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.

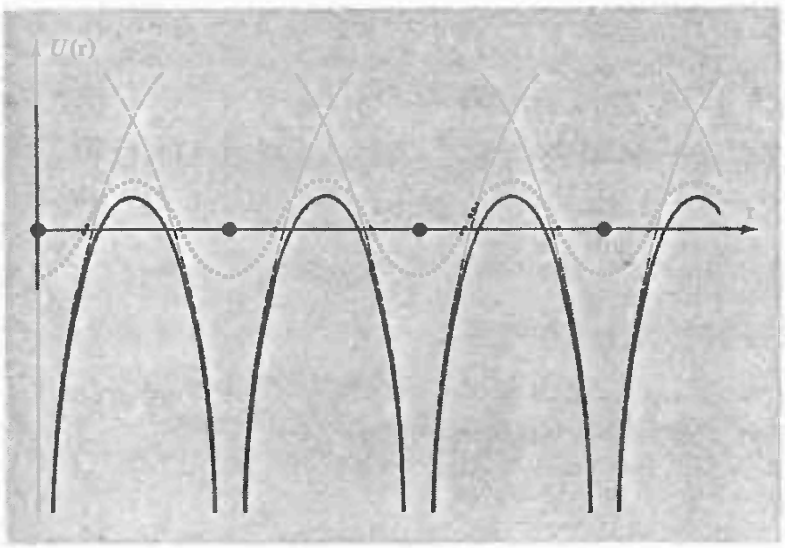

Figure 8.1
A typical crystalline periodic potential, plotted along a line of ions and along a line midway between a plane of ions. (Closed circles are the equilibrium ion sites; the solid curves give the potential along the line of ions; the dotted curves give the potential along a line between planes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

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

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

where

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}) \tag{8.4}$$

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

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

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

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

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

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 $\mathbf{R}$:

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

Since the Hamiltonian is periodic, we have

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

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

$$T_{\mathbf{R}}H = HT_{\mathbf{R}}. \tag{8.9}$$

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

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

Therefore

$$T_{\mathbf{R}}T_{\mathbf{R}'} = T_{\mathbf{R}'}T_{\mathbf{R}} = T_{\mathbf{R}+\mathbf{R}'}. \tag{8.11}$$

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 $T_{\mathbf{R}}$:

$$\begin{aligned} H\psi &= \varepsilon\psi, \\ T_{\mathbf{R}}\psi &= c(\mathbf{R})\psi. \end{aligned} \tag{8.12}$$

---

[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.

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

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

while, according to (8.11),

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

It follows that the eigenvalues must satisfy

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

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

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

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

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

then

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

But this is precisely equivalent to

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

where

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

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 $\mathbf{R}$,

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

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

[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 $N = N_1N_2N_3$ 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 $\Delta\mathbf{k}$ of k-space per allowed value of $\mathbf{k}$ is just the volume of the little parallelepiped with edges $\mathbf{b}_i/N_i$:

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

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:

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

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

---

[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 $N_1 = N_2 = N_3 = L/a$.