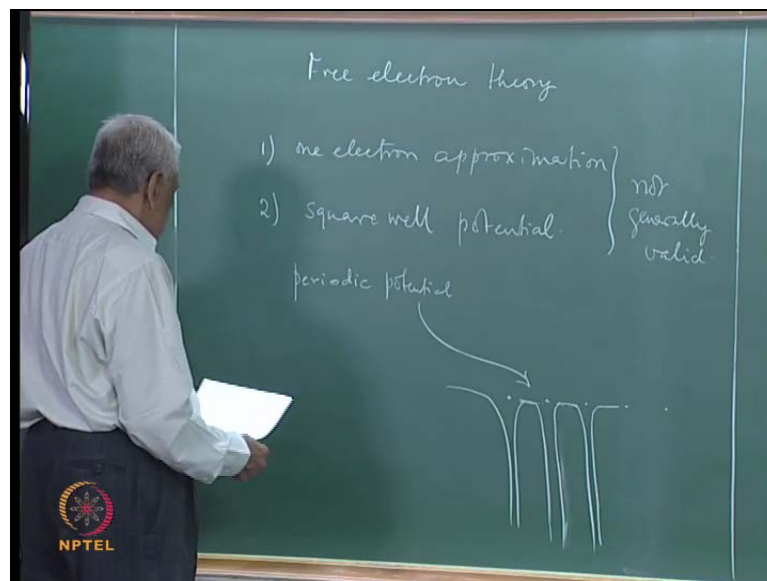


Condensed Matter Physics
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Lecture - 34
Energy Bands in Solids

The free electron theory, which was successful in explaining the physical properties of metallic materials has its serious limitations.

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Because it is based on the free electron theory is based on one - one electron approximation, which means that we look at one electron and considered the effect of all the other conductional electrons on it in the form of a square well potential, which is constant throughout the metal. And to which this electron is subject and which prevent it from getting out of the metal as whole. These are the two approximation and they are not generally valid.

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Free Electron Theory

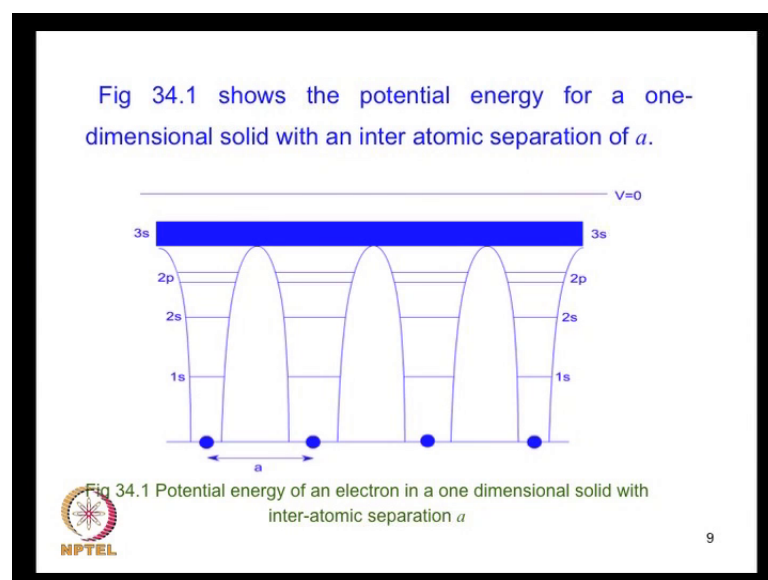
1. One electron approximation
2. Square well potential
Periodic potential

} not generally valid



So, in order to make further progress, it is necessary to go beyond this approximation mainly consider the more realistic situation in which we consider the periodic potential experienced by an electron due to all the ion cores in the lattice - crystal lattice. So, there are ion cores which are regularly arranged in a crystal lattice in all three dimension, I am showing one-dimensional situation. So, the potential is something like there will be...

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So, and this will repeated self everywhere so and so on. So, this is the periodic potential which we are talking about. This potential has a periodicity of the crystal lattice. So we

have to consider the motion of the electron subject to this given by the Schrodinger equation in quantum mechanics.

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$$V(\vec{r}) = V(\vec{r} + \vec{r}_n)$$

$$\vec{r}_n = n_1 \hat{a}_1 + n_2 \hat{a}_2 + n_3 \hat{a}_3, \quad n_1, n_2, n_3 \text{ are integers.}$$

periodicity

$$\mathcal{H}\psi(\vec{r}) = \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right\} \psi(\vec{r}) = E \psi(\vec{r})$$

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i \vec{G} \cdot \vec{r}}$$

\vec{G} is a reciprocal lattice vector

Subject to this periodic potential V of r , which has the periodicity of the crystal lattice. In other words V of r equals where r_n is a general lattice vector $n_1 a_1 + n_2 a_2 + n_3 a_3$ and n_1, n_2, n_3 are integers and a_1, a_2, a_3 are the basic translation vectors.

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$$V(\vec{r}) = V(\vec{r} + \vec{r}_n)$$

$$\vec{r}_n = n_1 \hat{a}_1 + n_2 \hat{a}_2 + n_3 \hat{a}_3, \quad n_1, n_2, n_3 \text{ are integers.}$$

$$H\psi(\vec{r}) = \left\{ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right\} \psi(\vec{r}) = E \psi(\vec{r})$$

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i \vec{G} \cdot \vec{r}}$$

\vec{G} is a reciprocal lattice vector

So, this is simply the condition of periodicity that the potential remains same at any given lattice point, and it is equal to the value of potential at any other lattice point given

by the position vector \vec{r} plus $\vec{r} \cdot \vec{n}$. So, this is the condition and we have to solve the Schrodinger equation $H \psi$ of \vec{r} equals minus $\hbar^2 / 2m$ ∇^2 plus V of \vec{r} ψ of \vec{r} equal to $E \psi$ of \vec{r} . So, we have to find energy Eigen values E by solving this Schrodinger equation subject to this. And because of the periodicity, it is possible to expand this in the Fourier series of the lattice periodic potential in the form where \vec{G} is a reciprocal lattice vector we already consider this well discussing diffraction of x-rays by a crystal lattice.

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The chalkboard shows the following derivation:

$$\psi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$

$$\sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} + \sum_{\vec{k}, \vec{G}} C_{\vec{k}} V_{\vec{G}} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} = \sum_{\vec{k}} E C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$

$$\sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \left[\left(\frac{\hbar^2 k^2}{2m} - E \right) C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k} - \vec{G}} \right] = 0$$

valid for all \vec{r} .

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And we can also expand the plain ψ of \vec{r} in the form of plain waves where \vec{k} is the wave vector of z electron. So, using this substituting this and this we get equals $E \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$ to the power $i\vec{k} \cdot \vec{r}$.

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$$\psi(\vec{r}) = \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$

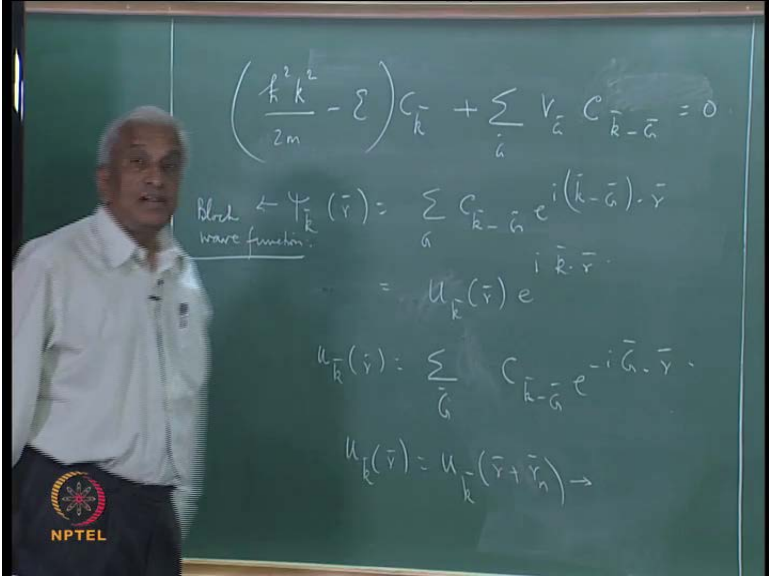
$$\sum_{\vec{k}} \frac{\hbar^2 k^2}{2m} C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} + \sum_{\vec{k}, \vec{G}} C_{\vec{k}-\vec{G}} V_{\vec{G}} e^{i(\vec{k}-\vec{G}) \cdot \vec{r}}$$

$$= E \sum_{\vec{k}} C_{\vec{k}} e^{i\vec{k} \cdot \vec{r}}$$

$$\sum_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \left[\left(\frac{\hbar^2 k^2}{2m} - E \right) C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} \right] = 0$$


That will be the equation that we have to solve and this can be written also in the form factoring out a to the power $i \vec{k} \cdot \vec{r}$ we can write this as which is valued for all \vec{r} which means the square bracket at quantity should vanish.

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$$\left(\frac{\hbar^2 k^2}{2m} - E \right) C_{\vec{k}} + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} = 0$$

Block wave function $\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G}) \cdot \vec{r}}$


$$= u_{\vec{k}}(\vec{r}) e^{i\vec{k} \cdot \vec{r}}$$

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}-\vec{G}} e^{-i\vec{G} \cdot \vec{r}}$$

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{r}_n) \rightarrow$$


So, we get. So, that we can therefore, write $\psi_{\vec{k}}(\vec{r})$ as $\sum_{\vec{G}} C_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G}) \cdot \vec{r}}$.

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$$\left(\frac{\hbar^2 k^2}{2m} - E\right) C_k + \sum_{\vec{G}} V_{\vec{G}} C_{\vec{k}-\vec{G}} = 0$$

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}-\vec{G}} e^{i(\vec{k}-\vec{G})\cdot\vec{r}}$$

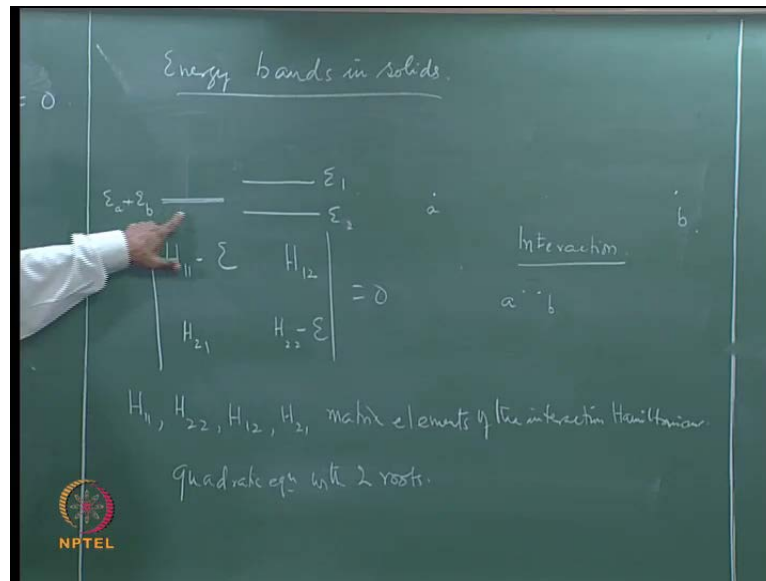
$$= u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$$

$$u_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} C_{\vec{k}-\vec{G}} e^{-i\vec{G}\cdot\vec{r}}$$

$$u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + \vec{r}_n) \rightarrow$$

Which can also be written as $u_{\vec{k}}(\vec{r}) e^{i\vec{k}\cdot\vec{r}}$ where $u_{\vec{k}}(\vec{r})$ is. So, we get the automatic property that the wave function $\psi_{\vec{k}}(\vec{r})$ this modulator is a free electron wave function E to the power $i\vec{k}\cdot\vec{r}$ modulator by the function $u_{\vec{k}}(\vec{r})$ such that $u_{\vec{k}}(\vec{r})$ equals $u_{\vec{k}}(\vec{r} + \vec{r}_n)$. So, this as the modulating function as the periodicity of the lattice and so this is known as Bloch wave function. So, the consequences of translational invariance of the periodic crystalline lattice is that the wave function $\psi_{\vec{k}}(\vec{r})$ is no longer the free electron plane wave function E to the power $i\vec{k}\cdot\vec{r}$ that E to the power $i\vec{k}\cdot\vec{r}$ modulated by the $u_{\vec{k}}(\vec{r})$ which is also translational invariance. And this is the form of the Bloch wave function which we should use in our description of the energy Eigen values of an electron moving in a perfectly periodic potential. So, this is step one this is one important result which we will use in our discussion of the formation of so-called energy bands in solids.

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So, we move on to the discussion of energy bands in solids. In this discussion, we have to answer the question how bands are found. We already saw in our discussion of the energetic of a homo nuclear diatomic molecule that if you have two molecules which are far apart and therefore, non-interacting. The energy Eigen value of the two atom system is just twice the energy of the individual atoms and I am showing them together here in the form in which they are degenerate. So, this is energy of E_a plus E_b where a and b are atoms which are not interacting now as the atoms are brought together we saw that the atoms start interacting we turn on an interaction. In atomic interaction the electronic and nuclear the electron and nucleus start interacting by as a coulomb potential. So, this interaction when it turns on and the two molecules come close together then we saw that the energy Eigen value is going to be given by the secular determinant where H_{11} , H_{22} , H_{12} and H_{21} are matrix elements of the interaction potential. Or interaction Hamiltonians between the individual atomic states represented by ψ_1 and ψ_2 . So, solving this we see that we get a quadratic equation with two roots.


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$$\epsilon^2 - \epsilon(H_{11} + H_{22}) - H_{12}H_{21} = 0$$

$$\epsilon = \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} + H_{22})^2 + 4H_{12}H_{21}}}{2}$$

$$\epsilon_1 = \frac{(\epsilon_1 + \epsilon_2) + \sqrt{(H_{11} + H_{22})^2 + 4H_{12}H_{21}}}{2}$$

$$\epsilon_2 = \frac{(\epsilon_1 + \epsilon_2) - \sqrt{(H_{11} + H_{22})^2 + 4H_{12}H_{21}}}{2}$$



So, these quadratic equation has this form for which the roots are. So, this shows this will be this is the $H_{11} + H_{22}$ is what we call $E_1 + E_2$ these are the energies of individual non interacting atoms and the resulting energy. Now in the presents of the interaction one of this is E_1 is plus square root of $H_{11} + H_{22}$ square plus $4k_{12}H_{21}$.


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$$E^2 - E(H_{11} + H_{22}) - H_{12}H_{21} = 0$$

$$E = \frac{[(H_{11} + H_{22})] \pm \sqrt{(H_{11} + H_{22})^2 + 4H_{12}H_{21}}}{2}$$

$$E_1 = \frac{(\epsilon_1 + \epsilon_2) + \sqrt{(H_{11} + H_{22})^2 + 4H_{12}H_{21}}}{2}$$

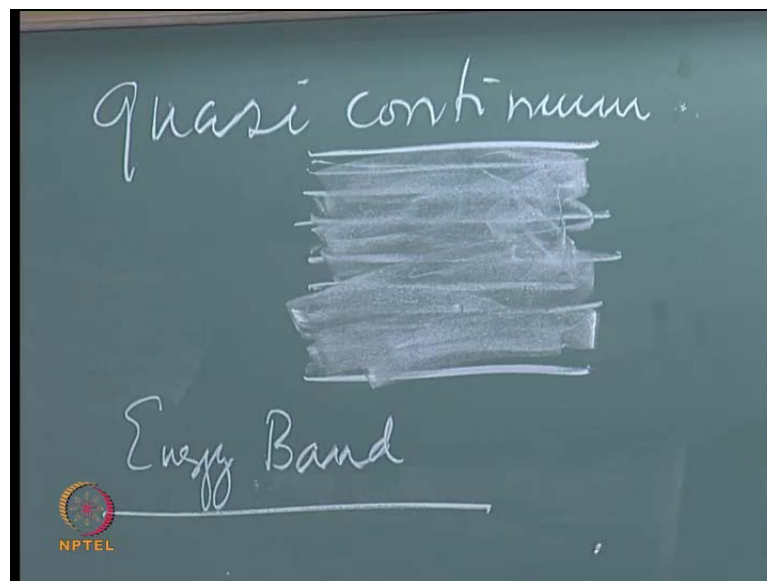
$$E_2 = \frac{(\epsilon_1 + \epsilon_2) - \sqrt{(H_{11} + H_{22})^2 + 4H_{12}H_{21}}}{2}$$



Yes and the other one will be E_2 will be minus. So, there are two routes one corresponding to a lower value corresponding to the negative sign there, and a higher

energy value corresponding to... So, these are the E_2 E_1 . So, you see that any interaction when it is stand on the two atom systems the energy level are split into in a such a way, the two fold degenerate is lifted and there are two non-degenerated energy levels one the higher energy Eigen value, and another with the lower energy Eigen value. Now this is the situation when two atoms interact. We are now considering the periodic potential due to the entire lattice of all the ten to power 23 electrons. So, these are going to give you a large number of interaction of the same kind the solid is after all large molecule.

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So, we are going to have a large number of splitting in this. So, of this finally, becomes a quasi I continuum when the number of interaction is very large so. This is a quasi I continuum. So, this continuum what we call an energy band in the presence of the perfectly periodic crystalline potential the electron energy going to sprodon into the form of energy bands. So, this is the mechanism of energy bands in order to discuss the detailed nature of the energy band.

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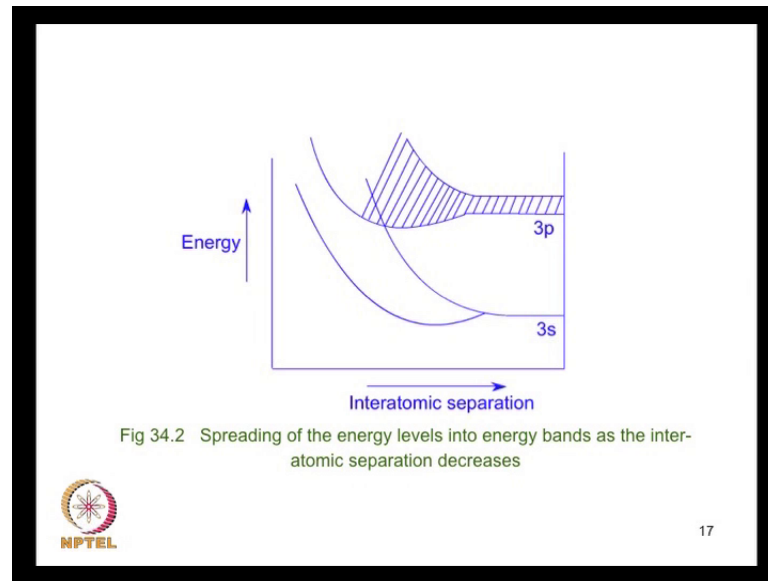
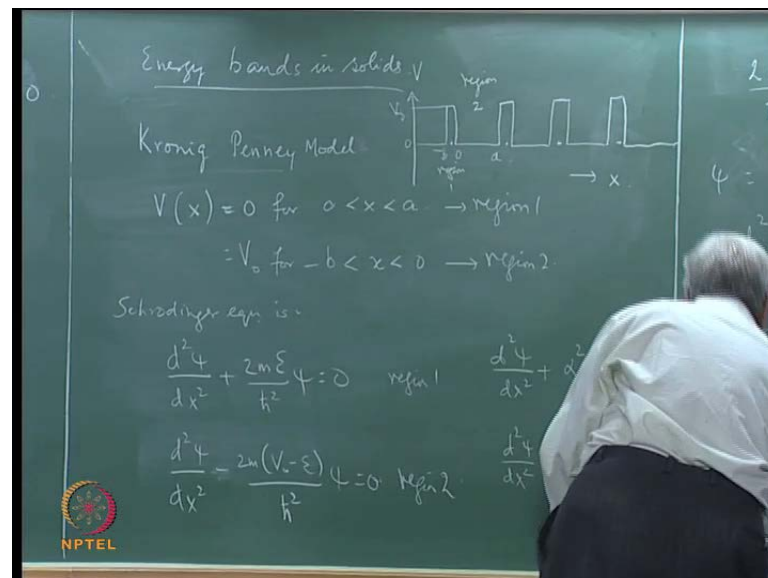


Fig 34.2 Spreading of the energy levels into energy bands as the interatomic separation decreases

Energy band it is necessary to go a little for other this is only a qualitative description of the interaction. Now let us consider a specific model in which we will be position to calculate the energy band structure.

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So, this model is simplify one-dimensional model known as Kronig-Penney model. This discusses the motion of the electron in is one-dimensional potential which is 0 for 0 less than X less than area.

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A simple one-dimensional model known as the *kronig-Penney model* assumed for the periodic potential illustrates the behaviour of the electrons in a solid. In this model the potential function is described by

$$V(x) = 0 \text{ for } 0 < x < a \text{ (region 1)}$$
$$V(x) = V_0 \text{ for } -b < x < 0 \text{ (region 2)}$$

Here the periodicity of the lattices is $(a+b)$.



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And equals V_0 for minus b less than x less than 0 . So this is known as less than 0 region one, this is region two pictorially this mean that we have atoms which are situated like this.


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Energy bands in solids

Kronig Penney Model

$$V(x) = 0 \text{ for } 0 < x < a \rightarrow \text{region 1}$$
$$= V_0 \text{ for } -b < x < 0 \rightarrow \text{region 2}$$

Schrodinger equation is

$$\frac{d^2 \psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0$$
$$\frac{d^2 \psi}{dx^2} - \frac{2m(V_0 - E)}{\hbar^2} \psi = 0$$


And then you have a potential which is 0 here potentially is represented here which is 0 and when it reaches the neighborhood of ion core then the potential goes up like that. So, this is V_0 this is minus b this is 0 this is a .

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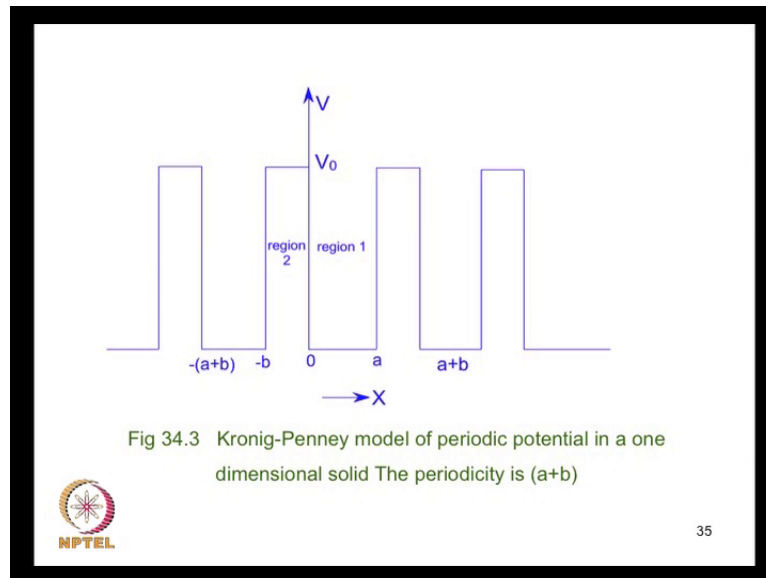


Fig 34.3 Kronig-Penney model of periodic potential in a one dimensional solid The periodicity is (a+b)

So, in the torsion the Schrodinger equations in one-dimensional $\psi'' + 2m(V - E)\psi = 0$ this is region one where V of x is 0 then. So, this is region one this is region 2 this region one this is region 2 let us first short and write $2mE$ by H^2 cross square.

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Yes alpha square and two m into V naught minus E by H^2 cross square as beta square. So, that this becomes and this is now we have the black solution the black form which we discuss already in the form. So, that substituting this and making differentiation and

substitute that we get the two equation these equation become and there u_1 , u_2 are the function u here in the region 1 2. So, these are the equation to be satisfy solved for u_1 and u_2 the solution u_1 and u_2 should satisfy boundary condition which are such that at the interface were at minus b at 0 and a they have to be matched in other words u_1 of 0 . They matched two wave function match at x equal to 0 .


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Where A, B, C and D are constants. The function $u(x)$ which are related to the wave function ψ must satisfy the conditions for continuity and single valued nature; i.e. they must obey the following boundary conditions:

$$u_1(0) = u_2(0), \quad u_1(a) = u_2(-b); \quad (34.12)$$

$$\left(\frac{du_1}{dx}\right)_{x=0} = \left(\frac{du_2}{dx}\right)_{x=0}; \quad \left(\frac{du_1}{dx}\right)_{x=a} = \left(\frac{du_2}{dx}\right)_{x=-b} \quad (34.13)$$

Substituting for u_1 and u_2 from Eqs(34.10) and (34.11) into Eqs (34.12) and & (34.13)



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And there are again match at u_1 of minus B equals u_2 of a for u_1 of a . These 2 minus B this a consequent of translation in variance and also condition on the derivatives $d u_1$ by $d x$ at the x equal to 0 matches $d u_2$ by $d x$ at x is equal to 0 . And a similar condition on $d u_1$ by $d x$ x equal to a equals $d u_2$ by $d x$ at x equal to minus b . If I take the forms this gives forms u_1 equals $A e^{i \alpha x} + B e^{-i \alpha x}$ plus $C e^{i \alpha x} + D e^{-i \alpha x}$. And u_2 is $C' e^{i \beta x} + D' e^{-i \beta x}$ plus $D' e^{i \beta x} + C' e^{-i \beta x}$. So, we required the solution u_1 and u_2 to satisfied this condition and that gives you a determinant which a 4 by 4 determinant because 4 conditions there and which when expanded leads to the following condition to be satisfied.

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$$\lim_{\beta b \rightarrow 0} \frac{\sinh \beta b}{\beta b} = 1$$
$$\begin{vmatrix} \beta a b \\ \sin \alpha a + \cos \alpha a \end{vmatrix} = \cos k a$$
$$P = \frac{\beta^2 a b}{2}$$


Namely $\beta^2 a b = 2 \alpha \beta \sin \alpha a + \cos \alpha a$. So, that will be the condition to be satisfied which is got by expanding by the four by four determinants now we specify to the situation where V_0 tends to infinity and b tends to 0 in other words it is extremely thin barrier it is infinitely high.

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The relation between E and k . i.e it gives the dispersion relation.

Meaningful interpretation is possible by making the following valid assumptions:

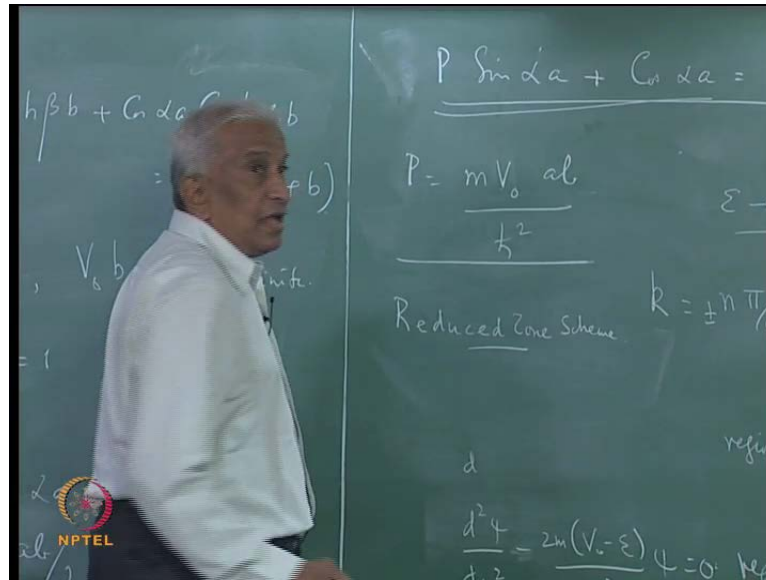
The height of the potential barrier is very large. i.e $V_0 \rightarrow \infty$ and simultaneously the width of the barrier $b \rightarrow 0$ in such a way that the product $V_0 b$ remains finite.



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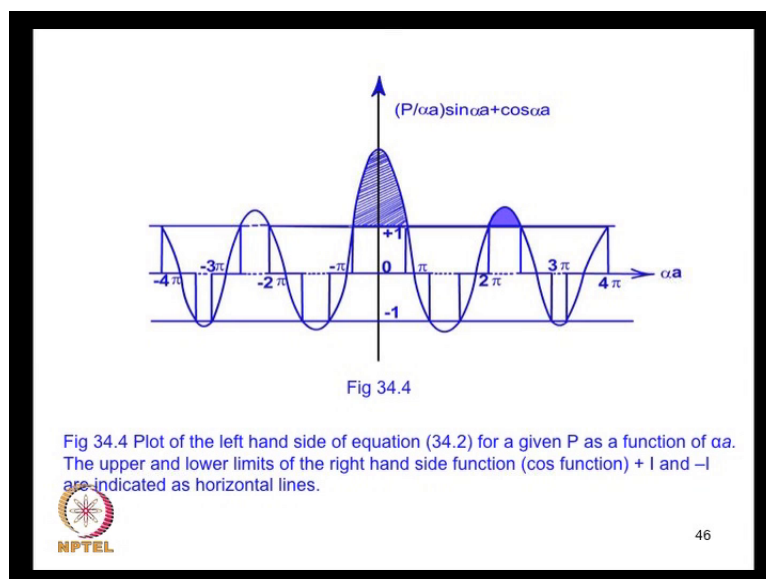
Such that V naught b remains this case we get limit $\beta b \rightarrow 0$ $\sin H \beta b$ by b equal to 1 and therefore, the derivative condition $b \sin \alpha a + \cos \alpha a = \cos k a$.

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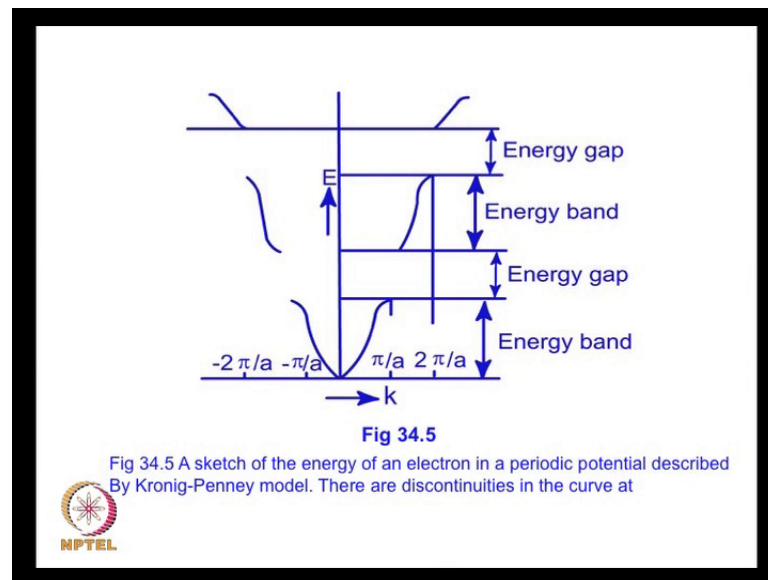
So, this p is nothing but $m V$ naught $a b$ by H cross square. So, this is the parameter which involves the highest of the potential barrier and the thickness of the potential barrier. So, this is the basic condition which determines the energy Eigen values.

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We can see the nature of these energy bands by looking at the graphical representation of these energy bands. So, the figure shows the plot of the right hand side of this equation for a given value of p as a function of αa . So, we can see that the shaded portions on the left hand side are plotted since the right hand side is just a cosine function. So, it cannot go beyond the value of plus one or minus one and therefore, you find shaded regions in the figure correspond to such values of $\cos k a$ which are unreasonable and therefore, are forbidden they are not allowed. So, you find that energy values get into two regions one the unshaded one corresponding to the allowed energy values and the shaded regions which correspond to the forbidden regions the energy Eigen values.

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So, these energy Eigen values when plotted look like this they are shown the energy E versus k curve we shown in. So, this gives the energy versus the wave vector for an electron in a periodic potential described by the chronic penny model. So, you can see that there are discontinuities at k equal to π/a and k equal to $-\pi/a$ and then k equal to $2\pi/a$ and k equal to $-2\pi/a$ and so on. So, in general, for all k equal to $n\pi/a$ plus or minus there are discontinuities in a energy. So, the energy Eigen value goes from the value suddenly it is this and all the energy Eigen values in this region are not allowed.

So, these are the allowed energy Eigen values these are the forbidden energy Eigen values in the gap region again these are allowed set up Eigen values then followed by energy gap again in the next band so on for the third band and so on. So, this goes on and we find that this can be represented a bit more effectively in the. So, called reduced zones scheme this only means that the states k and k plus or minus in into 2π by a into π by a .

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The wave function in the same but only the energy values is different.

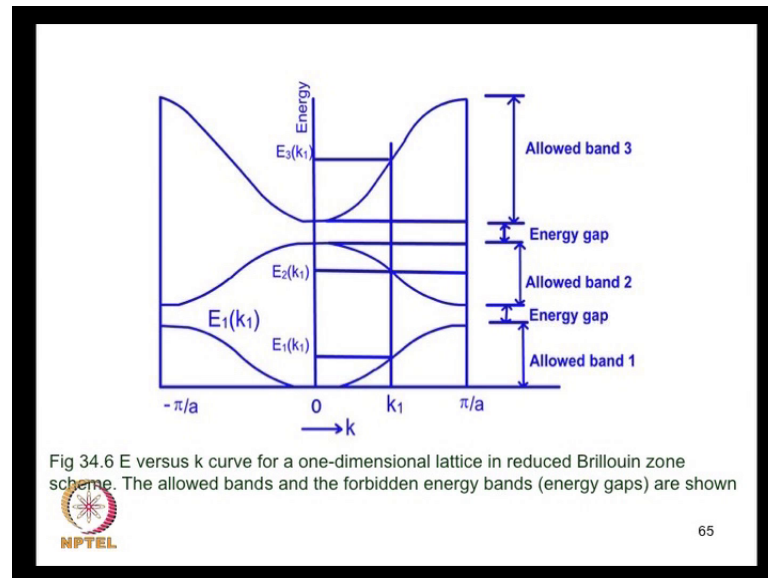
Therefore the E versus k curve can be drawn restricting the k values in the range $-\pi/a$ to $+\pi/a$ to plot all the possible energy values. Such a curve is called the reduced E versus k curve. The reduced E versus k curve is shown in Fig 34.6



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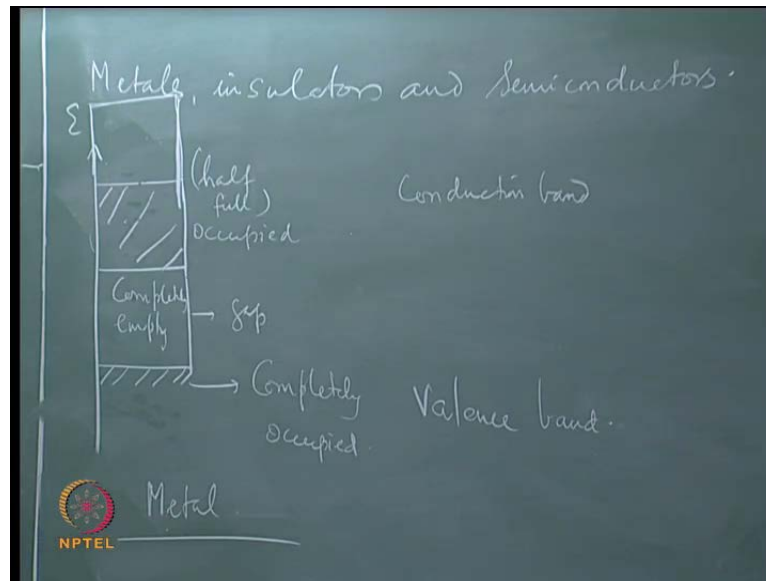
These are all equal and they are identical functions while the functions while the energies are different. So, the energies are different, but they are discovered by the same function. So, these versus k curve can be done by restricting the k values in the range minus π by a to plus π by a

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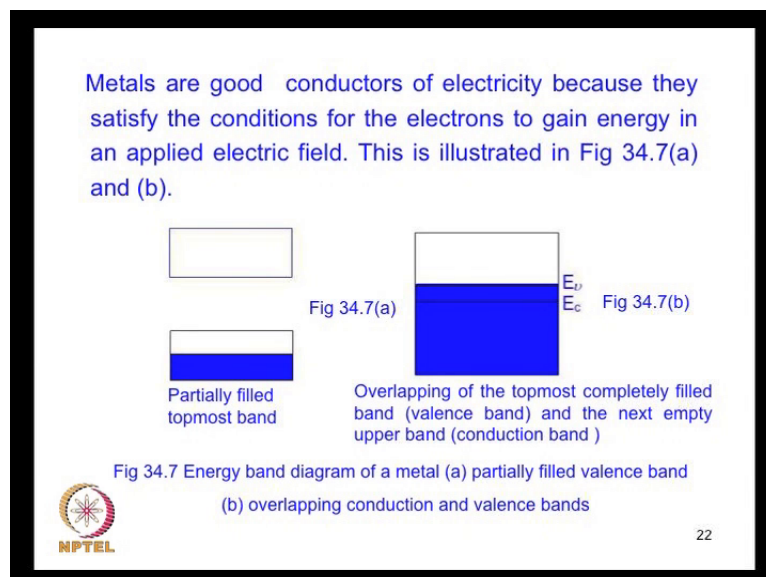
And all the energy values can be plotted within this region. So, such a plot is shown in figure where the first band as energies shown in the lowermost curve these are we allowed value and then E_2 is the corresponding energy values for the second band plotted in the reduced zone scheme. Therefore, there is a gap between these two. So, there is an energy gap and then the next allowed band comes here that is the k_2 and similarly E_3 with a gap here. So, this shows the entire energy band structure within this first Brillouin zone which is the region between $-\pi/a$ and π/a . So, this describes the band structure of the typical band structure. So, the Kronig-Penney model gives as an easy way to understand the formation of energy bands in periodic solid.

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And this is very important in a discussion of the property of metals insulators and semiconductor these are new class of materials which we are going to discuss from now on in a unified way how do you discuss this the matter let me just sketch the band structure in a simple way. So, this is the E energy and this is the band structure in a very crude form.

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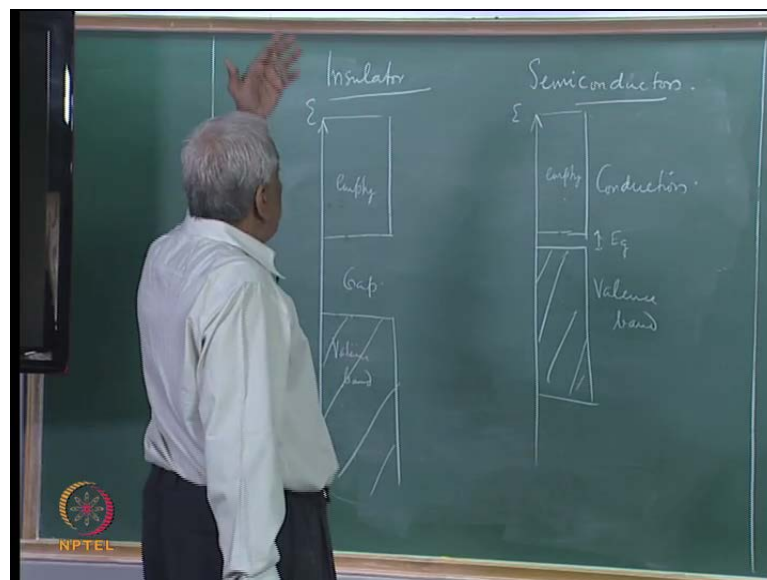


So, we have states lying here this is empty and there are states here. So, these are states which are occupied and these are states which are forbidden and therefore, these states allow

forbidden an occupy empty and this is an occupied band the bands. And of course, the extent of to this energy value and it is only of full this band is completely occupy the lower bands and this is completely empty this is the gap. So, this is the picture of a metal in a metal there is a completely occupy band separated from a partially occupied or of full conduction band this is known as the valance band and this is the conduction band. So, the valance band is completely occupied whenever a band is completely occupied states are free for an electron to get into because of Pawley's fusion principle and. So, conduction in a such a band is not possible the electron cannot move on one state to another similarly if there is a completely empty band that is also something in which there are no electrons therefore, is there is no conduction.

So, for conduction to be possible in a material request have a band structure with an uppermost band which is only partially feel in this case the metal is only of filled and therefore, of the band is empty and off of the band is occupied. So, the electrons the conduction electron is can move from the occupied states into the empty states there by facilitating conduction. So, conduction is possible. So, this is the band structure which renders a metal conducting coming to the case of an insulators and insulators how is its band structure.

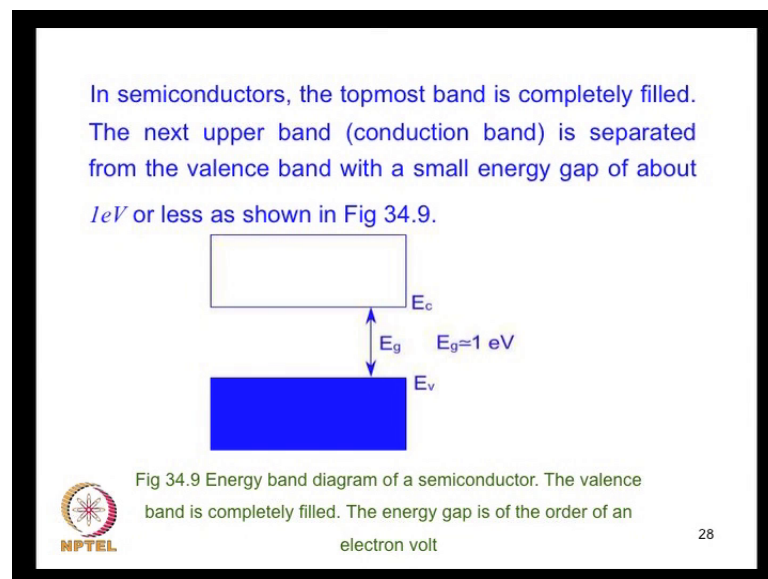
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Band structure again we shown in schematically in this way. So, you have a upper band and a lower band this is a gap. So, this is the valence band which is completely occupied

and a conduction band which is empty, but separated. The conduction band which is empty is separated from the valence band which is completely occupied by a very large energy gap. So, for carriers to go into this empty band from the occupied band they have to cross over this barrier produced by this energy gap and they have to get in from the state in the valence band they have to get into the state in the empty unoccupied band upper band. So, this is possible only there as the energy which is more than the gap energy and then an insulator does not happen and therefore this is not conducting.

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Now we come to another interesting class of material which we have not talked about so far which is known as semiconductors. So, here the band structure is very similar that of an insulator. And there is a valence band below which is completely occupied with an energy gap which in contrast to an insulator the energy gap is as a very small value. In other words, the occupied valence band is separated from the unoccupied conduction band only by an extremely small amount of energy of the order of an electron hole. So, it is easily possible for carriers to get excited across the gap from getting to conduction band. Therefore, they are neither an insulator nor a metal like this, but they are semiconducting.

So, this is the new class of material, which will be discussed from now on. And the band structure theory, the theory of energy band provides a convenient mechanism or convenient way to understand the difference between an insulator, a metal and a

semiconductor from the point of view of their band structures. And there relate these electronic band structure to the nature of the conduction band in these material. We will discuss semiconductors in the next session.

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