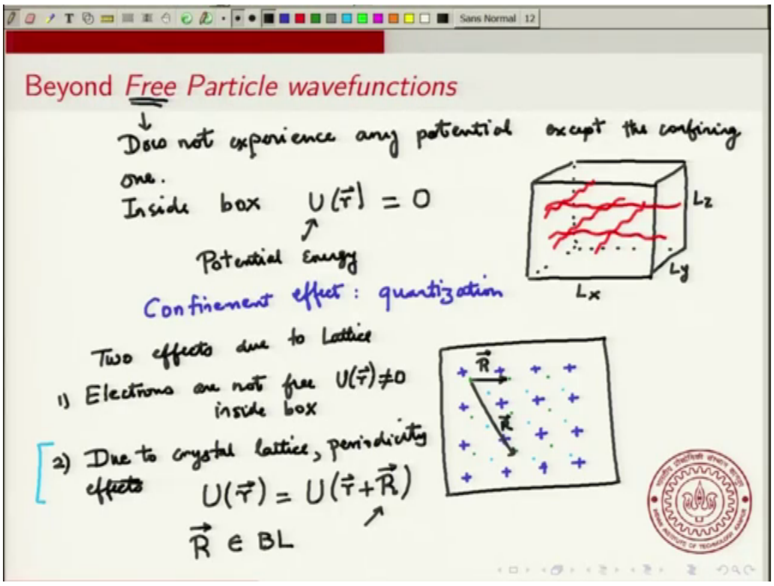
Solid State Chemistry
Prof. Madhav Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 52
Bloch Theorem

Now, I will go to the second lecture of this 11th week. And in this lecture we will be doing the most important idea in electronic structure of solids that is that of Bloch Theorem.

(Refer Slide Time: 00:38)



Beyond Free Particle wavefunctions

Does not experience any potential except the confining one.

Inside box $U(\vec{r}) = 0$

Potential Energy

Confinement effect : quantization

Two effects due to Lattice

1) Electrons are not free inside box $U(\vec{r}) \neq 0$

2) Due to crystal lattice, periodicity effects

$$U(\vec{r}) = U(\vec{r}+\vec{R})$$

$$\vec{R} \in BL$$

So, week 11 lecture 2 we will be talking about Bloch Theorem. To give you a perspective we have been discussing about free particle wave function ok. And one of the things we will do when we are dealing, when we are doing the Bloch theorem is to go beyond free particle wave functions. Now what do I what did we mean by free particles free in what sense?

So, it is free in the sense that it does not experience any potential, except the confining one. So, that is what we meant by free particles. So, in the sense so what we mean is that these electrons or these electrons were treated as free particles; that means, if this is my crystal ok, then the electrons are treated as particles that are just freely moving within this box ok. So, they were treated as so the free electrons they are just treated as particles that are moving within this box.

So, it is in that sense that they are free and they do not see any potential, they do not interact inside the box the potential of interaction is 0; so inside box U of r which is the potential energy function equal to 0. So that means, inside the box the particle does not feel anything and it is a free particle inside the box, but there is still confinement is there. So, the confinement effect is quantization of energy level ok. So, the energy levels are quantized, because the particle is confined to be within this box ok.

So, the particle is confined to be within this box. But so that makes the energy levels quantized ok, but inside the box it does not have any potential of interaction and this is like a particle in a three-dimensional box ok. So now what we want to do is we want to go beyond these free particle wave functions ok. What is it that we want to say? What we want to say is something like this. I will just show this using a two dimensional picture. What we want to say is that inside this box there are lots of atoms ok, and I will show them as positive charged species because we took out the valence electrons.

So, what is left behind is some is ions and they form some lattice and let me just draw a lattice for example, and so what you would like to take into account is that because of this lattice there are two things that will happen. The first thing is that the electrons are not free anymore electrons are not like free particles. So, what you had here electrons are moving freely now they do not move freely ok.

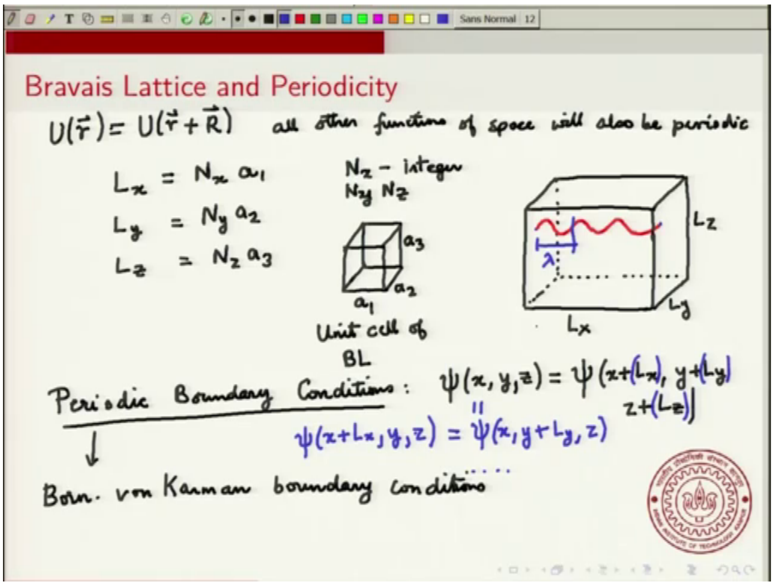
So, the two effects due to lattice first one is that electrons are not free anymore; that means, they it is the potential is not 0. So, that is U of r is not equal to 0 inside box ok; that means, that means at various positions the electron will feel some potential. The second probably more profound effect that is there is that this is due to the due to crystal lattice ok; there is a periodicity ok. So, there are periodicity is imposed effects and this is probably the more profound one which we will be discussing in lot of detail ok.

So, what it means is that U of r is equal to U of r plus some lattice translation vector ah. So, r belongs to Bravais lattice ok; that means, what we mean is that the potential experienced by the electrons ok. So, whatever it experiences here, will be the same here, it will be the same here, it will be the same here, it will be the same here, same here and so on. Similarly whatever it experiences in let us say this point will be the same as what is experienced here, it will be the same as what is the experience here this is just due to the periodicity of the Bravais lattice ok.

So, what it means is that your potential is a periodic function with a period of the Bravais lattice and in general this is a three dimensional lattice and so it should be true in all dimensions all three dimensions. So, in general if you take a point and you look at this point and this point they are related by a lattice translation vector they are related by a lattice translation vector. So, if two points are related by a lattice translation vector, similarly if you take this green point and you take this a green point all the way here ok, these two are also related through some lattice translation vectors ok.

So, there is a lattice translation vector for that connects each green point to every other green point. And so you immediately conclude that the potential energy is a periodic function, where with the periodicity of the Bravais lattice. So, these are the two effects and today first I will be talking about just this effect. So, this is the main, this is the effect that we will be talking about, for most of today and then and then we will also be saying that of course, you will be saying that U of r is not equal to 0 ah, but the interesting results will come because of this periodic nature of the Bravais lattice ok. Now, notice we used a box now the size of the box size of the box was taken as L x L y and L z ok; and we will see how this size also imposes a periodicity ok.

(Refer Slide Time: 08:42)



Bravais Lattice and Periodicity

$U(\vec{r}) = U(\vec{r}+\vec{R})$ all other functions of space will also be periodic

$L_x = N_x a_1$

$L_y = N_y a_2$

$L_z = N_z a_3$

N_x - integer

N_y N_z

Periodic Boundary Conditions : $\psi(x,y,z) = \psi(x+(L_x), y+(L_y), z+(L_z))$

$\psi(x+L_x,y,z) = \psi(x,y+L_y,z)$ ⋯

↓

Born. von Karman boundary conditions

So, let us now go to the next point ok. So, the Bravais lattice introduces a periodicity and what we said is that, U of r is equal to U of r plus R that is the potential energy you expect. In fact, you expect all functions other functions, of space will be periodic will also be periodic. So, if you have a scalar function of phase of space then it should be periodic. So, this is what you expect. Now I also mentioned that there is a periodicity that comes from the overall size of the cell and let us look at this.

So, we have this overall box and again this is L x L y L z ok. Now we in the in the free particle solutions; in the free particle solutions ok; we imposed a condition that the wave function should be same at the two boundaries that the wave function should vanish at the boundaries and that is how you got the free particle solutions ok. Now, what we will do is we will this we can take this lattice parameter L x and L y and L z as integer multiples of the unit of translation ok. So, this is the unit of translation of the Bravais lattice and this can be I will call it a 1, a 2, a 3 ok.

So, what we are saying is that the L x is taken as an integer multiple. So, N x is an integer and this, a 1, a 2, a 3 are basically the lattice translation vectors of your Bravais lattice. So, the magnitude of each of the lattice translation vector magnitude of this is a 1, this is a 2, a 3 this is a unit cell of corresponding to the Bravais lattice ok. So, what we are saying is that we are going to take this length ok.

So, this length is typically many times the length of the crystal is many times that of the unit cell ok. And what we will do is for simplicity we will take this length as an integer multiple of this lattice parameter. So N x, N y, N z are all integers ok. Now what that implies? So that, implies if you look at this quantity I will write this quantity right now and then we will worry about it a little later ok. Now another restriction that is put is that your functions are chosen to be periodic with L z ok.

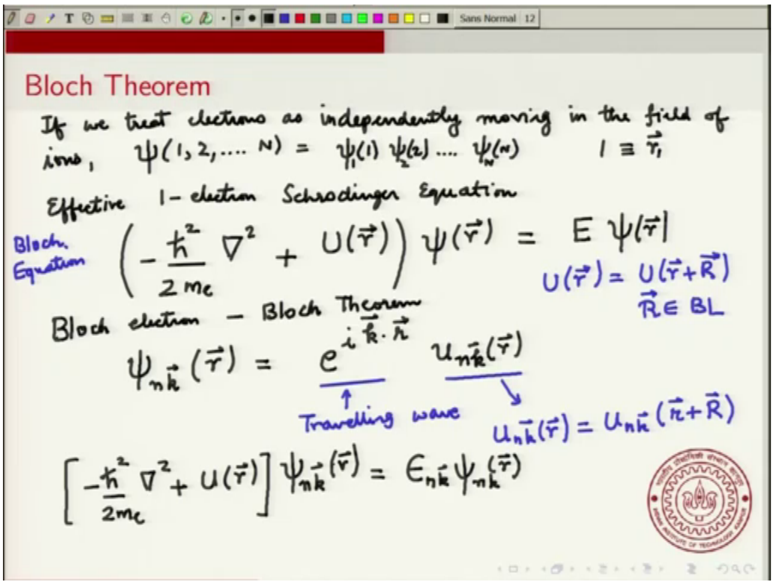
So, there is a different periodicity, so periodic boundary conditions on the entire system ok; that means, any function for example, the wave function of x y z is equal to psi of x plus L x y z y if you want you can take y plus, L y and z plus L z it is you can do one or two you can take any in all directions in all the directions there is periodicity ok. So, let me put these in brackets.

So, you might just take x plus L x or you might just take y plus L y or you might just take z plus l is L z and keep the others the same. So, in other words in other words so what I want to say psi of x plus, this is same as psi of x plus L x y z and this is same as psi of x y plus L y z and so on and you can make two of them different ok.

So, basically you are saying that all functions are periodic with this overall system size ok. This is a tool this is also referred to this is a general tool that is used general principle that is used; this is also referred to as the Born-von Karman boundary conditions ok. Now what this imposes? What this imposes is that we will we will see what this imposes it says that if your if your wave function has to be a periodic function; that means, whatever value of the wave function is here it should be the same value here ok. Now, if that has to be true then your wave function whatever it does in between it should come back to here, ok. And there is a typical function that is periodic with this is either a sin or a cosine function.

So, suppose you have a sin or a cosine function then it could be periodic this is not periodic; so it could be periodic it could be periodic ok. Provided the provided the wavelength of this sine wave is wave length multiplied by an integer and gives you the overall length of the system ok. This is what we will see; we will see how this Born von Karman boundary conditions effects the choice of wave functions ok.

(Refer Slide Time: 16:17)



Bloch Theorem

If we treat electrons as independently moving in the field of ions, $\psi(1, 2, \dots N) = \psi_1(1)\, \psi_2(2) \dots \psi_N(N)$ $\quad 1 \equiv \vec{r}_1$

Effective 1-electron Schrodinger Equation

Bloch Equation $$\left(-\frac{\hbar^2}{2m_e}\nabla^2 + U(\vec{r})\right)\psi(\vec{r}) = E\,\psi(\vec{r})$$

$U(\vec{r}) = U(\vec{r}+\vec{R})$
$\vec{R} \in BL$

Bloch electron – Bloch Theorem

$$\psi_{n\vec{k}}(\vec{r}) = \underbrace{e^{i\vec{k}\cdot\vec{r}}}_{\text{Travelling wave}}\ \underline{u_{n\vec{k}}(\vec{r})}$$

$u_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r}+\vec{R})$

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + U(\vec{r})\right]\psi_{n\vec{k}}(\vec{r}) = \epsilon_{n\vec{k}}\,\psi_{n\vec{k}}(\vec{r})$$

Now, let us go to the Bloch theorem which is the central idea of this of this lecture. So, so here what we say is that, if we treat electrons as independently moving in the field of the ions ok. Then you can write the total wave function, which is a function of coordinates of all the electrons as a product of coordinates of each of the electrons.

So, you can write it as a, where 1 is supposed to represent a coordinate of first electron second electron and so on. So, 1 is equivalent to r 1, this is a wave function of I will write psi 1 of 1 psi 2 of 2 psi N of N and so on. So, what I am trying to get it is now we can write an effective one electron Schrodinger equation. So, if you just look at 1 electron, if you just look at any one of these electrons ok, then it satisfies an effective one electron Schrodinger equation that is written in the following way.

So, there is a kinetic energy of the electron that is minus h cross square by 2 m e ok, times the Laplacian square. So, the kinetic energy in three dimensions is given by this by this Laplacian or the square of the gradient, plus U of r; U of r is the potential that is felt by the electron U of r.

Now, there is only one coordinate, there is only one electron and you just have some wave function. Now let me so times psi of r this should be E times psi of r ok. This is a one electron wave function; this is a wave function for a single electron that is moving in this potential U ok. So, such an electron is called a Bloch electron and it is basically moving in this field of these ions. And now there is a theorem now we go to the Bloch theorem.

So, Bloch theorem says so this is let me remind you that that we have the condition the periodicity U of r is equal to U of r plus R I where R belongs to the Bravais lattice, R is some lattice translation vector ok. So, now you can see what we have here, what we have is kinetic energy term and a potential energy term and that potential energy is periodic with the periodicity of the Bravais lattice. So, if you have such a and this kinetic energy involves a second derivative.

So, if you have such an equation then there is a general theorem which is called the Bloch theorem in solid state physics; it says that your wave function ok. And let me I will write it explicitly in terms of indices n k, k is a vector of r is equal to e to the i k dot r u n k of r. So, I will tell you what I mean by this n and k, we will we will see that n is like the nth.

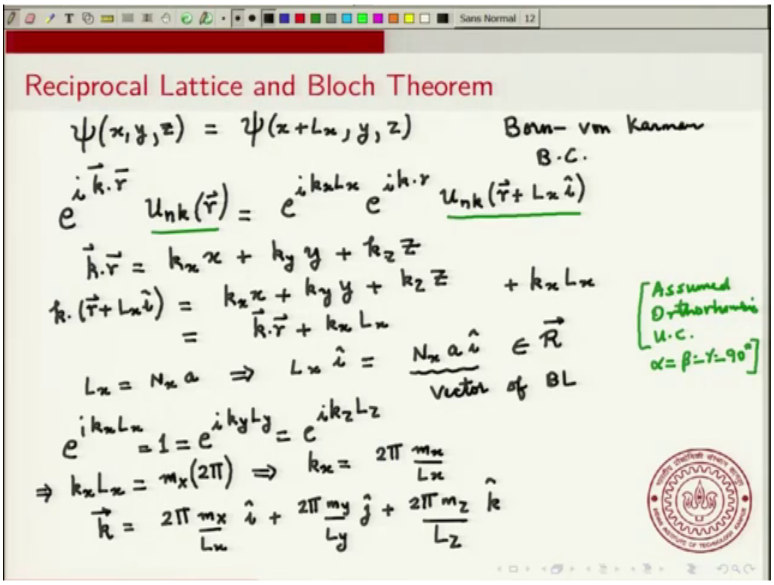
So, whenever you have a Schrodinger equation and you solve it you will get several solutions. So, you get not just one solution, but several solutions and n. And so this n index that is used to say which solution you are looking at ok. And now what we are saying is that you can write a general solution in terms of this k, in terms of this wave vector k ok.

So, the general solution can be written in terms of this wave vector as a product of two terms. The first term is just e to the ikr there is a travelling wave this is a travelling wave solution this part is a travelling wave. The second part is some function of r and there is a restriction that this should be periodic, should be equal to U nk of r plus R where R is capital R is any vector in the Bravais lattice ok. So, what it says that the wave functions for this Bloch electrons with the solution of this equation.

This equation is called the Bloch equation. So, Bloch equation is the effective one electron Schrodinger equation ok. So, this Bloch equation and the solution of it according to Bloch theorem can be written in this form can be written as some travelling wave times a periodic function and there are several solutions each indexed by this letter n ok.

So, if I just go back and write this equation again write the Bloch equation in a slightly more slightly more illustrative way. So, U now I can write psi n k of r is equal to epsilon n psi n k of epsilon n k ok. So, I am just writing the same Bloch equation in a slightly more explicit form with the indices and n k ok. And as I said k corresponds to this particular wave vector that is there in the solution, k corresponds to the wave vector that is there in the solution ok.

(Refer Slide Time: 24:36)



Reciprocal Lattice and Bloch Theorem

$$\psi(x,y,z) = \psi(x+L_x, y, z)$$

Born- von Karman B.C.

$$e^{i\vec{k}\cdot\vec{r}}\,\underline{u_{nk}(\vec{r})} = e^{ik_xL_x}\,e^{ik\cdot r}\,\underline{u_{nk}(\vec{r}+L_x\hat{i})}$$

$$\vec{k}\cdot\vec{r} = k_x x + k_y y + k_z z$$

$$\vec{k}\cdot(\vec{r}+L_x\hat{i}) = k_x x + k_y y + k_z z \quad + k_x L_x$$

$$= \vec{k}\cdot\vec{r} + k_x L_x$$

$$L_x = N_x a \Rightarrow L_x\hat{i} = \underbrace{N_x a\hat{i}}_{\text{vector of BL}} \in \vec{R}$$

[Assumed Orthorhombic U.C. $\alpha=\beta=\gamma=90^\circ$]

$$e^{ik_xL_x} = 1 = e^{ik_yL_y} = e^{ik_zL_z}$$

$$\Rightarrow k_xL_x = m_x(2\pi) \Rightarrow k_x = 2\pi\frac{m_x}{L_x}$$

$$\vec{k} = 2\pi\frac{m_x}{L_x}\hat{i} + 2\pi\frac{m_y}{L_y}\hat{j} + \frac{2\pi m_z}{L_z}\hat{k}$$

Now, what does this imply for the, what does this imply for the first we will see what it implies for the for the Born von Karman boundary condition. So, we can write so we are going to use a periodic boundary condition, so that says that psi of x, y, z should be equal to psi of x plus L x, y, z ok. So, this is the one the Born von Karman boundary condition, von Karman boundary condition ok. And what this allows us to write, what this allows us to write?

Now, if you go back and substitute the form of psi; so if you substitute this form of psi, so what you will get is that you will have a term that looks like e to the i k dot r ok. Now and you will have U nk of r ok, this should be equal to, now if I change if I change x to x plus L x ok; then k dot r will look like the following. So, if I use k dot r equal to k x x plus k y, y, plus k z, z; then you will have k dot r plus L x i that is like, changing x to x plus l x. So, this is equal to k x now instead of x I have x plus L x ok.

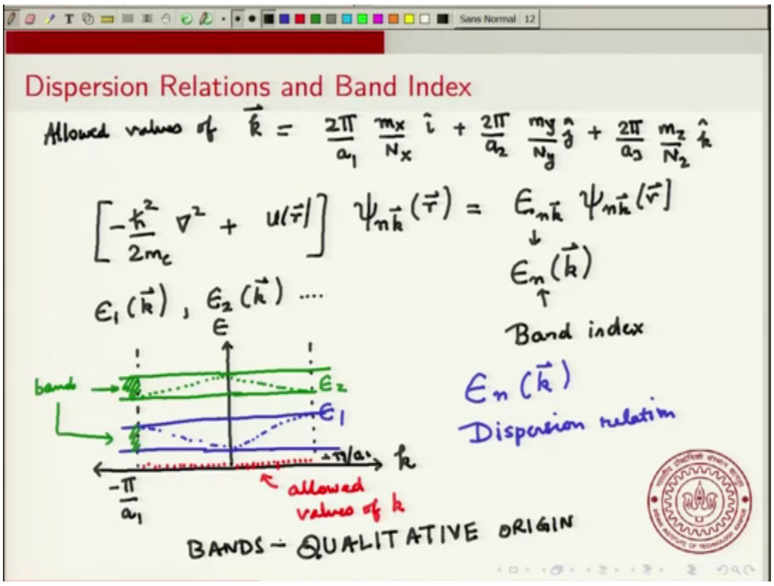
So, I will write the x term and I will write the plus kx L x the y and the z term will remain as they are ok. So, this is equal to so now the first part is just k dot r plus kx L x. So, now what I will write this as so e to the ik dot so on, the right hand side I will have e to the i k dot I will write k x L x multiplied by e to the I k dot r ok. And I have U nk of r plus L x i. Now remember we chose our L x to be N x a ok, this implies that L x times i is equal to N x times a i ok.

And so it is just a times i multiplied by N x, so this is a this is a vector of the Bravais lattice ok. So, this is a vector of the Bravais lattice. In other words since we said that, the L x is N x times a is just an integer multiple of a. So, a translation by L x; a translation by L x is also a translation in the Bravais lattice ok. So, what that will imply? That will imply that U nk and that will imply that these two terms are equal ok. So, according to the Bloch theorem these two terms are equal ok.

So, then we get a condition so this gives you a condition that e to the i kx L x equal to 1; and similarly we can also get conditions for ky L y and kz L z. And so if e to the i times something as 1 ok. So, this implies that k x times L x should be an integer multiple I will call this m 1 or m x is an integer multiple of 2 pi ok. So, it should be two pi times an integer then you have exponential of i kx L x equal to 1 ok; and this implies that k x should be equal to equal to 2 pi m x by L x and what this implies is that the k all the ks should be.

So, in general you can write your k vector as L z k ok. Now, notice that I have assumed I will show you I should mentioned this clearly that I have assumed, orthorhombic unit cell ok. So, in other words alpha equal to beta equal to gamma equal to 90 degrees ok, this just makes the calculations easy I can talk in terms of unit vectors ijk so I have made this assumption ok. Now what it says is that your k has to satisfy this kind of relation. So, this is an important result and I can further I can further if I take if I replace L by n x a ok, then I can also write this in terms of m x by N x and so on ok. So, I will not bother doing that, but basically we can we can see that something like this should be true ok.

(Refer Slide Time: 32:27)



Dispersion Relations and Band Index

Allowed values of $\vec{k} = \frac{2\pi}{a_1}\frac{m_x}{N_x}\hat{i} + \frac{2\pi}{a_2}\frac{m_y}{N_y}\hat{j} + \frac{2\pi}{a_3}\frac{m_z}{N_z}\hat{k}$

$$\left[-\frac{\hbar^2}{2m_e}\nabla^2 + u(\vec{r})\right]\psi_{n\vec{k}}(\vec{r}) = \underset{\substack{\downarrow \\ \epsilon_n(\vec{k}) \\ \uparrow \\ \text{Band index}}}{\epsilon_{n\vec{k}}}\,\psi_{n\vec{k}}(\vec{r})$$

$\epsilon_1(\vec{k})$, $\epsilon_2(\vec{k})$ ....

$\epsilon_n(\vec{k})$

Dispersion relation

BANDS – QUALITATIVE ORIGIN

So, now let me go to the dispersion relations and the band index ok. Now what this says is that your wave vector, now usually you would expect L x to be quite large, in your N x to be a very large number. So, the crystal will is likely to be very big ok. So, your m x by N x will be a very very small fraction of a ok.

So, what you would expect is that your k; your allowed values of k ok, so the allowed values of k are basically I can write as 2 pi now if I will write it as m x by N x 2 pi divided by a by b mx or a 1 a 2 a 3. So, these are the other values of k and these are fairly closely spaced because N x is m x can go from 0 to infinity N x is slightly to be a very large number ok. So, these are going to be quite fairly closely spaced ok. The next thing is that if you just look at your Bloch equation.

So you have, let us say I have psi n k of r is equal to now I will write this as E nk just make sure I use the same notation I use the epsilon. So, let me write this as epsilon n k epsilon n k is not a function of r times. So, now for each allowed value of k you have some energy ok. So, let me write this in a slightly different way, I will write this as epsilon n as a function of k ok.

So, for each allowed value of k you have some energy associated with it and you have various energy levels. So, n is called the band index ok. So, what I when you solve this if you could imagine solving such an equation then what you will get the solutions will look like epsilon 1 of k epsilon 2 of k and so on ok. And now suppose I plot, suppose I make a plot of epsilon versus k, suppose I make a plot of epsilon versus k, and I will just show it schematically.

So we will come to the boundaries little later will describe this, but if you just make a plot then you will get some energy. So, for each value of k you will have some energy for a different value you will have some energy. And if you join all these let me mention that let me mention that k can take several values. So, these are the allowed values of k and I am just showing as though you were in a one dimensional system, but you can do this in three dimensions two ok.

So, you have several values of k that are allowed ok. So, these are the allowed values of k ok, remember k has to be this of this form ok. So, it has to be 2 pi m x by N x a a 1 ok. So, it has to be integer multiple of 2 pi by L x, a a 1 times n x is L x. So, there are only certain values, but actually its a very very large number of values these values are very closely spaced. And for each of them you will have some energy, so if you look at epsilon 1 let me this is for epsilon 1 will have all these values ok.

So this is and epsilon 2, so this is epsilon 1 of k, if I look at epsilon 2 of k it might look something like this and so on ok. Now what this what you see from here is that epsilon 2 has a range of values ok, so this is a range of values of epsilon epsilon 2. So, epsilon 2 lies can be anywhere in this range of values ok; similarly epsilon 1 can be anywhere in this range of values ok.

So, there is a range of values of epsilon 1 and epsilon 2. We will come to this boundary condition we will come to this part in the next lecture what we mean by this ok. This is actually minus pi by a 1 and this is plus pi by a 1 ok. We will come to this; this is actually the first Brionne zone ok, but we will just show explicitly that you only need the wave function or the energy relation in this region ok. Now what you see is that this set of states are closely spaced and this is called a band, this is also this is also a band ok.

So, there so there is a band of energy. So, you say that this whole range of energies is what is called this band of energies ok. And this comes because your wave function as a function of k has this kind of behaviour ok. Now n is called the band index and the relation epsilon n of k this relation is called the dispersion relation ok. And this basically tells you how this epsilon changes with k, how this energy of the nth band changes with k that is called a dispersion relation ok. So we have qualitatively seen how bands appear in this case ok.

And so this is the qualitative origin of bands. So, we have seen the qualitative origin of bands ok. And in the next lecture we will see this more quantitatively; we will see this qualitative origin of bands ok, that just comes from this dispersion relation and we will see this more quantitatively in the next lecture ok. So, with this I will conclude this second lecture of week 11 ok. In the next lecture we will look at this in a little bit more detail and we will refine the band theory of solids.

Thank you.