

Subject Material science

Production of Courseware

 **-Content for Post Graduate Courses**

Paper No. : Crystallography & crystal growth

Module : Motion of electrons in periodic potential



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Description of Module	
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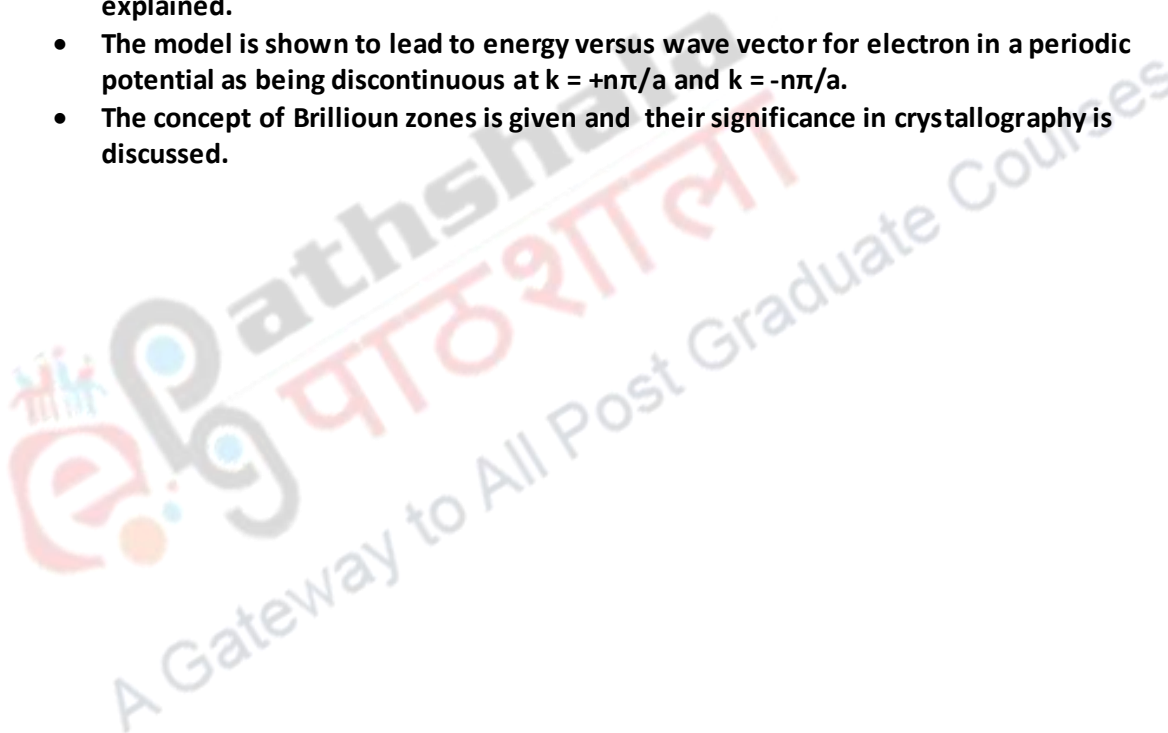
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LEARNING OBJECTIVES

- In this module motion of electrons in a periodic potential is described and discussed.
- Significance of translational periodicity in a crystalline solid is explained.
- Sommerfeld's model where electron is assumed to travel in a potential which is constant everywhere inside the metal is described.
- The concept of De Broglie wave or Sommerfeld waves or Bloch waves are given
- The kinetic energy of the electron is shown to be proportional to the square of wave number and the model leads to a relationship between energy and wave vector for a free electron that is parabolic.
- The Bloch theorem is explained.
- Kronig Penney model describing the motion of electrons in a periodic potential is explained.
- The model is shown to lead to energy versus wave vector for electron in a periodic potential as being discontinuous at $k = +n\pi/a$ and $k = -n\pi/a$.
- The concept of Brillouin zones is given and their significance in crystallography is discussed.



23.1 Motion of electrons in a periodic potential

Atoms in a crystalline solid are positioned at regular intervals because of which it exhibits periodicity in the arrangement of atoms in all dimensions. On account of this periodicity, it exhibits various types of symmetries and as such the atoms or molecules composing the solid are always related by some symmetry elements. Crystalline solids exhibit various types of physical properties which are structure sensitive. So, the physical behaviour of crystalline solids cannot be explained unless we have a sound background of crystallography. The symmetry elements have already been discussed in the previous sections. It is essential to describe the significance of symmetry in crystalline solids in so far as its relevance to the development of theory in the understanding of their physical properties is concerned. One of the physical properties is that of conduction in crystalline solids. Metals have been considered as being composed of atoms with their valence electrons roaming freely inside the solid. The classical theory considered these electrons as moving freely inside the solids like molecules of a gas in an enclosure. Drude and Lorentz theory assumed that these electrons behave like classical particles, move in a constant potential field and as such applied Maxwell Boltzmann statistics to understand and explain the behaviour of solids. However, it was modified by Sommerfeld by applying quantum mechanical concepts which could explain some of the physical properties of solids. The free electron theory, however, could not explain as to why some solids are good conductors like metals, some semiconductors or insulators. It is in situations of this type that crystallography in general and periodicity of crystals in particular becomes significant in the development of solid state theory.

23.2 Significance of translational periodicity.

We may select some function say $f(\mathbf{r})$ in the direct lattice space. It is well known that atoms exhibit translational periodicity in a crystalline solid and because of this fact, this function is also expected to be periodic in the sense that it should be the same at physically equivalent points in the crystal lattice. The periodicity of the function $f(\mathbf{r})$ could be expressed as:

$$f(\mathbf{r} + \mathbf{R}) = f(\mathbf{r}) \dots \dots \dots 23.1$$

for all points located at \mathbf{r} . The vector \mathbf{R} by virtue of translational periodicity is represented by:

$$\mathbf{R} = l\mathbf{a} + m\mathbf{b} + n\mathbf{c},$$

where l, m, n are integers and $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are translational periodicities along x, y and z directions. Let us start with a one-dimensional case for the sake of convenience and simplicity of mathematical treatment and represent equation 23.1 for one-dimensional case as:

$$f(x + a) = f(x) \dots \dots \dots 23.2$$

Since the function of equation 23.2 is periodic, it may be expressed in the form of Fourier series. The expression of equation 23.2, if expressed in the Fourier series form can be written as:

$$f(x) = \sum_n F_n e^{2\pi i n x / a} \dots \dots \dots 23.3$$

where n is an integer, a is period of the function.

We may express equation 23.3 as:

$$f(x) = \sum_{\phi} A_{\phi} e^{i\phi x}, \text{ where } |\phi_n| = n.2\pi/a \dots \dots \dots 23.4$$

The ϕ 's represent the reciprocal lattice vectors for the linear lattice in one-dimension:

The Fourier coefficients A_{ϕ} in equation 23.4 are given by:

$$A_{\phi} = 1/a \int_0^a f(x) e^{-i\phi x} dx \dots\dots\dots 23.5$$

In terms of the Fourier coefficient the L.H.S. of equation 23.2 may be expressed as:

$$\begin{aligned} f(x+a) &= \sum_{\phi} A_{\phi} e^{i\phi(x+a)} \dots\dots\dots 23.6 \\ &= \sum_{\phi} A_{\phi} e^{-i\phi x} \cdot e^{i\phi a} \end{aligned}$$

Making substitution for ϕ from equation 23.4

$$e^{i\phi a} = e^{in(2\pi/a)a} = e^{2in\pi} = 1,$$

or,
$$f(x+a) = \sum_{\phi} A_{\phi} e^{i\phi x} = f(x), \quad \text{using equation 23.4}$$

It shows that the function $f(x) = \sum_{\phi} A_{\phi} e^{i\phi x}$ is a function in the direct lattice space.

We may extend the expressions 23.2, 23.3 & 23.4 to the more general case by considering lattice periodicity along the three orthogonal axes which may be represented by \vec{a} , \vec{b} and \vec{c} . In that case, we have on using equation 23.1,

$$f(\vec{r} + \vec{R}) = f(\vec{r} + l\vec{a} + m\vec{b} + n\vec{c}) = f(\vec{r}) \dots\dots\dots 23.8$$

As in the case of one-dimensions, the expression for three-dimensions may be written as:

$$\vec{f}(\vec{r}) = \sum_{\vec{\phi}} B_{\vec{\phi}} e^{i(\phi_1 x + \phi_2 y + \phi_3 z)} \dots\dots\dots 23.9$$

Equation 23.9 may also be written in the form:

$$\vec{f}(\vec{r}) = \sum_{\vec{\phi}} B_{\vec{\phi}} e^{i\vec{A} \cdot \vec{r}} \dots\dots\dots 23.10$$

where $\vec{\phi}$ is the reciprocal lattice vector with components ϕ_1 , ϕ_2 and ϕ_3 along the x, y and z axes. As in the one-dimensional case above, here also:

$$e^{i\vec{\phi} \cdot \vec{R}} = e^{2\pi i n} = 1, \text{ which leads to the expression:}$$

$$\begin{aligned} f(\vec{r} + \vec{R}) &= \sum_{\vec{\phi}} A_{\vec{\phi}} e^{i\vec{\phi} \cdot (\vec{r} + \vec{R})} \\ &= \sum_{\vec{\phi}} A_{\vec{\phi}} e^{i\vec{\phi} \cdot \vec{r}} \cdot e^{i\vec{\phi} \cdot \vec{R}} \\ &= \sum_{\vec{\phi}} A_{\vec{\phi}} e^{i\vec{\phi} \cdot \vec{r}} \cdot 1 \\ &= \sum_{\vec{\phi}} A_{\vec{\phi}} e^{i\vec{\phi} \cdot \vec{r}} \\ &= f(\vec{r}), \end{aligned}$$

Which is in agreement with equation no. 23.1

23.3 Periodic Boundary Conditions & Wave Vector.

In the Sommerfeld's model, the free electrons are assumed to travel in a potential which is constant everywhere inside the metal. The electron is considered bound inside a cubical crystal of side say 'l'. The potential inside the crystal is assumed to be zero and the potential outside the crystal is infinity. The motion of the electrons is calculated by solving the Schrodinger equation:

$$\nabla^2 \psi + (8\pi^2 m/h^2) E \psi = 0$$

Instead of assuming that the electron wave function vanishes at $x=0$ and at $x= l$, it is considered more realistic to assume that the electron wave function is periodic with a period l . That means there must be integral number of wavelengths of the electron wave (de Broglie wave) in the distance ' l ' of the crystal. It can be expressed mathematically as:

$$\psi [(x+l), y, z] = \psi (x, y, z),$$

with similar expressions for y and z coordinates.

This is popularly known as periodic boundary condition, also known as cyclic boundary condition. It is an important concept in solid state physics.

Considering the fact that atoms in a crystal are arranged in an orderly manner consequently leading to periodicity of the lattice, one can express the periodic boundary condition for the electron wave function as:

$$\psi (x + a) = \psi (x),$$

where a is the lattice constant

The relation between the wave vector k and the energy E is given by :

$$K = \frac{2\pi (2mE)^{1/2}}{h}$$

The De Broglie waves, also known as Sommerfeld waves or Bloch waves in so far as motion of electrons in a crystalline solids is concerned, are expressed in terms of the wave vector.

We know $E = p^2/2m$,

Since $p = h/\lambda$, $E = h^2/2\lambda^2 m$

Substituting this expression for E in the above equation, we get:

$$K = 2\pi/\lambda$$

Therefore, k is a vector whose magnitude is $2\pi/\lambda$ and whose direction is the same as the direction of propagation of electron wave or the De Broglie wave (Sommerfeld waves or Bloch waves). It is also called wave vector or wave number. The kinetic energy of the electron is proportional to the square of the wave number and the relationship between E and k for a free electron is parabolic as shown in the figure 23.1

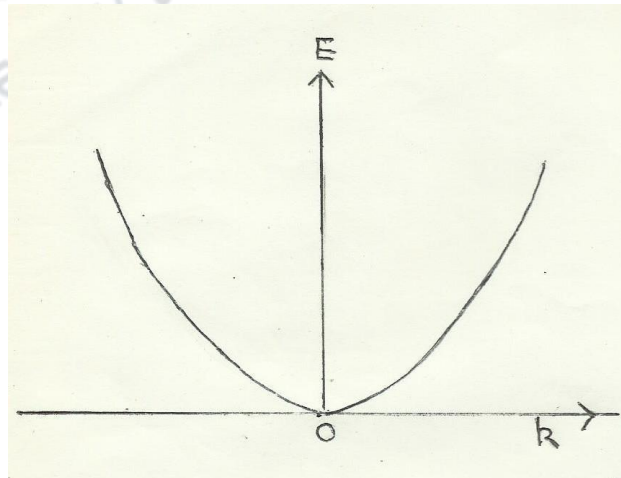


Figure 23.1: Plot of E Vs. wave vector k for a free electron

23.4 Bloch Theorem

What has been discussed above is regarding general functions with the periodicity of the lattice. It is general case of any such function. We shall now consider here a specific function of periodic potential. We know that the atoms or ions in a crystalline solid are positioned in regular periodic arrays and as such the electrostatic potential exhibited by them is also periodic which may be expressed as:

$$V(\vec{r} + \vec{R}) = V(\vec{r}) \dots\dots\dots 23.11$$

for all Bravais lattice vectors \vec{R} .

This potential assumes significance when we deal with an understanding of motion of electrons in a crystalline solid. The periodicity of the electrostatic potential V is of the order of 1\AA which is almost the same as the wavelength of an electron as assumed in the Sommerfeld's free electron model for motion of electrons in a crystalline solid. On account of this nearness between the sizes of the electron wavelength and the periodic potential, the use of quantum mechanics in understanding the motion of electrons in a crystalline solid becomes necessary. However, it is assumed here that the crystal is free from any imperfection which is rather an ideal concept. The real crystalline solid is not free from any imperfection because of which the periodicity breaks down in the region around imperfection. The imperfections influence the physical properties of crystalline solids. However, it is necessary to assume that we are dealing with an ideal crystalline solid in order to be able to develop the theory regarding physical properties of solids in the background of symmetries and periodicity in crystals. It is in this ideal crystal that we shall consider the motion of electrons as represented by one-electron potential $V(r)$ which follows the expression no. 23.11 for an ideal crystal, i.e.,

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

The motion of electrons is described by Schrodinger equation:

$$H\Psi = (-\hbar^2/2m\nabla^2 + V(\vec{r}))\Psi = E\Psi \dots\dots\dots 23.12$$

Where H stands for Hamiltonian, m is the effective mass of the electron; $\hbar = h/2\pi$ (where h represents Planck's constant), Ψ is the wave function, ∇^2 is the operator $\partial^2/\partial r^2$ and E is the total energy). In order to describe the motion of the electrons in crystalline solid, equation 23.12 is required to be solved with the periodic potential of an ideal crystal lattice $V(\vec{r} + \vec{R}) = V(\vec{r})$. The solution of this equation is given by:

$$\psi_k(\vec{r}) = V_k(\vec{r}) e^{i\vec{k}\cdot\vec{r}} \dots\dots\dots 23.13$$

$$\text{Where } V_k(\vec{r} + \vec{R}) = V_k(\vec{r}) \dots\dots\dots 23.14$$

Functions of the type of equation 23.13 are called Bloch functions, k the wave vector ($= \lambda/2\pi$). It was Bloch who in 1928 showed that the solutions are of the form as given by equation 23.13.

From equations 23.13, 23.14, we have:

$$\psi_k(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}} \cdot \psi_k(\vec{r}) \dots\dots\dots 23.15$$

Bloch function can also be expressed by the following equation by selecting Eigen states of H in such a way that corresponding to each Ψ there is a wave vector k so that:

$$\psi(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi(\vec{r}) \dots\dots\dots 23.16$$

for all possible Bravais lattice vectors \vec{R} .

Referring to Schrodinger equation no. 23.12, its solution is given by:

$$\psi(\vec{r}) = f(\vec{r}) u(\vec{r}) \dots \dots \dots 23.17$$

where $u(\vec{r})$ is a periodic function . Since the potential $u(\vec{r})$ is periodic, all the quantities associated with the electron are also periodic. The quantity $|\psi(\vec{r})|^2$ has also to be periodic provided $f(\vec{r})$ satisfies the condition :

$$|f(\vec{r} + \vec{R})|^2 = |f(\vec{r})|^2 \dots \dots \dots 23.18$$

The solution of this equation is expressed to be of this form:

$$\psi(\vec{r}) = u(\vec{r}) e^{i\vec{k}\vec{r}} \dots \dots \dots 23.19$$

This equation represents Bloch theorem.

If one considers the periodicity of atoms in the crystalline solid, it is obvious that the electron moves in the field of periodic potential. For example, figure 23.2 indicates the qualitative form of the electrostatic potential energy of conduction electrons in the field of positive ion cores of monatomic linear lattice. The ion cores left out by conduction electrons are positively charged. The potential energy of an electron in the field of these positive ion cores is negative.

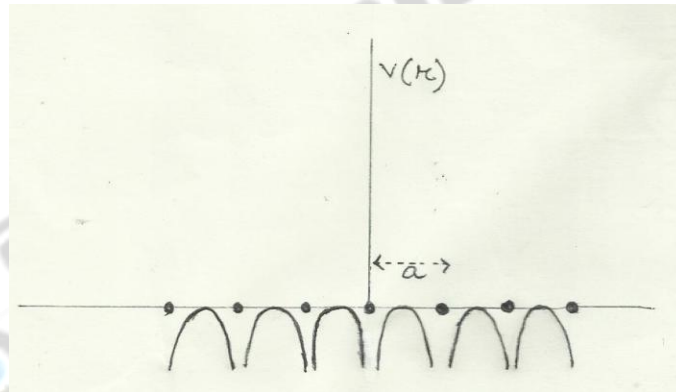


Figure 23.2: Variation of electrostatic potential energy of electrons in the field of ions monoatomic linear lattice

23.5 Kronig-Penney Model

Here, we consider the motion of electrons in a simple one-dimensional periodic potential and use Bloch theorem to understand about the allowed and forbidden electronic energy bands in a one-dimensional lattice. For this purpose we shall consider Kronig-Penney model in which the potential energy variation is assumed to be of the form as shown in figure 23.3. It shows an ideal periodic square well potential used in Kronig-Penney Model to illustrate the general characteristics of the quantum behaviour of the electrons in periodic lattices.

The essential features of the behaviour of electrons in a periodic potential may be studied by considering the model first discussed by Kronig and Penney (1931) and so is named after them. In this model, it is assumed that the potential energy of an electron moving in one-dimensional perfect crystal lattice is represented in the form of a periodic array of rectangular wells as indicated in the figure; the period of potential being $(a+b)$. In regions ranging $0 < x < a$ a potential energy is assumed to be zero whereas in the regions ranging $-b < x < 0$, the potential energy is V_0 . Each of the potential energy may be treated as a rough approximation for the potential in the vicinity of an atom. With this infinite one-dimensional rectangular well potential, it is possible to obtain an exact solution of the Schrodinger equation.

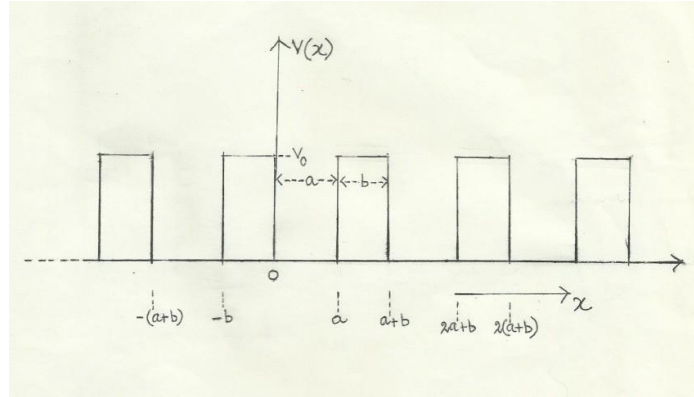


Figure 23.3: A one-dimensional periodic potential of periodicity $(a+b)$ for the Kronig-Penney model

Although it is somewhat an idealized periodic potential which in reality is just a crude approximation to what in reality exists in the real crystal, it is nevertheless very useful because it serves the purpose of illustrating the most explicit way with the help of which several important characteristic features of the quantum behaviour of electrons in a periodic lattice can be described.

As shown in figure 23.3:

$$\left. \begin{array}{l} V = 0 \quad \text{for } 0 < x < a \\ V = V_0 \quad \text{for } -b < x < 0 \end{array} \right\} \dots\dots\dots 23.20$$

$$\text{And } V(x + a + b) = V(x) \dots\dots\dots 23.21$$

So, the periodicity of the potential as represented by the figure is $(a + b)$. The Schrodinger equations for the two regions are given by:

$$d^2 \psi / dx^2 + (2m/\hbar^2) E \psi(x) = 0 \quad \text{for } 0 < x < a \dots\dots\dots 23.22$$

$$d^2 \psi / dx^2 + (2m/\hbar^2)(E - V_0) \psi(x) = 0 \quad \text{for } -b < x < 0 \dots\dots\dots 23.23$$

Here, it may be assumed that the energy E of the electrons is smaller than V_0 i.e., $E < V_0$. We also put two real quantities α and β by:

$$\alpha^2 = 2mE/\hbar^2 \text{ and } \beta^2 = \frac{2m(V_0 - E)}{\hbar^2} \dots\dots\dots 23.24$$

$E < V_0$, because α and β are real quantities.

If $E > V_0$ then β will be imaginary.

The Schrodinger equation 23.22 and 23.23 may be written as :

$$d^2 \psi / dx^2 + \alpha^2 \psi(x) = 0 \quad \text{for } 0 < x < a \dots\dots\dots 23.25$$

$$\& \quad d^2 \psi / dx^2 - \beta^2 \psi(x) = 0 \quad \text{for } -b < x < 0 \dots\dots\dots 23.26$$

From Bloch theorem we know that the solution of wave equation for a periodic potential will be of the form of a plane wave modulated with the periodicity of the lattice of the form:

$$\psi(x) = e^{ikx} \cdot U_k(x) \dots\dots\dots 23.27$$

Where $u_k(x)$ is the periodic function in x with the period $(a+b)$.

$$\text{Or,} \quad d\psi(x)/dx = ik e^{ikx} u_k(x) + e^{ikx} du_k/dx \dots\dots\dots 23.28$$

$$\begin{aligned}
 d^2 \psi / dx^2 &= ik \cdot ike^{ikx} u_k(x) + ike^{ikx} du_k/dx + ike^{ikx} du_k/dx + e^{ikx} d^2 u_k/dx^2 \\
 &= -k^2 e^{ikx} u_k(x) + ike^{ikx} du_k/dx + ike^{ikx} du_k/dx + e^{ikx} d^2 u_k/dx^2 \\
 &= -k^2 e^{ikx} u_k(x) + 2ik e^{ikx} du_k/dx + e^{ikx} d^2 u_k/dx^2 \dots\dots\dots 23.29
 \end{aligned}$$

Substituting from equations 23.27 and 23.29 in equation no. 23.25 we get:

$$-k^2 e^{ikx} u_k(x) + 2ik e^{ikx} du_k/dx + e^{ikx} d^2 u_k/dx^2 + \alpha^2 e^{ikx} u_k(x) = 0 \text{ for } 0 < x < a$$

For the sake of convenience let us drop the subscripts and write the above expression as:

$$d^2 u/dx^2 + 2ik du/dx + (\alpha^2 - k^2)u = 0 \text{ for } 0 < x < a \dots\dots\dots 23.30$$

Similarly, substituting equations 23.27 and 23.29 in equation 23.26, we have:

$$-k^2 e^{ikx} u + 2ike^{ikx} du/dx + e^{ikx} d^2 u/dx^2 - \beta^2 e^{ikx} u = 0$$

$$\text{Or, } d^2 u/dx^2 + 2ik du/dx - (\beta^2 + k^2) u = 0 \text{ for } -b < x < 0 \dots\dots\dots 23.31$$

Representing the value of $u(x)$ in the interval $0 < x < a$ by $u_1(x)$ and in the interval $-b < x < 0$ by $u_2(x)$, equation 23.30 and 23.31 may be written as :

$$d^2 u_1/dx^2 + 2ik du_1/dx + (\alpha^2 - k^2) u_1 = 0 \text{ for } 0 < x < a \dots\dots\dots 23.32$$

$$d^2 u_2/dx^2 + 2ik du_2/dx - (\beta^2 + k^2) u_2 = 0 \text{ for } -b < x < 0 \dots\dots\dots 23.33$$

The differential equations 23.32 and 23.33 are easily solved by the standard procedure as follows:

In solving these differential equations, it is assumed that the solution is of the following form :

$$\begin{aligned}
 &u = e^{mx} \\
 \text{So that } &\left. \begin{aligned} du/dx &= m e^{mx} \\ d^2 u/dx^2 &= m^2 e^{mx} \end{aligned} \right\} 23.34 \\
 \&
 \end{aligned}$$

Substituting it in equation no. 23.32, we get :

$$m^2 e^{mx} + 2ik m e^{mx} + (\alpha^2 - k^2) e^{mx} = 0 \text{ for } 0 < x < a$$

Or,

$$\begin{aligned}
 m^2 + 2ik m + (\alpha^2 - k^2) &= 0 \\
 m &= \frac{-2ik \pm \sqrt{4k^2 - 4(\alpha^2 - k^2)}}{2} \\
 &= \frac{-2ik \pm \sqrt{-4\alpha^2}}{2} \\
 &= \frac{-2ik \pm 2i\alpha}{2} \\
 &= -ik \pm i\alpha
 \end{aligned}$$

i.e., $m_1 = i(\alpha - k)$ & $m_2 = -i(\alpha + k)$,

Hence, the general solution of equation 23.32 is:

$$\begin{aligned}
 u_1 &= Ae^{m_1 x} + Be^{m_2 x} \\
 &= Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x} \text{ for } 0 < x < a \dots\dots\dots 23.35
 \end{aligned}$$

Following a similar procedure and substituting values of equation 23.34 in equation no. 23.33, we get:

$$\begin{aligned}
 m^2 e^{mx} + 2ik m e^{mx} - (\beta^2 + k^2) e^{mx} &= 0 \text{ for } -b < x < 0, \\
 \text{or } m^2 + 2ik m - (\beta^2 + k^2) &= 0
 \end{aligned}$$

$$\begin{aligned}
 m &= \frac{-2ik \pm \sqrt{4k^2 + 4(\beta^2 + k^2)}}{2} \\
 &= \frac{-2ik \pm 2\beta}{2}
 \end{aligned}$$

$$= -ik_{\pm} \beta$$

$$\text{i.e., } m_1 = (\beta - ik) ;$$

$$m_2 = -(\beta + ik)$$

Hence, the general solution for equation 23.33 is:

$$u_2 = C e^{m_1 x} + D e^{m_2 x},$$

$$\text{Or } u_2 = C e^{(\beta - ik)x} + D e^{-(\beta + ik)x} \quad \text{for } -b < x < 0, \dots\dots\dots 23.36$$

Where A, B, C, D are arbitrary constants. These constants are chosen in such a manner that the following four conditions are satisfied.

$$u_1(x)_{x=0} = u_2(x)_{x=0} \dots\dots\dots 23.37(a)$$

[One could also write it as $u_1(0) = u_2(0)$]

$$(du_1/dx)_{x=0} = (du_2/dx)_{x=0} \dots\dots\dots 23.37(b)$$

$$\& u_1(x)_{x=a} = u_2(x)_{x=-b} \dots\dots\dots 23.38(a)$$

[One could also write it as $u_1(a) = u_2(-b)$]

$$(du_1/dx)_{x=a} = (du_2/dx)_{x=-b} \dots\dots\dots 23.38b$$

The first two conditions under equations 23.37(a) and 23.37(b) are imposed because of the requirements of continuity of the wave functions. Because of continuity at $x=0$, the two wave functions and their derivatives must have the same value at $x=0$. The other two conditions viz., 23.38(a) & 23.38(b) are required because of the periodicity of $u_k(x)$. Thus, the function $u_k(x)$ should have the same value at $x=a$ and $x=-b$.

Imposition of the first two conditions 23.37(a) & 23.37 (b) in equations 23.34 and 23.36 leads to:

$$U_1(x)_{x=0} = A e^0 + B e^0 = u_2(x)_{x=0} = C e^0 + D e^0.$$

$$\text{Or, } A + B = C + D \dots\dots\dots 23.39$$

$$\text{and } i(\alpha - k)A - i(\alpha + k)B = (\beta - ik)C - (\beta + ik)D \dots\dots\dots 23.40$$

The derivation of equation no.23.40 is given as under:

From equation 23.35, we have:

$$du_1/dx = A e^{i(\alpha-k)x} \{ i(\alpha-k) \} + B e^{-i(\alpha+k)x} \{ -i(\alpha+k) \}$$

$$(du_1/dx)_{x=0} = i(\alpha - k)A - i(\alpha + k)B$$

Similarly, from equation 23.36, we have:

$$du_2/dx = C e^{(\beta-ik)x} \cdot (\beta - ik) + D e^{-(\beta+ik)x} \{ -(\beta + ik) \}$$

$$(du_2/dx)_{x=0} = (\beta - ik)C - (\beta + ik)D \quad (du_1/dx)_{x=0} =$$

$$(du_2/dx)_{x=0}$$

$$\text{So, } i(\alpha - k)A - i(\alpha + k)B = (\beta - ik)C - (\beta + ik)D.$$

Equation 23.40 is thus derived here. Moving forward we have:

Imposition of the next two conditions 23.38 (a & b) in equations 23.34 and 23.36, we have:

$$(u_1)_{x=a} = A e^{i(\alpha-k)a} + B e^{-i(\alpha+k)a}$$

$$(u_2)_{x=-b} = C e^{-(\beta-ik)b} + D e^{(\beta+ik)b}$$

$$\text{So, } A e^{i(\alpha-k)a} + B e^{-i(\alpha+k)a} = C e^{-(\beta-ik)b} + D e^{(\beta+ik)b} \dots\dots\dots 23.41.$$

$$\text{and, } i(\alpha - k)A e^{i(\alpha-k)a} - i(\alpha+k)B e^{-i(\alpha+k)a} = (\beta - ik)C e^{-(\beta-ik)b} - (\beta+ik)D e^{(\beta+ik)b} \dots\dots\dots 23.42$$

Thus application of 23.37(a, b) on equation no. 23.34 and 23.36 leads to four linear homogeneous equations in the constants A, B, C and D. The coefficients A, B, C and D can thus be determined as the solution of a set of these four simultaneous linear homogeneous equations in these quantities. There is no solution other than $A=B=C=D=0$, unless the determinant of the coefficients vanishes. That means these four equations 23.39 to 23.42 have a solution only if the determinant of the coefficients of A, B, C, and D vanishes.

That means:

$$\begin{vmatrix} 1 & 1 & -1 & -1 \\ i(\alpha-k) & -i(\alpha+k) & -(\beta-ik) & (\beta+ik) \\ e^{i(\alpha-k)a} & e^{-i(\alpha+k)a} & e^{-(\beta-ik)b} & e^{(\beta+ik)b} \\ i(\alpha-k)e^{i(\alpha-k)a} & -i(\alpha+k)e^{-i(\alpha+k)a} & -(\beta-ik)e^{-(\beta-ik)b} & (\beta+ik)e^{(\beta+ik)b} \end{vmatrix} = 0 \quad \dots\dots 23.43$$

On expansion of this determinant, one can show after rigorous and straight forward algebra that equation 23.43 can be expressed as:

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh \beta b \sin \alpha a + \cosh \beta b \cos \alpha a = \cos k(a+b) \dots\dots\dots 23.44$$

In order to obtain a more convenient equation, Kronig and Penney considers the case for which the potential barriers become delta functions i.e., $V_0 \rightarrow \infty$ & $b \rightarrow 0$ but the product $V_0 b$ or $\beta^2 b$ remains finite. Such a function is known as delta function. Under these circumstances equation 23.44 reduces to:

$$\frac{\beta^2 b}{2\alpha} \sin \alpha a + \cos \alpha a = \cos ka \dots\dots\dots 23.45$$

It is because when $b \rightarrow 0$ $\sinh \beta b \rightarrow \beta b$ and $\cosh \beta b \rightarrow 1$ and because $E < V_0$ and $V_0 \rightarrow \infty$ so E is very small, α^2 may be neglected but β cannot be neglected on account of involvement of the term $(V_0 - E)$.

Equation 23.45 can be further expressed as:

$$\frac{\beta^2 ab}{2\alpha a} \sin \alpha a + \cos \alpha a = \cos ka$$

Let us put $\beta^2 ab/2 = P$ in the above equation, we get:

$$P \frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \dots\dots\dots 23.46$$

The quantity P is defined by the expression:

$$P = \beta^2 ab/2 = \frac{2mV_0 ab}{2\hbar^2} = \frac{mV_0 ab}{\hbar^2}$$

It means that the solutions for the wave functions exist only if equation 23.46 is satisfied. We are now in a position to define the quantity P . Since $V_0 \rightarrow \infty$ i.e., P is a measure of the “area” $V_0 b$ of the potential barrier. The physical significance of this quantity is that if P is increased, the area of the potential barrier is increased and so a given electron is bound more strongly to a particular potential well. When $P \rightarrow 0$, the potential barrier becomes very weak which in other words means that electrons are free electrons

When $P \rightarrow 0$ i.e., for free electrons, expression at 23.46 can be written as:

$$\cos \alpha a = \cos ka$$

$$\alpha a = ka$$

$$\alpha = k$$

Or

From equation 23.24, we know that: $\alpha^2 = 2mE/\hbar^2$

So,

$$\alpha^2 = 2mE/\hbar^2 = k^2,$$

So,

$$E = \hbar^2 k^2 / 2m = \hbar^2 k^2 / 8\pi^2 m \quad (\text{on substitution for } \hbar = h/2\pi) \dots\dots\dots 23.47$$

The expression at 23.47 resembles the result as was obtained by considering the Sommerfeld model of metals.

A plot of the function $(P \sin \alpha a / \alpha a + \cos \alpha a)$ when drawn against αa for $P = 3\pi/2$ appears as shown in figure 23.4.

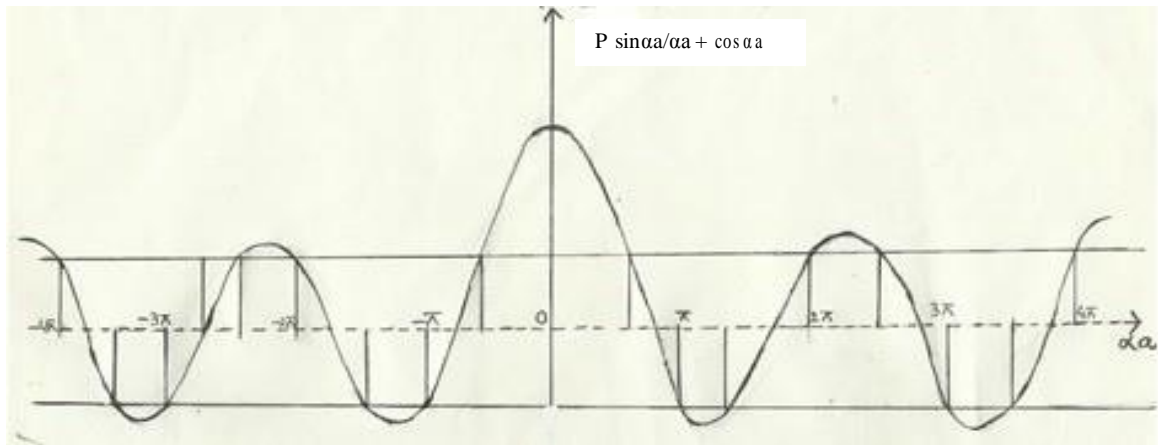


Figure 23.4: Variation of function $(P \sin \alpha a / \alpha a + \cos \alpha a)$ with αa for $P = 3\pi/2$. The allowed values of energy are given by those ranges of $\alpha = (2mE/\hbar^2)^{1/2}$ for which the function lies between -1 and $+1$

We know that $\alpha = (2mE/\hbar^2)^{1/2}$ which suggests that α^2 is proportional to energy E . The abscissa is a measure of energy and in order to calculate the energy represented by the function at a point, the value of αa corresponding to that point is determined. The values of αa which satisfy equation 23.46 are found out by drawing a line parallel to αa axis at a distance $\cos ka$ from it. If ka is continuously varied from 0 to π , i.e., $\cos ka$ from $+1$ to -1 , one is able to find all possible values of αa and hence that of energy. It is important to realize that the right hand side of equation 23.46 can accept only values between -1 and $+1$ (i.e., ka continuously varying from 0 to π and $\cos ka$ from $+1$ to -1) as indicated by the horizontal lines in the figure. Therefore, the condition as imposed by equation 23.46 can be met only for values of αa for which the L.H.S. lies between ± 1 .

In figure 23.4, we have plotted the left side of equation 23.46 as a function of αa , for the arbitrary value $P=3\pi/2$. As the cosine term on the right side can have values between $+1$ and -1 , only those values of αa are allowed for which the left side falls in this range. The allowed ranges of αa are indicated in the figure, and through the relation $\alpha = (2mE/\hbar^2)^{1/2}$ they correspond to allowed ranges of the energy E . The boundaries of the allowed ranges of αa correspond to the values $n\pi/a$ for k .

In figure 23.4, the function: $f(\alpha a) = P \sin \alpha a / \alpha a + \cos \alpha a$ is plotted against αa . Obviously, for k to be real $|f(\alpha a)|$ should be less than 1 . Those values of E for which $|f(\alpha a)| > 1$ will be forbidden. Those values of E for which $f(\alpha a) \leq 1$ will correspond to allowed values of energy. It may also be noted that if k is replaced by $k+2n\pi/a$ (where $n = \pm 1, \pm 2, \pm 3, \dots$), the right hand side of equation 23.46 will remain the same. That means one cannot uniquely determine the value of k . It is usually restricted to the domain:

$$-\pi/a \leq k \leq +\pi/a$$

which is known as the first Brillouin zone.

The $E - k$ diagram showing the allowed and forbidden energy bands are shown in figures 23.5 & 23.6. At the zone boundaries ($k = \pm \pi/a$) the Bloch wave function satisfies the Bragg condition and the group velocity $[(1/\hbar)dE/dk]$ is zero which corresponds to a standing wave.

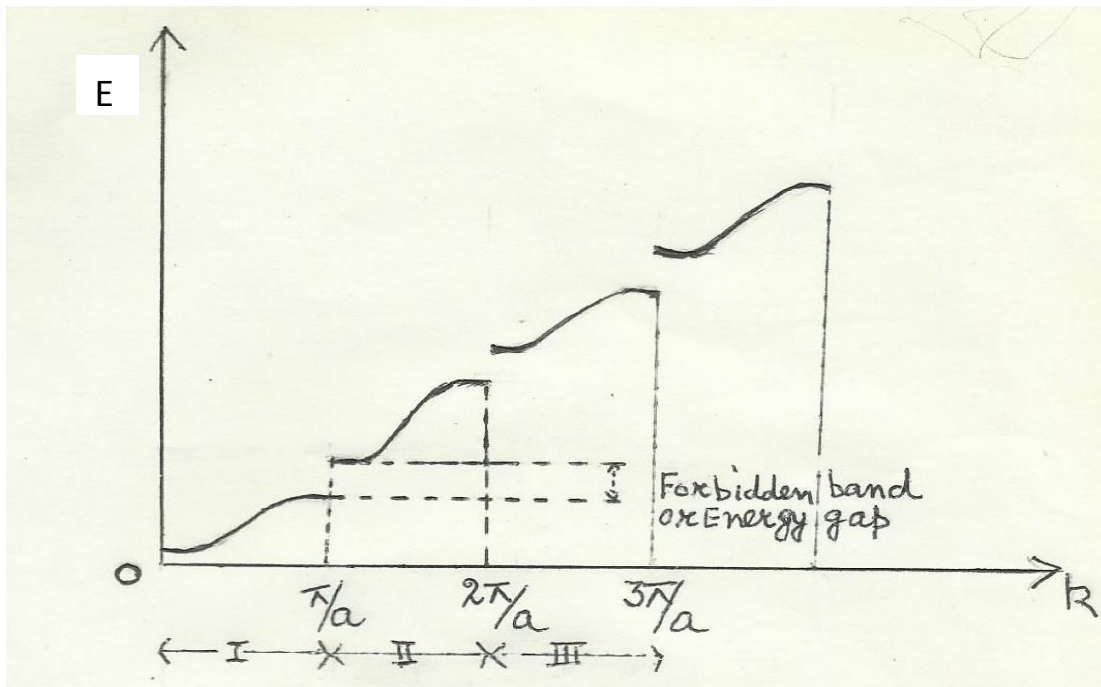


Figure 23.5: E Vs. wave vector K for electron in a periodic potential

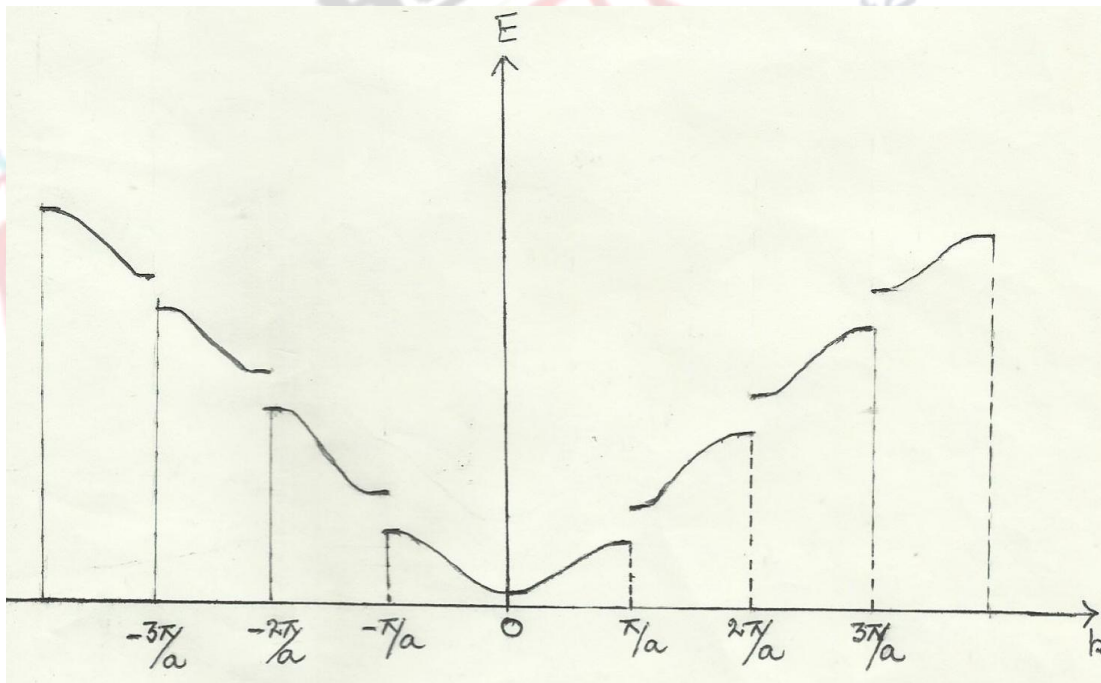


Figure 23.6: Full curve of E Vs. wave vector k showing discontinuities at $k = \pm n\pi/a$ (where $n = 1, 2, 3, \dots$)

Let us analyse the details of what may be concluded from the figure drawn on the basis of equation 23.46.

(i) There are infinite numbers of allowed energy bands separated by intervals in which there are no energy levels. Such regions are known as forbidden regions.

The boundaries of the allowed ranges of ka correspond to the values for which $\cos ka = \pm 1$

That happens if $ka = n\pi$, or $k = n\pi/a$, where $n = 1, 2, 3, \dots$.

(ii) The first term in the expression for $f(\alpha a)$ i.e., $P \sin \alpha a / \alpha a$ decreases on an average with increasing αa . It suggests that the width of the allowed energy bands increases and the forbidden regions get narrower as αa increases or as energy increases.

(iii) As P increases, the width of the allowed band decreases. Increase in the value of P means the increase in “binding energy” of the electrons. In the extreme case, when P is infinite, the allowed energy bands get infinitely narrower, consequently the energy spectrum becomes line spectrum and are independent of k .

If $P \rightarrow \infty$, the allowed energy ranges of αa reduce to points given by:

$$\begin{aligned} \alpha a &= \pm n\pi \\ \alpha &= \pm n\pi/a ; \\ \text{or } \alpha^2 &= n^2 \pi^2 / a^2, \text{ Substituting} \\ \text{for } \alpha &= (2mE/\hbar^2)^{1/2} \\ \alpha^2 &= 2mE/\hbar^2 = n^2 \pi^2 / a^2 \\ \text{or, } E &= \frac{n^2 \pi^2 \hbar^2}{2ma^2} \dots\dots\dots 23.48 \end{aligned}$$

It shows that E is independent of k .

The energy levels in this case are discrete and the electron is completely bound. It is trapped within the potential wells and moves only in one cell of width ‘ a ’.

From the discussion on analysis of equation 23.46, we come to the conclusion that in the one-dimensional problem for the limiting case, the spectrum of energy values that are permitted is found to be consisting of continuous regions separated by finite intervals. By varying the quantity P (i.e., $V_0 b$) from zero to infinity, we move from the case of free electrons to that of bound electrons and so are able to study the changes in the allowed and forbidden ranges of energy and the wave function.

We may also use equation 23.46 to study the variation of energy E with the wave number k . The variation is as shown in figures 23.5 & 23.6. From these figures one arrives at the following conclusions:

- (i) The energy spectrum of the electrons consists of a number of allowed energy bands separated by forbidden regions.
- (ii) The width of the allowed energy bands increases with increase of energy values.
- (iii) If V_0 is made zero, the E versus k curve becomes a continuous parabola, the same as that of free electrons (see figure 23.1)
- (iv) There are discontinuities in the E versus k curve which occur for $k = n\pi/a$, where $n = \pm 1, \pm 2, \pm 3$. The range of allowed values of k between $-\pi/a$ and $+\pi/a$ constitutes the first Brillouin zone. The range of values of k between $-\pi/a$ and $-2\pi/a$ and between $+\pi/a$ and $+2\pi/a$ constitutes the second Brillouin zone.

The energy E is represented as function of k for $P = 3\pi/2$. Analyzing the curve of E against k further regarding the discontinuities in the E versus k at $k = n\pi/a$, where $n = 1, 2, 3, \dots$. The k -values define the boundaries of the first (I), second (II), third (III) and so on Brillouin zones. Figure 23.5 shown here provides only half of the E - k curve; the first zone in fact extends from $k = -\pi/a$ to $+\pi/a$. Similarly, the second Brillouin zone is composed of two parts; the one extending from $+\pi/a$ to $+2\pi/a$ as shown in the figure and the other part extending from $-\pi/a$ to $-2\pi/a$. Figure 23.6 represents the full E - k curve. We may call each position of the curve as a band. The curve of E - k has the following characteristics:

- 1. The curves are horizontal at the top and bottom.
- 2. The curves are parabolic near the top and the bottom having curvatures in opposite directions.
- 3. d^2E/dk^2 is positive in the lower portion of the band and negative in the upper portion of the band.

Let us consider a linear lattice of lattice constant a . According to free electron theory E versus wave vector k is continuous as shown in figure 23.1. The low energy part of the band structure is shown in figure 23.7 for electrons which are nearly free but with an energy gap at wave vector $k = \pm\pi/a$ resulting into creation of forbidden gap as a result of our assumption that electron is moving in a periodic potential (unlike in the case of free electron theory where electron is assumed to be moving

in a constant potential field). The curve of E versus wave vector k for an electron in a monatomic linear lattice with lattice constant a appears as shown in figure 23.7. The energy gap E_g is associated with the first Bragg reflection at $k = \pm\pi/a$.

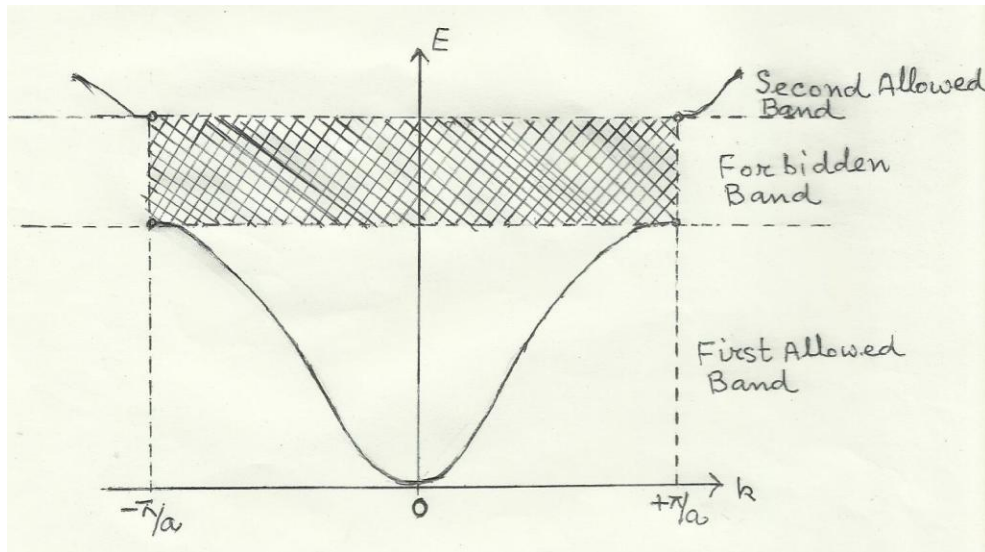


Figure 23.7: E as a function of wave vector k for an electron in a monatomic linear lattice of lattice constant a . The forbidden band associated with the energy gap E_g is shown. The band gap is associated with the first Bragg reflection at $k = \pm\pi/a$.

The Bragg condition in terms of the reciprocal lattice implies that:

$$(\vec{K} + \vec{G})^2 = \vec{K} \cdot \vec{K} + \vec{G} \cdot \vec{G} + 2\vec{K} \cdot \vec{G} = k^2$$

for diffraction of a wave vector k , if taken in one dimension becomes on expanding the dot product and simplifying

$$2\vec{K} \cdot \vec{G} + G^2 = 0 \quad \dots\dots\dots 23.49$$

where \vec{G} is 2π times a vector from the origin to a lattice point of the reciprocal lattice and \vec{k} is a vector of magnitude $2\pi/\lambda$ along the direction of the incident x-ray beam. Equation 23.49 is the vector form of the Bragg equation.

In one dimension equation 23.49 becomes:

$$k = \pm \frac{1}{2} G = \pm n\pi/a, \quad \dots\dots\dots 23.50$$

Where $G = \pm 2n\pi/a$ is the reciprocal lattice vector.

The first reflection and the first energy gap results at $k = \pm\pi/a$; other energy gaps result for other values of integer in equation 23.50.

The reflection at the wave vector $k = \pm\pi/a$ takes place because the wave reflected from one atom in the linear lattice meets constructive interference with the wave from a nearest neighbour atom. The phase difference between the two reflected waves is $\pm 2\pi$ for these two values of k . The region in the k -space between $-\pi/a$ and $+\pi/a$ is called the first Brillouin zone.

23.6 Brillouin Zones

Kronig-Penney model has shown that the energy discontinuities in the monatomic one dimensional lattice result when the wave vector satisfies the relation:

$$k = n\pi/a, \text{ where } n \text{ is an integer which may be positive or negative.}$$

In the one-dimensional monatomic lattice a line representing the value of k is divided up by the energy discontinuities into segments of length π/a as shown in figure 23.8

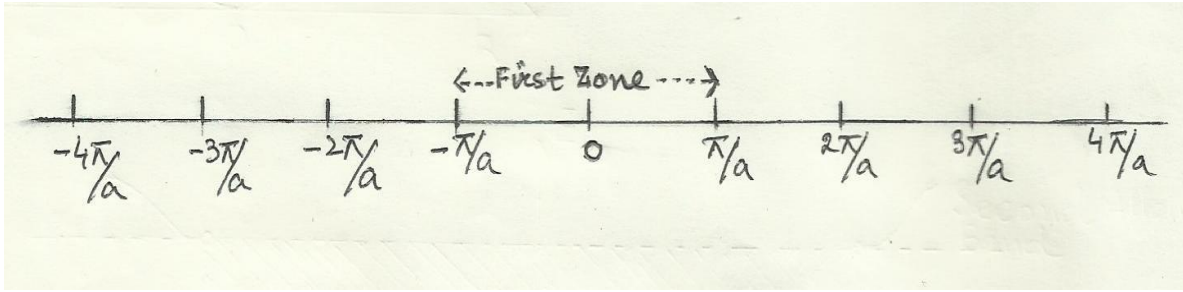


Figure 23.8: Line representing the value of k for one-dimensional monatomic lattice is shown divided into segments of length $\pm n\pi/a$ ($n=1, 2, 3, \dots$)

These line segments are known as Brillouin zones. The segment $-\pi/a < k < \pi/a$ represents first Brillouin zone; the two segments $-2\pi/a < k < -\pi/a$ and $\pi/a < k < 2\pi/a$ form the second Brillouin zone and so on. Brillouin zones are characteristic of a particular crystal structure and as such each crystal structure form its own characteristic Brillouin zones.

Let us take the example of two dimensional simple square lattice as shown in figure 23.9. The first Brillouin zone for this lattice will be a square ABCD whose boundaries are defined by:

$$k_x = \pm\pi/a; \quad k_y = \pm\pi/a$$

Similarly, the boundaries of the second Brillouin zone are defined by:

$$\pm k_x = \pm k_y = \pi/a \text{ as represented by the diagram EFGH.}$$

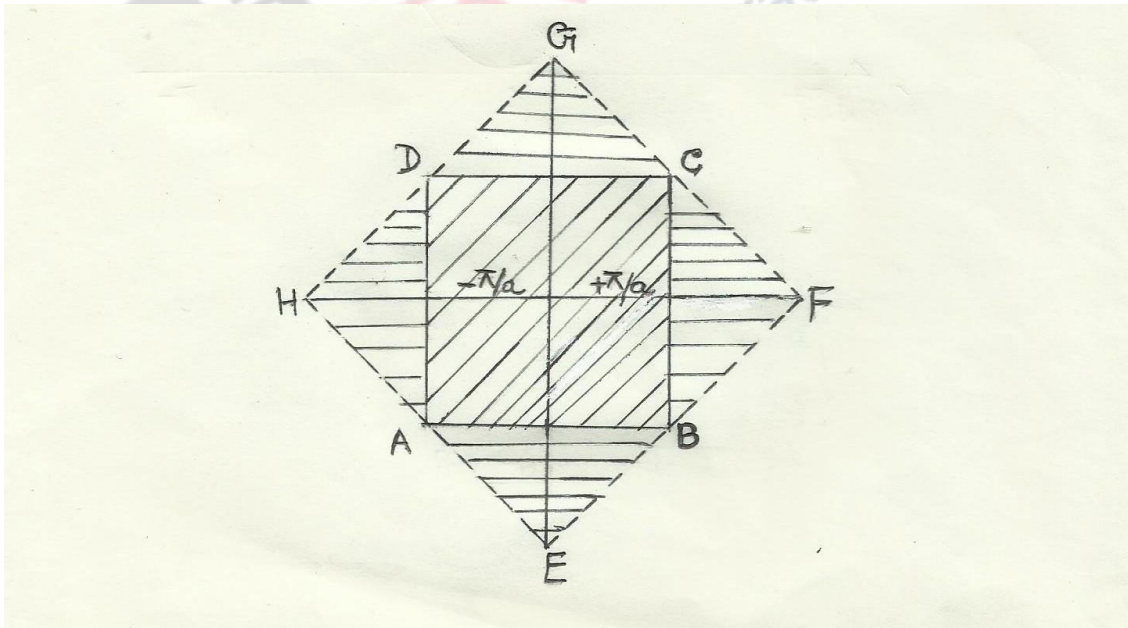


Figure 23.9: Brillouin zones in two dimensional simple square lattice

One can apply the same principle for the three dimensional crystal structures. For a simple cubic lattice, the first Brillouin zone is a cube of edge $2\pi/a$.

23.7 Significance of Brillouin Zones

(i) Looking at the curve shown in figure 23.6 one finds that electron energy increases continuously from zero until the value of k reaches π/a . Thereafter, it gets stopped as if it meets an obstacle or a wall at that instant and consequently gets reflected.

Treating electrons as waves and the propagation of electrons through a crystal as analogous to the propagation of electromagnetic waves, we arrive at a very important conclusion. We know that x-ray will suffer reflection if incident normal to a set of planes of interplanar spacing 'a' provided this equation is satisfied:

$$n\lambda = 2a \sin 90^\circ \quad (\text{for x-ray is at right angles to the planes})$$

$$n\lambda = 2a$$

For electron $k = n\pi/a$ and $k = 2\pi/\lambda$

So, $2\pi/\lambda = n\pi/a$, or $n\lambda = 2a$, which is the same condition as for Bragg reflection. Thus, we may conclude that electron suffers Bragg reflection when $n = \pm 1, \pm 2, \pm 3, \dots$ corresponding to first, second, third order reflections and so on. The zones between the values of $k = -\pi/a$ and $+\pi/a$ constitutes the first Brillouin zone and so on.

- (ii) The zone boundaries represent the maximum energies that the electron can have without developing any discontinuity.
- (iii) The energy gap at the zone boundary is called the Forbidden zone or band; electrons cannot have those energies.
- (iv) Considering velocity of electrons in a periodic potential (given $v_g = 2\pi \cdot dv/dk$; $E = h\nu$ and so $v_g = 2\pi/h \cdot dE/dk$)
 Slope $dE/dk = 0$ when $k = 0$,
 & $dE/dk = 0$ when $k = \pm\pi/a$.

Therefore, the velocity of electron is zero both at the bottom and at the top of the first Brillouin zone or band. At intermediate regions in the zone the electron velocity reaches the free electron velocity $h\hbar/2\pi m$.

- (v) Let us now consider the motion of the electron in the first Brillouin zone, under the continued application of a force F (either due to electric field or any other agency). Velocity of the electron at $k = 0$ will increase but when it approaches the value of k close to $+\pi/a$ its velocity begins to decrease and at $k = +\pi/a$ the velocity becomes zero, indicating that the electron wave packet suffers a Bragg reflection and begins to travel in a direction opposite to the applied force. The propagation in the negative direction continues until it becomes equal to $-\pi/a$. Once again the electron suffers Bragg reflection and the forward propagation starts until value of k reaches $+\pi/a$. In other words, the electron is shunted back and forth in the first Brillouin zone under the application of a constant unidirectional force. It means that a stationary electron wave is set up in the first Brillouin zone instead of a travelling wave.
- (vi) An electron remaining in one zone or band cannot cross over to another zone by continuous application of force. Two consecutive Brillouin zones are separated by a forbidden energy gap. So, unless and until the electron in the first zone absorbs an energy equal to that of the forbidden gap in a single dose, the electron cannot cross over to the next Brillouin zone irrespective of the duration of the applied force.
- (vii) If the electrons continue to move back and forth in their respective Brillouin zones there is no change in the sum of the momenta of all the electrons and, as a result, no net current is conducted by the crystal. It, obviously, means that the material is an insulator. Now suppose the forbidden gap is small enough or if impurity atoms provide some localized electronic states within the forbidden energy gap, one will find a semiconductor behaviour. The third situation is that there is no forbidden energy gap. In that case there is no restriction for increase in the value of k and so electric conduction can take place. The material in this case is a good conductor.

SUMMARY

- We have discussed motion of electrons, both in a constant potential field (as assumed by Sommerfeld) as well as in a periodic potential field as assumed in Kronig Penney model.
- Significance of translational periodicity in a crystalline solid is explained.
- The concept of De Broglie wave or Sommerfeld waves or Bloch waves are given.
- It is shown that Sommerfeld's model of motion of a free electrons in a constant potential field leads to a relation between energy and wave vector for a free electron that is parabolic.
- Bloch theorem is explained.
- It is shown that if electron is assumed to travel in a periodic potential as proposed by Kronig Penney model it leads to energy versus wave vector that shows discontinuities at $k = \pm \frac{n\pi}{a}$.
- The concept of Brillouin zones and their significance in crystallography is explained

