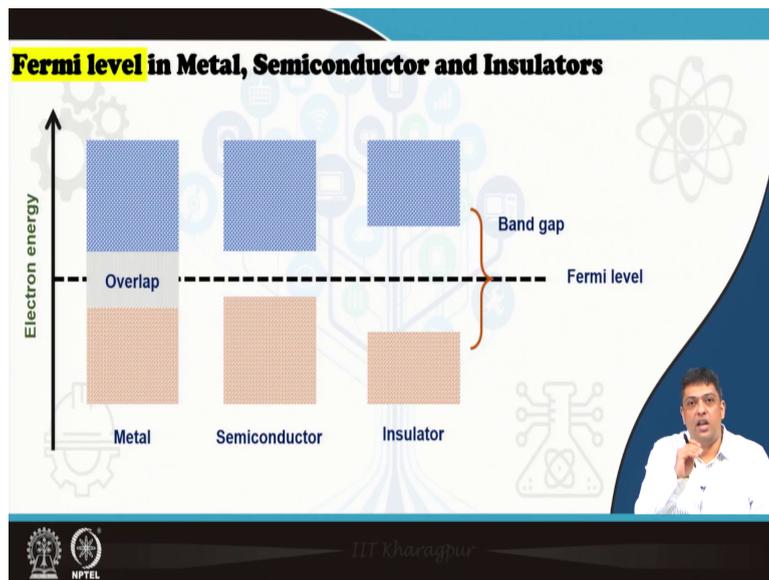
Insulator (band gap  $E_g > 3 \text{ eV}$ )      Semiconductor (band gap  $0.1 < E_g \leq 3 \text{ eV}$ )

The diagram illustrates the energy band structure for three types of materials: Metal, Insulator, and Semiconductor. In the Metal diagram, the valence band (VB) and conduction band (CB) overlap, allowing electrons to move between them. In the Insulator diagram, there is a large band gap ( $E_g$ ) between a completely filled valence band and an empty conduction band. In the Semiconductor diagram, there is a smaller band gap ( $E_g$ ) between a completely filled valence band and an empty conduction band. The slide also includes the NPTEL logo and the name 'IIT Kharagpur' at the bottom.

And now, let me put this slide back once again and can you now explain the concepts of metal, insulator and semiconductor easily to every anybody, I hope you are able to do it now, so metals are the ones where they have the overlapping valence band and conduction, so for electrons from valence band can go to conduction band and then they can take part in the conduction mechanism.

Insulators are the one which have the largest band gap amongst metal semiconductors and conductors and semiconductors are the one which have band gap but the values are much less than that observed in insulators. So, I hope it is clear what is the difference between metal insulator and semiconductor in terms of band gap and what is the origin of band gap.

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The next concept which one tries to explain is the Fermi level in metal semiconductor or insulator Fermi level the highest level up to which the electrons are completely filling the energy levels, so in metals, because there is an overlap region the Fermi level can be in any of these points in semiconductors if you call it intrinsic semiconductors the Fermi level is in the centre of the gap and in insulators also the band gap is much larger and the Fermi level again lies somewhere in this energy band gap.

So, you can explain the concept of Fermi level in metals semiconductors and insulators also, we will explain further in following lectures when we start making the devices and the importance of understanding this Fermi level and how it shifts when we make a P or an n-type semiconductor or a pn-type semiconductor junction.

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**CONCLUSION**

- *The origin of energy band gap in solids was explained.*
- *Based on the value of energy band gap, the materials can be classified as metals, semiconductors and insulators.*

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So, in today's lecture, I have tried to give you a brief overview about the origin of energy band gap in solid and then, we have tried to give the explanation as to why materials can be classified as metals semiconductors or insulators based on energy band gap. If you want to develop more understanding about each of these models, which were described in today's lecture, please refer to many of the basic books on Solid State Physics.

(Refer Slide Time: 36:59)

**REFERENCES**

- "Photoelectrochemical Solar Cells" by Suresh Chandra (Gordon and Breach Publishers, 1985).
- Physics of semiconductors devices (2<sup>nd</sup> Edition) by S.M. Sze (Wiley)
- "Physics of Energy Sources" by George C. King
- "Advance Renewable Energy Systems" by S. C. Bhatia

For today's lecture, the main references which I have followed are the books by professor Suresh Chandra by S.M. Sze George C. King and by S.C. Bhatia, and the name of the books

are also given. I thank you very much for attending today's lecture and in next lecture, we will try to develop further understanding about semiconductors and then how that understanding on semiconductors can be used to fabricate photovoltaic devices. Thank you very much.