

# Electron Energy Bands in Solids

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**Abstract:** A solid can be considered as a lattice structure of positive ions which offer a periodic potential to the motion of valence electrons. Consequently, the energy states of an electron in a solid will not be continuous but bunch together into energy bands separated by forbidden energy gaps. This enables one to classify solids into metals, semi-metals, semiconductors and insulators. In metals, the valence band is half-filled and the next higher band known as conduction band overlaps with the valence band. In semi-metals, the valence band is filled but it is continuous with the conduction band without any energy gap. In semiconductors, the valence band is filled and the conduction band is separated by a small energy gap of the order of 1 eV. In the case of insulators, the valence band is completely filled and the conduction band is well above the valence band with a large energy gap of the order of 5 eV. The one-dimensional model of Kronig and Penney clearly demonstrates the existence of energy bands separated by forbidden energy gaps for an electron in a periodic potential.

## 1 Introduction

Any theory is based on certain postulates and the theory yields meaningful results only in situations where those postulates are valid. Free electron theory is based on the postulate that the valence electrons are free to move but confined within the solid. Such a model is applicable only to metals and the free valence electron theory [1] when treated quantum-mechanically yields quantitative agreement with the experiments on electrical and thermal conductivity in metals. But it miserably fails to explain the properties of semiconductors and insulators.

To explain the properties of semiconductors and insulators, one has to consider the lattice structure of solids and the motion of electrons in the Coulomb field of the

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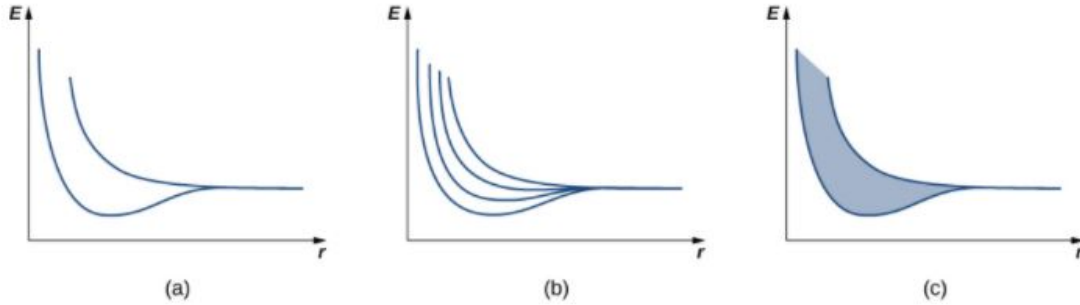


Figure 1: Splitting of an energy level of an atom (a) when two atoms are brought together, (b) when four atoms are brought together and (c) when a large number of atoms are brought together. This is depicted as a function of inter-atomic distance  $r$

periodic structure of atoms in the solid. This is a challenging task and let us treat this problem first qualitatively and then quantitatively using an one-dimensional model.

Let us start with the simple case of hydrogen atom. The electron has discrete energy levels:  $1s, 2s, 2p, \dots$ . If two hydrogen atoms are brought together to form a hydrogen molecule, it is found that each energy level is split into two closely spaced energy levels. If four atoms are brought together, then each energy level is split into four closely spaced levels. In a similar way, if  $N$  atoms are brought close together, then each energy level can be expected to form  $N$  closely-spaced levels, known as an energy band. This is illustrated in Fig. 1. Each energy band is separated from the other by an energy gap. Since we consider the solid as a lattice structure of positive ions, in which the electron is moving, then the energy levels of electron will assume a band structure separated by energy gaps. In metals, the valence electrons occupy the outermost shell which is only partially filled and it corresponds to the valence band. The next higher shell which is empty corresponds to the conduction band. In metals, there is an overlap of valence band with the conduction band and they are found to be good conductors of electric current. In semiconductors, the valence band is completely filled and the conduction band is separated by a small energy gap of less than 1 eV. So, with a slight increase in temperature, the valence electrons can jump into the conduction band and consequently, in semiconductors, the resistance decreases with increase of temperature; whereas in metals, the resistance increases with increase of temperature. In insulators, the energy gap is much larger and hence offers great resistance to the flow of electricity. This is a qualitative picture of conductors, semiconductors and insulators that emerges from the band theory of solids using hand-waving arguments.

Since it is a formidable task to treat quantitatively the three-dimensional problem with the actual periodic potential, Kronig and Penney considered an one-

dimensional problem of propagation of an electron in a highly simplified potential. This simple model clearly shows the existence of energy bands and energy gaps for an electron in a periodic potential [2,3,4,5].

## 2 The Kronig-Penney Model

Let us consider the propagation of an electron in an one-dimensional lattice structure of ions with positive charge  $Ze$ , where  $Z$  denotes the charge of the ion. The electron will experience a periodic potential

$$V(x_0) = -\frac{Ze^2}{x_0},$$

where  $x_0$  denotes the distance of the electron from any one of the ions. The negative sign indicates that it is an attractive potential. This is displayed in Fig.2.

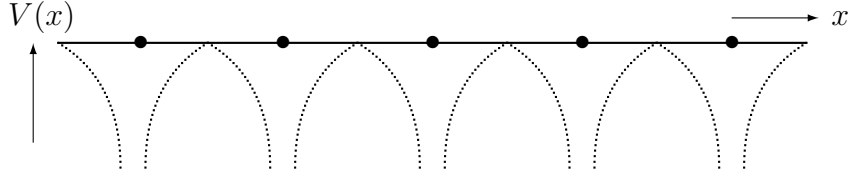


Figure 2: Variation of potential energy  $V(x)$  for an electron moving through a one-dimensional lattice of ions with charge  $Ze$ , where  $Z$  denotes the charge of the ion. The  $\bullet$  represents the position of the ions and the dotted curves the potential  $V(x)$  experienced by the electron.

It is the usual convention to shift the zero of the energy scale to the lowest conceivable energy so that all the energies that we come across in our study are positive.

Kronig and Penney in the year 1930 devised an one-dimensional model as a prelude to the study of electron propagation in the periodic potential due to the ions arranged in a lattice structure in the solid. For the sake of analytical treatment of the problem, he considered an highly artificial but simple periodic potential of the form that extends both on the positive and negative side of  $x$ -axis, as shown in Fig. 3.

$$V = \begin{cases} 0, & 0 < x < a, \quad a + b < x < 2a + b, \dots \\ V_0, & -b < x < 0, \quad a < x < a + b, \dots \end{cases}$$

The time-independent Schrödinger equation for the two regions can be written as

$$\frac{d^2\psi}{dx^2} + \left(\frac{2m}{\hbar^2}\right) E\psi = 0, \quad 0 < x < a \quad (1)$$

$$\frac{d^2\psi}{dx^2} + \left(\frac{2m}{\hbar^2}\right) (E - V_0)\psi = 0, \quad -b < x < 0 \quad (2)$$

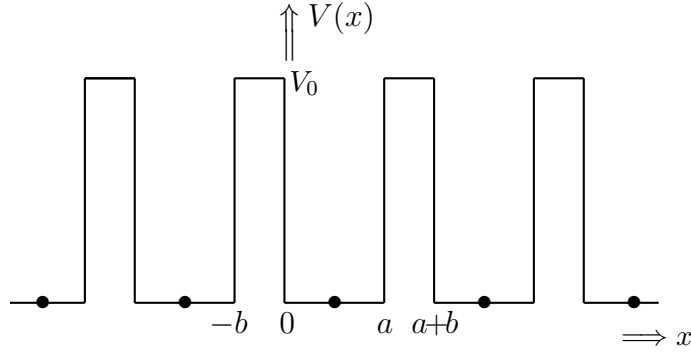


Figure 3: Periodic square well potential used by Kronig and Penney. The dot ( $\bullet$ ) represents the positive ion,  $a$  the width of the potential well,  $b$  the width of the barrier and  $V_0$  the barrier height. The distance between any two positive ions is  $a + b$ .

In the above equations,  $\psi$  denotes the electron wave function and  $\hbar = h/(2\pi)$ ,  $h$  being the Planck constant. The potential  $V_0$  is much larger than the electron energy  $E$ . By defining two variables,

$$\alpha^2 = \frac{2mE}{\hbar^2}; \quad \beta^2 = \frac{2m(V_0 - E)}{\hbar^2} \quad (3)$$

the above differential equations can be written as

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0, \quad 0 < x < a \quad (4)$$

$$\frac{d^2\psi}{dx^2} - \beta^2\psi = 0, \quad -b < x < 0 \quad (5)$$

Following Bloch, we can write the solutions of the above equations in the form

$$\psi(x) = u(x)e^{ikx}, \quad (6)$$

where  $e^{ikx}$  is a plane wave and  $u(x)$  which depends on the wave number  $k$  represents a periodic function  $u(x) = u(x + a + b)$ , where  $a$  represents the width of the potential well and  $b$  denotes the width of the barrier. Substituting (6) in Eqs. (4) and (5), we obtain second order differential equations in  $u(x)$ .

$$\frac{d^2u_1}{dx^2} + 2ik\frac{du_1}{dx} + (\alpha^2 - k^2)u_1(x) = 0; \quad 0 < x < a \quad (7)$$

$$\frac{d^2u_2}{dx^2} + 2ik\frac{du_2}{dx} - (\beta^2 + k^2)u_2(x) = 0; \quad -b < x < 0 \quad (8)$$

Since Eqs. (7) and (8) are second order linear differential equations, each of them will have two linearly independent solutions. Try the following forms for the solutions.

$$u_1 = e^{px}; \quad u_2 = e^{rx}.$$

On substitution in Eqs. (7) and (8), we obtain quadratic equations in  $p$  and  $r$ , each yielding two solutions.

$$\begin{aligned} p^2 + 2ikp + (\alpha^2 - k^2) &= 0; & r^2 + 2ikr - (\beta^2 + k^2) &= 0; \\ p_1 = i(\alpha - k), p_2 = -i(\alpha + k); & r_1 = (\beta - ik), r_2 = -(\beta + ik) \end{aligned}$$

For convenience of writing, let us redefine  $p_1, p_2, r_1, r_2$  as  $p, q, r, s$ .

$$p = i(\alpha - k), q = -i(\alpha + k); \quad r = (\beta - ik), s = -(\beta + ik) \quad (9)$$

Using the above data, we can write the general solutions of Eqs. (7) and (8) using four constants  $A, B, C, D$  as given below:

$$u_1 = Ae^{px} + Be^{qx} = Ae^{i(\alpha-k)x} + Be^{-i(\alpha+k)x}; \quad 0 < x < a \quad (10)$$

$$u_2 = Ce^{rx} + De^{sx} = Ce^{(\beta-ik)x} + De^{-(\beta+ik)x}, \quad -b < x < 0 \quad (11)$$

The values of the constants can be determined using the boundary conditions.

$$[u_1(x)]_{x=0} = [u_2(x)]_{x=0}; \quad \left[ \frac{du_1(x)}{dx} \right]_{x=0} = \left[ \frac{du_2(x)}{dx} \right]_{x=0} \quad (12)$$

$$[u_1(x)]_{x=a} = [u_2(x)]_{x=-b}; \quad \left[ \frac{du_1(x)}{dx} \right]_{x=a} = \left[ \frac{du_2(x)}{dx} \right]_{x=-b} \quad (13)$$

The boundary conditions (12) and (13) represent respectively the continuity conditions and the periodic conditions for the functions  $u_1(x)$  and  $u_2(x)$  and they lead to the following four equations, involving the constants  $A, B, C, D$ .

$$A + B = C + D \quad (14)$$

$$pA + qB = rC + sD \quad (15)$$

$$e^{pa}A + e^{qa}B = e^{-rb}C + e^{-sb}D \quad (16)$$

$$pe^{pa}A + qe^{qa}B = re^{-rb}C + se^{-sb}D \quad (17)$$

They can be rewritten as

$$A + B - C - D = 0 \quad (18)$$

$$pA + qB - rC - sD = 0 \quad (19)$$

$$e^{pa}A + e^{qa}B - e^{-rb}C - e^{-sb}D = 0 \quad (20)$$

$$pe^{pa}A + qe^{qa}B - re^{-rb}C - se^{-sb}D = 0 \quad (21)$$

The above four homogeneous linear equations will yield non-vanishing solutions for  $A, B, C, D$ , only if the determinant  $\Delta$  of the  $4 \times 4$  matrix formed with their coefficients is zero.

$$\Delta = \begin{vmatrix} 1 & 1 & -1 & -1 \\ p & q & -r & -s \\ e^{pa} & e^{qa} & -e^{-rb} & -e^{-sb} \\ pe^{pa} & qe^{qa} & -re^{-rb} & -se^{-sb} \end{vmatrix} = 0 \quad (22)$$

where the quantities  $p, q, r, s$  are defined in Eq: (9). The determinant is invariant if the two columns, third and fourth, are multiplied by  $-1$ .

$$\Delta = \begin{vmatrix} 1 & 1 & 1 & 1 \\ p & q & r & s \\ e^{pa} & e^{qa} & e^{-rb} & e^{-sb} \\ pe^{pa} & qe^{qa} & re^{-rb} & se^{-sb} \end{vmatrix} = 0 \quad (23)$$

It is possible to use the other properties of determinant to reduce it to a simple structure but it is found that what we gain on the swings is lost on the roundabouts in obtaining the final result. So, we shall take the straight route of finding the determinant [2], the details of which is given in Appendix A.

The condition that the determinant  $\Delta = 0$  leads to the following relation:

$$\frac{(\beta^2 - \alpha^2)}{2\alpha\beta} \sin(\alpha a) \sinh(\beta b) + \cosh(\beta b) \cos(\alpha a) = \cos\{k(a + b)\}. \quad (24)$$

Kronig and Penney further simplified the above relation by assuming that  $V_0 \rightarrow \infty$  and  $b \rightarrow 0$  in such a way that  $V_0 b$  remains finite. Since

$$\sinh x = \frac{e^x - e^{-x}}{2} \rightarrow x \quad \text{and} \quad \cosh x = \frac{e^x + e^{-x}}{2} \rightarrow 1, \quad \text{as } x \rightarrow 0,$$

the relation (24) reduces to

$$\frac{(\beta^2 - \alpha^2)}{2\alpha\beta} \beta b \sin(\alpha a) + \cos(\alpha a) = \cos(ka). \quad (25)$$

The quantities  $\alpha$  and  $\beta$  are defined in Eq. (3). Accordingly,

$$\beta^2 - \alpha^2 = \frac{2m}{\hbar^2} (V_0 - 2E) \approx \frac{2m}{\hbar^2} V_0, \quad \text{since } V_0 \gg E.$$

Defining a quantity

$$P = \frac{(\beta^2 - \alpha^2)ab}{2} = \frac{mV_0ab}{\hbar^2}, \quad (26)$$

Eq. (25) can be written as

$$P \frac{\sin(\alpha a)}{\alpha a} + \cos(\alpha a) = \cos(ka), \quad \text{where } \alpha = \frac{\sqrt{2mE}}{\hbar}. \quad (27)$$

The quantity  $V_0 b$  is sometimes referred to as the potential barrier strength and  $P$  as the scattering power of the potential barrier. Eq. (27) gives the primary condition for the existence of a solution for the electron in a periodic potential and yields the allowed and forbidden energy regions for the electron.

## 2.1 Allowed energy bands and forbidden energy region

The quantity  $\cos(ka)$  on the right-hand side (R.H.S.) of Eq. (27) can have a limited range of values from  $-1$  to  $+1$ . So, the left-hand side (L.H.S.) which is a function of  $\alpha$  that depends on the electron energy  $E$  should necessarily be restricted to the range of values that satisfy the R.H.S. Thus we obtain the allowed energy bands and the forbidden energy regions. The allowed energy bands are the range of electron energies permitted by Eq. (27) and the forbidden regions are those electron energies that violate the condition (27).

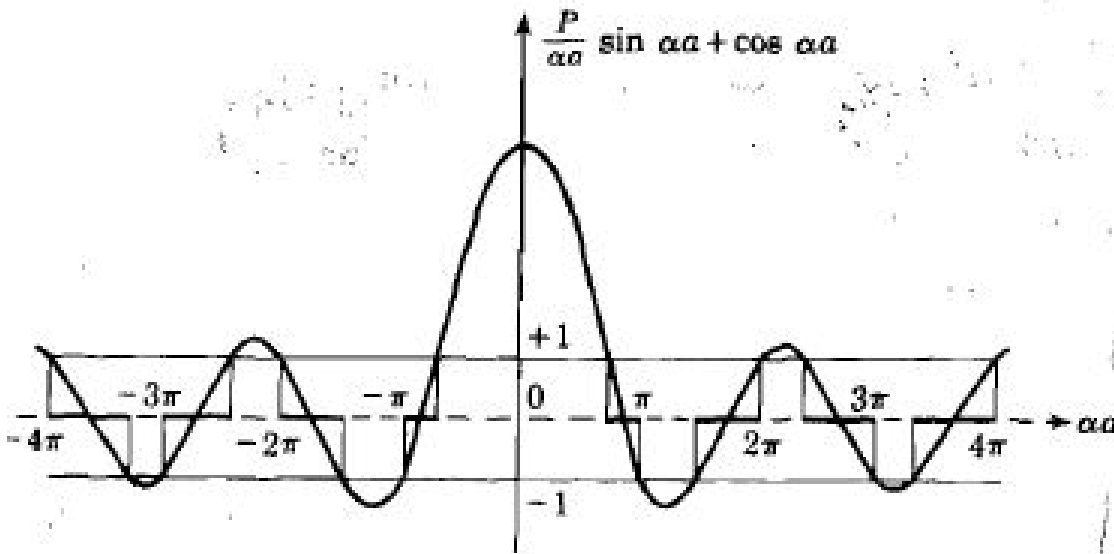


Figure 4: Graph of  $\frac{P}{\alpha a} \sin(\alpha a) + \cos(\alpha a)$  vs  $\alpha a$ . The curve within the range  $-1$  and  $+1$  yields the allowed values of electron energy and the curve beyond this region gives the forbidden energy range. (Source: Dekker [4])

This is depicted in Fig. 4. A curve is drawn with  $\frac{P}{\alpha a} \sin(\alpha a) \cos(\alpha a)$  as Y-axis and  $\alpha a$  as X-axis. It is a wavy curve which cuts the parallel lines drawn through  $y = -1$  and  $y = +1$  at points  $\alpha a = n\pi$  alternatively with  $n = \pm 1, \pm 2, \pm 3$ . The electron energies that correspond to the wavy curve within the parallel lines are allowed and the energies that correspond to the wavy curve outside this region are forbidden.

Let us consider the two extreme cases:  $P \rightarrow \infty$  which corresponds to  $V_0 \rightarrow \infty$  and  $P \rightarrow 0$  which corresponds to  $V_0 \rightarrow 0$ .

If  $P \rightarrow \infty$ , then  $\sin \alpha a$  should tend to zero. That corresponds to  $\alpha a = n\pi$ , where  $n$  is an integer.

$$\begin{aligned}\alpha^2 a^2 &= \frac{2mE}{\hbar^2} a^2 = n^2 \pi^2 \\ E &= \frac{n^2 \pi^2 \hbar^2}{2ma^2}\end{aligned}\quad (28)$$

This corresponds to the discrete energy levels of electron in an infinite square well potential of width  $a$  and the energy levels are independent of  $k$ . This is what is expected since the electron cannot tunnel through an infinite potential barrier.

If  $P \rightarrow 0$ , then Eq. (27) reduces to

$$\cos \alpha a = \cos ka \quad \text{or} \quad \alpha = k.$$

This corresponds to the state of free electrons.

$$\begin{aligned}\alpha^2 &= \frac{2mE}{\hbar^2} = k^2 \\ E &= \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m},\end{aligned}\quad (29)$$

where  $p$  denotes the momentum of the electron.

Thus the variation of  $P$  from zero to  $\infty$ , covers the entire range of electron state, from completely free to completely bound.

## 2.2 Electron energy as a function of wave number $k$

The free electron energy

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

is quadratic in  $k$  and consequently  $E$  vs  $k$  curve is a parabola. In Fig. 5, it is shown by the dotted curve. In the periodic potential, the energy of the electron shows discontinuity at values of  $k = \pm \frac{n\pi}{a}$ , where  $n$  is an integer as depicted in Fig. 5 and this leads to allowed energy bands and forbidden energy regions. The allowed energy bands are often known as Brillouin zones.

From Fig. 5, we find that the first energy band is spread over the  $k$  values ranging from  $-\frac{\pi}{a}$  to  $\frac{\pi}{a}$ . The range of  $k$  values for the second and higher energy bands are fragmented. The second energy band covers the range of  $k$  values from  $-\frac{2\pi}{a}$  to  $-\frac{\pi}{a}$  and from  $\frac{\pi}{a}$  to  $\frac{2\pi}{a}$ . This is depicted in Fig. 6.



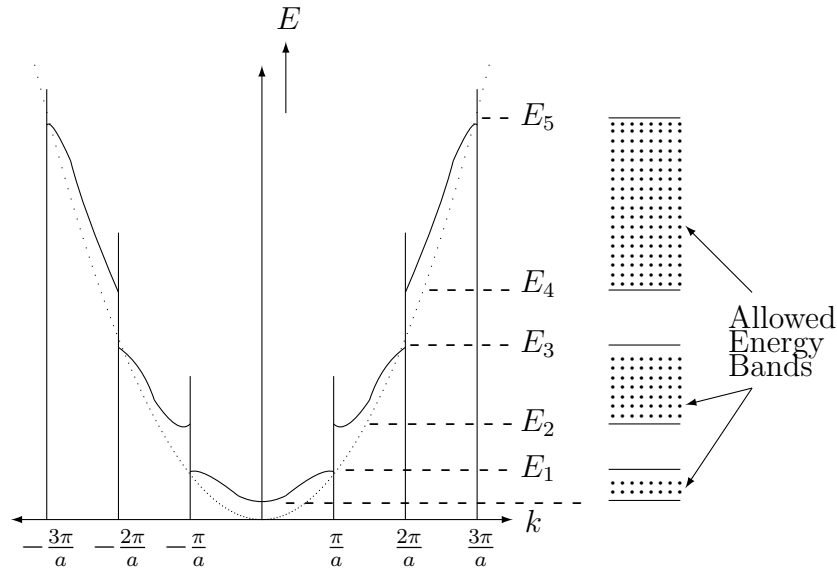


Figure 5: The dotted curve is the parabola  $E = (\hbar^2/2m)k^2$  representing the motion of a free electron and the discontinuous solid curves represent the allowed energies for an electron in a periodic potential. The allowed energy bands are shown on the left side in the figure.

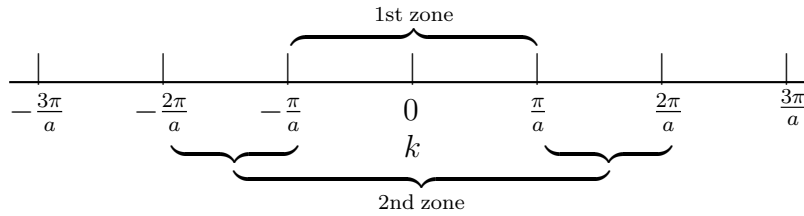


Figure 6: The first two allowed energy bands known as Brillouin zones along with their  $k$  values.

Further, one may observe that within an energy band, the energy is a periodic function of  $k$ , since the value of  $\cos(ka)$  that occurs on the right hand side of Eq. (27) is not altered if  $ka$  is replaced by  $ka+2n\pi$  or  $k$  by  $k+\frac{2n\pi}{a}$ , where  $n$  is an integer (positive or negative). Since  $k$  is not uniquely determined, it is possible to represent second and higher energy bands also in the same way as the first energy band within the range of  $k$  values from  $-\frac{\pi}{a}$  to  $\frac{\pi}{a}$ . This is known as the "Reduced wave vector" representation of energy bands [4]. Fig. 7 depicts the first four energy bands (known as Brillouin zones) in the reduced vector space.

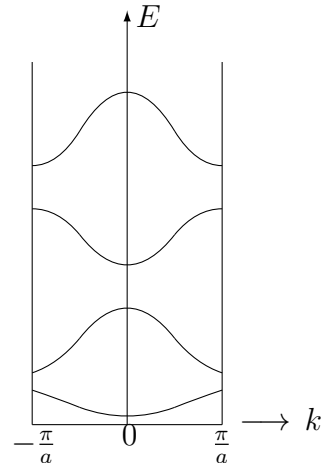


Fig. 7: Energy bands in reduced wave vector space

Let us explicitly show how the second energy band, usually expressed in terms of  $k$ , can be represented in the reduced vector space using the corresponding reduced wave number  $k'$ .

$$\begin{aligned} k = -\frac{2\pi}{a} & \text{ can be replaced by } k' = k + \frac{2\pi}{a} = 0. \\ k = -\frac{\pi}{a} & \text{ can be replaced by } k' = k + \frac{2\pi}{a} = \frac{\pi}{a}. \\ k = \frac{\pi}{a} & \text{ can be replaced by } k' = k - \frac{2\pi}{a} = -\frac{\pi}{a}. \\ k = \frac{2\pi}{a} & \text{ can be replaced by } k' = k - \frac{2\pi}{a} = 0. \end{aligned}$$

Thus we have folded the second energy band and expressed it in terms of reduced wave vector with values ranging from  $k' = -\frac{\pi}{a}$  to  $k' = \frac{\pi}{a}$ . In a similar way, higher energy bands also can be expressed in terms of the reduced wave vector  $k'$ .

### 2.3 Number of energy states in a band

Let us consider one-dimensional solid of length  $L$  with  $N$  lattice points. If  $a$  is the distance between two lattice points, then  $L = Na$ . Due to the periodicity of the wave function and Born cyclic condition [3,4],

$$\psi(x) = \psi(x + L), \quad (30)$$

where

$$\psi(x) = u_k(x)e^{ikx}; \quad \psi(x + L) = u_k(x + L)e^{ik(x+L)} \quad (31)$$

The modulating function  $u_k(x)$  obeys the Bloch condition of periodicity of lattice.

$$u_k(x) = u_k(x + a) = u_k(x + 2a) = \cdots = u_k(x + Na).$$

Since  $Na = L$ , it follows that

$$u_k(x) = u_k(x + L). \quad (32)$$

From Eqs. (30), (31) and (32), it follows that

$$e^{ikL} = 1 \longrightarrow \cos kL = 1 \longrightarrow kL = 2n\pi, \quad (33)$$

where  $n$  is an integer, either positive or negative. Since  $k$  is the wave number of the propagating electron in the solid, the set of values that  $n$  can take can be considered as the number of energy states, available for the electron in the solid with wave

number  $k$ . It follows that in a small interval of wave number  $dk$ , the number of energy states  $dn$  available for the electron is

$$dn = \frac{L}{2\pi} dk. \quad (34)$$

From Fig. 5, we find that for the first energy band  $k$  varies from  $-\frac{\pi}{a}$  to  $+\frac{\pi}{a}$  and consequently the number of energy states available for the electron is

$$n = \frac{L}{2\pi} \int_{-\pi/a}^{+\pi/a} dk = \frac{L}{2\pi} [k]_{-\pi/a}^{\pi/a} = \frac{L}{a} = N, \text{ since } L = Na. \quad (35)$$

Thus, the number of states available for the electron in a band is  $N$  which is equal to the number of lattice points or the number of ions in the one-dimensional solid.

In a similar way, we find that for the second energy band also, the electron has  $N$  available states. The limiting values of  $k$  for the second energy band can be found from Figs. 5 and 6.

$$n = \frac{L}{2\pi} \left( \int_{-(2\pi/a)}^{-(\pi/a)} dk + \int_{(\pi/a)}^{(2\pi/a)} dk \right) = \frac{L}{2\pi} \left( \frac{\pi}{a} + \frac{\pi}{a} \right) = \frac{L}{a} = N \quad (36)$$

It follows that every other higher energy band also contains  $N$  levels.

If we use the reduced vector representation, then it follows from Eq. (35) that all energy bands will have the same number of energy states  $N$ . Since two electrons (one with spin up and another spin down) can occupy each energy state, a total number of  $2N$  electrons can be accommodated in each energy band.

## 2.4 Effective mass of the electron

Invoking the wave-particle duality, the velocity of electron  $v$  can be identified with the group velocity of de Broglie waves. In this dual role, the velocity of electron can be defined as

$$v = \frac{dE}{dp}, \quad (37)$$

where  $E$  denotes the energy of electron and  $p$  its momentum. If  $m$  is the rest mass of the electron, then in the particle picture,

$$E = \frac{p^2}{2m}; \quad \frac{dE}{dp} = \frac{p}{m} = v,$$

In the wave picture,

$$E = \hbar\omega, \quad p = \hbar k,$$

where  $\omega$  denotes the angular frequency,  $k$  denotes the wave number and  $\hbar = h/(2\pi)$ . Consequently,

$$v = \frac{dE}{dp} = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk}. \quad (38)$$

If a force acts on an electron, it will be accelerated. The acceleration  $a$  of the electron in terms of  $E$  becomes

$$a = \frac{dv}{dt} = \frac{1}{\hbar} \frac{d}{dk} \left( \frac{dE}{dk} \right) \frac{dk}{dt} = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt}. \quad (39)$$

Now, let us subject a free electron to an Electric field  $\mathcal{E}$ . The electron will experience a force  $e\mathcal{E}$  and will be accelerated. The energy gained by the electron in a small interval of time  $dt$  will be

$$\begin{aligned} dE &= e\mathcal{E}vdt = \frac{e\mathcal{E}}{\hbar} \frac{dE}{dk} dt. \\ \text{Force} &= e\mathcal{E} = \frac{dp}{dt} = m \frac{dv}{dt} = \hbar \frac{dk}{dt} = ma; \\ \text{So, } a &= \frac{e\mathcal{E}}{m} = \frac{\hbar}{m} \frac{dk}{dt}. \end{aligned} \quad (40)$$

This is for a free electron. For an electron in a periodic potential, let us define an effective mass  $m^*$  for the electron. Then, using Eqs. (40) and (39), we obtain

$$a = \frac{e\mathcal{E}}{m^*} = \frac{\hbar}{m^*} \frac{dk}{dt} = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt}. \quad (41)$$

From the above equation, we obtain an expression for the effective mass  $m^*$ .

$$m^* = \frac{\hbar^2}{(d^2 E/dk^2)}. \quad (42)$$

The effective mass  $m^*$  of an electron in a periodic potential depends on  $d^2 E/dk^2$  which can take both positive and negative values. So,  $m^*$  can assume both positive and negative values. This is shown in Fig. 8(c).

Figs. 8(a) and 8(b) depict  $E$  and  $v$  as a function of  $k$  for an electron in a periodic potential.  $v$  is a sine wave ( $v = 0$  at  $k = 0$  and at  $k = \pm\pi/2$ ) for electron in a periodic potential but proportional to  $k$  for a free electron.

The degree of freedom of an electron in a periodic potential is given by a factor  $f_k$ .

$$f_k = \frac{m}{m^*} = \frac{m}{\hbar^2} \frac{d^2 E}{dk^2}. \quad (43)$$

The factor  $f_k$  is a measure of the extent to which an electron is free. If  $m^*$  is large,  $f_k$  is small and the electron behaves as a heavy particle. If  $f_k = 1$ , then the electron behaves as a free particle. From Fig. 8(d), it can be observed that  $f_k$  is positive in the lower half of the band and negative in the upper half of the band.

## 2.5 Effective number of free electrons

The effective number of free electrons in a band is equal to (since 2 electrons can occupy an energy state)

$$N_{\text{eff}} = 2 \sum_k f_k,$$

where the summation  $k$  extends over all occupied states in a band. For one-dimensional lattice of length  $L$ , the effective number of free electrons in the interval  $-k_1$  to  $k_1$  is obtained from Eqs.(34) and (43), as shown in Fig.9.

$$dN_{\text{eff}} = 2 \frac{L}{2\pi} f_k dk \longrightarrow N_{\text{eff}} = \frac{L}{\pi} \int_{-k_1}^{k_1} f_k dk.$$

$$N_{\text{eff}} = \frac{2L}{\pi} \frac{m}{\hbar^2} \int_0^{k_1} \frac{d^2 E}{dk^2} dk = \frac{2mL}{\pi \hbar^2} \left[ \frac{dE}{dk} \right]_{k=0}^{k_1}.$$

At  $k = \pm n\pi/a$ ,  $dE/dk = 0$ . Hence  $N_{\text{eff}} = 0$  for a completely filled band.  $dE/dk = 1$  when the energy band is half-filled and so  $N_{\text{eff}}$  is maximum for half filled bands.

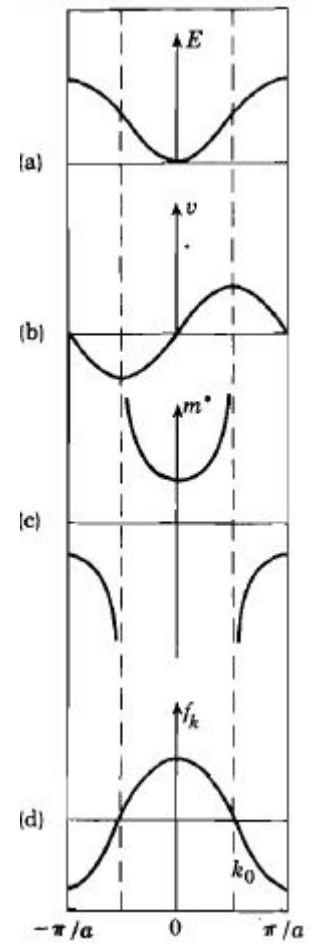


Fig. 8: Energy, velocity, effective mass and  $f_k$  as a function of  $k$

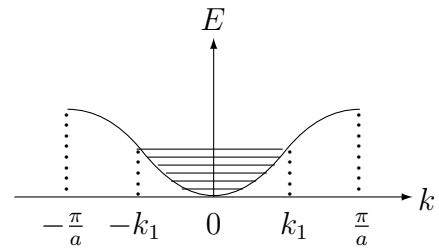


Fig.9: Partially filled valence band

### 3 Metals, Semiconductors and Insulators

The study of electron energy bands enables us to classify solids into metals, semiconductors and insulators. In solids, the lower energy bands are completely filled and the top-most energy band which is partially or completely filled is known as "valence band" and the next higher energy band which is empty is known as the "conduction band". The relative location of the conduction band from the valence band distinguishes metals from semiconductors and insulators as depicted in Fig. 10.

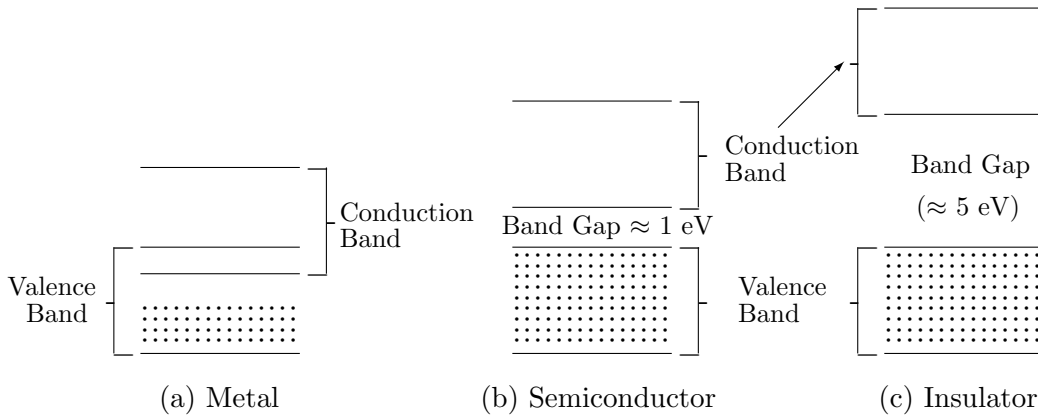


Figure 10: Relative location of valence band and conduction band in metal, semiconductor and insulator.

In metals, the valence band is partially filled and the conduction band slightly overlaps with valence band. This facilitates the free movement of electrons, enabling good electrical and thermal conductivity. In semiconductors, the valence band is completely filled and the conduction band is slightly above with a small energy band gap of energy ( $\approx 1 \text{ eV}$ ). Silicon and Germanium are semiconductors with an energy gap of 1.11 eV and 0.67 eV between valence and conduction bands. On thermal heating, the electrons gain energy and move to conduction band and the semiconductor becomes a conductor. The resistance of semiconductor decreases with raise of temperature whereas in metals, the resistance increases with raise of temperature. In the case of insulators, the band gap energy is larger than 5 eV and so the insulators remain as insulators even when heated.

### 4 Concluding Remarks

The Kronig-Penney one-dimensional model clearly demonstrates the existence of electron energy bands in solids with energy gaps. For more quantitative study, one

has to resort to many three-dimensional models that have been developed subsequently. Augmented Plane Wave (APW) method, Korringa-Kohn-Rostoker (KKR) method, the Density-Functional theory and many variations thereof are available for detailed investigations.

## Appendix A

In this Appendix, we shall evaluate the determinant  $\Delta$  and find the condition that is to be satisfied for  $\Delta = 0$ . We shall follow essentially the method given in the book by S.O. Pillai [2] but here it is presented in a way that the reader may find it easy to understand.

$$\Delta = \begin{vmatrix} 1 & 1 & 1 & 1 \\ p & q & r & s \\ e^{pa} & e^{qa} & e^{-rb} & e^{-sb} \\ pe^{pa} & qe^{qa} & re^{-rb} & se^{-sb} \end{vmatrix} = 0 \quad (\text{A.1})$$

It is possible to use the properties of determinant to reduce it to a simpler structure but, as stated earlier, it offers no great advantage. So, we shall take the straight route of finding the determinant.

$$\begin{aligned} \Delta = & \underbrace{\begin{vmatrix} q & r & s \\ e^{qa} & e^{-rb} & e^{-sb} \\ qe^{qa} & re^{-rb} & se^{-sb} \end{vmatrix}}_{(\mathcal{A})} - \underbrace{\begin{vmatrix} p & r & s \\ e^{pa} & e^{-rb} & e^{-sb} \\ pe^{pa} & re^{-rb} & se^{-sb} \end{vmatrix}}_{(\mathcal{B})} \\ & + \underbrace{\begin{vmatrix} p & q & s \\ e^{pa} & e^{qa} & e^{-sb} \\ pe^{pa} & qe^{qa} & se^{-sb} \end{vmatrix}}_{(\mathcal{C})} - \underbrace{\begin{vmatrix} p & q & r \\ e^{pa} & e^{qa} & e^{-rb} \\ pe^{pa} & qe^{qa} & re^{-rb} \end{vmatrix}}_{(\mathcal{D})} \end{aligned} \quad (\text{A.2})$$

where

$$\mathcal{A} = q(s-r)e^{-rb}e^{-sb} - r(s-q)e^{qa}e^{-sb} + s(r-q)e^{qa}e^{-rb} \quad (\text{A.3})$$

$$\mathcal{B} = p(s-r)e^{-rb}e^{-sb} - r(s-p)e^{pa}e^{-sb} + s(r-p)e^{pa}e^{-rb} \quad (\text{A.4})$$

$$\mathcal{C} = p(s-q)e^{qa}e^{-sb} - q(s-p)e^{pa}e^{-sb} + s(q-p)e^{qa}e^{pa} \quad (\text{A.5})$$

$$\mathcal{D} = p(r-q)e^{qa}e^{-rb} - q(r-p)e^{pa}e^{-rb} + r(q-p)e^{qa}e^{pa} \quad (\text{A.6})$$

$$\begin{aligned}
\Delta &= \mathcal{A} - \mathcal{B} + \mathcal{C} - \mathcal{D} \\
&= pq (e^{qa}e^{-rb} + e^{pa}e^{-sb} - e^{pa}e^{-rb} - e^{qa}e^{-sb}) \\
&\quad + pr (e^{-rb}e^{-sb} - e^{qa}e^{-rb} - e^{pa}e^{-sb} + e^{qa}e^{pa}) \\
&\quad + ps (-e^{-rb}e^{-sb} + e^{qa}e^{-sb} + e^{pa}e^{-rb} - e^{qa}e^{pa}) \\
&\quad + qr (-e^{-rb}e^{-sb} + e^{qa}e^{-sb} + e^{pa}e^{-rb} - e^{qa}e^{pa}) \\
&\quad + qs (e^{-rb}e^{-sb} - e^{qa}e^{-rb} - e^{pa}e^{-sb} + e^{qa}e^{pa}) \\
&\quad + rs (-e^{qa}e^{-sb} + e^{qa}e^{-rb} + e^{pa}e^{-sb} - e^{pa}e^{-rb}) \\
\Delta &= pq \{e^{qa} (e^{-rb} - e^{-sb}) - e^{pa} (e^{-rb} - e^{-sb})\} \\
&\quad + pr \{e^{qa} (e^{pa} - e^{-rb}) - e^{-sb} (e^{pa} - e^{-rb})\} \\
&\quad + ps \{e^{qa} (e^{-sb} - e^{pa}) - e^{-rb} (e^{-sb} - e^{pa})\} \\
&\quad + qr \{e^{qa} (e^{-sb} - e^{pa}) - e^{-rb} (e^{-sb} - e^{pa})\} \\
&\quad + qs \{e^{qa} (e^{pa} - e^{-rb}) - e^{-sb} (e^{pa} - e^{-rb})\} \\
&\quad + rs \{e^{qa} (e^{-rb} - e^{-sb}) - e^{pa} (e^{-rb} - e^{-sb})\} \\
&= (pq + rs) (e^{qa} - e^{pa}) (e^{-rb} - e^{-sb}) \\
&\quad + (pr + qs) (e^{qa} - e^{-sb}) (e^{pa} - e^{-rb}) \\
&\quad + (ps + qr) (e^{qa} - e^{-rb}) (e^{-sb} - e^{pa})
\end{aligned}$$

The condition that the determinant  $\Delta = 0$  leads to the following relation.

$$\begin{aligned}
(pr + qs) (e^{qa} - e^{-sb}) (e^{pa} - e^{-rb}) + (ps + qr) (e^{qa} - e^{-rb}) (e^{-sb} - e^{pa}) \\
= (pq + rs) (e^{qa} - e^{pa}) (e^{-sb} - e^{-rb}), \tag{A.7}
\end{aligned}$$

where the quantities  $p, q, r, s$  are given by Eq. (9).

$$p = i(\alpha - k); \quad q = -i(\alpha + k); \quad r = \beta - ik; \quad s = -(\beta + ik).$$

Substituting the values of  $p, q, r, s$  in Eq. (A.7), we obtain

$$\begin{aligned}
pr + qs &= i(\alpha - k)(\beta - ik) + \{-i(\alpha + k)\}\{-(\beta + ik)\} \\
&= 2i\alpha\beta - 2k^2. \tag{A.8}
\end{aligned}$$

$$\begin{aligned}
ps + qr &= i(\alpha - k)\{-(\beta + ik)\} - i(\alpha + k)(\beta - ik) \\
&= -2i\alpha\beta - 2k^2 \tag{A.9}
\end{aligned}$$

$$\begin{aligned}
pq + rs &= i(\alpha - k)\{-i(\alpha + k)\} - (\beta - ik)(\beta + ik) \\
&= \alpha^2 - \beta^2 - 2k^2. \tag{A.10}
\end{aligned}$$



$$\begin{aligned} (e^{pa} - e^{qa}) &= e^{i(\alpha-k)a} - e^{-i(\alpha+k)a} \\ &= (e^{i\alpha a} - e^{-i\alpha a}) e^{-ika} = 2i(\sin \alpha a) e^{-ika}. \end{aligned} \quad (\text{A.11})$$

$$\begin{aligned} (e^{pa} - e^{-rb}) &= e^{i(\alpha-k)a} - e^{-(\beta-ik)b} \\ &= e^{i\alpha a} e^{-ika} - e^{-\beta b} e^{ikb}. \end{aligned} \quad (\text{A.12})$$

$$\begin{aligned} (e^{pa} - e^{-sb}) &= e^{i(\alpha-k)a} - e^{(\beta+ik)b} \\ &= e^{i\alpha a} e^{-ika} - e^{\beta b} e^{ikb}. \end{aligned} \quad (\text{A.13})$$

$$\begin{aligned} (e^{qa} - e^{-rb}) &= e^{-i(\alpha+k)a} - e^{-(\beta-ik)b} \\ &= e^{-i\alpha a} e^{-ika} - e^{-\beta b} e^{ikb}. \end{aligned} \quad (\text{A.14})$$

$$\begin{aligned} (e^{qa} - e^{-sb}) &= e^{-i(\alpha+k)a} - e^{(\beta+ik)b} \\ &= e^{-i\alpha a} e^{-ika} - e^{\beta b} e^{ikb}. \end{aligned} \quad (\text{A.15})$$

$$\begin{aligned} (e^{-rb} - e^{-sb}) &= e^{-(\beta-ik)b} - e^{(\beta+ik)b} \\ &= (e^{-\beta b} - e^{\beta b}) e^{ikb} = -2(\sinh \beta b) e^{ikb} \end{aligned} \quad (\text{A.16})$$

Substituting the above relations in Eq. (A.7), we obtain

$$\begin{aligned} &(pr + qs) (e^{qa} - e^{-sb}) (e^{pa} - e^{-rb}) \\ &= (2i\alpha\beta - 2k^2) (e^{-i(\alpha+k)a} - e^{(\beta+ik)b}) (e^{i\alpha a} e^{-ika} - e^{-\beta b} e^{ikb}) \\ &= (2i\alpha\beta - 2k^2) \{e^{-2ika} + e^{2ikb} - e^{-ik(a-b)} (e^{-i\alpha a} e^{-\beta b} + e^{i\alpha a} e^{\beta b})\} \\ &= (2i\alpha\beta - 2k^2) e^{-ik(a-b)} \{e^{-ik(a+b)} + e^{ik(a+b)} - (e^{-i\alpha a} e^{-\beta b} + e^{i\alpha a} e^{\beta b})\} \\ &= (2i\alpha\beta - 2k^2) e^{-ik(a-b)} \{2 \cos k(a+b) - (e^{-i\alpha a} e^{-\beta b} + e^{i\alpha a} e^{\beta b})\} \end{aligned} \quad (\text{A.17})$$

$$\begin{aligned} &(ps + qr) (e^{qa} - e^{-rb}) (e^{-sb} - e^{pa}) \\ &= (-2i\alpha\beta - 2k^2) (e^{-i\alpha a} e^{-ika} - e^{-\beta b} e^{ikb}) (e^{\beta b} e^{ikb} - e^{i\alpha a} e^{-ika}) \\ &= (-2i\alpha\beta - 2k^2) \{e^{-i\alpha a + \beta b} e^{-ik(a-b)} - e^{-2ika} - e^{2ikb} + e^{i\alpha a - \beta b} e^{-ik(a-b)}\} \\ &= (-2i\alpha\beta - 2k^2) e^{-ik(a-b)} \{e^{-i\alpha a + \beta b} + e^{i\alpha a - \beta b} - e^{-ik(a+b)} - e^{ik(a+b)}\} \\ &= (-2i\alpha\beta - 2k^2) e^{-ik(a-b)} \{e^{-i\alpha a + \beta b} + e^{i\alpha a - \beta b} - 2 \cos k(a+b)\} \\ &= (2i\alpha\beta + 2k^2) e^{-ik(a-b)} \{2 \cos k(a+b) - (e^{-i\alpha a + \beta b} + e^{i\alpha a - \beta b})\} \end{aligned} \quad (\text{A.18})$$

$$\begin{aligned} &(pq + rs) (e^{qa} - e^{pa}) (e^{-sb} - e^{-rb}) \\ &= (\alpha^2 - \beta^2 - 2k^2) \{-2i(\sin \alpha a) e^{-ika}\} \{2(\sinh \beta b) e^{ikb}\} \\ &= (\alpha^2 - \beta^2 - 2k^2) e^{-ik(a-b)} \{-2i(\sin \alpha a)\} \{2(\sinh \beta b)\} \end{aligned} \quad (\text{A.19})$$

Let us substitute Eqs. (A.17) - (A.19) into Eq. (A.7). Since  $e^{-ik(a-b)}$  is a common factor that occurs on both sides, it cancels away.

$$\begin{aligned} &(2i\alpha\beta - 2k^2) \{2 \cos k(a+b) - (e^{-i\alpha a} e^{-\beta b} + e^{i\alpha a} e^{\beta b})\} \\ &\quad + (2i\alpha\beta + 2k^2) \{2 \cos k(a+b) - (e^{-i\alpha a + \beta b} + e^{i\alpha a - \beta b})\} \\ &= (\alpha^2 - \beta^2 - 2k^2) \{-2i(\sin \alpha a)\} \{2(\sinh \beta b)\}. \end{aligned} \quad (\text{A.20})$$

It can be easily checked that the terms involving the factor  $2k^2$  in Eq. (A.20) mutually cancel away.

$$\begin{aligned}
& (-2k^2) \{2 \cos k(a+b) - (e^{-i\alpha a} e^{-\beta b} + e^{i\alpha a} e^{\beta b})\} \\
& \quad + (2k^2) \{2 \cos k(a+b) - (e^{-i\alpha a} e^{\beta b} + e^{i\alpha a} e^{-\beta b})\} \\
& = (-2k^2) \{e^{-im\alpha a} (e^{\beta k} - e^{-\beta k}) + e^{im\alpha a} (e^{-\beta k} - e^{\beta k})\} \\
& = (-2k^2) \{(e^{-im\alpha a} - e^{im\alpha a}) (e^{\beta k} - e^{-\beta k})\} \\
& = (-2k^2) \{-2i(\sin \alpha a)\} \{2(\sinh \beta b)\} \tag{A.21}
\end{aligned}$$

So, Eq. (A.20) reduces to a simple form.

$$\begin{aligned}
& (2i\alpha\beta) \{4 \cos k(a+b) - e^{-i\alpha a}(e^{-\beta b} + e^{\beta b}) - e^{i\alpha a}(e^{\beta b} + e^{-\beta b})\} \\
& = -4i(\alpha^2 - \beta^2)(\sin \alpha a)(\sinh \beta b). \tag{A.22}
\end{aligned}$$

This can be rewritten as

$$(2\alpha\beta) \{4 \cos k(a+b) - 4 \cos \alpha a \cosh \beta b\} = 4(\beta^2 - \alpha^2)(\sin \alpha a)(\sinh \beta b), \tag{A.23}$$

which reduces to a simple relation

$$(2\alpha\beta) \{\cos k(a+b) - \cos \alpha a \cosh \beta b\} = (\beta^2 - \alpha^2)(\sin \alpha a)(\sinh \beta b). \tag{A.24}$$

Thus, we obtain Eq. (24) of Kronig and Penney, which is the condition for the determinant  $\Delta = 0$  and consequently for the existence of a solution for the energy states of electron in a periodic potential.

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

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