CHAPTER SEVENTEEN

The Band Theory of Electrons in Crystals

We have considered in early chapters of this book the quantum properties of single particles and of some two-particle systems. These included the hydrogen atom (Chapter 7), a particle in a potential well (Chapter 4), and as an example of a two-particle system, the helium atom (Section 8.2). In the last chapter we discussed the statistical properties of a many-electron gas.

In this chapter we consider the problem of an electron (or particle) in a spatially periodic potential field. The analysis is relevant to the electronic properties of crystals.

We encounter here, for the first time, some concepts of central importance in solid state physics. These include the ideas of forbidden energy gaps and of Brillouin zones. These concepts reflect the lattice periodicity and arise in other branches of physics that involve wave propagation in periodic media. Some examples are: The propagation of acoustic waves in crystals[1] and of electromagnetic waves in periodic waveguides.

17.1 THE KRONIG–PENNEY MODEL

The basic features of the wavefunctions of electrons in crystals may be demonstrated with the aid of the one-dimensional Kronig–Penney model. The potential field used in this model is shown in Fig. 17.1. The plot is that of the potential energy profile $V(x)$ experienced by a single electron. The wavefunction $\psi(x)$ of an electron in this model obeys the Schrödinger

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[1] C. Kittel, *Introduction to Solid State Physics*, 5th ed. (John Wiley & Sons, New York, 1976).

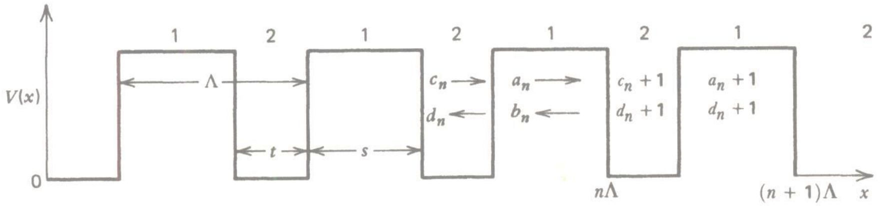

Figure 17.1 A one-dimensional periodic potential.

equation:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}=[E-V(x)]\psi(x) \tag{17.1}$$

Before proceeding to solve for $\psi(x)$, we consider some general properties of wavefunctions in periodic media. According to the Floquet theorem in mathematics (also known as the Bloch theorem in solid state physics[2]), the solution of the wave equation in a periodic medium is of the form

$$\psi_{\mathbf{K}}(\mathbf{r})=u_{\mathbf{K}}(\mathbf{r})e^{i\mathbf{K}\cdot\mathbf{r}} \tag{17.2}$$

where $u_{\mathbf{K}}(\mathbf{r})$ has the same periodicity as the medium. In one dimension (17.2) becomes

$$\psi_K(x)=u_K(x)e^{iKx} \tag{17.3}$$

where

$$u_K(x+\Lambda)=u_K(x) \tag{17.4}$$

Λ is the periodic distance.

To prove that the wavefunction $\psi(x)$ has the Bloch form (17.3), we introduce the translation operation $\hat{T}_\Lambda$ defined by

$$\hat{T}_\Lambda f(x)=f(x+\Lambda) \tag{17.5}$$

where $f(x)$ is any arbitrary function. We will first prove that $\hat{T}_\Lambda$ commutes with the Hamiltonian $\hat{\mathcal{H}}$. Since $\psi(x)$ is an eigenfunction of $\hat{\mathcal{H}}$, $\hat{\mathcal{H}}\psi(x)=E\psi(x)$, where E is the energy of the electron. Using (17.5) we write

$$\begin{aligned}\hat{T}_\Lambda\hat{\mathcal{H}}\psi(x)&=E\hat{T}_\Lambda\psi(x)\\&=E\psi(x+\Lambda)\\\hat{\mathcal{H}}\hat{T}_\Lambda\psi(x)&=\hat{\mathcal{H}}\psi(x+\Lambda)\\&=E\psi(x+\Lambda)\end{aligned}$$

so that

$$\hat{\mathcal{H}}\hat{T}_\Lambda-\hat{T}_\Lambda\hat{\mathcal{H}}=0$$

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[2] F. Bloch, *Z. Physik* **52**, pp. 555–560 (1928).

and $\hat{\mathcal{H}}$ and $\hat{T}_\Lambda$ commute. Two commuting operators have common eigenfunctions so that $\psi(x)$ can be chosen to be an eigenfunction of $\hat{T}_\Lambda$ as well as of $\hat{\mathcal{H}}$ (see the discussion in Chapter 3). Let the corresponding eigenvalue be c so that

$$\begin{aligned}\hat{T}_\Lambda\psi(x) &= \psi(x+\Lambda)\\ &= c\psi(x)\end{aligned} \tag{17.6a}$$

where c is some constant. Then

$$\psi(x+g\Lambda)=c^g\psi(x) \tag{17.6b}$$

To determine c we need to impose boundary conditions on $\psi(x)$. The one commonly used[3] is that $\psi(x)=\psi(x+L)$, where $L=N\Lambda$ is the length of our one-dimensional crystal:

$$\begin{aligned}\psi(x+N\Lambda) &= c^N\psi(x)\\ &= \psi(x)\end{aligned} \tag{17.7}$$

so that

$$C^N=1, \qquad C=e^{i(2\pi g/N)}\,(g=0,1,2,\ldots,N-1) \tag{17.8}$$

A solution satisfying (17.3) and (17.7) can be taken as

$$\psi_g(x)=e^{i2\pi g(x/N\Lambda)}u_g(x) \tag{17.9}$$

where $u_g(x)$ *is periodic in* Λ. Defining

$$K=\frac{2\pi g}{N\Lambda}=\frac{2\pi}{L}g(g=0,\pm1,\pm2,\ldots) \tag{17.10}$$

the total eigenfunction can thus be written as

$$\psi_K(x)=u_K(x)e^{iKx} \tag{17.11}$$

which is the Bloch form.

We are now ready to proceed with the solution of the Schrödinger equation:

$$\frac{d^2\psi}{dx^2}+\frac{2m}{\hbar^2}[E-V(x)]\psi=0 \tag{17.12}$$

Since $V(x)$ has a constant value of V_0 in regions 1 and is zero in regions 2, the solution of (17.12) in each region is a superposition of the two linearly independent exponential solutions:

$$\psi(x)=a_n e^{k_1(x-n\Lambda)}+b_n e^{-k_1(x-n\Lambda)} \quad \text{in regions 1} \tag{17.13}$$

$$\psi(x)=c_n e^{ik_2(x-n\Lambda)}+d_n e^{-ik_2(x-n\Lambda)} \quad \text{in regions 2} \tag{17.14}$$

with

$$k_1=\frac{\sqrt{2m(V_0-E)}}{\hbar} \tag{17.15}$$

$$k_2=\frac{\sqrt{2mE}}{\hbar} \tag{17.16}$$

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[3] C. Kittel, *Introduction to Solid State Physics*, 5th ed. (John Wiley & Sons, New York, 1975).

Our next task is that of solving for the coefficients a_n, b_n, and d_n that uniquely determine $\psi(x)$. Requiring that $\psi(x)$ and $d\psi/dx$ be continuous at $x = n\Lambda$ yields

$$\begin{aligned} a_n + b_n &= c_{n+1}e^{-ik_2\Lambda} + d_{n+1}e^{ik_2\Lambda} \\ k_1 a_n - k_1 b_n &= ik_2 c_{n+1}e^{-ik_2\Lambda} - ik_2 d_{n+1}e^{ik_2\Lambda} \end{aligned} \tag{17.17}$$

while the same boundary conditions applied at $x = n\Lambda + t = (n+1)\Lambda - s$ gives

$$\begin{aligned} c_{n+1}e^{-ik_2 s} + d_{n+1}e^{ik_2 s} &= a_{n+1}e^{-k_1 s} + b_{n+1}e^{k_1 s} \\ ik_2 c_{n+1}e^{-ik_2 s} - ik_2 e^{ik_2 s} d_{n+1} &= k_1 a_{n+1}e^{-k_1 s} - k_1 b_{n+1}e^{k_1 s} \end{aligned} \tag{17.18}$$

Equations (17.17) and (17.18) can be expressed using matrix notation as

$$\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \begin{pmatrix} a_n \\ b_n \end{pmatrix} = \begin{pmatrix} e^{-ik_2\Lambda} & e^{ik_2\Lambda} \\ i\dfrac{k_2}{k_1}e^{-ik_2\Lambda} & -i\dfrac{k_2}{k_1}e^{ik_2\Lambda} \end{pmatrix} \begin{pmatrix} c_{n+1} \\ d_{n+1} \end{pmatrix} \tag{17.19}$$

and

$$\begin{pmatrix} e^{-ik_2 s} & e^{ik_2 s} \\ e^{-ik_2 s} & -e^{ik_2 s} \end{pmatrix} \begin{pmatrix} c_{n+1} \\ d_{n+1} \end{pmatrix} = \begin{pmatrix} e^{-k_1 s} & e^{k_1 s} \\ -i\dfrac{k_1}{k_2}e^{-k_1 s} & i\dfrac{k_1}{k_2}e^{k_1 s} \end{pmatrix} \begin{pmatrix} a_{n+1} \\ b_{n+1} \end{pmatrix} \tag{17.20}$$

By obvious matrix manipulation (pre- and post-multiplication) we can relate (a_n, b_n) to (a_{n+1}, b_{n+1}):

$$\begin{vmatrix} a_n \\ b_n \end{vmatrix} = \begin{vmatrix} A & B \\ C & D \end{vmatrix} \begin{vmatrix} a_{n+1} \\ b_{n+1} \end{vmatrix} \tag{17.21}$$

where

$$\begin{aligned} A &= e^{-k_1 s}\left[\cos k_2 t + \frac{1}{2}\left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\sin k_2 t\right] \\ B &= e^{k_1 s}\left[\frac{1}{2}\left(\frac{k_2}{k_1} + \frac{k_1}{k_2}\right)\sin k_2 t\right] \\ C &= e^{-k_1 s}\left[-\frac{1}{2}\left(\frac{k_2}{k_1} + \frac{k_1}{k_2}\right)\sin k_2 t\right] \\ D &= e^{k_1 s}\left[\cos k_2 t - \frac{1}{2}\left(\frac{k_2}{k_1} - \frac{k_1}{k_2}\right)\sin k_2 t\right] \end{aligned} \tag{17.22a}$$

The matrix (A, B, C, D) is referred to as the unit cell transformation matrix. From (17.22a) it follows that

$$AD - BC = 1 \tag{17.22b}$$

that is, the transformation matrix is unimodular.

Using (17.21) we can obtain the coefficients a_n, b_n in any unit cell once their values in some cell are known. We can then solve—using (17.19)—for c_n, d_n, given a_{n-1}, b_{n-1}.

Consider the basic solution of $\psi(x)$ in region 1 of the nth unit cell, Eq. (17.13):

$$\psi(x)=a_n e^{k_1(x-n\Lambda)}+b_n e^{-k_1(x-n\Lambda)}$$

so that

$$\begin{aligned}\psi(x+\Lambda)&=a_{n+1}e^{k_1[x+\Lambda-(n+1)\Lambda]}+b_{n+1}e^{-k_1[x+\Lambda-(n+1)\Lambda]}\\&=a_{n+1}e^{k_1(x-n\Lambda)}+b_{n+1}e^{-k_1(xn-\Lambda)}\end{aligned}$$

The Bloch form of $\psi(x)$ imposed by the periodicity was given by (17.11) as

$$\psi(x)=\psi(x+\Lambda)e^{iK\Lambda}$$

The last two forms of $\psi(x)$ can be reconciled provided

$$\begin{vmatrix}a_n\\b_n\end{vmatrix}=\begin{vmatrix}a_{n+1}\\b_{n+1}\end{vmatrix}e^{-iK\Lambda}\tag{17.23}$$

which, using (17.21) and then letting $n+1\rightarrow n$, leads to

$$\begin{vmatrix}A&B\\C&D\end{vmatrix}\begin{vmatrix}a_n\\b_n\end{vmatrix}=e^{-iK\Lambda}\begin{vmatrix}a_n\\b_n\end{vmatrix}\tag{17.24}$$

Equation (17.24) is in the form of the general operator eigenvalue problem

$$\hat{A}u_n=a_n u_n$$

where the matrix (A,B,C,D) can be considered as a matrix representation of the unit cell translation operator in a 2×2 function space, and the column matrix (a_n,b_n) is the eigenvector. The factor $\exp(-iK\Lambda)$ is thus the eigenvalue of the matrix. By subtracting the right side of (17.24) from the left side, we obtain

$$\begin{vmatrix}A-e^{-iK\Lambda}&B\\C&D-e^{-iK\Lambda}\end{vmatrix}\begin{vmatrix}a_n\\b_n\end{vmatrix}=0\tag{17.25}$$

which is a set of two homogeneous equations for the unknowns a_n and b_n. The condition for the existence of nontrivial solutions is that the determinant vanish. After using (17.22*a*), this leads to

$$e^{-iK_{1,2}\Lambda}=\tfrac{1}{2}(A+D)\pm i\left\{1-\left[\tfrac{1}{2}(A+D)\right]^2\right\}^{1/2}\tag{17.26}$$

where the 1,2 subscripts correspond to + and − on the right side, respectively. The eigenvectors corresponding to the eigenvalues (17.26) are obtained by substituting (17.26) in (17.25), leading to

$$\begin{vmatrix}a_0\\b_0\end{vmatrix}=N\begin{vmatrix}B\\e^{-iK_{1,2}\Lambda}-1\end{vmatrix}\tag{17.27}$$

where N is a normalization constant to ensure that $\int \psi\psi^* \, dV = 1$. Given a_0 and b_0 we can use (17.13) to write the eigenfunction $\psi_K(x)$ in region 1 of the nth unit cell:

$$\psi_K(x) = N\left[\left(a_0 e^{k_1(x-n\Lambda)} + b_0 e^{-k_1(x-n\Lambda)}\right)e^{-iK(x-n\Lambda)}\right]e^{iKx} \qquad (17.28)$$

The expression for $\psi(x)$ has the required Bloch form (17.11), since the portion of the function within the square brackets is periodic in Λ. The propagation constant K is obtained from (17.26):

$$\cos(K\Lambda) = \tfrac{1}{2}(A + D) \qquad (17.29)$$

which is the basic dispersion relation for the propagation of the wavefunction. Using the specific form of A and D (17.22), we obtain

$$\cos(K\Lambda) = \cos(k_2 t)\cosh(k_1 s) + \sin(k_2 t)\sinh(k_1 s)\left(\frac{k_1^2 - k_2^2}{2k_1 k_2}\right) \qquad (17.30)$$

A contemplation of the dispersion relation (17.30) is in order. The right side is, according to (17.15) and (17.16), a function of the particle energy $E = \hbar^2 k_2^2/2m$. Given any value of E, we can thus use (17.30) to obtain $K\Lambda$ (to within a multiple of 2π). We distinguish between two regimes:

(a) Values of energy E such that

$$|\tfrac{1}{2}(A + D)| < 1 \qquad (17.31)$$

It follows from (17.29) that in this case K is real and $\psi_K(x)$, according to (17.28), is a (modulated) propagating wave. These regions of E are referred to as "*allowed.*"

(b) Values of E such that

$$|\tfrac{1}{2}(A + D)| > 1 \qquad (17.32)$$

Here $|\cos K\Lambda| > 1$ and K must be complex. Since $\frac{1}{2}(A + D)$ is real, it follows that

$$K = \frac{m\pi}{\Lambda} + iK_i \quad (m = \pm\pi, \pm 2\pi, \ldots) \qquad (17.33)$$

[The simple proof of (17.33) is assigned as a problem.] In this regime the factor $\exp(iKx)$ in (17.28) becomes

$$\exp(iKx) = e^{i(m\pi/\Lambda)x}\exp(-|K_i|x)$$

and the $\psi_K(x)$ is an exponentially evanescent function. In the interior of a large crystal $\psi_K(x)$ is thus zero. (The solution corresponding to $\exp(|K_i|x)$ is ruled out, since it leads to unphysical solutions that increase exponentially without limit.

The energy intervals for which $|\frac{1}{2}(A + D)| > 1$ so that K is complex are referred to as the *forbidden energy gaps*. No electrons with "forbidden" energies can "exist" in the interior of a large crystal. In practice, we can find such electrons only within a few times K_i^{-1} from an interface or some other discontinuity in the crystal structure.

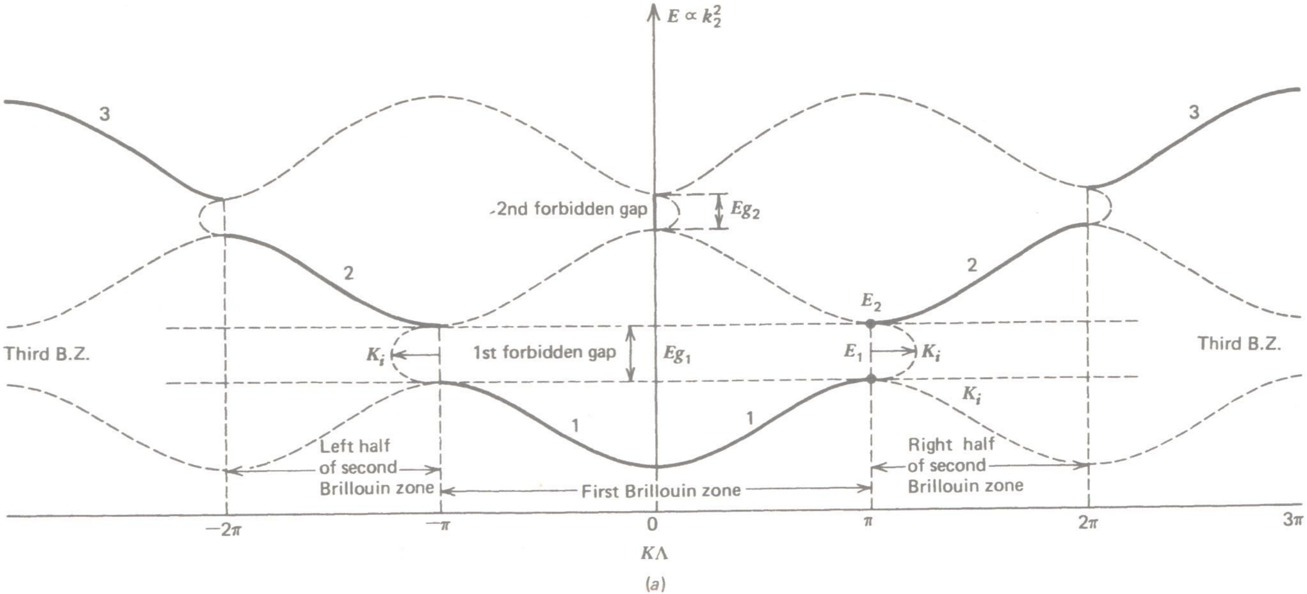

Figure 17.2 (*a*) The dispersion diagram E vs. $K\Lambda$ for electrons in the Kronig–Penney potential field.

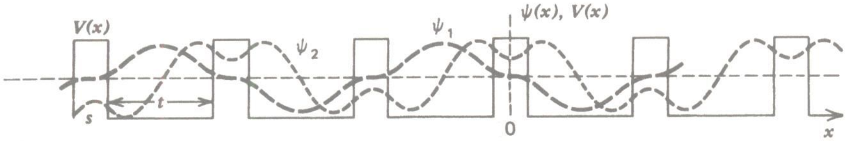

Figure 17.2 (*b*) A schematic representation of the eigenfunctions ψ_1 (odd symmetry) and ψ_2 at the edge of the forbidden gap, that is, $K\Lambda = m\pi$, $K_i = 0$. ψ_1 has its nodes inside the potential barriers, while ψ_2 has its maxima inside them. The eigenenergy E_1 of ψ_1 is thus lower than the energy E_2 of ψ_2.

A typical plot of E vs. K (and K_i) obtained from (17.30) is shown in Fig. 17.2*a*. We notice that the decay constant K_i is maximum at midgap.

The condition $K\Lambda = m\pi$ that, according to (17.33), marks the boundary of a forbidden gap, is formally equivalent to the one-dimensional Bragg condition for X rays.[4] When this condition is satisfied, the reflections of the electron wavefunction $\psi_K(x)$ from neighboring unit cells are in phase and reinforce each other since the round-trip phase delay is $2\ K\Lambda\ =\ 2m\pi$. Under these conditions $\psi_K(x)$ is strongly reflected and cannot "penetrate" into the bulk of the crystal, which results in the evanescent behavior of (17.33).

The perfect reflection of the particle wave that occurs when $K\Lambda = m\pi$ causes the wavefunction to behave like a standing wave rather than a running wave. (A standing sinusoidal wave, we recall, results from the interference of e^{iKx} and e^{-iKx}.) There are two independent standing wave solutions corresponding to the same value of $K = m\pi/\Lambda$—one even and one odd—since the eigenfunctions must possess definite parity. Since one of these two functions has its extrema inside the potential barriers, its eigenenergy E_2 is higher than that of the second function that has its nodes at the barriers. There are thus two eigenfunctions with the same value of $K = m\pi/\Lambda$ but with two different energies. These two energies E_1 and E_2 in Fig. 17.2 correspond to the top and bottom of the forbidden gap. The schematic behavior of the two eigenfunctions at the edge of the gap is illustrated in Fig. 17.2*b*.

The region $-\pi < K\Lambda \leq \pi$ is called the first Brillouin zone.[5] The two regions $\pi < K\Lambda < 2\pi$ and $-2\pi < K\Lambda < -\pi$ are designated collectively as the second Brillouin zone, and so on.

Since the dispersion relation (17.30) only determines $K\Lambda$ to within $2m\pi$, m being an integer, and since $\psi_K(x)$ as given by (17.28) is invariant when K is replaced by $K + m(2\pi/\Lambda)$, we may "collapse" the dispersion diagram (Fig. 17.2) to the interval $-\pi/\Lambda < K < \pi/\Lambda$ by shifting the dark portions of the curves horizontally by $(2\pi/\Lambda)l$ (l=some integer). The result, known as the reduced zone energy band diagram, is shown in Fig. 17.3.

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[4] See Kittel, *ibid.*

[5] L. Brillouin is responsible for many of the basic concepts involving propagation in periodic media. See, for example, his book *Wave Propagation in Periodic Structures* (McGraw-Hill, New York, 1946).

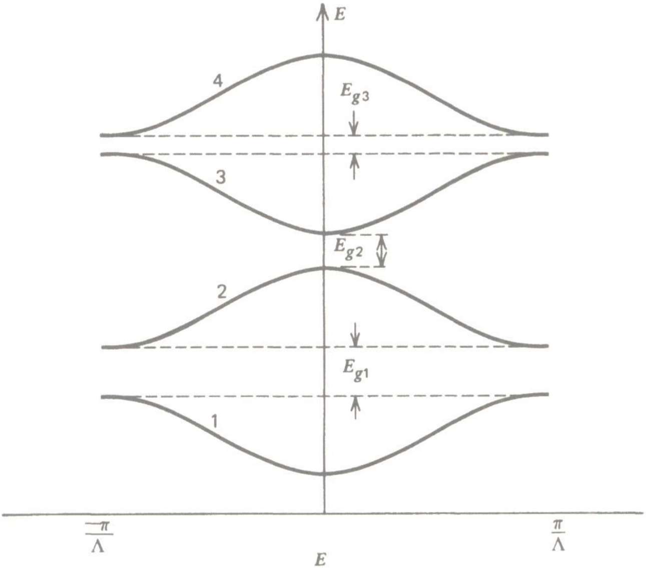

Figure 17.3 A reduced zone band diagram. The numerical designation corresponds to Fig. 17.2.

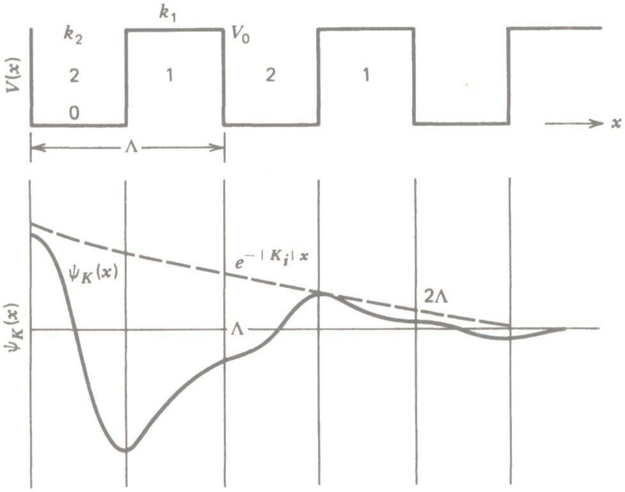

Figure 17.4 The behavior of the wavefunction of an electron whose energy is inside the first forbidden gap.

A schematic plot of the wavefunction $\psi_K(x)$ (17.28) for an energy E somewhere in the first forbidden gap ($K\Lambda = \pi + iK_i$) is shown in Fig. 17.4. Note the phase reversal [$\exp(iK\Lambda) = -1$] in each unit cell. The basic behavior of $\psi_K(x)$ is one of sinusoidal variation in region 2 and exponential in region 1. The whole pattern fits under an evanescent envelope $\exp(-K_i X)$ so that it decays quickly upon penetration into the bulk of the crystal and is thus associated with "surface electron states."

17.2 THE MULTIELECTRON CRYSTAL

The solution of the Schrödinger equation in a periodic potential field resulted in the one-particle eigenfunctions (17.28)

$$\psi_K(x) = u_K(x)e^{iKx} \tag{17.34}$$

and the associated energy E_K. If we neglect the interaction between electrons, we can treat the case of a real crystal with many electrons by associating with each allowed value of K one electron, until all the electrons are used up.

In the deliberations leading to (17.10), we showed that in a (one-dimensional) crystal *consisting of N unit cells*, the allowed set of K numbers is restricted to the set

$$K = \frac{2\pi g}{N\Lambda} = \frac{2\pi}{L} g \quad (g = 0, \pm 1, \pm 2, \ldots)$$

so that two adjacent K numbers are separated by $\Delta K = 2\pi/L$. These are shown as dots in Fig. 17.5. Since the length of a Brillouin zone is $2\pi/\Lambda$ there are

$$\frac{2\pi/\Lambda}{\Delta K} = \frac{2\pi/\Lambda}{2\pi/L} = \frac{L}{\Lambda} = N$$

allowed K values in each zone. Since with each K value we may associate 2 spin states ($m_s = \pm\frac{1}{2}$), each Brillouin zone can accommodate $2N$ electrons, where N, we recall, is the number of unit cells in the crystal. If the number of valence electrons per unit cell[6] is 2, then the first zone is exactly full. If the number is 1, the zone is only half full. In general, an even number of electrons per unit cell leads to fully occupied zones, while an odd number requires that the uppermost zone (band) is only half full.

When an electric field is applied to a crystal with an even number of valence electrons per unit cell so that the uppermost Brillouin zone is filled with no electrons left over for the next higher zone, as in Fig. 17.5, there is *no current flow.* This astounding fact follows from the symmetry of a filled band. For each electron moving to the right ($K > 0$), there is a corresponding electron with ($K < 0$) with an equal but oppositely directed velocity,[7] so that

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[6] We assume that the inner atomic electrons are tightly bound and do not play a significant role in the electronic conduction process.

[7] The more precise explanation of this fact should use the concept of the electron group velocity, which is introduced in Section 17.3.