

# *PYL102 Course*

## *Lecture-4 on 16-08-2021*

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## *PYL102:*

# *Principles of Electronic Materials*

- Electrons in periodic potential.....
- K-P model...energy band theory...
- Schrödinger equation for a periodic potential .....
- Bloch theorem....

# Free electron theory:

In free electron theory, the conduction electrons are described by free electron wave functions, and these have certain allowed values of wave vector  $k$  that are analogous to the quantum numbers  $n$ ,  $l$ , and  $m$  that describe the permitted states of an electron in an atom.

In fact, the energy of a free electron in a metal is related to its wave vector,  $k$ , by

$$E = \frac{\hbar^2 k^2}{2m}$$

Since the energy of a free electron is entirely energy due to its motion—in other words, due to its kinetic energy, so we can write as below:

$$\frac{1}{2}mv^2 = \frac{\hbar^2 k^2}{2m}, \text{ which can be written as } mv = \hbar k$$

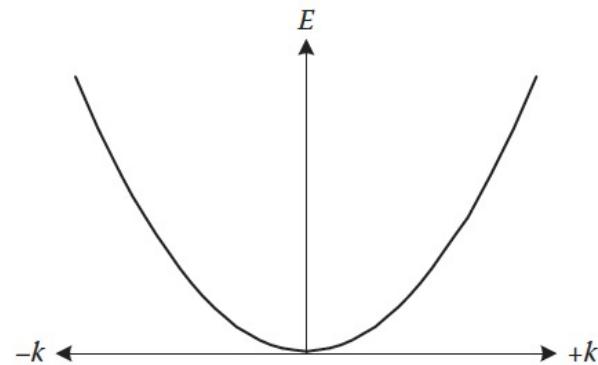
So, we can see that the wave vector,  $k$ , is a measure of the momentum of a totally free electron, as momentum,  $p$ , is equal to  $mv$ . (In fact,  $k$  is often referred to as the “quasi-momentum”.

This is because although it gives an indication of the momentum—and hence the velocity---of a totally free conduction electron,

but we will see in the next slides, it does not always do so for conduction electrons influenced by the lattice ions.

# Electrons in periodic potentials:

Now let's plot the form of the relationship between  $E$  and  $k$ , which is parabolic because in Cartesian coordinates any parabola has a standard equation of  $y = ax^2$ :



This is the E-k relationship for a totally free electron, which does not interact with the crystal lattice but behaves as though it is a particle in a quantum gas.

After Pauli's free electron theory, we can give a good explanation of many of the properties of metals, including their thermal and electrical conductivities.

But it still fails to explain why some materials are conductors, some semiconductors, and some insulators, and cannot account for the electron mean free path being around a hundred or more atomic spacings.

A better way to understand these topics is to view solids in terms of energy bands instead, and as we will see, there are two totally different ways of considering how energy bands come about.

# Electrons in periodic potentials:

This model is an extension of Pauli's quantum free electron model that takes into account the effect that the ions in the lattice have on the sea of electrons.

In Pauli's model, the conduction electrons are assumed to have a uniform potential energy because the positive charge of the lattice ions is effectively spread out across the whole of the specimen of metal being considered.

In fact, the potential energy of electrons within a metal was actually taken to be zero for simplicity, while the potential energy outside the metal is assumed to be infinite so that the electrons are confined within the metal.

However, the potential energy of the electrons is like that shown below:

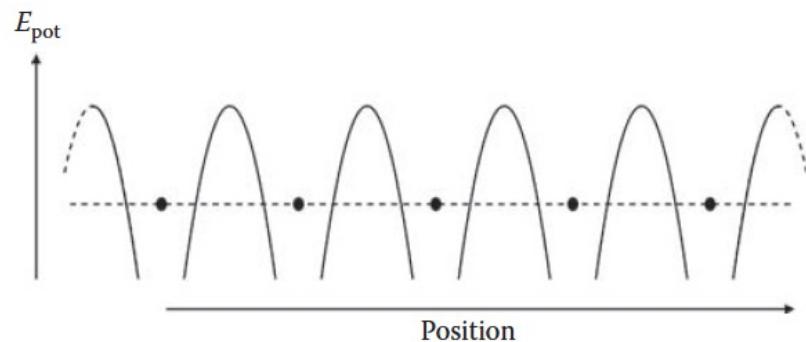


Fig.: Potential energy for conduction electrons in hypothetical 1D solids

Once the interaction of the conduction electrons with the positively charged lattice ions is considered. As the above diagram shows, the potential energy of an electron is lower than its average value when that electron is near a positive ion, and is at its highest when the electron is exactly in between two ions.

# Electrons in periodic potentials:

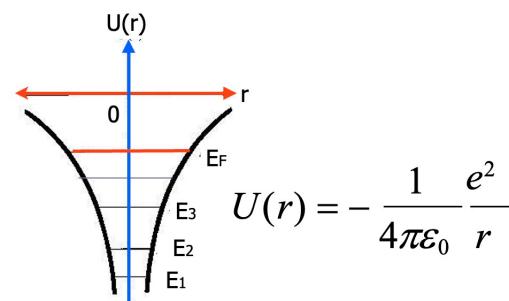
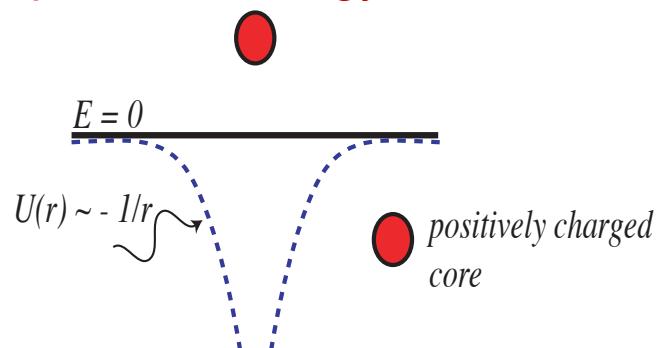
This is because any object will have a lower potential energy when it is near to something it is attracted to than when it is far apart.

We will discuss Schrödinger equation for a periodic potential:

Electrons motion in a crystal will now be considered from a quantum mechanical point of view based on Schrödinger equation.

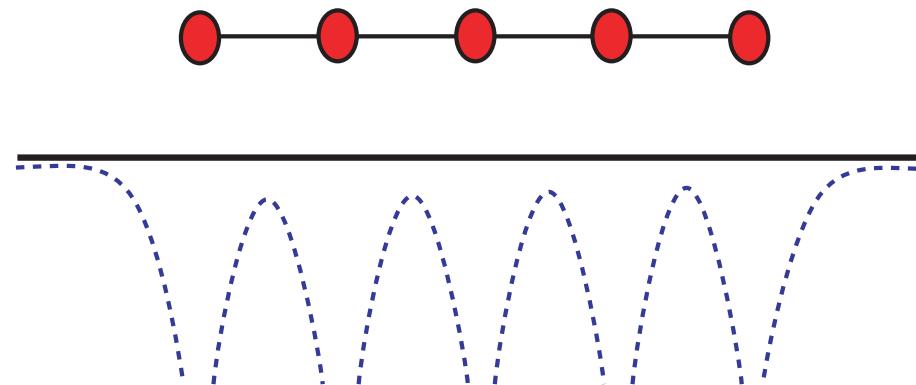
The crystal may be viewed as a periodic arrangement of atoms, i.e., positively-charged ion cores comprising the positively charged nuclei and non-valence electrons that may be assumed stationary in the lattice points.

The potential energy of a valence electron in a single isolated atom is shown:

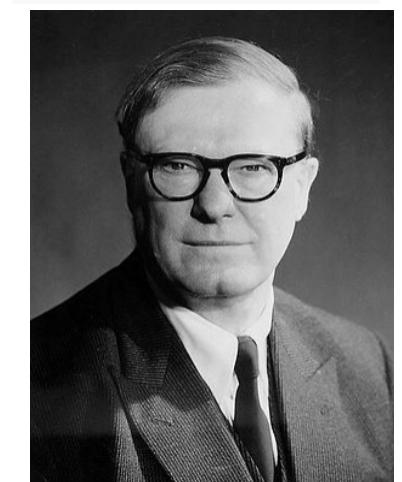
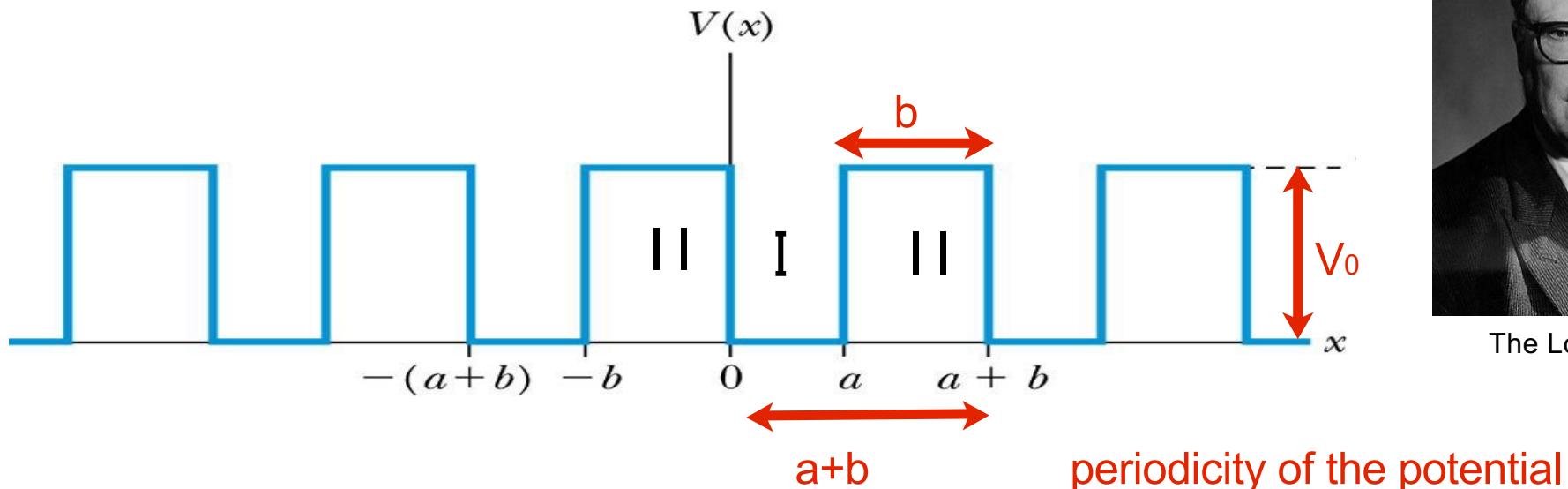


If several of these atoms are placed in close proximity and equidistant from each other, the potential functions of neighboring atoms overlap so that the net potential function will look like the potential function as shown in the next slide:

# Electrons in periodic potentials:



However, we can simplify the potential function by using the potential function shape (referred to as Kronig-Penny Model).



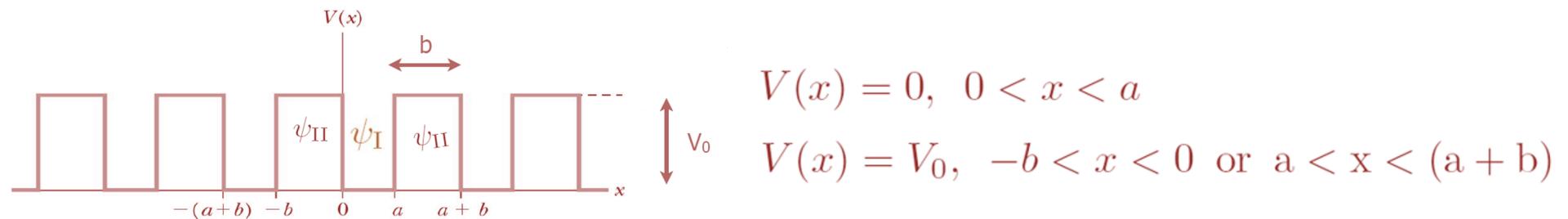
In the Kronig-Penney model, a single electron is considered which moves in a one-dimensional crystal of certain length  $L$ .

Potential energy is periodic array of square wells with period  $(a+b)$

# Kronig-Penney simplification of 1D potential:

Now we can write the time-independent Schrödinger equation for the motion of the electron in the one-dimensional periodic potential takes the form

$$H\psi = \left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \psi = E\psi \quad \text{we can write as} \quad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)] \psi = 0$$



It is of course implicit in the equation above that the time-dependent component of the wave-function is of the form:

$$e^{-i\left(\frac{E}{\hbar}\right)t} \quad \text{where} \quad E = \text{total energy}$$

Now, we can write the Schrödinger equation in both the regions:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_I}{dx^2} = E\psi_I, \quad \text{for } 0 < x < a$$

$$-\frac{\hbar^2}{2m} \frac{d^2\psi_{II}}{dx^2} + V_0\psi_{II} = E\psi_{II}, \quad \text{for } -b < x < 0$$

# *PYL102 Course*

## *Lecture-5 on 18-08-2021*

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## *PYL102:*

# *Principles of Electronic Materials*

- Electrons in periodic potential.....
- K-P model...energy band theory...
- Schrödinger equation for a periodic potential .....
- Bloch theorem....

# Bloch theorem:

To obtain the solution to the Schrödinger equation, we utilize a mathematical theorem by Bloch....

Independent e<sup>-</sup>s, each of which obeys a one e<sup>-</sup> equation with a periodic potential, are known as Bloch e<sup>-</sup>s instead of free e<sup>-</sup>s.....

**Bloch's theorem:** The eigenstates  $\Psi$  of the one e<sup>-</sup> Hamiltonian

$$H = -\frac{\hbar^2 \nabla^2}{2m} + V(r) \text{ where } V(r + R) = V(r). \quad \text{for all } \mathbf{R} \text{ in a Bravais lattice}$$

$$\psi(x) = u(x)e^{ikx}$$

- Wave function which satisfies Schrödinger equation for perfect periodicity of lattice
- Due to periodicity of the potential the wavefunction is also periodic
- Bloch function is a function which is a product of plane wave and a function which contains periodicity of lattice vector.
- The function  $u(x)$  is called Bloch function and it is periodic with the same periodicity as that of the potential function.
- As this Bloch function satisfies Schrödinger equation, therefore, it can be used to solve periodic potential problems.

# Kronig-Penney model:

Now let's first consider:

$$\alpha^2 = \frac{2mE}{\hbar^2} \quad \beta^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

And use the following Bloch function in the above two equations on last slide:

$$\psi(x) = e^{ikx} u_k(x)$$

We get the following forms:

$$\frac{d^2 u_I}{dx^2} + 2ik \frac{du_I}{dx} + (\alpha^2 - k^2) u_I = 0, \quad 0 < x < a$$

$$\frac{d^2 u_{II}}{dx^2} + 2ik \frac{du_{II}}{dx} + (\beta^2 + k^2) u_{II} = 0, \quad -b < x < 0$$

Solutions of these equations in two regions can be written as following:

$$u_I = A e^{i(\alpha-k)x} + B e^{-i(\alpha+k)x}, \quad 0 < x < a$$

$$u_{II} = C e^{(\beta-i k)x} + D e^{-(\beta+i k)x}, \quad -b < x < 0$$

# Kronig-Penney model:

- Now we need to determine the constants, let's use the boundary conditions at  $x = 0$ ,  $x = -b$  and at  $x = a$ ,  
the wave function and their derivative must be continuous and periodic:

$$\left. \begin{array}{l} u_I(0) = u_{II}(0) \\ \left( \frac{du_I}{dx} \right)_{(x=0)} = \left( \frac{du_{II}}{dx} \right)_{(x=0)} \\ u_I(a) = u_{II}(-b) \\ \left( \frac{du_I}{dx} \right)_{(x=a)} = \left( \frac{du_{II}}{dx} \right)_{(x=-b)} \end{array} \right\} \begin{array}{l} \text{continuity requirement} \\ \text{periodicity requirement} \end{array}$$

Calculate wave functions & energy What are the energy values for which satisfactory solution to these equations are obtained?

Putting this boundary condition and making the determinants of A, B, C and D to be zero, one gets the form:

$$\left| \frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin h\beta b \cdot \sin \alpha a + \cos h\beta b \cdot \cos \alpha a = \cos k(a+b) \right.$$

# Kronig-Penney model:

Further assumption, let's consider potential barrier as a delta function...i.e.,

$$V_0 \rightarrow \infty, \quad b \rightarrow 0 \quad V_0 \cdot b \neq 0$$

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sin h\beta b \cdot \sin \alpha a + \cos h\beta b \cdot \cos \alpha a = \cos k(a+b)$$

$$\Rightarrow \frac{mV_0 b}{\hbar^2 \alpha} \sin \alpha a + \cos \alpha a = \cos ka$$

Let's take  $P = \frac{mV_0 ba}{\hbar^2}$

$$P \rightarrow 0 \implies \alpha = k$$

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

Since  $\cos(ka)$  can take values only between +1 to -1. Only certain values of  $k$  are allowed OR we can say not all  $\alpha a$  values (i.e., energy) are allowed in the left-hand side of the equation.

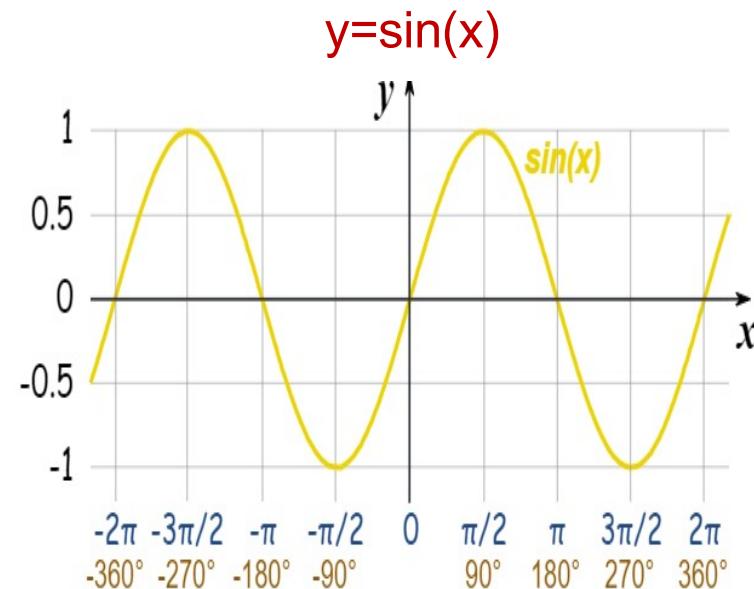
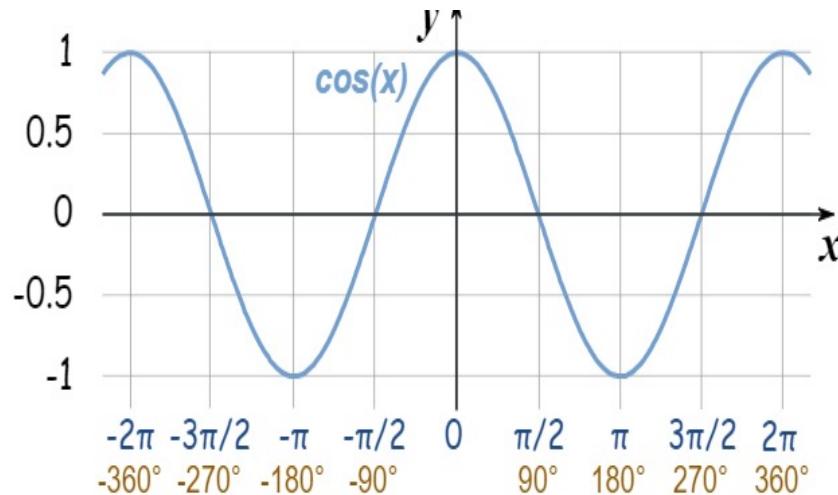
The equation gives a simple relationship between  $E$  (through  $\alpha$ ) and the wave vector  $k$  for a simple potential described by a finite product  $V_0 \cdot b$

# Energy bands in Solid:

This is energy wave vector dispersion relation for conduction electrons...

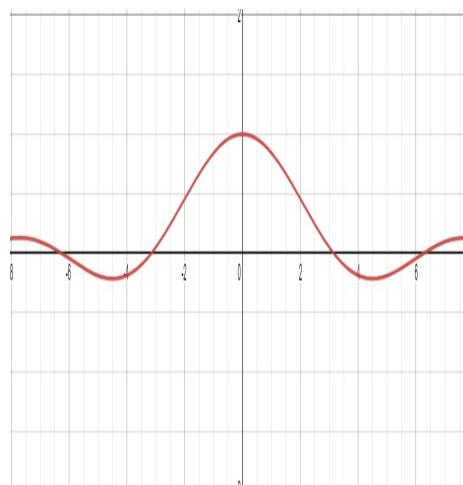
How to understand the above equation graphically?

let's first see the graph of  $y=\cos(x)$  and



Now let's see the graph of  $\sin(x)/x$ :

→ We can see that the amplitude of the oscillations decreases very quickly as  $x$  is increasing.

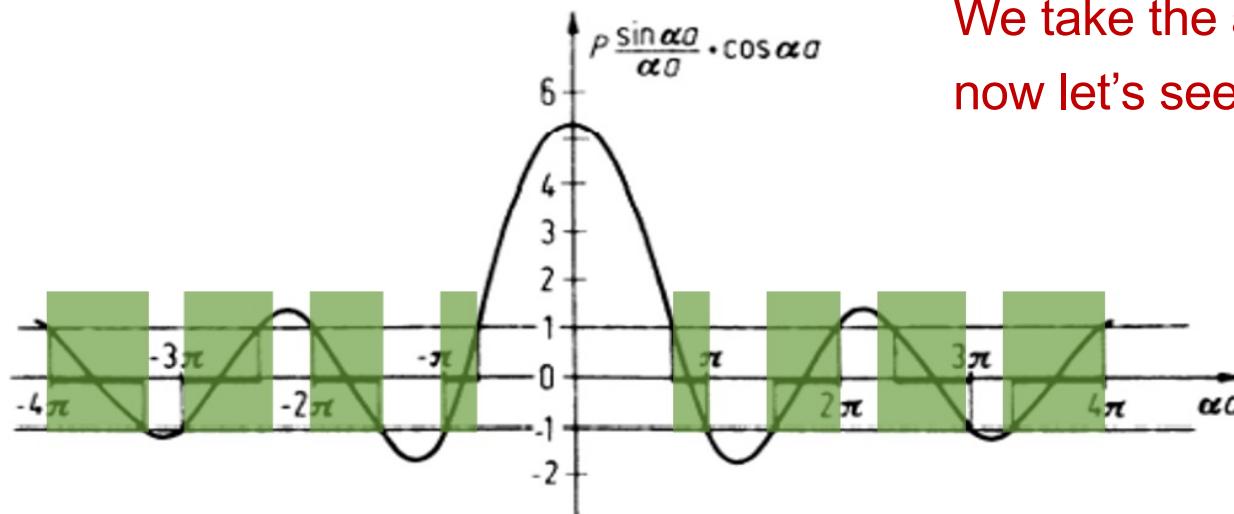


→ This is because  $x$  in the denominator dominates at higher values of  $x$ .

# Energy bands in Solid:

→ It provide relationships between the total energy of the electron and its momentum (or wave-number) and their dependence on the shape and magnitude of the barrier.

→ Now we add  $\cos(x)$  to this in order to get the graphical representation of that equation



We take the arbitrary value of  $P = \frac{3\pi}{2}$ ,  
now let's see how the plot looks like...

This will result in allowed energy bands and forbidden energy gaps...

It is important to understand that in free electron model, electrons were not considered to be affected by periodic potential.

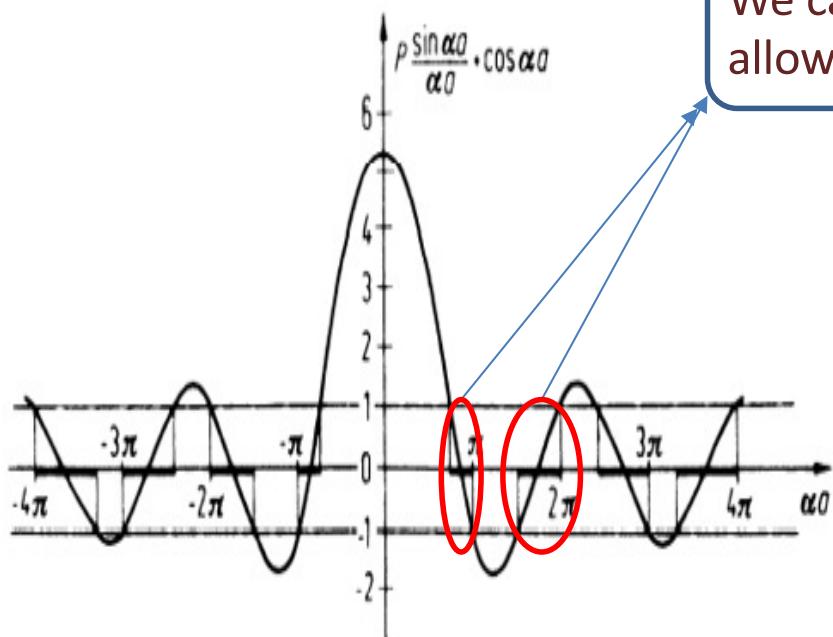
Important: at some ranges of values of the energy, there is no solution according to these equations, and thus, the system will not have those energies: energy gaps.

These are the so-called band-gaps, which can be shown to exist in *any* shape of periodic potential (not just delta or square barriers).

# Energy bands in Solid:

What do we find from KP model? Energy spectrum --> allowed and forbidden bands...  
Width of the allowed bands increases with energy (x-axis)...

- Electrons that move in a periodically varying potential field can only occupy certain allowed energy zones.
- Energies outside of these allowed zones or “bands” are prohibited.
- When we increase the value of energy, the value ( $\alpha a$ ) increases, the amplitude is decreasing with the value of ( $\alpha a$ ), size of the forbidden bands become narrower.



We can clearly see in the increase in the size of allowed energy bands with ( $\alpha a$ ).

What is the influence of  $P$  on the energy spectrum?

The size of the allowed and forbidden bands depends on the value of  $P$ ...

Let's see in the next slide, how?

# *PYL102 Course*

## *Lecture-6 on 19-08-2021*

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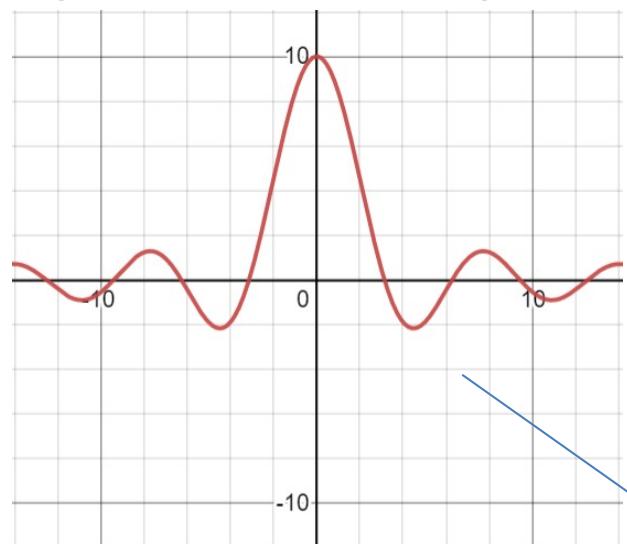
# Energy bands in Solid:

Case 1) When the “potential barrier strength” ( $V_0 b$ ) is large  $\rightarrow P$  is also large and the curve proceeds more steeply. The allowed bands are narrow.

Let's see the graphs of  $P[\sin(x)/x]$

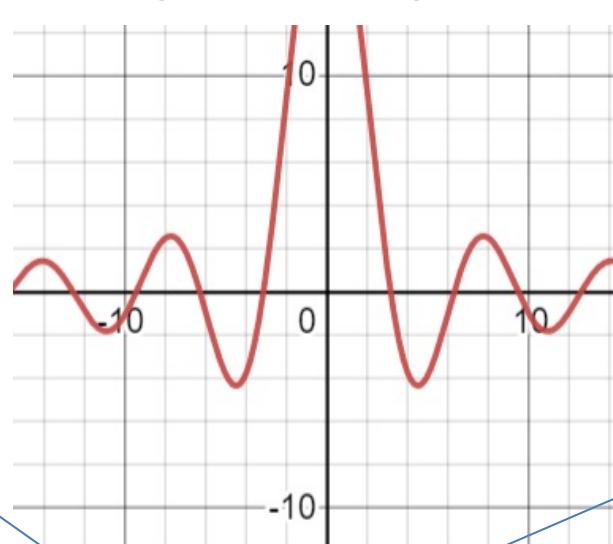
when

$P=10$

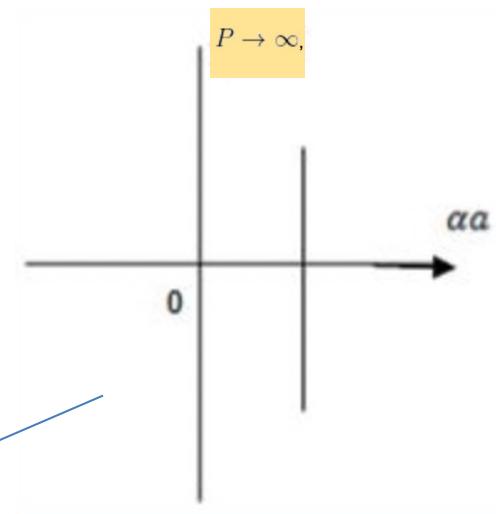


when

$P=20$



when  $P$  is infinity



When  $P$  is increased the amplitude is also increasing. Since the same number of crests are occupied in an interval, The steepness increases.

Similarly,  
if the potential barrier strength,  
and therefore  $P$ , is small,  
the allowed bands become wider.

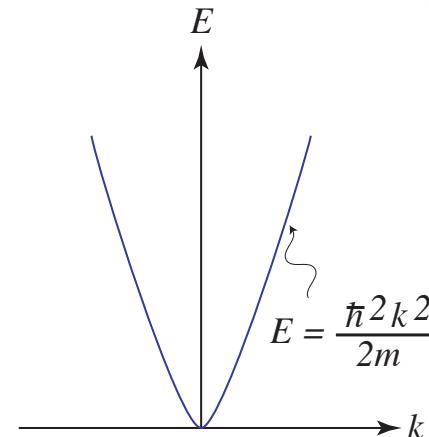
# Energy bands in Solid:

Case 2) When  $P$  goes to zero, i.e., when potential barrier strength approaches zero, we have the following situation...

$$\cos \alpha a = \cos ka \quad \rightarrow \quad \alpha = k. \quad E = \frac{\hbar^2 k^2}{2m}.$$

In this case only  $\cos(\alpha a)$  contribute to the graph from the left-hand side of that equation.

This is similar to the case of free electron model.



Case 3) If the potential barrier strength is very large,  $P$  approaches infinity. However, because the left-hand side of equation has to stay within the limits  $\pm 1$ , i.e., it has to remain finite, it follows that

$$\frac{\sin \alpha a}{\alpha a} \rightarrow 0, \quad \rightarrow \quad \alpha a = n\pi$$

So, we can write as following:

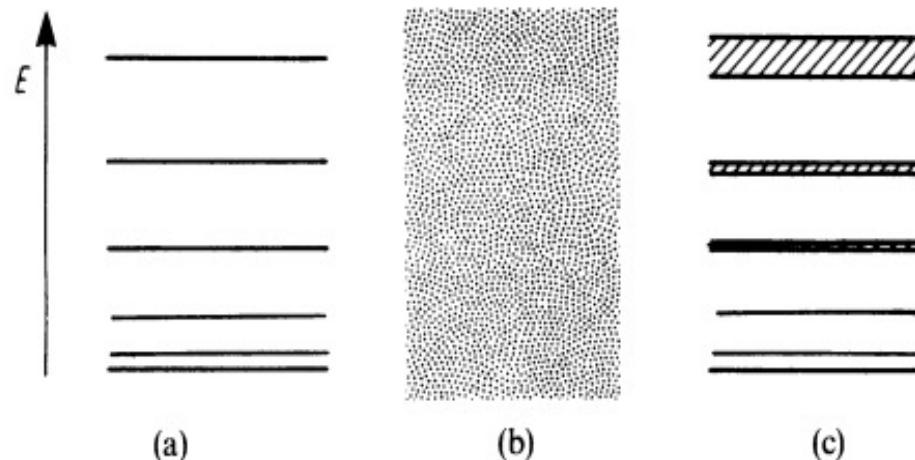
$$\alpha^2 = \frac{n^2 \pi^2}{a^2} \quad \text{for } n = 1, 2, 3, \dots$$

# Energy bands in Solid:

And we know that:

$$\alpha^2 = \frac{2m}{\hbar^2} E, \quad \rightarrow \quad E = \frac{\pi^2 \hbar^2}{2ma^2} \cdot n^2,$$

Now we can see the allowed energy levels for (a) bound electrons, (b) free electrons, and (c) electrons in a solid:

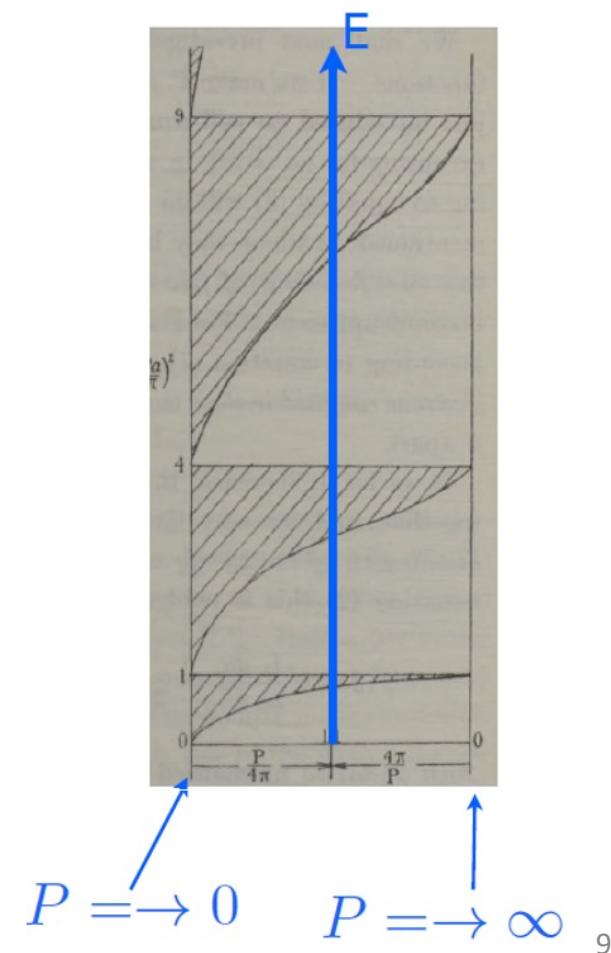


So, let's conclude, say when  $P \neq 0$

width of an allowed band decreases with increasing  $P$

( $P \rightarrow$  binding energy of electrons)

Shaded area: allowed bands



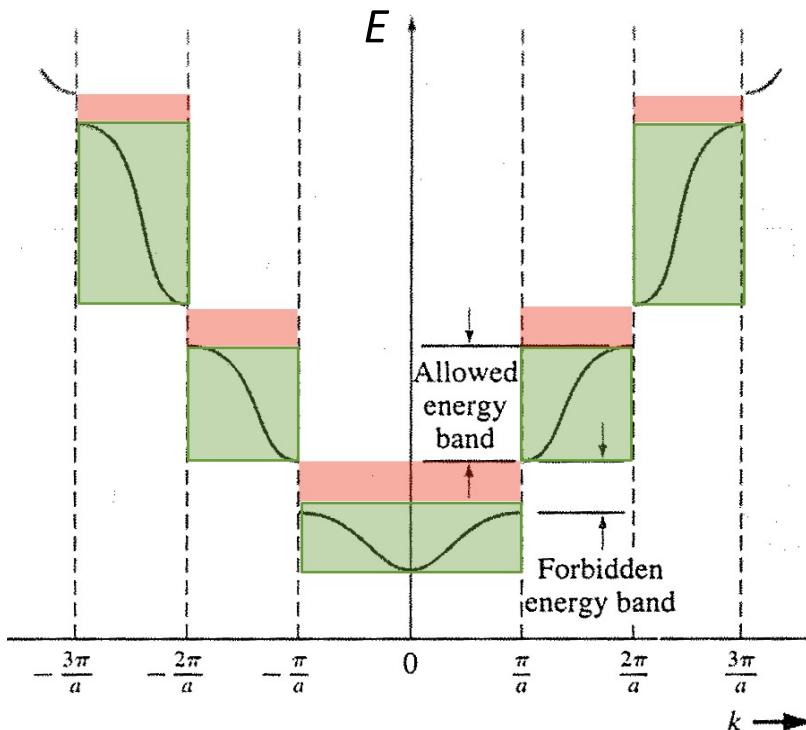
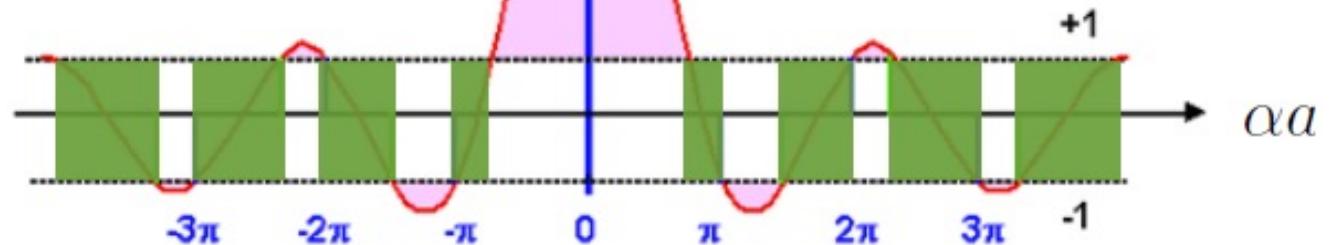
# Energy bands in Solid:

Dispersion relation: Relation between E and k

Graphical solution of

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka$$

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a$$



❖ discontinuities appear at

$$k = \frac{n\pi}{a}, \quad n = 1, 2, 3, \dots$$

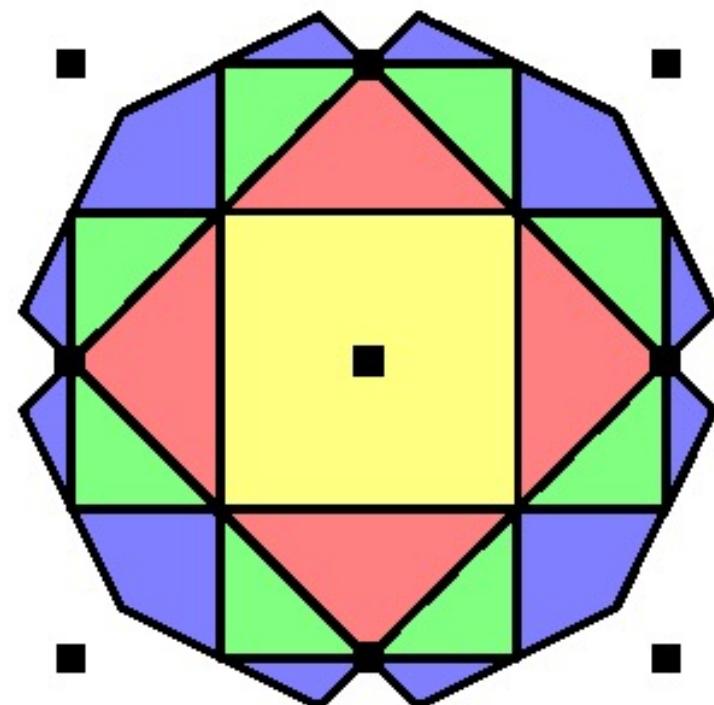
- ❖ represent the boundaries of the Brillouin Zones.
- ❖ energy ranges between the allowed energy bands which are not accessible to the electrons, due to the interaction of the conduction electrons with the periodic potential of the lattice.

❖ This energy range is called energy gap....

# Energy bands in Solid:

Self-reading material

- ❖ Any physical property of an electron has the periodicity of the reciprocal lattice, so energy is plotted in a primitive unit cell of the reciprocal space.
- ❖ Brillouin Zone is simply a geometrical representation of the Wigner Seitz primitive cell in the reciprocal ( $k$ -space).
- ❖ In reciprocal space, the planes which bisect the lines joining the reciprocal lattice points from the origin are described as Bragg Planes.
- ❖ First Brillouin Zone is the set of points in the  $k$ -space that can be reached from the origin without crossing any Bragg plane.
- ❖ Second Brillouin Zone is the set of points that can be reached from the first zone by crossing just one Bragg Plane.
- ❖ In general,  $n$ th Brillouin zone is defined as the set of points that can be reached from the origin by crossing the  $(n-1)$ th Bragg Planes.

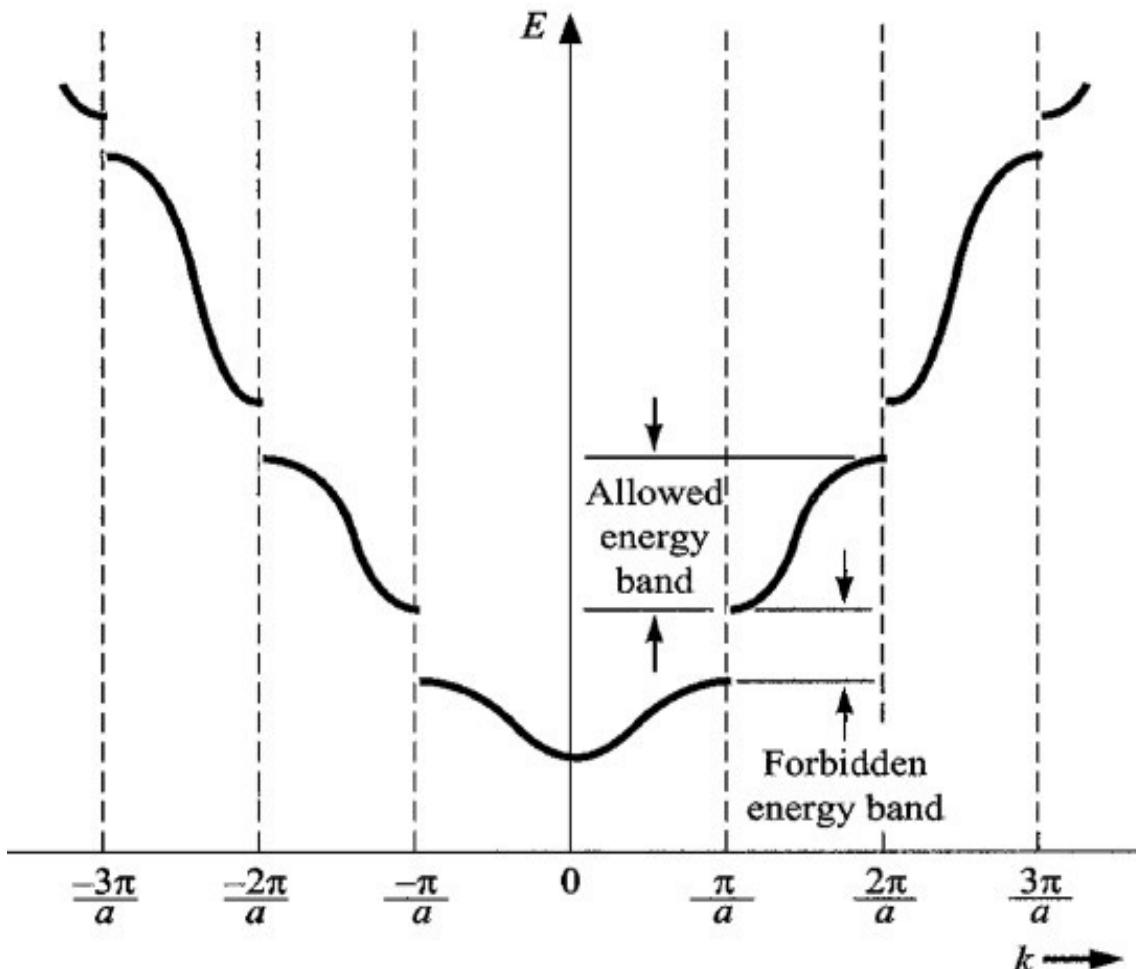


First 4 Brillouin Zones of the Two-dimensional lattice. <sub>21</sub>

# Energy bands in Solid:

Dispersion relation: Relation between E and k, extended zone scheme.....

When all the Bragg Planes and their associated Fourier components are included, energy levels are depicted by the shown set of curves.



- This representation of depicting the energy levels is called the Extended Zone Scheme.
- It is easier to identify the deviations from the free electron parabolic curves at the  $kx = n\pi/a$ .

# Energy bands in Solid:

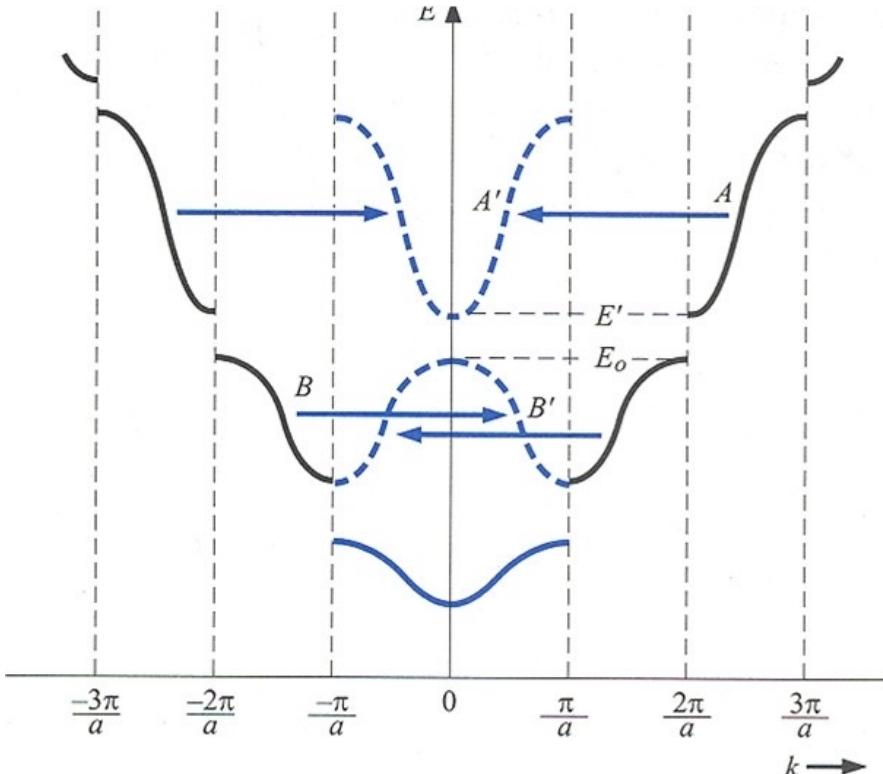
Dispersion relation: Relation between E and k, reduced zone scheme.....

As we know that energy is a periodic function of k.

$$\cos ka = \cos(ka + 2\pi) = \cos(ka - 2\pi) \quad k \rightarrow \left(k + \frac{2\pi n}{a}\right), (n \text{ is an integer})$$

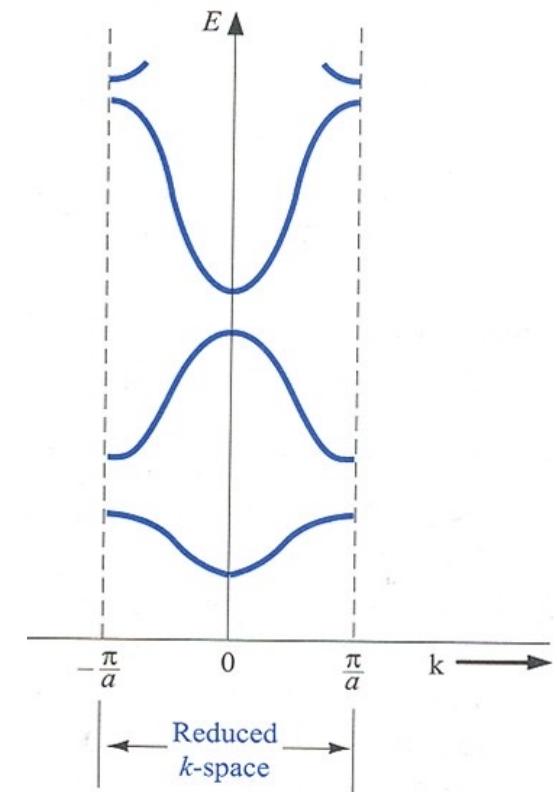
Hence, allowed energy ranges of the E-k diagram can be shifted by the  $n(2\pi/a)$ .

i.e., all k values can be limited to  $-\pi \leq ka \leq \pi$



Translating the wave vectors k by  $2\pi/a$ , into the first Brillouin zone, gives the **Reduced Zone Representation** for the E-k diagram.

So, we have, reduced wave vector, confined in the region **( $-\pi/a \leq k \leq \pi/a$ )**



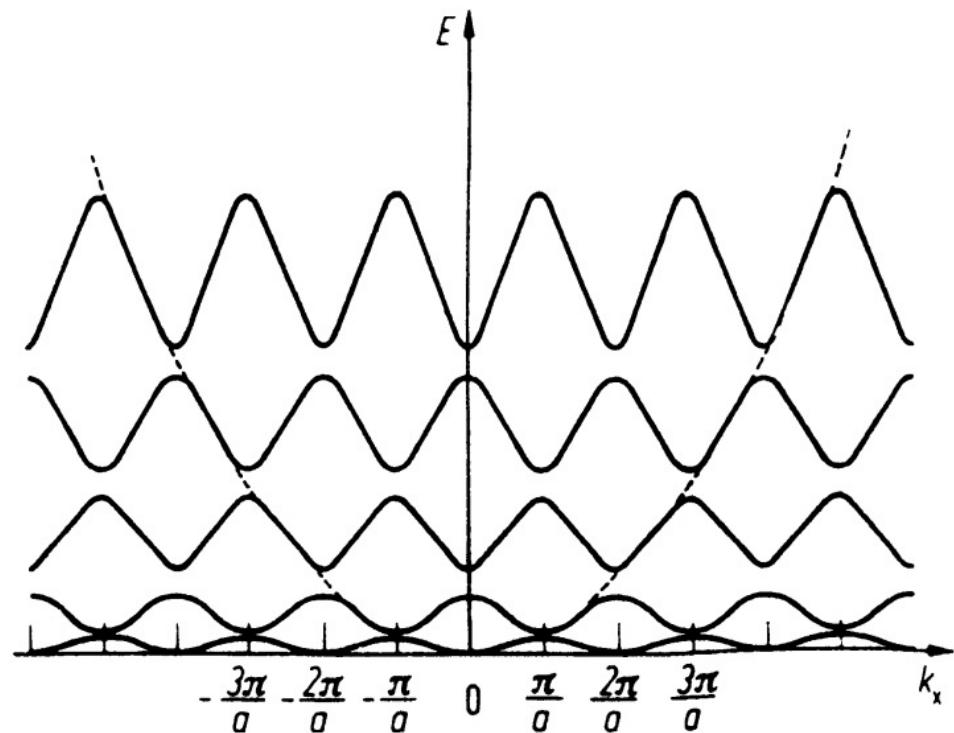
# Energy bands in Solid:

Dispersion relation: Relation between E and k,

Repeated Zone scheme

Self-reading material

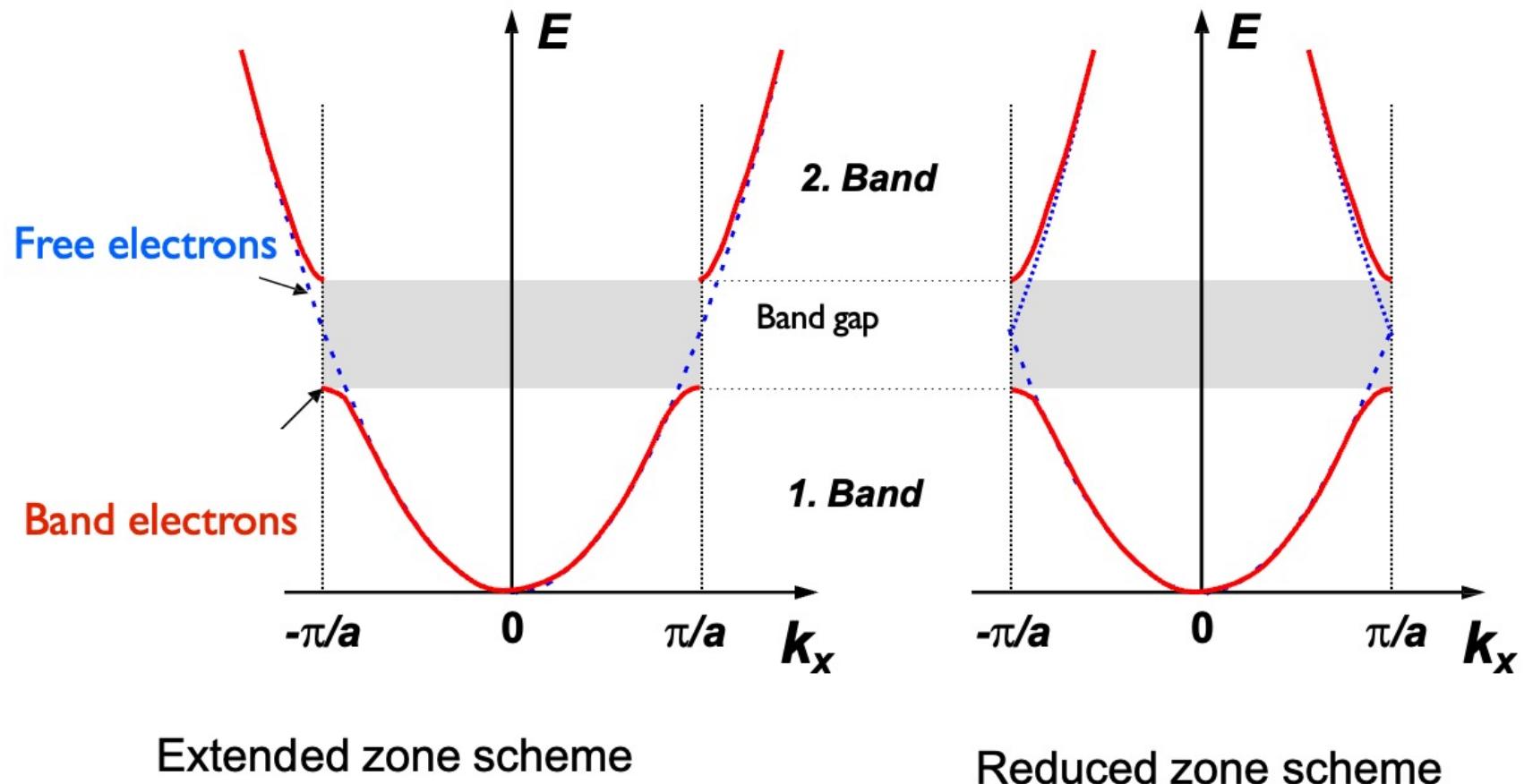
- ❖ Repeated zone scheme is the general representation for the energy levels.
- ❖ Takes into account the periodicity of the k-space, throughout all of the k-space.
- ❖ Particular level at k can be represented by any wave vector, differing from the k by reciprocal lattice vector, in the repeated Zone Scheme.
- ❖ The Band structure can be represented by the repetition of the dispersion curves over the whole k-space.
- ❖ Presents a way of labelling, which shows continuity with the free electron levels.



# Energy bands in Solid:

Dispersion relation: Relation between E and k,

Now let's see the difference between free electrons and band electrons



Extended zone scheme

Reduced zone scheme