Because the ions in a perfect crystal are arranged in a regular periodic array, we are led to consider the problem of an electron in a potential $U(\mathbf{r})$ with the periodicity of the underlying Bravais lattice; i.e.,

$$U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r}) \tag{8.1}$$

for all Bravais lattice vectors $\mathbf{R}$.

Since the scale of periodicity of the potential U ($\sim 10^{-8}$ cm) is the size of a typical de Broglie wavelength of an electron in the Sommerfeld free electron model, it is essential to use quantum mechanics in accounting for the effect of periodicity on electronic motion. In this chapter we shall discuss those properties of the electronic levels that depend only on the periodicity of the potential, without regard to its particular form. The discussion will be continued in Chapters 9 and 10 in two limiting cases of great physical interest that provide more concrete illustrations of the general results of this chapter. In Chapter 11 some of the more important methods for the detailed calculation of electronic levels are summarized. In Chapters 12 and 13 we shall discuss the bearing of these results on the problems of electronic transport theory first raised in Chapters 1 and 2, indicating how many of the anomalies of free electron theory (Chapter 3) are thereby removed. In Chapters 14 and 15 we shall examine the properties of specific metals that illustrate and confirm the general theory.

We emphasize at the outset that perfect periodicity is an idealization. Real solids are never absolutely pure, and in the neighborhood of the impurity atoms the solid is not the same as elsewhere in the crystal. Furthermore, there is always a slight temperature-dependent probability of finding missing or misplaced ions (Chapter 30) that destroy the perfect translational symmetry of even an absolutely pure crystal. Finally, the ions are not in fact stationary, but continually undergo thermal vibrations about their equilibrium positions.

These imperfections are all of great importance. They are, for example, ultimately responsible for the fact that the electrical conductivity of metals is not infinite. Progress is best made, however, by artificially dividing the problem into two parts: (a) the ideal fictitious perfect crystal, in which the potential is genuinely periodic, and (b) the effects on the properties of a hypothetical perfect crystal of all deviations from perfect periodicity, treated as small perturbations.

We also emphasize that the problem of electrons in a periodic potential does not arise only in the context of metals. Most of our general conclusions apply to all crystalline solids, and will play an important role in our subsequent discussions of insulators and semiconductors.

THE PERIODIC POTENTIAL

The problem of electrons in a solid is in principle a many-electron problem, for the full Hamiltonian of the solid contains not only the one-electron potentials describing the interactions of the electrons with the massive atomic nuclei, but also pair potentials describing the electron-electron interactions. In the independent electron approximation these interactions are represented by an effective one-electron potential $U(\mathbf{r})$. The problem of how best to choose this effective potential is a complicated one, which we shall return to in Chapters 11 and 17. Here we merely observe that whatever detailed form the one-electron effective potential may have, if the crystal is perfectly

periodic it must satisfy (8.1). From this fact alone many important conclusions can already be drawn.

Qualitatively, however, a typical crystalline potential might be expected to have the form shown in Figure 8.1, resembling the individual atomic potentials as the ion is approached closely and flattening off in the region between ions.
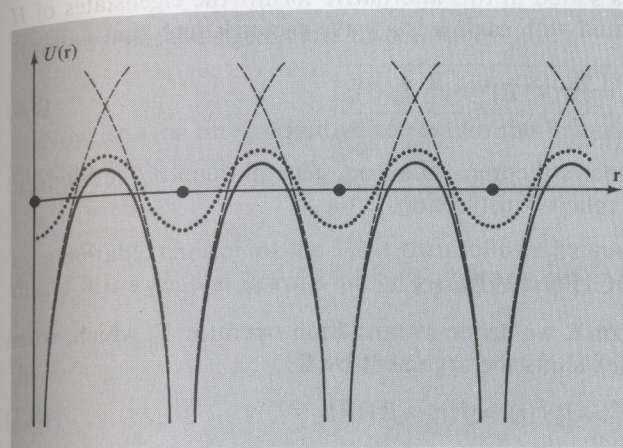

Figure 8.1
A typical crystalline periodic potential, plotted along a line of ions and along a line midway between a plane of ions. (Closed circles are the equilibrium ion sites; the solid curves give the potential along the line of ions; the dotted curves give the potential along a line between planes of ions; the dashed curves give the potential of single isolated ions.)

We are thus led to examine general properties of the Schrödinger equation for a single electron,

$$H\psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right) \psi = \varepsilon\psi, \tag{8.2}$$

that follow from the fact that the potential U has the periodicity (8.1). The free electron Schrödinger equation (2.4) is a special case of (8.2) (although, as we shall see, in some respects a very pathological one), zero potential being the simplest example of a periodic one.

Independent electrons, each of which obeys a one electron Schrödinger equation with a periodic potential, are known as *Bloch electrons* (in contrast to "free electrons," to which Bloch electrons reduce when the periodic potential is identically zero). The stationary states of Bloch electrons have the following very important property as a general consequence of the periodicity of the potential U:

BLOCH'S THEOREM

Theorem.[1]   The eigenstates ψ of the one-electron Hamiltonian $H = -\hbar^2\nabla^2/2m + U(\mathbf{r})$, where $U(\mathbf{r} + \mathbf{R}) = U(\mathbf{r})$ for all $\mathbf{R}$ in a Bravais lattice, can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice:

$$\boxed{\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}),} \tag{8.3}$$

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[1]   The theorem was first proved by Floquet in the one-dimensional case, where it is frequently called *Floquet's theorem.*

where

$$u_{nk}(\mathbf{r} + \mathbf{R}) = u_{nk}(\mathbf{r}) \qquad (8.4)$$

for all $\mathbf{R}$ in the Bravais lattice.[2]

Note that Eqs. (8.3) and (8.4) imply that

$$\psi_{nk}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{nk}(\mathbf{r}). \qquad (8.5)$$

Bloch's theorem is sometimes stated in this alternative form:[3] the eigenstates of H can be chosen so that associated with each ψ is a wave vector $\mathbf{k}$ such that

$$\boxed{\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r}),} \qquad (8.6)$$

for every $\mathbf{R}$ in the Bravais lattice.

We offer two proofs of Bloch's theorem, one from general quantum-mechanical considerations and one by explicit construction.[4]

FIRST PROOF OF BLOCH'S THEOREM

For each Bravais lattice vector $\mathbf{R}$ we define a translation operator $T_\mathbf{R}$ which, when operating on any function $f(\mathbf{r})$, shifts the argument by $\mathbf{R}$:

$$T_\mathbf{R} f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}). \qquad (8.7)$$

Since the Hamiltonian is periodic, we have

$$T_\mathbf{R} H\psi = H(\mathbf{r} + \mathbf{R})\psi(\mathbf{r} + \mathbf{R}) = H(\mathbf{r})\psi(\mathbf{r} + \mathbf{R}) = HT_\mathbf{R}\psi. \qquad (8.8)$$

Because (8.8) holds identically for any function ψ, we have the operator identity

$$T_\mathbf{R} H = HT_\mathbf{R}. \qquad (8.9)$$

In addition, the result of applying two successive translations does not depend on the order in which they are applied, since for any $\psi(\mathbf{r})$

$$T_\mathbf{R} T_{\mathbf{R}'}\psi(\mathbf{r}) = T_{\mathbf{R}'} T_\mathbf{R}\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R} + \mathbf{R}'). \qquad (8.10)$$

Therefore

$$T_\mathbf{R} T_{\mathbf{R}'} = T_{\mathbf{R}'} T_\mathbf{R} = T_{\mathbf{R}+\mathbf{R}'}. \qquad (8.11)$$

Equations (8.9) and (8.11) assert that the $T_\mathbf{R}$ for all Bravais lattice vectors $\mathbf{R}$ and the Hamiltonian H form a set of commuting operators. It follows from a fundamental theorem of quantum mechanics[5] that the eigenstates of H can therefore be chosen to be simultaneous eigenstates of all the $T_\mathbf{R}$:

$$H\psi = \mathcal{E}\psi,$$
$$T_\mathbf{R}\psi = c(\mathbf{R})\psi. \qquad (8.12)$$

The eigenvalues $c(\mathbf{R})$ of the translation operators are related because of the condition (8.11), for on the one hand

$$T_\mathbf{R} T_{\mathbf{R}'}\psi = c(\mathbf{R}) T_{\mathbf{R}'}\psi = c(\mathbf{R})c(\mathbf{R}')\psi, \qquad (8.13)$$

while, according to (8.11),

$$T_\mathbf{R} T_{\mathbf{R}'}\psi = T_{\mathbf{R}+\mathbf{R}'}\psi = c(\mathbf{R} + \mathbf{R}')\psi. \qquad (8.14)$$

It follows that the eigenvalues must satisfy

$$c(\mathbf{R} + \mathbf{R}') = c(\mathbf{R})c(\mathbf{R}'). \qquad (8.15)$$

Now let $\mathbf{a}_i$ be three primitive vectors for the Bravais lattice. We can always write the $c(\mathbf{a}_i)$ in the form

$$c(\mathbf{a}_i) = e^{2\pi i x_i} \qquad (8.16)$$

by a suitable choice[6] of the x_i. It then follows by successive applications of (8.15) that if $\mathbf{R}$ is a general Bravais lattice vector given by

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3, \qquad (8.17)$$

then

$$c(\mathbf{R}) = c(\mathbf{a}_1)^{n_1} c(\mathbf{a}_2)^{n_2} c(\mathbf{a}_3)^{n_3}. \qquad (8.18)$$

But this is precisely equivalent to

$$c(\mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}}, \qquad (8.19)$$

where

$$\mathbf{k} = x_1\mathbf{b}_1 + x_2\mathbf{b}_2 + x_3\mathbf{b}_3 \qquad (8.20)$$

and the $\mathbf{b}_i$ are the reciprocal lattice vectors satisfying Eq. (5.4): $\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij}$.

Summarizing, we have shown that we can choose the eigenstates ψ of H so that for every Bravais lattice vector $\mathbf{R}$,

$$T_\mathbf{R}\psi = \psi(\mathbf{r} + \mathbf{R}) = c(\mathbf{R})\psi = e^{i\mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r}). \qquad (8.21)$$

This is precisely Bloch's theorem, in the form (8.6).

THE BORN–VON KARMAN BOUNDARY CONDITION

By imposing an appropriate boundary condition on the wave functions we can demonstrate that the wave vector $\mathbf{k}$ must be real, and arrive at a condition restricting the allowed values of $\mathbf{k}$. The condition generally chosen is the natural generalization of the condition (2.5) used in the Sommerfeld theory of free electrons in a cubical box. As in that case, we introduce the volume containing the electrons into the theory through a Born–von Karman boundary condition of macroscopic periodicity (page 33). Unless, however, the Bravais lattice is cubic and L is an integral multiple of the lattice constant a, it is not convenient to continue to work in a cubical volume of side L. Instead, it is more convenient to work in a volume commensurate with a

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[2] The index n is known as the *band index* and occurs because for a given $\mathbf{k}$, as we shall see, there will be many independent eigenstates.

[3] Equation (8.6) implies (8.3) and (8.4), since it requires the function $u(\mathbf{r}) = \exp(-i\mathbf{k} \cdot \mathbf{r})\psi(\mathbf{r})$ to have the periodicity of the Bravais lattice.

[4] The first proof relies on some formal results of quantum mechanics. The second is more elementary, but also notationally more cumbersome.

[5] See, for example, D. Park, *Introduction to the Quantum Theory*, McGraw-Hill, New York, 1964, p. 123.

[6] We shall see that for suitable boundary conditions the x_i must be real, but for now they can be regarded as general complex numbers.

primitive cell of the underlying Bravais lattice. We therefore generalize the periodic boundary condition (2.5) to

$$\psi(\mathbf{r} + N_i\mathbf{a}_i) = \psi(\mathbf{r}), \qquad i = 1, 2, 3, \tag{8.22}$$

where the $\mathbf{a}_i$ are three primitive vectors and the N_i are all integers of order $N^{1/3}$, where $N = N_1 N_2 N_3$ is the total number of primitive cells in the crystal.

As in Chapter 2, we adopt this boundary condition under the assumption that the bulk properties of the solid will not depend on the choice of boundary condition, which can therefore be dictated by analytical convenience.

Applying Bloch's theorem (8.6) to the boundary condition (8.22) we find that

$$\psi_{n\mathbf{k}}(\mathbf{r} + N_i\mathbf{a}_i) = e^{iN_i\mathbf{k}\cdot\mathbf{a}_i}\psi_{n\mathbf{k}}(\mathbf{r}), \qquad i = 1, 2, 3, \tag{8.23}$$

which requires that

$$e^{iN_i\mathbf{k}\cdot\mathbf{a}_i} = 1, \qquad i = 1, 2, 3. \tag{8.24}$$

When $\mathbf{k}$ has the form (8.20), Eq. (8.24) requires that

$$e^{2\pi i N_i x_i} = 1, \tag{8.25}$$

and consequently we must have

$$x_i = \frac{m_i}{N_i}, \qquad m_i \text{ integral.} \tag{8.26}$$

Therefore the general form for allowed Bloch wave vectors is[7]

$$\mathbf{k} = \sum_{i=1}^{3} \frac{m_i}{N_i}\mathbf{b}_i, \qquad m_i \text{ integral.} \tag{8.27}$$

It follows from (8.27) that the volume Δk of k-space per allowed value of $\mathbf{k}$ is just the volume of the little parallelepiped with edges $\mathbf{b}_i/N_i$:

$$\Delta k = \frac{\mathbf{b}_1}{N_1} \cdot \left(\frac{\mathbf{b}_2}{N_2} \times \frac{\mathbf{b}_3}{N_3}\right) = \frac{1}{N}\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3). \tag{8.28}$$

Since $\mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3)$ is the volume of a reciprocal lattice primitive cell, Eq. (8.28) asserts that *the number of allowed wave vectors in a primitive cell of the reciprocal lattice is equal to the number of sites in the crystal.*

The volume of a reciprocal lattice primitive cell is $(2\pi)^3/v$, where $v = V/N$ is the volume of a direct lattice primitive cell, so Eq. (8.28) can be written in the alternative form:

$$\boxed{\Delta k = \frac{(2\pi)^3}{V}.} \tag{8.29}$$

This is precisely the result (2.18) we found in the free electron case.

SECOND PROOF OF BLOCH'S THEOREM[8]

This second proof of Bloch's theorem illuminates its significance from a rather different point of view, which we shall exploit further in Chapter 9. We start with the observation that one can always expand any function obeying the Born–von Karman boundary condition (8.22) in the set of all plane waves that satisfy the boundary condition and therefore have wave vectors of the form (8.27):[9]

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}. \tag{8.30}$$

Because the potential $U(\mathbf{r})$ is periodic in the lattice, its plane wave expansion will only contain plane waves with the periodicity of the lattice and therefore with wave vectors that are vectors of the reciprocal lattice:[10]

$$U(\mathbf{r}) = \sum_{\mathbf{K}} U_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}. \tag{8.31}$$

The Fourier coefficients $U_{\mathbf{K}}$ are related to $U(\mathbf{r})$ by[11]

$$U_{\mathbf{K}} = \frac{1}{v}\int_{\text{cell}} d\mathbf{r}\, e^{-i\mathbf{K}\cdot\mathbf{r}} U(\mathbf{r}). \tag{8.32}$$

Since we are at liberty to change the potential energy by an additive constant, we fix this constant by requiring that the spatial average U_0 of the potential over a primitive cell vanish:

$$U_0 = \frac{1}{v}\int_{\text{cell}} d\mathbf{r}\, U(\mathbf{r}) = 0. \tag{8.33}$$

Note that because the potential $U(\mathbf{r})$ is real, it follows from (8.32) that the Fourier coefficients satisfy

$$U_{-\mathbf{K}} = U_{\mathbf{K}}^*. \tag{8.34}$$

If we assume that the crystal has inversion symmetry[12] so that, for a suitable choice of origin, $U(\mathbf{r}) = U(-\mathbf{r})$, then (8.32) implies that $U_{\mathbf{K}}$ is real, and thus

$$U_{-\mathbf{K}} = U_{\mathbf{K}} = U_{\mathbf{K}}^* \quad \text{(for crystals with inversion symmetry).} \tag{8.35}$$

We now place the expansions (8.30) and (8.31) into the Schrödinger equation (8.2). The kinetic energy term gives

$$\frac{p^2}{2m}\psi = -\frac{\hbar^2}{2m}\nabla^2\psi = \sum_{\mathbf{q}} \frac{\hbar^2}{2m} q^2 c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}. \tag{8.36}$$

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[7] Note that (8.27) reduces to the form (2.16) used in free electron theory when the Bravais lattice is simple cubic, the $\mathbf{a}_i$ are the cubic primitive vectors, and $N_1 = N_2 = N_3 = L/a$.

[8] Although more elementary than the first proof, the second is also notationally more complicated, and of importance primarily as a starting point for the approximate calculations of Chapter 9. The reader may therefore wish to skip it at this point.

[9] We shall subsequently understand unspecified summations over $\mathbf{k}$ to be over all wave vectors of the form (8.27) allowed by the Born–von Karman boundary condition.

[10] A sum indexed by $\mathbf{K}$ shall always be understood to run over all reciprocal lattice vectors.

[11] See Appendix D, where the relevance of the reciprocal lattice to Fourier expansions of periodic functions is discussed.

[12] The reader is invited to pursue the argument of this section (and Chapter 9) without the assumption of inversion symmetry, which is made solely to avoid inessential complications in the notation.

The term in the potential energy can be written[13]

$$U\psi = \left(\sum_{\mathbf{K}} U_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}\right)\left(\sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}\right)$$

$$= \sum_{\mathbf{K}\mathbf{q}} U_{\mathbf{K}} c_{\mathbf{q}} e^{i(\mathbf{K}+\mathbf{q})\cdot\mathbf{r}} = \sum_{\mathbf{K}\mathbf{q}'} U_{\mathbf{K}} c_{\mathbf{q}'-\mathbf{K}} e^{i\mathbf{q}'\cdot\mathbf{r}}. \tag{8.37}$$

We change the names of the summation indices in (8.37)—from $\mathbf{K}$ and $\mathbf{q}'$, to $\mathbf{K}'$ and $\mathbf{q}$—so that the Schrödinger equation becomes

$$\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left\{\left(\frac{\hbar^2}{2m} q^2 - \mathcal{E}\right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{q}-\mathbf{K}'}\right\} = 0. \tag{8.38}$$

Since the plane waves satisfying the Born–von Karman boundary condition are an orthogonal set, the coefficient of each separate term in (8.38) must vanish,[14] and therefore for all allowed wave vectors $\mathbf{q}$,

$$\boxed{\left(\frac{\hbar^2}{2m} q^2 - \mathcal{E}\right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{q}-\mathbf{K}'} = 0.} \tag{8.39}$$

It is convenient to write $\mathbf{q}$ in the form $\mathbf{q} = \mathbf{k} - \mathbf{K}$, where $\mathbf{K}$ is a reciprocal lattice vector chosen so that $\mathbf{k}$ lies in the first Brillouin zone. Equation (8.39) becomes

$$\left(\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - \mathcal{E}\right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'} c_{\mathbf{k}-\mathbf{K}-\mathbf{K}'} = 0, \tag{8.40}$$

or, if we make the change of variables $\mathbf{K}' \to \mathbf{K}' - \mathbf{K}$,

$$\boxed{\left(\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - \mathcal{E}\right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} U_{\mathbf{K}'-\mathbf{K}} c_{\mathbf{k}-\mathbf{K}'} = 0.} \tag{8.41}$$

We emphasize that Eqs. (8.39) and (8.41) are nothing but restatements of the original Schrödinger equation (8.2) in momentum space, simplified by the fact that because of the periodicity of the potential, $U_{\mathbf{k}}$ is nonvanishing only when $\mathbf{k}$ is a vector of the reciprocal lattice.

For fixed $\mathbf{k}$ in the first Brillouin zone, the set of equations (8.41) for all reciprocal lattice vectors $\mathbf{K}$ couples only those coefficients $c_{\mathbf{k}}$, $c_{\mathbf{k}-\mathbf{K}}$, $c_{\mathbf{k}-\mathbf{K}'}$, $c_{\mathbf{k}-\mathbf{K}''}$, ... whose wave vectors differ from $\mathbf{k}$ by a reciprocal lattice vector. Thus the original problem has separated into N independent problems: one for each allowed value of $\mathbf{k}$ in the first Brillouin zone. Each such problem has solutions that are superpositions of plane waves containing only the wave vector $\mathbf{k}$ and wave vectors differing from $\mathbf{k}$ by a reciprocal lattice vector.

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[13]   The last step follows from making the substitution $\mathbf{K} + \mathbf{q} = \mathbf{q}'$, and noting that because $\mathbf{K}$ is a reciprocal lattice vector, summing over all $\mathbf{q}$ of the form (8.27) is the same as summing over all $\mathbf{q}'$ of that form.

[14]   This can also be deduced from Eq. (D.12), Appendix D, by multiplying (8.38) by the appropriate plane wave and integrating over the volume of the crystal.

Putting this information back into the expansion (8.30) of the wave function ψ, we see that if the wave vector $\mathbf{q}$ only assumes the values $\mathbf{k}$, $\mathbf{k} - \mathbf{K}'$, $\mathbf{k} - \mathbf{K}''$, ..., then the wave function will be of the form

$$\psi_{\mathbf{k}} = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{i(\mathbf{k}-\mathbf{K})\cdot\mathbf{r}}. \tag{8.42}$$

If we write this as

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \left(\sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{r}}\right), \tag{8.43}$$

then this is of the Bloch form (8.3) with the periodic function $u(\mathbf{r})$ given by[15]

$$u(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}-\mathbf{K}} e^{-i\mathbf{K}\cdot\mathbf{r}}. \tag{8.44}$$

GENERAL REMARKS ABOUT BLOCH'S THEOREM

1. Bloch's theorem introduces a wave vector $\mathbf{k}$, which turns out to play the same fundamental role in the general problem of motion in a periodic potential that the free electron wave vector $\mathbf{k}$ plays in the Sommerfeld theory. Note, however, that although the free electron wave vector is simply $\mathbf{p}/\hbar$, where $\mathbf{p}$ is the momentum of the electron, in the Bloch case $\mathbf{k}$ is not proportional to the electronic momentum. This is clear on general grounds, since the Hamiltonian does not have complete translational invariance in the presence of a nonconstant potential, and therefore its eigenstates will not be simultaneous eigenstates of the momentum operator. This conclusion is confirmed by the fact that the momentum operator, $\mathbf{p} = (\hbar/i)\nabla$, when acting on $\psi_{n\mathbf{k}}$ gives

$$\frac{\hbar}{i}\nabla\psi_{n\mathbf{k}} = \frac{\hbar}{i}\nabla(e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}))$$

$$= \hbar\mathbf{k}\psi_{n\mathbf{k}} + e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\hbar}{i}\nabla u_{n\mathbf{k}}(\mathbf{r}), \tag{8.45}$$

which is not, in general, just a constant times $\psi_{n\mathbf{k}}$; i.e., $\psi_{n\mathbf{k}}$ is not a momentum eigenstate.

Nevertheless, in many ways $\hbar\mathbf{k}$ is a natural extension of $\mathbf{p}$ to the case of a periodic potential. It is known as the *crystal momentum* of the electron, to emphasize this similarity, but one should not be misled by the name into thinking that $\hbar\mathbf{k}$ is a momentum, for it is not. An intuitive understanding of the dynamical significance of the wave vector $\mathbf{k}$ can only be acquired when one considers the response of Bloch electrons to externally applied electromagnetic fields (Chapter 12). Only then does its full resemblance to $\mathbf{p}/\hbar$ emerge. For the present, the reader should view $\mathbf{k}$ as a quantum number characteristic of the translational symmetry of a periodic potential, just as the momentum $\mathbf{p}$ is a quantum number characteristic of the fuller translational symmetry of free space.

2. The wave vector $\mathbf{k}$ appearing in Bloch's theorem can always be confined to the first Brillouin zone (or to any other convenient primitive cell of the reciprocal

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[15]   Note that there will be (infinitely) many solutions to the (infinite) set of equations (8.41) for a given $\mathbf{k}$. These are classified by the band index n (see footnote 2).

lattice). This is because any $\mathbf{k}'$ not in the first Brillouin zone can be written as

$$\mathbf{k}' = \mathbf{k} + \mathbf{K} \tag{8.46}$$

where $\mathbf{K}$ is a reciprocal lattice vector and $\mathbf{k}$ does lie in the first zone. Since $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ for any reciprocal lattice vector, if the Bloch form (8.6) holds for $\mathbf{k}'$, it will also hold for $\mathbf{k}$.

3. The index n appears in Bloch's theorem because for given $\mathbf{k}$ there are many solutions to the Schrödinger equation. We noted this in the second proof of Bloch's theorem, but it can also be seen from the following argument:

Let us look for all solutions to the Schrödinger equation (8.2) that have the Bloch form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u(\mathbf{r}), \tag{8.47}$$

where $\mathbf{k}$ is fixed and u has the periodicity of the Bravais lattice. Substituting this into the Schrödinger equation, we find that u is determined by the eigenvalue problem

$$H_{\mathbf{k}}u_{\mathbf{k}}(\mathbf{r}) = \left(\frac{\hbar^2}{2m}\left(\frac{1}{i}\nabla + \mathbf{k}\right)^2 + U(\mathbf{r})\right)u_{\mathbf{k}}(\mathbf{r})$$

$$= \mathcal{E}_{\mathbf{k}}u_{\mathbf{k}}(\mathbf{r}) \tag{8.48}$$

with boundary condition

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{R}). \tag{8.49}$$

Because of the periodic boundary condition we can regard (8.48) as a Hermitian eigenvalue problem restricted to a single primitive cell of the crystal. Because the eigenvalue problem is set in a fixed finite volume, we expect on general grounds to find an infinite family of solutions with *discretely* spaced eigenvalues,[16] which we label with the band index n.

Note that in terms of the eigenvalue problem specified by (8.48) and (8.49), the wave vector $\mathbf{k}$ appears only as a parameter in the Hamiltonian $H_{\mathbf{k}}$. We therefore expect each of the energy levels, for given $\mathbf{k}$, to vary continuously as $\mathbf{k}$ varies.[17] In this way we arrive at a description of the levels of an electron in a periodic potential in terms of a family of continuous[18] functions $\mathcal{E}_n(\mathbf{k})$.

4. Although the full set of levels can be described with $\mathbf{k}$ restricted to a single primitive cell, it is often useful to allow $\mathbf{k}$ to range through all of k-space, even though this gives a highly redundant description. Because the set of all wave functions and energy levels for two values of $\mathbf{k}$ differing by a reciprocal lattice vector must be

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[16] Just as the problem of a free electron in a box of fixed finite dimensions has a set of discrete energy levels, the vibrational normal modes of a finite drumhead have a set of discrete frequencies, etc.

[17] This expectation is implicit, for example, in ordinary perturbation theory, which is possible only because small changes in parameters in the Hamiltonian lead to small changes in the energy levels. In Appendix E the changes in the energy levels for small changes in $\mathbf{k}$ are calculated explicitly.

[18] The fact that the Born–von Karman boundary condition restricts $\mathbf{k}$ to discrete values of the form (8.27) has no bearing on the continuity of $\mathcal{E}_n(\mathbf{k})$ as a function of a continuous variable $\mathbf{k}$, for the eigenvalue problem given by (8.48) and (8.49) makes no reference to the size of the whole crystal and is well defined for any $\mathbf{k}$. One should also note that the set of $\mathbf{k}$ of the form (8.27) becomes dense in k-space in the limit of an infinite crystal.

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identical, we can assign the indices n to the levels in such a way that *for given n, the eigenstates and eigenvalues are periodic functions of $\mathbf{k}$ in the reciprocal lattice:*

$$\boxed{\begin{aligned}\psi_{n,\,\mathbf{k}+\mathbf{K}}(\mathbf{r}) &= \psi_{n\mathbf{k}}(\mathbf{r}), \\ \mathcal{E}_{n,\,\mathbf{k}+\mathbf{K}} &= \mathcal{E}_{n\mathbf{k}}.\end{aligned}} \tag{8.50}$$

This leads to a description of the energy levels of an electron in a periodic potential in terms of a family of continuous functions $\mathcal{E}_{n\mathbf{k}}$ (or $\mathcal{E}_n(\mathbf{k})$), each with the periodicity of the reciprocal lattice. The information contained in these functions is referred to as the *band structure* of the solid.

For each n, the set of electronic levels specified by $\mathcal{E}_n(\mathbf{k})$ is called an *energy band.* The origin of the term "band" will emerge in Chapter 10. Here we only note that because each $\mathcal{E}_n(\mathbf{k})$ is periodic in $\mathbf{k}$ and continuous, it has an upper and lower bound, so that all the levels $\mathcal{E}_n(\mathbf{k})$ lie in the band of energies lying between these limits.

5. It can be shown quite generally (Appendix E) that an electron in a level specified by band index n and wave vector $\mathbf{k}$ has a nonvanishing mean velocity, given by

$$\boxed{\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\nabla_{\mathbf{k}}\,\mathcal{E}_n(\mathbf{k}).} \tag{8.51}$$

This is a most remarkable fact. It asserts that there are stationary (i.e., time-independent) levels for an electron in a periodic potential in which, in spite of the interaction of the electron with the fixed lattice of ions, it moves forever without any degradation of its mean velocity. This is in striking contrast to the idea of Drude that collisions were simply encounters between the electron and a static ion. Its implications are of fundamental importance, and will be explored in Chapters 12 and 13.

THE FERMI SURFACE

The ground state of N free electrons[19] is constructed by occupying all one-electron levels $\mathbf{k}$ with energies $\mathcal{E}(\mathbf{k}) = \hbar^2k^2/2m$ less than $\mathcal{E}_F$, where $\mathcal{E}_F$ is determined by requiring the total number of one-electron levels with energies less than $\mathcal{E}_F$ to be equal to the total number of electrons (Chapter 2).

The ground state of N Bloch electrons is similarly constructed, except that the one-electron levels are now labeled by the quantum numbers n and $\mathbf{k}$, $\mathcal{E}_n(\mathbf{k})$ does not have the simple explicit free electron form, and $\mathbf{k}$ must be confined to a single primitive cell of the reciprocal lattice if each level is to be counted only once. When the lowest of these levels are filled by a specified number of electrons, two quite distinct types of configuration can result:

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[19] We shall not distinguish notationally between the number of conduction electrons and the number of primitive cells when it is clear from the context which is meant; they are equal, however, only in a monovalent monatomic Bravais lattice (e.g., the alkali metals).