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

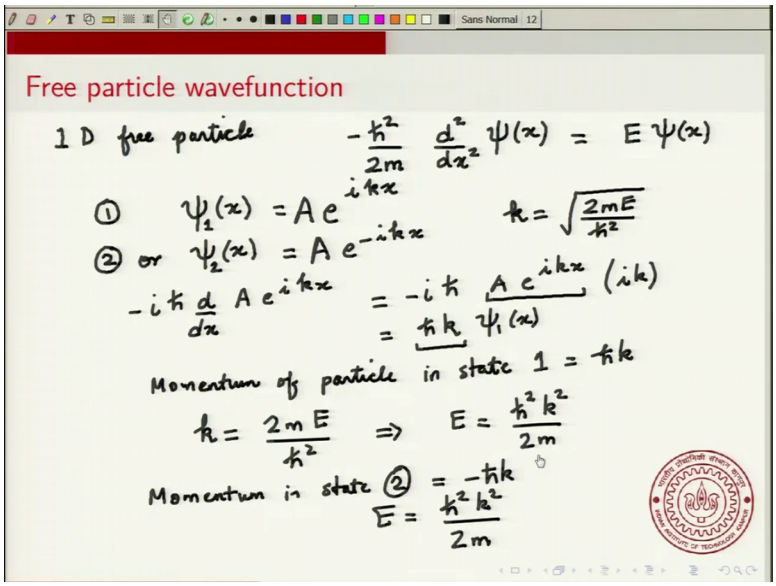
Lecture - 51
Free electron models

Now, I will start the 11th week of this course, and in the last 2 weeks of this course the 11th and 12th week, I will change topics and I will start talking about topic that is extremely relevant for solids and this is the theory of electronic structure of solids which is also known as the band theory of solids. So, I will try to give the basic picture of the band theory of solids and how it is used to describe the electronic structure of a crystal ok.

And so; obviously, this will involve some mathematics in particular it will involve quantum mechanics. But the level of quantum mechanics that will be required is quite low. So, you will require just basics of particle in a box and maybe free particle and a little bit of qualitative theory of bonding ok. So, that is about the level of quantum mechanics that I would expect you to know ok. So, if at any time during these lectures you feel that you do not understand the quantum mechanics then you should go back and read the basic quantum mechanics of these topics ok. And; obviously, these are going to be short lectures and they are going to be I am going to get at the crux of the band theory of solids.

So, I mean band theory of solids is a very detailed and a very vast topic ok, but I will just look at us at a few basic features of band theory of solids ok. So, we will start this in the first lecture with free electron models and this is the first step, this is a step actually prior to the construction of bands ok, but it is useful to learn this topic and it will also give you a refresher of your basic quantum mechanics ok. So, week 11 lecture 1 will be free electron models.

(Refer Slide Time: 02:23)



So, let us write the wave function of a free particle; free particle and I will start with 1 dimensional free particle ok. So, just to remind you if you have just one particle in 1 dimensions then you can write the Schrodinger equation for this particle as minus h cross square by 2 m d square by d x square and there is a wave function which is a function of x, x is the one-dimensional coordinate; this should be some energy times the wave function of x. So, this is the basic Schrodinger equation and you can see that up to constants, it is just saying that d square y by dx square is a constant times psi ok. The solution of this is what is called a travelling wave. So, psi of x if you solve this differential equation, you will get psi of x equal to e to the I will write it as i k x or psi of x equal to e to the and I should put a normalization constant. So, I will just say I will put a constant of proportionality before this A e to the minus i k x, where k is equal to square root of 2 m E by h cross square.

So, you should be able to verify this, you should be able to substitute this wave function in this differential equation and you should be able to see that it satisfies it and it is fairly easy to see ok. So, what do these two wave functions represent? To find out what the first let me call this the first wave function and this the second wave function ok. So, I will denote it by psi 1 and psi 2 ok.

So, now, if you take psi 1 of x and you calculate the momentum; so, how do you calculate the momentum? You operate by the momentum operator. So, if you calculate

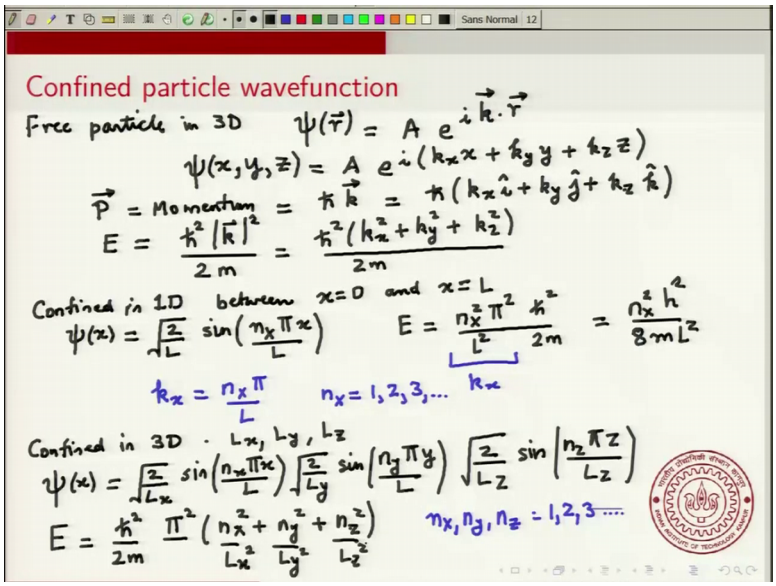
the momentum of the particle in state 1 ok. So, the momentum operator is minus i h cross d by dx and if I operate this on the wave function on A e to the i kx what I will get is. So, I have minus i h cross and then I have i k e to the ikx. So, I will let me write it out explicitly i h cross d by dx I do not want to write d by dx.

So, if I take the derivative I will get A e to the i kx multiplied by i k and i into minus i is i square is minus 1. So, minus i square is plus 1. So, you just get h cross k and what you are left with is the same wave function that started with which is psi 1 of x ok; that means, this h cross k is the eigenvalue of momentum. So, the momentum of particle in state 1 equal to h cross k ok; so basically k, the k that we use in the wave function is such that h cross k is the momentum, what about the energy?

The energy, so we have k is equal to 2 m E by h cross square implies E is equal to h cross square k square by 2 m ok. So, the energy of the particle is h cross square k square by 2 m and since it is a free particle there is no quantization, what we mean is that k can take any value and energy can take any value ok. Now in state 2, the momentum in of particle in state 2 will be minus h cross k minus h cross k the energy will be the same ok.

And so, this state 1 and state 2 are the state 1 represents a free particle with momentum h cross k. So, it is travelling in the forward in the positive x direction, state 2 represents a free particle with momentum minus h cross k. So, it is travelling in the negative x direction. So, this is a free particle wave function in one dimension, you can extend this to three dimensions and we have already seen this. I will come to that and before I talk about confined particle wave functions.

(Refer Slide Time: 08:23)



So, in 3 D, so the free particle in 3 D satisfy psi, now it is a function of x y z or r. So, r is basically x y z this is A e to the i k is a vector and r is a vector ok. If you want to write in more expanded form, you can write psi of x y z is equal to A times e to the i and you can write k x times x plus k y times y plus k z times z, where momentum ok.

So, the momentum is a vector. So, P is a vector momentum and that is equal to h cross k vector which can also be written as h cross k x i plus k yj plus kz k hat; ijk are the unit vectors in the x y z direction ok. The energy of this particle is just h cross square, now you have k vector square that is same as k dot k divided by 2 m. So, I can also write this as h cross square. So, k square is k dot k I can write it as kx square plus ky square plus kz square divided by 2 m ok.

So, this is a free particle wave function in 3 D and this is the energy and again the particle is moving with this momentum ok. So, now, momentum has components and again there is no restriction on kx ky and kz ok. So, now let us go to a confined particle.

So, confined particle; so, let us say the particle is confined particle in 1 D between x equal to 0 and x equal to L. You should have done this problem in your basic quantum mechanics; this is a particle in a box in a box from 0 to L; so, your; so the wave function psi of x. Now this wave function can be normalized and the normalization constant is root 2 by L sin and now there is quantization. So, there is n x pi x by L ok.

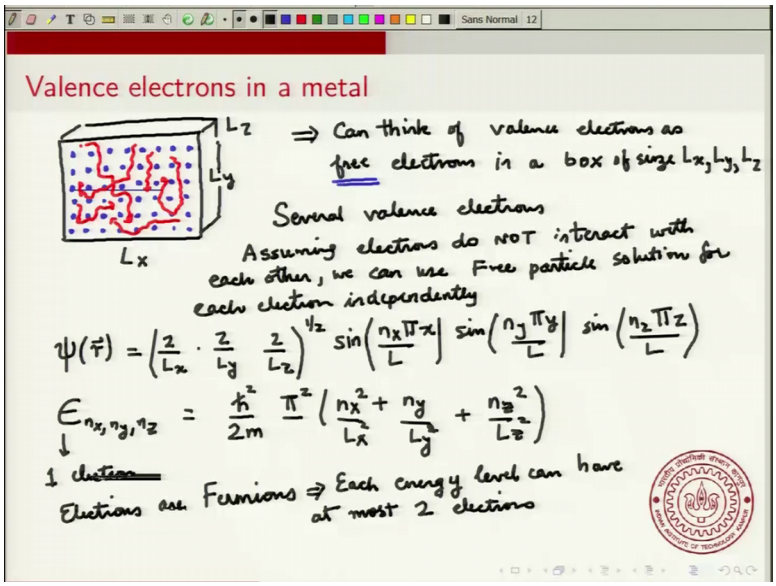
So, this has energy equal to n x square pi square h cross square by x square pi square by L square into h cross square by 2 m ok. I am deliberately writing it in this form, you might also see it in the form n x square h square by 8 mL square; you might also have seen it in that form. This is the, but it is equivalent I am writing it in this way just to emphasize that this is your k x ok. So, what it says is that your k x is quantized by L and n x equal to 1 2 3. So, k x can take only distinct values.

So, and since the k x can take only distinct values, the energy can also take on the distinct values ok. So, this is a confined particle in 1D, if you have a confined particle in 3D with between with box size being L x, L y and L z ok. So, a 3D box with sides L x, L y and L z will be represented by a wave function psi of x, that just looks like a product of the 3 wave functions.

So, root 2 by L x sin n x pi x by L times root 2 by L y sin n y pi y by L and root 2 by L z sin n z pi z by L z ok. So, that is a wave function and the energy is given by. So, I will write it by h cross square by 2 m and then you have pi square by L square times n x square plus n y square plus n z square and each of n x, n y, n z can be n x, n y n z; each of them can take values 1 2 3 etcetera ok.

And now all this is all this should be familiar to you and if you are not familiar as I said, you can go back to your basics of quantum mechanics and look at the particle in a one dimensional box and particle in a three dimensional box. So, these are exactly these functions.

(Refer Slide Time: 15:21)



So, now let us; so, what is the basic idea of band theory of solids ok? This the idea here is to describe the valence electrons in a metal and the general physical picture that we have is the following that if I take a piece of metal; if I take a piece of metal this is a crystal of the metal and there are several atoms. So, let us say there are several atoms ordered in some array.

So, I am just showing some schematic picture, where there are several atoms in each atom I am showing in blue ok. Now the basic idea here is that in a metal in a typical metal each of these atoms some of the valence electrons of the metal will actually leave the parent atom and it will freely move in the crystal.

So, I am just showing these valence electrons. So, let us say there is a valence electron on the first atom on this blue atom. So, it actually leaves the atom and it goes it moves freely around in the crystal. So, it moves around in the crystal and this will be true of all the valence electrons in all the atoms and so you will have all these valence electrons that are just roaming around and they come from different atoms and so, the idea is that these valence electrons are not tied to any anyone atom and they are going to freely go around in the metal, and this is what gives the metal lots of its properties like conductivity etcetera ok.

So, the valence electrons of the metal they roam around throughout the solid and if you take this piece of metal as having dimensions L x, L y and let me now just briefly show

the third dimension its L z L z then the basic idea is you can think of can think of valence electrons as free electrons and I am using the term free in a slightly different context here. So, here the context free means it is not interacting with anything ok.

So, they can move around freely, free electrons in a box in a 3D box ok. In the 3D box has dimensions L x, L y and L z ok. So, you can think of valence electrons in a metal in this way and this is what gives you what is called the free electron model and what it will say is that your wave function for the valence electrons will have this free electron form. Now, so, psi of so now, the idea is that there are lot of valence electrons in the crystal ok.

So, several valence electrons; so and if we assume that the electrons do not interact with each other, so assume assuming electrons do not interact with each other then we can use a free particle solution ok. So, the free particle solution let me write here. So, we can use free particle solution for each electron each electron independently ok.

So, this is the idea of this is one of the ideas of the free electron model and. So, what happens here? So, if you use this then for each electron I can write a wave function just that just depends on the coordinates of the electron and that will look like that will look like the following form. So, it will look like 2 by L x 2 by L y 2 by L z I am just taking all these at the beginning and you will have sin n x pi x by L sin n y pi y by L, exactly the expression that we had before sin n z pi z by L.

So, this is what the wave function will look like and the energy of the electron I will denote it by energy this is by epsilon, this is energy of the electron when it is in state n x, n y, n j; I am using that term, I am using the notation epsilon because this is 1 electron and there are several electrons in the system.

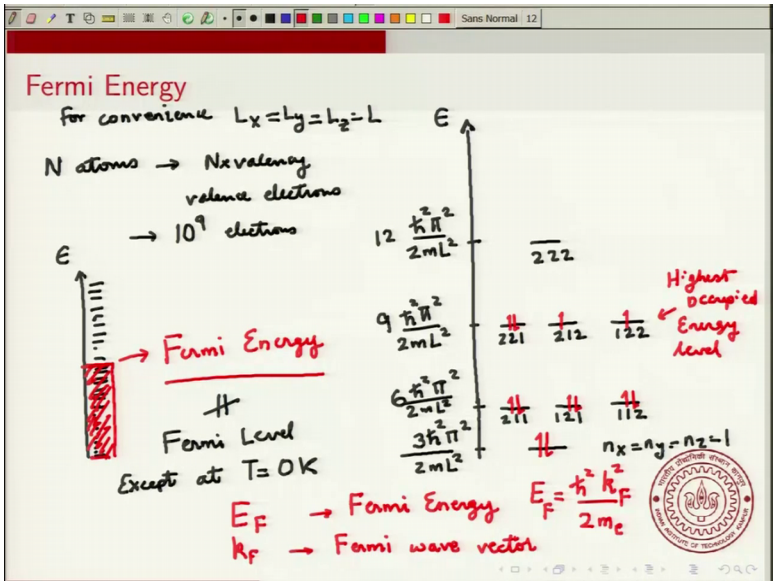
So, for 1 electron this energy will look like h cross square by 2 m and then k square will look like will look like pi square by L square times n x square plus n y; that is not correct ok.

So, pi square n x square by L x square n y square by L y square plus n z square by L z square and I think I have to make this correction in the previous slide also. So, I will just go back and make this correction in the previous slide. So, this should be n x square by L x square plus n y square by L y square plus n z square by L z square sorry about that. So,

this is going to be the energy per electron. Now what there is something else about electrons, ok.

So, electrons are fermions; so, are fermions and fermions satisfy the Fermi-Dirac statistics, but basically, so, each energy level can have at the most 2 electrons ok. So, this is one important restriction and this will turn out to be turn out to be important when we actually analyze the free electron model ok. So, the picture is that you have such energy levels for each of the electrons and each like each level can have at the most 2 electrons.

(Refer Slide Time: 24:07)



So, what happens here? So, if you look at the energy level ok. So, I will just plot it here. So, I will put energy on this axis epsilon and x, I will just call it epsilon this is the energy. Now the lowest possible value is when n x equal to n y equal to n z equal to 1 ok, and in this case you have and let me take for convenience take L x equal to L y equal to L z equal to L ok.

So, I will just take this for convenience just for this particular case and so, when n x equal to n y equal to n z equal to 1 then the energy will be equal to 3 h cross square by 3 h cross square pi square by 2 m L square ok. So, that is the energy. Now the next possible value of energy is when one of n x n y and n z is 2 and now you can have 3 different possibilities; I will just write them as 2 1 1.

So, n x is 2, n y is 1, n z is 1 or you can have 1 2 1 or you can have 1 1 2. And now the energy is equal to 6 times h cross square pi square by 2 m L square ok. Then similarly you can take the next level which will be 2 2 1, 2 1 2 and 1 2 2. So, I can write this as 2 2 1, 2 1 2, 1 2 2 and now the energy is equal to 9 h cross square pi square by 2 mL square ok. Notice that there are 3 states that have equal value of energy for this ok. So, this state is triply degenerate. The next one I will just show one more ok.

So, this is 2 2 2 and the energy is 12 h cross square pi square by 2 m L square ok. Now what I want to say is that each of the electrons will have such a distribution of energy; each of the electrons will have these energy levels ok. Now because these electrons are fermions in each level they can be at the most 2 electrons ok. And so, if you take all the valence electrons of the metal, then you keep filling them; you keep filling them, you keep filling till you have till you exhaust all the valence electrons. And you keep filling till how many? Let us say let us say you had a case where you had where you had 12 valence electrons ok.

So, if there are only 12 valence electrons this will be the configuration of the or this will be the electronic configuration. So, the 12 electrons will be in these 12 states and what you notice is that this is the highest occupied energy level.

Now, you can I am I mean here I took a case where you had only 12 electrons, but now you can extend this concept to saying that if you have a large number of electrons. So, if you have a if you have a piece of crystal which has N x which has N atoms then there will be a total of N times the valency; valence electrons. And if you have a piece of a crystal that is finite size, then this will be this could be a very large number ok.

So, N could be number of atoms could be billions of atoms ok. So, the number of; so, the total number of electrons that we are looking at is of the order of billions ok. So, 10 raised to 9 electrons and now so if you look at this diagram you have to keep extending this free electron picture all the way to 10 raised all the ways so that you can fill as many as 10 raised to 9 electrons. Well, if you go ahead and do that then what you will get is that you will have this energy and you will have several states and all you will have several states, you will have a very large number of states. And what you will find is that when you fill all the electrons then a certain number of them will be filled ok.

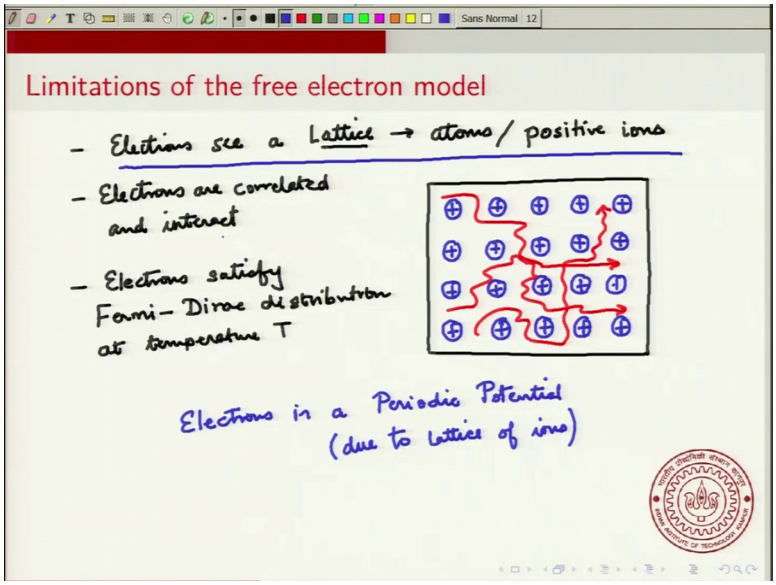
And the last energy level that is filled this is called the Fermi energy; this is called the Fermi energy. Now I will just I mean it is rather important to distinguish this from the, this is not equal to Fermi level, strictly this is not equal to except at T equal to 0.

So, except at T equal to 0 Kelvin and we will see this as we go along ok, but the point is that the Fermi energy is defined in terms of the energy levels and so, at T equal to 0 Kelvin, the this will be the at T equal to 0 Kelvin you will start filling the energy levels from the bottom and you will only fill the lowest energy levels. At higher temperatures you could have some higher levels also filled up and you could have some lower levels being empty, but at T equal to 0 you will only fill up starting from the lowest energy level and the energy level the highest energy level that is filled is called the Fermi energy and this is a concept that we will be using a lot.

It is denoted by the symbol E F this is the Fermi energy and we will see that for a free electron model since EF is related to the wave vector k, since for a free electron model you have EF; E is related to k. So, we have E is h cross square k square by 2 m, now we are talking about electron.

So, it will be mass of the electron ok then the Fermi energy has a wave vector corresponding to the Fermi energy that is called k F that is called the Fermi wave vector ok. So, these are two concepts that we will be using a lot and we will be considering the case where we do not have this free electron model ok.

(Refer Slide Time: 33:47)



So, now let me conclude this lecture by saying what are the limitations of the free electron model ok so, first thing is electrons see lattice ok. So, electrons are not just free they are actually they actually see a lattice ok. So, and so lattice has I would say, I mean atoms and since we removed the electrons, actually they are positive ions. Since we remove the valence electrons from these atoms, so, what will be left is actually positive ions and so what this picture of the metal will look like is the following.

So, if you look at valence electrons, now the valence electrons ok. So, even if the valence electrons were allowed to roam around in the crystal they would see a lattice of positive charges.

So, what the valence electrons? Even if they are allowed to go around in the within the crystal they will not just be able to freely move they will keep seeing the lattice ok. So, they will they are just not able; there they are not completely free as in they cannot just run from one end to the other, they will experience they will see this periodic lattice ok. And so that is the first thing.

The second thing second and third points are the second point is slightly more subtle is that, electrons are correlated and they interact; that means, since all the valence electrons are moving around this crystal they will see each other. So, one electron will see the other the other electron ok.

So, it is not just moving freely, it will encounter the other electrons. So, it will see the other electrons and it might and that might affect its motion and so this picture has to be modified to take electron interactions and electron ion interactions ok. So, these are some of the limitations. Now also you should keep in mind that electrons satisfy something called a Fermi Dirac statistical distribution; Dirac distribution at temperature T ok. So, what that means is that the distribution of electrons in different levels follows this Fermi Dirac distribution and we will see this in more detail ok.

Now, what we will do first is to take the effect of this periodic lattice ok. So, electrons should see a lattice. So, the electrons should experience some forces which are periodic ok. So, the next topic that we will be doing in the next lecture is to look at electrons in a periodic potential ok. This periodic potential is due to the lattice of ions, due to lattice of ions of ions ok. And at this point a couple of things I want to say I am not going to make

a distinction between lattice and crystal, I am just going to talk about lattices ok. So, you can think of them as a single atom basis ok.

So, I am just going to talk about lattices because that will be sufficient to give the basic concepts, the other thing is in this course. So, once we see electrons moving in the lattice we will automatically see the emergence of bands ok. So, I will not really be talking about correlated and interacting electrons ok. In the next lecture we will talk about how electrons move in a periodic potential, and we will see how, just even if you even if you have electrons that do not interact with each other, even if you have electrons that are freely moving throughout the crystal ok.

But so long as they experience this lattice of ions, you will see that they will naturally form bands ok. So, that will be in the next lecture.

Thank you.