7. The Electronic Bandstructure of Solids

Despite the success of the free-electron-gas model in describing electrons in crystals (Chap. 6), it must be recognized that the assumptions of the one-electron approximation and of a square-well potential, are oversimplifications. Thus one cannot expect this model to explain, for example, the fundamentally important optical and electronic properties of semiconductors. If one imagines, as discussed briefly in Chap. 1, that a solid is created by allowing initially free atoms to gradually approach one another, then the discrete nature of the energy levels of the isolated atoms should clearly by reflected in the properties of the solid. Indeed, discrete energy levels must be present in order to explain, e.g., the sharp resonance-like structures observed in the optical spectra of solids. An explanation of such features is beyond the scope of the free-electron-gas model. Furthermore, this model is unable to shed any light on the nature of semiconductors and insulators. To make further progress one has to take into account that the electronic states in solids form so-called bands. One can think of these as deriving from the states of the free atom.

In our present approximation, all deviations from perfect periodicity, be they static perturbations of the lattice or dynamic lattice vibrations, will be neglected. The assumption of an infinitely extended potential also means the neglect of all surface effects. To arrive at a finite crystal, i.e., one with a finite number of degrees of freedom, that is compatible with the infinite periodicity, one again makes use of the periodic boundary conditions introduced in Sect. 5.1.

7.1 General Symmetry Properties

We are now faced with the task of solving the time-independent Schrödinger equation for a single electron under the assumption that the potential $V(\boldsymbol{r})$ is periodic:

$$\mathscr{H}\psi(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r}) \right] \psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \ , \tag{7.1}$$

where

$$V(\boldsymbol{r}) = V(\boldsymbol{r}+\boldsymbol{r}_n); \quad \boldsymbol{r}_n = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3 \ . \tag{7.2}$$

As in Sect. 3.2, $\boldsymbol{r}_n$ represents an arbitrary translation vector of the three-dimensional periodic lattice, i.e., $\boldsymbol{r}_n$ consists of multiples (n_1, n_2, n_3) of the three basis vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$ of the real-space lattice.

Since the potential $V(\boldsymbol{r})$ has the same periodicity as the lattice, it can be expanded in the following Fourier series:

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} e^{i\boldsymbol{G}\cdot\boldsymbol{r}} \tag{7.3}$$

where the vector $\boldsymbol{G}$ must be a reciprocal lattice vector

$$\boldsymbol{G} = h\boldsymbol{g}_1 + k\boldsymbol{g}_2 + l\boldsymbol{g}_3, \quad h,k,l \text{ integers} \tag{7.4}$$

(in the one-dimensional case $\boldsymbol{G} \to G = h2\pi/a$). The most general plane-wave expansion of the required wavefunction $\psi(\boldsymbol{r})$ is

$$\psi(\boldsymbol{r}) = \sum_{\boldsymbol{k}} C_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \ . \tag{7.5}$$

Here $\boldsymbol{k}$ is a point in reciprocal space that is compatible with the periodic boundary conditions (Sects. 5.1 and 6.1). Substituting the expansions (7.3) and (7.5) into the Schrödinger equation (7.1) we obtain:

$$\sum_{\boldsymbol{k}} \frac{\hbar^2 k^2}{2m} C_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} + \sum_{\boldsymbol{k}'\boldsymbol{G}} C_{\boldsymbol{k}'} V_{\boldsymbol{G}} e^{i(\boldsymbol{k}'+\boldsymbol{G})\cdot\boldsymbol{r}} = E \sum_{\boldsymbol{k}} C_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \ . \tag{7.6}$$

After renaming the summation indices this becomes

$$\sum_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \left[\left(\frac{\hbar^2 k^2}{2m} - E \right) C_{\boldsymbol{k}} + \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} \right] = 0 \ . \tag{7.7}$$

Since this condition is valid for every position vector $\boldsymbol{r}$, the expression in brackets, which is independent of $\boldsymbol{r}$, must vanish for every $\boldsymbol{k}$, i.e.,

$$\left(\frac{\hbar^2 k^2}{2m} - E \right) C_{\boldsymbol{k}} + \sum_{\boldsymbol{G}} V_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} = 0 \ . \tag{7.8}$$

This set of algebraic equations, which is simply a representation of the Schrödinger equation (7.1) in reciprocal space, couples only those expansion coefficients $C_{\boldsymbol{k}}$ of $\psi(\boldsymbol{r})$ (7.5), whose $\boldsymbol{k}$-values differ from one another by a reciprocal lattice vector $\boldsymbol{G}$. Thus $C_{\boldsymbol{k}}$ is coupled to $C_{\boldsymbol{k}-\boldsymbol{G}}, C_{\boldsymbol{k}-\boldsymbol{G}'}, C_{\boldsymbol{k}-\boldsymbol{G}''}, \ldots$.

The original problem thus separates into N problems (N = number of unit cells), each corresponding to a $\boldsymbol{k}$-vector in the unit cell of the reciprocal lattice. Each of the N systems of equations yields a solution that can be represented as a superposition of plane waves whose wave vectors $\boldsymbol{k}$ differ only by reciprocal lattice vectors $\boldsymbol{G}$. The eigenvalues E of the Schrödinger equation (7.1) can thus be indexed according to $\boldsymbol{k}$, $E_{\boldsymbol{k}} = E(\boldsymbol{k})$, and the wavefunction belonging to $E_{\boldsymbol{k}}$ is

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} e^{i(\boldsymbol{k}-\boldsymbol{G})\cdot\boldsymbol{r}} \tag{7.9}$$

or

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} e^{-i\boldsymbol{G}\cdot\boldsymbol{r}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} = u_{\boldsymbol{k}}(\boldsymbol{r}) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \ . \tag{7.10a}$$

The function $u_{\boldsymbol{k}}(\boldsymbol{r})$ introduced here is a Fourier series over reciprocal lattice points $\boldsymbol{G}$ and thus has the periodicity of the lattice. The wave vector $\boldsymbol{k}$, which, for periodic boundary conditions, can take the values (Sect. 6.1)

$$k_x = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots, \frac{2\pi n_x}{L}$$

$$k_y = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots, \frac{2\pi n_y}{L} \qquad (7.10\text{b})$$

$$k_z = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots, \frac{2\pi n_z}{L}$$

(L = macroscopic dimension of the crystal), yields the correct quantum numbers k_x, k_y, k_z or n_x, n_y, n_z, according to which the energy eigenvalues and quantum states may be indexed. In other words, we have shown that the solution of the one-electron Schrödinger equation for a periodic potential can be written as a modulated plane wave

$$\psi_k(r) = u_k(r)e^{ik\cdot r} \qquad (7.10\text{c})$$

with a modulation function

$$u_k(r) = u_k(r+r_n) \qquad (7.10\text{d})$$

that has the periodicity of the lattice. This result is known as *Bloch's theorem*, and the wavefunctions given in (7.10a–d) are called the *Bloch waves* or Bloch states of an electron (Fig. 7.1).

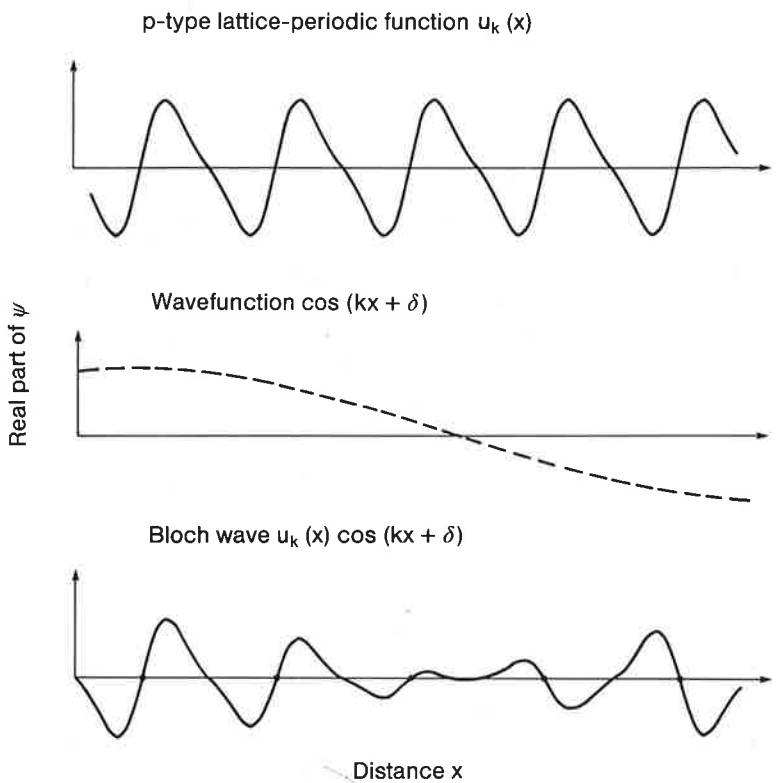

Fig. 7.1. Example of the construction of a Bloch wave $\psi_k(r) = u_k(r)e^{ik\cdot r}$ from a lattice-periodic function $u_k(r)$ with p-type bonding character and a plane wave

The strict periodicity of the lattice potential has further consequences that follow directly from the properties of the Bloch states. From the general representation of a Bloch wave (7.10a), and by renaming the reciprocal lattice vectors $\boldsymbol{G}'' = \boldsymbol{G}' - \boldsymbol{G}$, it follows that

$$\psi_{k+G}(\boldsymbol{r}) = \sum_{G'} C_{k+G-G'} e^{-iG'\cdot r} e^{i(k+G)\cdot r} = \left(\sum_{G''} C_{k-G''} e^{-iG''\cdot r} \right) e^{ik\cdot r} = \psi_k(\boldsymbol{r}) \ , \tag{7.11a}$$

i.e.,

$$\psi_{k+G}(\boldsymbol{r}) = \psi_k(\boldsymbol{r}) \ . \tag{7.11b}$$

Thus Bloch waves whose wave vectors differ by a reciprocal lattice vector are identical. The Schrödinger equation (7.1):

$$\mathscr{H}\psi_k = E(\boldsymbol{k})\,\psi_k \tag{7.12}$$

and that for the same problem displaced by $\boldsymbol{G}$:

$$\mathscr{H}\psi_{k+G} = E(\boldsymbol{k}+\boldsymbol{G})\,\psi_{k+G} \tag{7.13}$$

together with (7.11b) then yield

$$\mathscr{H}\psi_k = E(\boldsymbol{k}+\boldsymbol{G})\,\psi_k \ . \tag{7.14}$$

Comparing (7.12) with (7.14) we see that

$$E(\boldsymbol{k}) = E(\boldsymbol{k}+\boldsymbol{G}) \ . \tag{7.15}$$

Thus the energy eigenvalues $E(\boldsymbol{k})$ are a periodic function of the quantum numbers $\boldsymbol{k}$, i.e., of the wave vectors of the Bloch waves.

Similar to the case of phonons, whose $\omega(\boldsymbol{q})$ can be described by dispersion surfaces in reciprocal $\boldsymbol{q}$-space, the one-electron states of a periodic potential can be represented by energy surfaces $E = E(\boldsymbol{k})$ that are a periodic function of the wave vector (quantum number) in reciprocal $\boldsymbol{k}$-space. Taken together, these energy surfaces form the *electronic bandstructure* of the crystal. Since both $\psi_k(\boldsymbol{r})$ and $E(\boldsymbol{k})$ are periodic in reciprocal space, one only needs to know these functions for $\boldsymbol{k}$-values in the first Brillouin zone (Sect. 3.5). A periodic continuation of the functions then provides the values throughout the whole of $\boldsymbol{k}$-space.

7.2 The Nearly-Free-Electron Approximation

To understand the general concept of electronic bands it is particularly instructive to consider the limiting case of a vanishingly small periodic potential. We therefore imagine that the periodic potential starts at zero and is gradually "switched on". What happens then to the energy states of the free electrons which, in the square-well potential, were described by the energy parabola $E = \hbar^2 k^2/2m$? In the extreme case where the potential is still zero, i.e., where all Fourier coefficents V_G (7.3) vanish, one must nonetheless consider the symmetry requirements of the periodicity, since the requirements will be a decisive factor even for the smallest nonvanishing potential. This

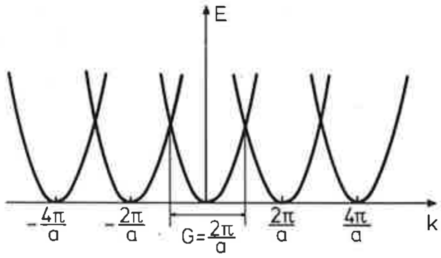

Fig. 7.2. The parabolic energy curves of a free electron in one dimension, periodically continued in reciprocal space. The periodicity in real space is a. This $E(\boldsymbol{k})$ dependence corresponds to a periodic lattice with a vanishing potential ("empty" lattice)

general demand of periodicity immediately implies, from (7.15), that the possible electron states are not restricted to a single parabola in $\boldsymbol{k}$-space, but can be found equally well on parabolas shifted by any $\boldsymbol{G}$-vector:

$$E(\boldsymbol{k}) = E(\boldsymbol{k}+\boldsymbol{G}) = \frac{\hbar^2}{2m}\,|\boldsymbol{k}+\boldsymbol{G}|^2 \;. \tag{7.16}$$

For the one-dimensional case $(\boldsymbol{G} \to G = h2\pi/a)$ this is depicted in Fig. 7.2.

Since the behavior of $E(\boldsymbol{k})$ is periodic in $\boldsymbol{k}$-space, it is sufficient to represent this in the first Brillouin zone only. To achieve this one simply displaces the part of the parabola of interest by the appropriate multiple of $G = 2\pi/a$. This procedure is called "*Reduction to the first Brillouin zone*".

In three dimensions, the $E(\boldsymbol{k})$ bands are already more complicated, even in the case of a vanishing potential, since in (7.16) one now has $\boldsymbol{G}$ contributions in all three coordinate directions. Figure 7.3 shows the $E(\boldsymbol{k})$ curves along k_x in the first Brillouin zone for a simple cubic lattice with vanishing potential.

The effect of a finite but very small potential can now be discussed with reference to Figs. 7.2 and 7.3.

In the one-dimensional problem of Fig. 7.2 there is a degeneracy of the energy values at the edges of the first Brillouin zone, i.e., at $+G/2 = \pi/a$ and $-G/2 = -\pi/a$, where two parabolas intersect. The description of the state of an electron with these k-values is necessarily a superposition of at least two corresponding plane waves. For a vanishing potential (zeroth-order approximation) these waves are

$$e^{iGx/2} \quad \text{and} \quad e^{i[(G/2)-G]x} = e^{-iGx/2} \;. \tag{7.17}$$

Equation (7.8) implies that waves with G-values larger than $2\pi/a$ must also be taken into account. However, on dividing (7.8) by $[(\hbar^2k^2/2m)-E]$, it follows that C_k is particularly large when E_k and E_{k-G} are both approximately equal to $\hbar^2k^2/2m$, and that the coefficient C_{k-G} then has approximately the same absolute magnitude as C_k. This is precisely the case for the two plane waves at the zone boundaries (7.17), and thus, to a first approximation, one can neglect contributions from other reciprocal lattice vectors. The appropriate expressions for a perturbation calculation of the influence of a small potential are therefore of the form

$$\psi_+ \sim (e^{iGx/2} + e^{-iGx/2}) \sim \cos\pi\frac{x}{a} \;, \tag{7.18a}$$

$$\psi_- \sim (e^{iGx/2} - e^{-iGx/2}) \sim \sin\pi\frac{x}{a} \;. \tag{7.18b}$$

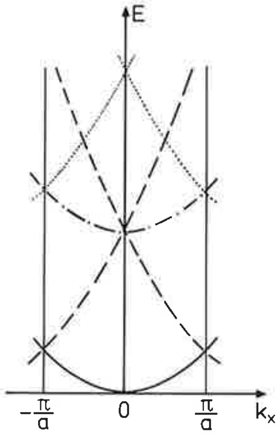

Fig. 7.3. Band structure for a free electron gas in a primitive cubic lattice (lattice constant a), represented on a section along k_x in the first Brillouin zone. The periodic potential is assumed to be vanishing ("empty" lattice). The various branches stem from parabolas whose origin in reciprocal space is given by the Miller indices hkl. (——) 000, (– – –) 100, $\bar{1}00$, (– · –) 010, $0\bar{1}0$, 001, $00\bar{1}$, (· · ·) 110, 101, $1\bar{1}0$, $10\bar{1}$, $\bar{1}10$, $\bar{1}01$, $\bar{1}\bar{1}0$, $\bar{1}0\bar{1}$

Fig. 7.4

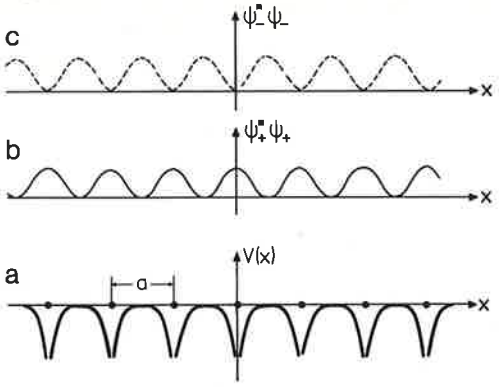

Fig. 7.5

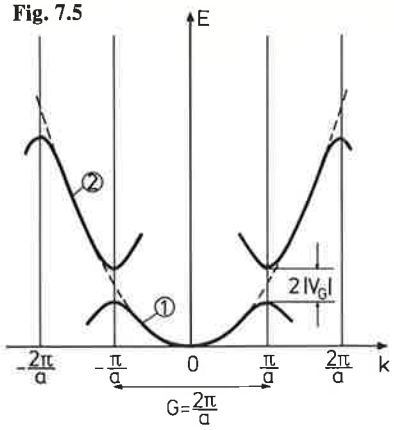

Fig. 7.4. (a) Qualitative form of the potential energy $V(x)$ of an electron in a one-dimensional lattice. The positions of the ion cores are indicated by the points with separation a (lattice constant). (b) Probability density $\varrho_+ = \psi_+^* \psi_+$ for the standing wave produced by Bragg reflection at $k = \pm\pi/a$ (upper edge of band ① in Fig. 7.5). (c) Probability density $\varrho_- = \psi_-^* \psi_-$ for the standing wave at the lower edge of band ② (Fig. 7.5) at $k = \pm\pi/a$

Fig. 7.5. Splitting of the energy parabola of the free electron (– – –) at the edges of the first Brillouin zone ($k = \pm\pi/a$ in the one-dimensional case). To a first approximation the gap is given by twice the corresponding Fourier coefficient V_G of the potential. Periodic continuation over the whole of k-space gives rise to continuous bands ① and ②, shown here only in the vicinity of the original energy parabola

These are standing waves possessing zeros at fixed positions in space. As seen in the discussion of diffraction from periodic structures (Chap. 3), these standing waves can be represented as a superposition of an incoming wave and a counter-propagating "Bragg-reflected" wave. The probability densities corresponding to ψ_+ and ψ_-,

$$\varrho_+ = \psi_+^* \psi_+ \sim \cos^2 \pi \frac{x}{a} , \tag{7.19a}$$

$$\varrho_- = \psi_-^* \psi_- \sim \sin^2 \pi \frac{x}{a} , \tag{7.19b}$$

are depicted in Fig. 7.4 together with a qualitative sketch of the potential. For an electron in the state ψ_+, the charge density is maximum at the position of the positive cores and minimum in between; for ψ_- the charge density is maximum between the cores. In comparison with the travelling plane wave e^{ikx}, which is a good approximation to the solution further away from the zone boundary, ψ_+ thus has a lower total energy (particularly potential energy), and ψ_- a higher energy than that of a free electron on the energy parabola (zero potential case). This increase and decrease in the energy of the states at the zone boundary represents a deviation from the free-electron energy parabola (Fig. 7.5).

Having gained insight into the problem from this qualitative discussion, it is now easy to carry out a formal calculation of the magnitude of the so-called band splitting or *energy gap* shown in Fig. 7.5.

Starting from the general representation of the Schrödinger equation in k-space (7.8), translation by a reciprocal lattice vector yields

$$\left(E-\frac{\hbar^2}{2m}\,|\boldsymbol{k}-\boldsymbol{G}|^2\right) C_{k-G} = \sum_{G'} V_{G'} C_{k-G-G'} = \sum_{G'} V_{G'-G} C_{k-G'} \,, \tag{7.20a}$$

i.e.

$$C_{k-G} = \frac{\sum_{G'} V_{G'-G} C_{k-G'}}{E-(\hbar^2/2m)\,|\boldsymbol{k}-\boldsymbol{G}|^2} \,. \tag{7.20b}$$

For small perturbations, a first approximation to the calculation of C_{k-G} can be made by setting the true eigenvalue E that we are seeking equal to the energy of the free electron ($\hbar^2 k^2/2m$). Furthermore, in this first approximation, only the largest coefficients C_{k-G} are of interest; in other words, we expect the greatest deviation from free-electron behavior when the denominator in (7.20b) vanishes, i.e., for

$$\boldsymbol{k}^2 \simeq |\boldsymbol{k}-\boldsymbol{G}|^2 \,. \tag{7.21}$$

This is identical to the Bragg condition (3.24). The strongest perturbations to the energy surface of the free electron (spheres in $\boldsymbol{k}$-space) produced by the periodic potential, occur when the Bragg condition is satisfied, i.e., for the $\boldsymbol{k}$-vectors at the edge of the first Brillouin zone. It follows from (7.20b), however, that besides C_{k-G}, the coefficient C_k is equally important. Thus, in the system of equations (7.20a), for this approximation we only need to consider two relations ($V_0 = 0$):

$$\begin{aligned} &\left(E-\frac{\hbar^2}{2m}\,k^2\right) C_k - V_G C_{k-G} = 0 \\ &\left(E-\frac{\hbar^2}{2m}|\boldsymbol{k}-\boldsymbol{G}|^2\right) C_{k-G} - V_{-G} C_k = 0 \,. \end{aligned} \tag{7.22}$$

We thus obtain the secular equation for the energy value

$$\begin{vmatrix} \left(\dfrac{\hbar^2}{2m}\,k^2 - E\right) & V_G \\ V_{-G} & \left(\dfrac{\hbar^2}{2m}|\boldsymbol{k}-\boldsymbol{G}|^2 - E\right) \end{vmatrix} = 0 \,. \tag{7.23}$$

With $E^0_{k-G} = (\hbar^2/2m)\,|\boldsymbol{k}-\boldsymbol{G}|^2$ as the energy of the free electrons, the two solutions to this secular equation may be written

$$E^{\pm} = \tfrac{1}{2}(E^0_{k-G} + E^0_k) \pm [\tfrac{1}{4}(E^0_{k-G} - E^0_k)^2 + |V_G|^2]^{1/2} \,. \tag{7.24}$$

Therefore, at the zone boundary itself, where the contributions of the two waves with C_k and C_{k-G} are equal – see (7.21) – and where $E^0_{k-G} = E^0_k$, the energy gap has a value

$$\Delta E = E_+ - E_- = 2\,|V_G| \,, \tag{7.25}$$

i.e., twice the Gth Fourier component of the potential.

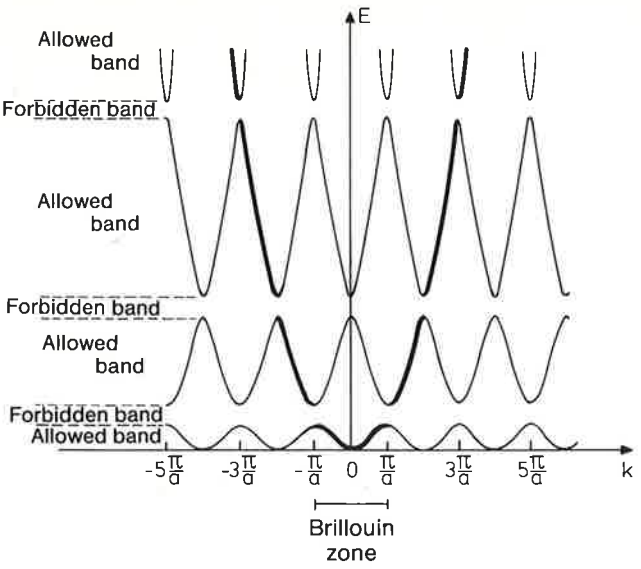

Fig. 7.6. Energy dispersion curves $E(k)$ for a one-dimensional lattice (lattice constant a) in the extended zone scheme. As can be seen, the quasi-free-electron approximation gives rise to forbidden and allowed energy regions due to the opening of band gaps, as shown in Fig. 7.5 (cf. the vanishing potential case of Fig. 7.2). The parts of the bands corresponding to the free-electron parabola are indicated by the thick lines

Near to the zone boundary, the form of the two energy surfaces that are separated by this gap is described by (7.24) (in which one again sets $E_k^0 = \hbar^2 k^2/2m$). Figure 7.5 illustrates this for the one-dimensional case near to the zero boundary at $k = G/2$.

The correspondence between the energy parabola of the free electrons and the periodic bandstructure, with its energy gaps due to the realistic potential, is depicted in Figs. 7.5 and 7.6, in both cases for the one-dimensional problem.

7.3 The Tight-Binding Approximation

The electrons that occupy the energetically low-lying core levels of a free atom are strongly localized in space. They naturally retain this strong localization when the atom participates in the formation of a crystal. It thus appears that the description of a solid's electronic structure in terms of quasi-free electrons must be inadequate. Since these core electrons largely retain the properties that they had in the free atom, an obvious approach is to describe the crystal electrons in terms of a linear superposition of atomic eigenfunctions. This procedure, also known as the LCAO method (Linear Combination of Atomic Orbitals), was already discussed qualitatively in Chap. 1 in relation to chemical bonding, in order to explain the existence of electronic bands in solids.

In formulating the problem, one assumes that the solutions to the Schrödinger equation for the free atoms that form the crystal

$$\mathcal{H}_A(\boldsymbol{r}-\boldsymbol{r}_n)\,\phi_i(\boldsymbol{r}-\boldsymbol{r}_n) = E_i\phi_i(\boldsymbol{r}-\boldsymbol{r}_n) \tag{7.26}$$

are known. $\mathcal{H}_A(\boldsymbol{r}-\boldsymbol{r}_n)$ is the Hamiltonian for a free atom at the lattice position $\boldsymbol{r}_n = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$ and $\phi_i(\boldsymbol{r}-\boldsymbol{r}_n)$ is the wavefunction for an electron in the atomic energy level E_i. One imagines the entire crystal to be built up of single atoms, i.e., the Hamiltonian for an electron (one-electron approximation!) in the total potential of all the atoms can be written: