Electronic Theory of Solids
Prof. Arghya Taraphder
Department of Physics
Indian Institute of Technology, Kharagpur

Lecture – 21
Graphene and Fermi Surfaces

We are discussing the situation where we have more than one atoms in a unit cell and how tight binding method works there.

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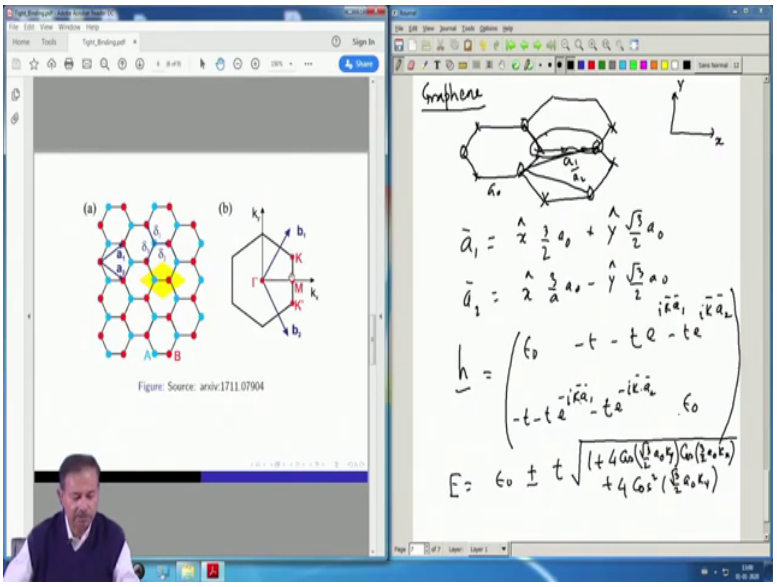

And we showed that the tight binding still works Bloch theorem still work, in all that you have to do is to replace your scalar elements. The scalar matrix elements which are the single elements by a matrix of the dimension of the number of unit number of atoms in the unit cell. For example in a 2 by 2 unit cell if each atom is contributing one orbital, then you have a 2 by 2 block matrix, that replaces your scalar for the one atom per unit cell case.

But the complications are not too much, it is the procedure is the same and instead of scalars you have to just to handle instead of just complex numbers you have to handle with 2 by 2 or n by n finite dimensional matrix that is all. So that means we can now take up the case of graphene for example and for graphene let me just draw the graphene unit cell, it is drawn already on your screen. So what I will do is that I let me just try to draw it again for my convenience and so on. I will have to draw one more ok.

So these two equivalent sites, so there is this circle here and cross here circle here and cross here circle here cross here circle cross cross circle and so on. And I choose my primitive vectors and these two I call them a 1 and a 2 ok. Remember these cross and the circle do not represent two different kinds of atoms in graphene, so they are both carbon but they are at equivalent sides.

So as we discussed the other day we have to choose unit cells which are kind of these are the unit cells; two Combination of two in the left hand side that the yellow region is the new unit cell. So that is what the red and blue are the two in equivalent carbon atoms and that is exactly what I am doing here.

So then I just do I have to just write down this a 1 and a 2 which I do, if these distance is a naught which is fixed distance for graphene. We can then write down a 1 along x direction root 3 by sorry 3 by 2 a naught plus in y direction root 3 by 2 a naught. And a 2 is again x 3 by 2 a naught minus y hat root 3 by 2 a naught. My x and y are these two axis x and y, x hat and y hat at the unit vectors along these two directions as conventionally we do. Then we have this Hamiltonian matrix here is very simple right, here remember that the hopping t 1 and t 2 are taken to be the same. So they are.

I remember this hopping t 1 was inter unit cell; so between the blue and the red and the t 2 is between two different units cells. But that distance is that is the same as this one right. So if you look at this blue to red in the same unit cell and the hopping is the same as that blue and this red in a different unit cell. So, that this one and this one sorry and this one belong in the same in the different unit cells, but the distances are the same and they are compared to the distance of the next the red one in the same unit cell. So the hoppings t 1 that we considered minus t 1 the values t 1 and t 2 they must be the same. So t 1 must be equal to t 2.

So for graphene life becomes simpler much simpler actually in this that the t 1 and t 2 are the same. So, that immediately tells us that gap will vanish in certain directions, so let us that gap can vanish in certain directions. So let us just look at this Hamiltonian matrix which is again as we did in the previous case is equal to epsilon naught. Epsilon naught then minus t 1 minus so let me just t 1 and t 2 distinction I do not make its, write as t minus t e to the power i K dot a 1 minus t e to the power i K dot a 2.

Similarly just the Hermitian conjugate of that; so minus t minus t e to the power of i K dot a 1 with minus sign minus t e to the power minus i K dot a 2 epsilon naught, this is the matrix. You can put minus ik here minus i K here and plus i K here, it just does not make anything different.

It is just your choice of how you took your directions and units cells and choose your beta beta transpose matrices. But all you have to do now is to diagonalize this matrix, this diagnolisation is already done in literature you will find it on. You can do it yourself it is straight forward. You will find that the energy has a fairly long form. t root over 1 plus 4 cos root 3 by 2 a naught K y into cosine 3 by 2 a naught K x plus 4 cosine square root 3 by 2 a naught K y.

So all on all these all the terms are under the root. So that is the energy and so what one now does is that one goes to these points in the Brillouin zone, so I leave it for you to check. It is all available everywhere but I would urge you to do it for yourself.

Go to this points K and K prime find their coordinates in the Brillouin first Brillouin zone and put those kx and K y values here and take it K point, it has a you can see that it has the kx and the ky and the K prime is basically kx and the same ky with the minus sign. So these two points you can check and you can actually check in every of these six points these are all equivalent points. There are three two three points which are like K three points which are equivalent to K prime. So at all these points you will find that this thing is this thing will give you a 0 and provided of course you choose your epsilon naught equal to 0 and.

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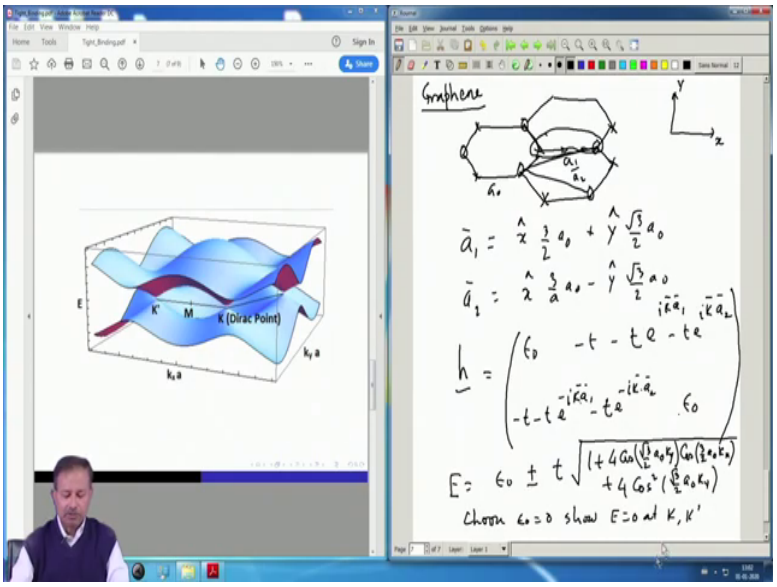

So this is a case this is what we have shown here, remember that these are this K and K prime points, where the spectrum is gapless at, you can also check it. At M point you will find that it has the largest gap in the spectrum, you can do it in a computer or you can do it by hand. The interesting thing to do is to expand this band structure around the point K and K prime, where this term in under the root vanishes.

So choose epsilon naught to be 0 and then show that E equal to 0 at K and K prime points in the Brillouin zone. So that is an exercise you can do and the other exercise which is bit more complicated, but you can still do it; is to make it Taylor expansion. For example about that point take any point K or any point or the point K prime make a Taylor expansion of this Hamiltonian.

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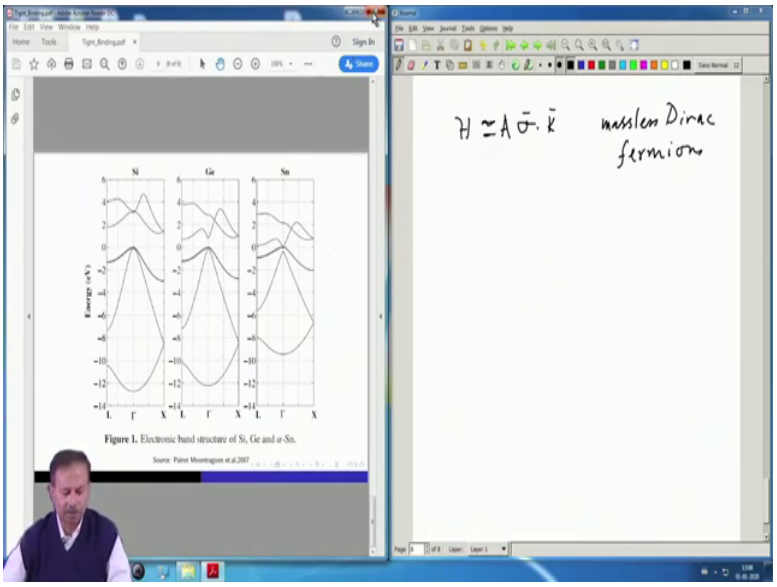

And interestingly what you will see is that the Hamiltonian has a form which is very similar to a Massless Dirac Fermion form of a Massless Dirac Fermion which is Hamiltonian will turn out to be sigma, will be some constant into sigma. Some constant sigma dot K, K is the momentum. So and this is the Massless Dirac form with a linear spectrum and sigma's are the Pauli matrices in two dimension.

So 2 by 2 Pauli matrices you can you know that what are these are these appear in our problems or spins and all that. So and that is the kind of matrix that the matrix Hamiltonian that you will get for this the system if you expand about K or K prime point, so these are like massless dirac fermions.

And that is a very important discovery in the sense that this was actually worked out in before 1950. So and it was after graphene came into being it was discovered by it was actually isolated by Geim and Novoselov and they the interest in graphene came back and people started working on it. And then of course they saw that there is a dirac spectrum at this point and that spectrum is extremely important.

So look at this spectrum as I just showed that these are 6 points where you have a, you have nodes, the two spectrum the anti-bonding and bonding bands touch each other. And by the way in graphene this one orbital that we are talking about comes from the pz orbital which is the pi orbital.

So in the carbon atom and so they are out of the plane along the z direction and their overlap gives rise to this band structure. So here is the band structure along three different directions the lower curve lower picture and you can see that at this point K there is a linear spectrum just like a V. So the two bands meet here like a V, but away as you go away from the point k, you can see there are deviations so that means the K, the linear in K spectrum works only close to the point K or K prime or their equivalent points in the Brillouin zone. So that is something one has to remember. So this is the band structure for other materials. For example I just wanted to show you that it is always plotted along certain symmetry directions in the Brillouin zone.

So this is for example some gamma X direction gamma L direction and so for silicon germanium and tin, it is the band structure is always plotted along certain symmetry directions and 0 is conventionally taken as the Fermi level. So that as we did this epsilon naught was set to 0, one choose one just sets the 0 of the scale to energy scale to at the Fermi level. So Fermi level is at 0 energy in most of these figures that is what you will find ok. So let me show you how actually these plots are done Fermi surfaces are plotted.

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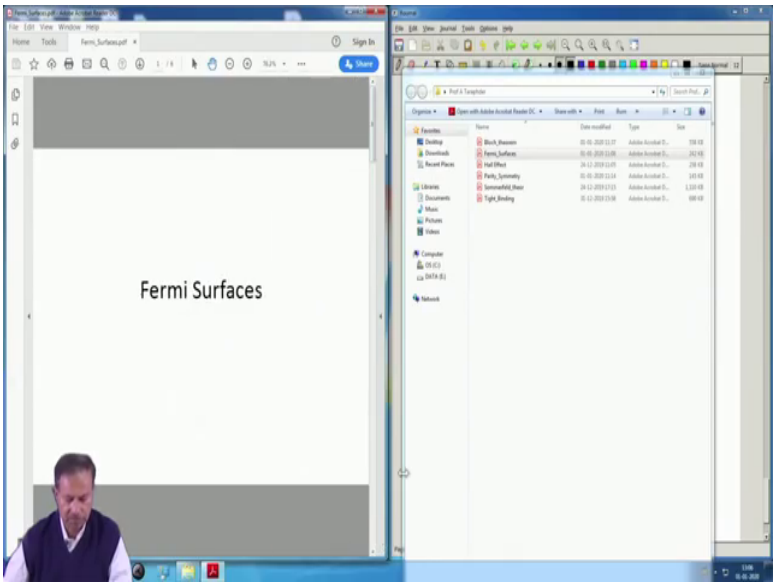

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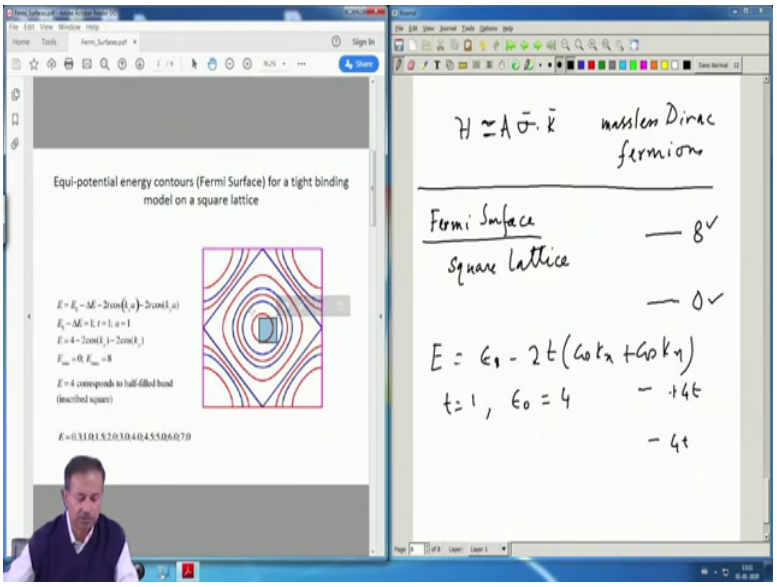

So let me show you a few examples of Fermi surfaces. For example this is something that we were discussing the other day. It is a 2 dimension square lattice, the tight burning models. So this is Fermi surface for example this is square lattice. Now this is the Brillouin zone.

So these points at the points at the extreme these points this is plus pi pi by A this is K y equal to pi by a and this is minus pi by a in K x. So this is pi by a 0 this is 0 pi by a this is minus pi by a 0, and this is 0 minus pi by a ok. So these are the 4 corners. Now let us look at this. This gives you the Brillouin zone. This equation for example is epsilon naught which is written as E naught here is so the it is taken to be 4 for example delta E is let us not bother about delta E. So E naught minus delta E is our epsilon naught, so that epsilon naught is taken to be 4 in this expression.

So epsilon naught is not set to 0, but it really does not matter at all. So we start or set of our energy starts from 4. So you can see that minimum of energy is this 2 cos k x and 2 cos k y will give you minus 4 that is the minimum possible, so 4 minus 4 will be 0 and maximum will be these cos kx and cos ky are both minus 1 and that will give you plus 4 so that will be 4 plus 4 equal to 8.

So the band goes here from 4 energy 4 in some units you can call it Ev or whatever, you do not need to mention the units at the moment. In some unit it is 4 and it goes up to 8. So that is the usual way theoreticians or even in an experimental paper will write the band the Fermi

surfaces. Because as I said this energy is are set to certain units certain values, t for example is set 1 here for you can see, a which is the lattice constant is set to 1. All these can be restored to get the real numbers for the proper correct lattice ok.

So this band basically goes from sorry it goes from 0 to 8. So this is 0, 0 is the minimum of this band and it goes all the way up to 8. Remember if you look at your expression remember E equal to epsilon naught minus twice t cos kx plus cos ky for a square lattice this is 2 dimensional square lattice. So this is the tight binding band. So t equal to 1, epsilon naught is chosen to be 4. So your bandwidth does a as we mentioned the other day has to be 8 t. So that is exact so here is for example it goes from minus 4 t to plus 4 t right, minus 4 t is minus 4 but there is a plus 4 here already epsilon naught is set to plus 4. So minus 4 plus 4 will give you 0 . So that is the band minimum here and the plus 4 t will take you all the way up to 8. 8 t is t becoming t being 1 is the bandwidth, so all the bands are within this.

Anyway so that is that we had done earlier, let us look at how to calculate how to do the Fermi surface. So these are Fermi surfaces for different values of E for example. See this E is basically controlled by the filling, so number of electrons you are putting in so that is called the chemical potential or the Fermi energy. And so for example for low filling you have a almost a circular Fermi surface. So that is the highest occupied level this is the circle is the highest occupied level. So that is for low filling this happens.

As we increase the filling your E goes up and you are going you are first of all you are going up towards the zone boundary which is this blue line and you are also becoming distorted from the circular shape. In three dimension, it is like a spherical at low densities you have a spherical Fermi surface and as you increase the Fermi surface becomes more distorted from its sphere.

So let us go on and at you can see at 4 E equal to 4 you hit this blue line. So this entire of Brillouin was the first Brillouin zone which is this entire region under this square given by this blue line is completely filled up. So that is where the bands the first Brillouin zone gets filled up that is the half filled situation.

So all the states here are filled up and so the Fermi surface is like a square. Now this kind of flat Fermi surfaces which is here is a Fermi surfaces is a line here 8 it is a rotated square and this blue square the blue line the perimeter of the square is your Fermi surface ok. Fermi

energy is 0 this energy here is 0 as you just put E equal to 4 and you can check that the energy here is 0.

So this is the half filled Fermi surface and the Fermi surface has flat regions which are lines here. In three dimension there will be like flat surfaces. Now when you have flat regions in the Fermi surface you can actually check for yourself the density of states becomes extremely large very large, because the density of states is actually proportional to the inverse of the gradient grad K of E. So the derivative of E with respect to K it is inverse comes inside an integral to calculate the density of states.

And that you see if you have a flat region the derivative goes to 0 and then you are really, so basically it means that if you change K your energy does not change. Your energy just remains at a particular value which is 0 here, E equal to 0 and nothing. So that means that there are large number of states at that energy, because you change your K slightly but your energy does not change that means there are lots of K states in that at that energy. And this kind of Fermi surfaces are prone to distortion, they do not survive much in real crystals. This is a topic of course physics of physics beyond this. But this is a fixed beyond single particle and in the sense that you need an interaction a scattering between these Fermi surfaces to make these Fermi surfaces unstable.

And in real systems this is always most of the times happen the system distorts either structurally or magnetic forms a magnetic order. So that this kind of Fermi surface it flat regions which can be brought onto one another. See if this Fermi this line can be translated can be brought to the opposite blue line by a by just translating with a vector which is the reciprocal lattice vector of this of the Brillouin zone.

So such cases the Fermi surface is very unstable, these are instabilities of Fermi surface that are commonly encountered. These singularities are often called Van Hove singularities they appear in many solid state; say properties of solid systems of crystalline systems. At some specific fillings densities where this similar the Fermi surface becomes this kind of flat becomes flat and one region can be brought to the other by translating with the vector in the Brillouin zone. Anyway so that is just to mention certain interesting things.

The other thing that I emphasized earlier was this form of this two electron band structure two electron per unit cell band structure. Now as you can see suppose I, suppose we started so let me draw it again.

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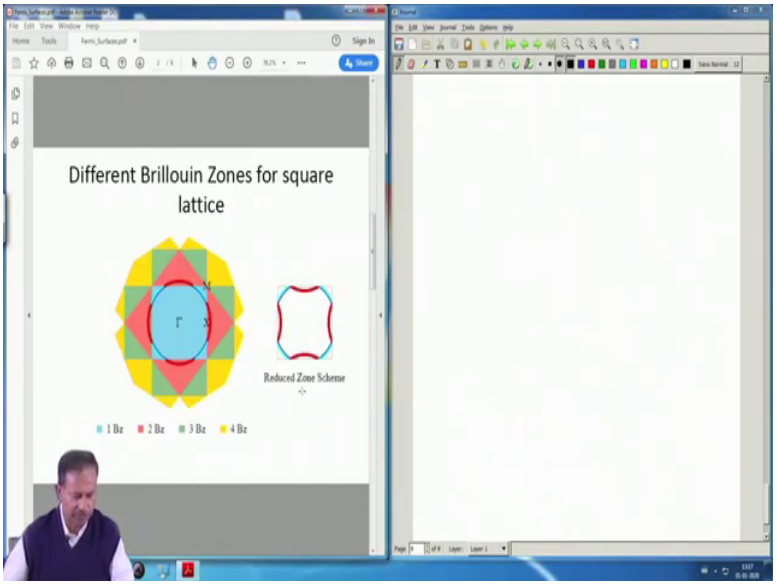

So let me just show you a bit more of this different Brillouin zones for square lattice. So this is a first blue one is the first Brillouin zone, the pink one is the second Brillouin zone, the greenish one is the third Brillouin zone, yellow is the fourth Brillouin zone and so on. And look at how the Fermi surface now look. It has gone beyond the first Brillouin zone, because your filling is such, your density is such that the Fermi surface has gone beyond the first Brillouin zone.

Now look at this red with this ring which is the Fermi surface. So now you have to bring it to the first Brillouin zone in the reduced zone scheme. So what you will do? You will just translate these red regions, it was from it was here on top, that red region has been translated here by a this translation of reciprocal lattice vector.

This red region at the bottom has gone up to here at the top and then and similarly this one on the left has gone to the right and the right one has gone to the left. So the right one has come here the left one has come here the red regions and that is how the prescription to draw a reduced Brillouin zone, draw the Fermi surface in a reduced Brillouin zone scheme works or you can draw any E versus K graph bring it to first Brillouin zone. So the Fermi surface

actually now looks like in the reducing zone scheme, this is how the Fermi surface looks like on the right hand side. Although in the extended zone scheme it has gone beyond the first Brillouin zone, entered the second Brillouin zone.

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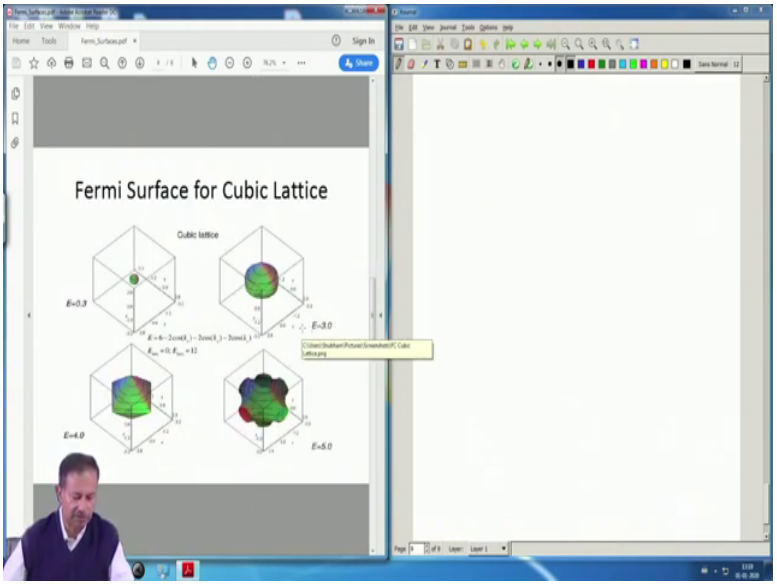

So these are other Fermi surfaces for cubic lattice at different fillings, here you can see that the Brillouin zone has crossed the first Brillouin zone. The Fermi surface has crossed the first Brillouin zone and become open it is called open Fermi surface in these regions, where it has crossed the first Brillouin zone.

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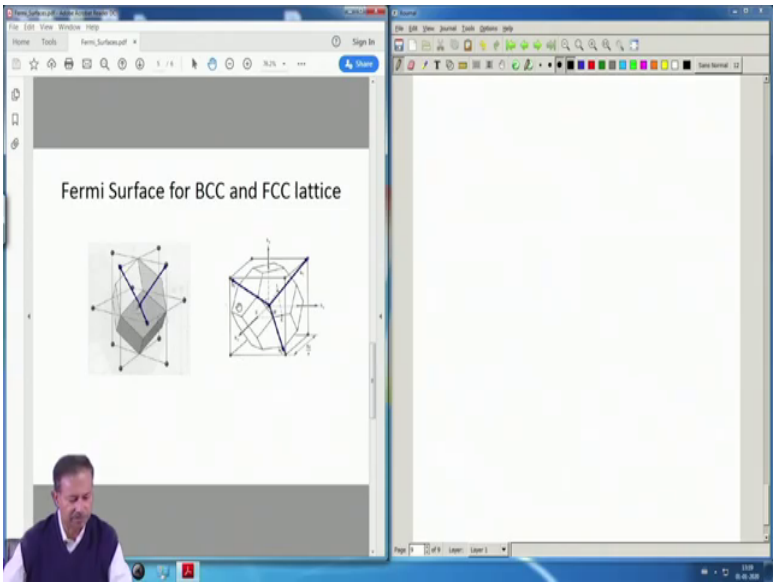

These are other Fermi surface BCC lattice FCC lattice these blue lines are the primitive vectors.

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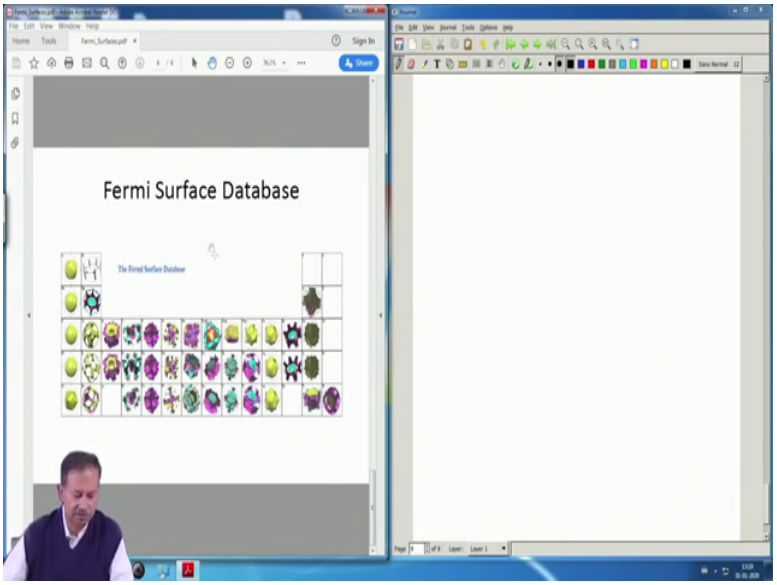

These are there are databases this is a databases for Fermi surface for different elements in the periodic table. You can look up if you like, they are very complicated looking simply because, they have been all translated into the first Brillouin zone. So they become sometimes they even become disjointed, so one part of the Fermi surface is completely separated from the other part of the Fermi surface. So that is possible and that happens and that has a that has consequences in solid state physics.

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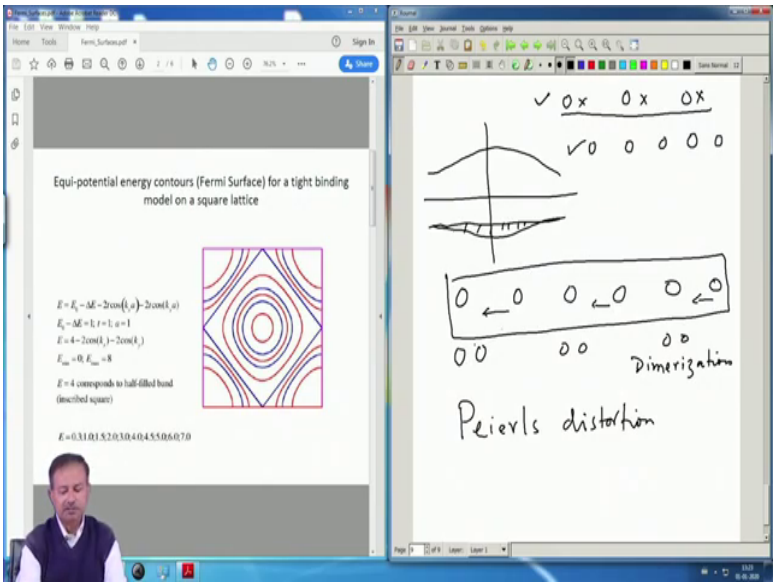

The thing that I was mentioning was that we were discussing this the formation of this band as they are these two bands. Now it happened when you had this kind of a lattice and so on.

But suppose I started with the lattice which is this the regular one atom per unit cell at a regular distance say A. Now as we just saw that this kind of a structure has stabilized it is energy by bringing one band down and filling in the half filled case filling up the lower band and gaining a lot of energy. So it is possible that if I can distort this bottom that is this lattice in such a way that it looks like this, then I might gain a lot of energy and that actually happens.

So in low dimensions one and two dimensions with the help of electron phonon coupling electron lattice coupling this kind of arrangement this regular arrangement can go to an arrangement where one of them moves to the left or right does not matter and forms a 2 atom unit cell and this kind of distortion do take place at low dimension systems one and two dimensions. And these of course it requires electron to couple to phonons and that kind of a calculation has been done it was done long back by Rudolf Peierls it is called Peierls distortion where it is shown that in one dimension it is hard to form a regular crystalline lattice, it is prone to a dimerization.

This kind of one atom shifting towards closer to another atom alternately is called a dimerization and this is one instability that you can see now that the Fermi surface is gone.

The Fermi there is no state 0 energy, there is the there is a gap at the Fermi level which was originally the Fermi level for this one for this lattice. There is now a gap that has opened one set of bands have come down and the system has gained a lot of energy by doing this. Of course distortion also cost some elastic energy but that cost is in lower dimensions it is less than the gain you have in electronic energies by doing this dimerization.

So it was shown by Peierls that in low dimension systems. The system is prone to basically destroy it is Fermi surface, it opens a gap and these kind this is again a Fermi surface instability and this class of a distortions are generally called Peierls distortions. We will not discuss it more here but it is just to show that there are instabilities of Fermi surface.