The Bloch theory (Chapter 8) extends the equilibrium free electron theory of Sommerfeld (Chapter 2) to the case in which a (nonconstant) periodic potential is present. In Table 12.1 we compare the major features of the two theories.

Table 12.1
COMPARISON OF SOMMERFELD AND BLOCH ONE-ELECTRON EQUILIBRIUM LEVELS

	SOMMERFELD	BLOCH
QUANTUM NUMBERS (EXCLUDING SPIN)	$\mathbf{k}$ ($\hbar\mathbf{k}$ is the momentum.)	$\mathbf{k}$, n ($\hbar\mathbf{k}$ is the crystal momentum and n is the band index.)
RANGE OF QUANTUM NUMBERS	$\mathbf{k}$ runs through all of k-space consistent with the Born-von Karman periodic boundary condition.	For each n, $\mathbf{k}$ runs through all wave vectors in a single primitive cell of the reciprocal lattice consistent with the Born-von Karman periodic boundary condition; n runs through an infinite set of discrete values.
ENERGY	$\mathcal{E}(\mathbf{k}) = \dfrac{\hbar^2 k^2}{2m}$.	For a given band index n, $\mathcal{E}_n(\mathbf{k})$ has no simple explicit form. The only general property is periodicity in the reciprocal lattice: $\mathcal{E}_n(\mathbf{k} + \mathbf{K}) = \mathcal{E}_n(\mathbf{k})$.
VELOCITY	The mean velocity of an electron in a level with wave vector $\mathbf{k}$ is: $\mathbf{v} = \dfrac{\hbar\mathbf{k}}{m} = \dfrac{1}{\hbar}\dfrac{\partial\mathcal{E}}{\partial\mathbf{k}}$.	The mean velocity of an electron in a level with band index n and wave vector $\mathbf{k}$ is: $\mathbf{v}_n(\mathbf{k}) = \dfrac{1}{\hbar}\dfrac{\partial\mathcal{E}_n(\mathbf{k})}{\partial\mathbf{k}}$.
WAVE FUNCTION	The wave function of an electron with wave vector $\mathbf{k}$ is: $\psi_{\mathbf{k}}(\mathbf{r}) = \dfrac{e^{i\mathbf{k}\cdot\mathbf{r}}}{V^{1/2}}$.	The wave function of an electron with band index n and wave vector $\mathbf{k}$ is: $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$ where the function $u_{n\mathbf{k}}$ has no simple explicit form. The only general property is periodicity in the direct lattice: $u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$.

To discuss conduction we had to extend Sommerfeld's equilibrium theory to nonequilibrium cases. We argued in Chapter 2 that one could calculate the dynamic behavior of the free electron gas using ordinary classical mechanics, provided that there was no need to localize an electron on a scale comparable to the interelectronic distance. Thus the trajectory of each electron between collisions was calculated according to the usual classical equations of motion for a particle of momentum $\hbar\mathbf{k}$:

$$\dot{\mathbf{r}} = \frac{\hbar\mathbf{k}}{m},$$

$$\hbar\dot{\mathbf{k}} = -e\left(\mathbf{E} + \frac{1}{c}\mathbf{v} \times \mathbf{H}\right). \tag{12.1}$$

If pressed to justify this procedure from a quantum-mechanical point of view we would argue that (12.1) actually describes the behavior of a wave packet of free electron levels,

$$\psi(\mathbf{r}, t) = \sum_{\mathbf{k}'} g(\mathbf{k}') \exp\left[i\left(\mathbf{k}' \cdot \mathbf{r} - \frac{\hbar k'^2 t}{2m} \right) \right],$$
$$g(\mathbf{k}') \approx 0, \quad |\mathbf{k}' - \mathbf{k}| > \Delta k, \tag{12.2}$$

where $\mathbf{k}$ and $\mathbf{r}$ are the mean position and momentum about which the wave packet is localized (to within the limitation $\Delta x\, \Delta k > 1$ imposed by the uncertainty principle).

This approach has a simple and elegant generalization to electrons in a general periodic potential, which is known as the *semiclassical model*. Justifying the semiclassical model in detail is a formidable task, considerably more difficult than justifying the ordinary classical limit for free electrons. In this book we shall not offer a systematic derivation. Our emphasis instead will be on how the semiclassical model is used. We shall therefore simply describe the model, state the limitations on its validity, and extract some of its major physical consequences.[1]

The reader who is dissatisfied with the very incomplete and merely suggestive bases we shall offer for the semiclassical model is urged to examine the broad array of mysteries and anomalies of free electron theory that the model resolves. Perhaps a suitable attitude to take is this: If there were no underlying microscopic quantum theory of electrons in solids, one could still imagine a semiclassical mechanics (guessed by some late nineteenth-century Newton of crystalline spaces) that was brilliantly confirmed by its account of observed electronic behavior, just as classical mechanics was confirmed by its accounting for planetary motion, and only very much later given a more fundamental derivation as a limiting form of quantum mechanics.

As with free electrons, two questions arise in discussing conduction by Bloch electrons[2]: (a) What is the nature of the collisions? (b) How do Bloch electrons move between collisions? The semiclassical model deals entirely with the second question, but the Bloch theory also critically affects the first. Drude assumed that the electrons collided with the fixed heavy ions. This assumption cannot be reconciled with the very long mean free paths possible in metals, and fails to account for their observed temperature dependence.[3] The Bloch theory excludes it on theoretical grounds as well. Bloch levels are *stationary* solutions to the Schrödinger equation in the presence of the full periodic potential of the ions. If an electron in the level $\psi_{n\mathbf{k}}$ has a mean nonvanishing velocity (as it does unless $\partial\varepsilon_n(\mathbf{k})/\partial\mathbf{k}$ happens to vanish), then that velocity persists forever.[4] One cannot appeal to collisions with static ions as a mechanism to degrade the velocity, because the interaction of the electron with the fixed periodic array of ions has been *fully* taken into account *ab initio* in the Schrödinger equation solved by the Bloch wave function. Thus the conductivity of a perfect periodic crystal is infinite.

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[1] For one of the more recent efforts at a systematic derivation see J. Zak, *Phys. Rev.* **168**, 686 (1968). References to much of the earlier work are given therein. A very appealing treatment of Bloch electrons in a magnetic field (perhaps the most difficult area in which to derive the semiclassical model) is given by R. G. Chambers, *Proc. Phys. Soc.* **89**, 695 (1966), who explicitly constructs a time-dependent wave packet whose center moves along the orbit determined by the semiclassical equations of motion.

[2] We shall use the term "Bloch electrons" to mean "electrons in a general periodic potential."

[3] Page 9.

[4] See page 141.

This result, so disconcerting to one's classical inclination to picture the electrons as suffering current degrading bumps with individual ions, can be understood as a simple manifestation of the wave nature of electrons. In a *periodic* array of scatterers a wave can propagate without attenuation because of the coherent constructive interference of the scattered waves.[5]

Metals have an electrical resistance because no real solid is a perfect crystal. There are always impurities, missing ions, or other imperfections that can scatter electrons, and at very low temperatures it is these that limit conduction. Even if imperfections could be entirely eliminated, however, the conductivity would remain finite because of thermal vibrations of the ions, which produce temperature-dependent distortions from perfect periodicity in the potential the electrons experience. These deviations from periodicity are capable of scattering electrons, and are the source of the temperature dependence of the electronic relaxation time that was noted in Chapter 1.

We defer a full discussion of the actual scattering mechanisms to Chapters 16 and 26. Here we only note that the Bloch theory now forces us to abandon Drude's naive picture of electron-ion scattering. We shall nevertheless continue to extract consequences that follow from the simple assumption that *some* scattering mechanism exists, irrespective of its detailed features.

Thus the main problem we face is how to describe the motion of Bloch electrons between collisions. The fact that the mean velocity of an electron in a definite Bloch level ψ_{nk} is[6]

$$\mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}} \tag{12.3}$$

is very suggestive. Consider a wave packet of Bloch levels from a given band, constructed in analogy to the free electron wave packet (12.2):

$$\psi_n(\mathbf{r}, t) = \sum_{\mathbf{k}'} g(\mathbf{k}')\psi_{nk'}(\mathbf{r}) \exp\left[-\frac{i}{\hbar}\varepsilon_n(\mathbf{k}')t\right], \qquad g(\mathbf{k}') \approx 0, \quad |\mathbf{k}' - \mathbf{k}| > \Delta k \tag{12.4}$$

Let the spread in wave vector Δk be small compared with the dimensions of the Brillouin zone, so that $\varepsilon_n(\mathbf{k})$ varies little over all levels appearing in the wave packet. The formula for the velocity (12.3) can then be viewed as the familiar assertion that the group velocity of a wave packet is $\partial\omega/\partial\mathbf{k} = (\partial/\partial\mathbf{k})(\varepsilon/\hbar)$.

The semiclassical model describes such wave packets when it is unnecessary to specify the position of an electron on a scale comparable with the spread of the packet.

Let us estimate how broad the wave packet (12.4) must be when the spread in wave vector is small compared with the dimensions of the Brillouin zone. We examine the wave packet at points separated by a Bravais lattice vector. Setting $\mathbf{r} = \mathbf{r}_0 + \mathbf{R}$, and using the basic property (8.6) of the Bloch function, we can write (12.4) as

$$\psi_n(\mathbf{r}_0 + \mathbf{R}, t) = \sum_{\mathbf{k}} [g(\mathbf{k}')\psi_{nk}(\mathbf{r}_0)] \exp\left[i\left(\mathbf{k}' \cdot \mathbf{R} - \frac{1}{\hbar}\varepsilon_n(\mathbf{k}')t\right)\right]. \tag{12.5}$$

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[5] For a unified view of a variety of such phenomena, see L. Brillouin, *Wave Propagation in Periodic Structures*, Dover, New York, 1953.

[6] See page 141. The result is proved in Appendix E.

Viewed as a function of $\mathbf{R}$ for fixed $\mathbf{r}_0$, this is just a superposition of plane waves, of the form (12.2), with a weight function $\bar{g}(\mathbf{k}) = [g(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}_0)]$. Thus if Δk measures the region within which g (and hence $\bar{g}$) is appreciable,[7] then $\psi_n(\mathbf{r}_0 + \mathbf{R})$, in accordance with the usual rules for wave packets, should be appreciable within a region of dimensions $\Delta R \approx 1/\Delta k$. Since Δk is small compared with the zone dimensions, which are of the order of the inverse lattice constant $1/a$, it follows that ΔR must be large compared with a. This conclusion is independent of the particular value of $\mathbf{r}_0$, and we therefore conclude that *a wave packet of Bloch levels with a wave vector that is well defined on the scale of the Brillouin zone must be spread in real space over many primitive cells.*

The semiclassical model describes the response of the electrons to externally applied electric and magnetic fields that vary slowly over the dimensions of such a wave packet (Figure 12.1) and therefore exceedingly slowly over a few primitive cells.

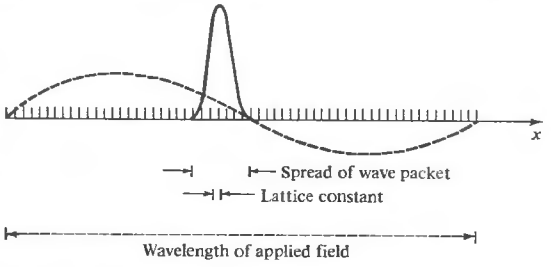

Figure 12.1
Schematic view of the situation described by the semiclassical model. The length over which the applied field (dashed line) varies is much greater than the spread in the wave packet of the electron (solid line), which in turn is much larger than the lattice constant.

In the semiclassical model such fields give rise to ordinary classical forces in an equation of motion describing the evolution of the position and wave vector of the packet. The subtlety of the semiclassical model that makes it more complicated than the ordinary classical limit of *free* electrons, is that the periodic potential of the lattice varies over dimensions that are *small* compared with the spread of the wave packet, and therefore cannot be treated classically. Thus the semiclassical model is a partial classical limit: The externally applied fields are treated classically, but the periodic field of the ions is not.

DESCRIPTION OF THE SEMICLASSICAL MODEL

The semiclassical model predicts how, in the absence of collisions, the position $\mathbf{r}$ and wave vector $\mathbf{k}$ of each electron[8] evolve in the presence of externally applied electric and magnetic fields. *This prediction is based entirely upon a knowledge of the band structure of the metal, i.e., upon the forms of the functions* $\mathcal{E}_n(\mathbf{k})$, *and upon no other explicit information about the periodic potential of the ions.* The model takes the $\mathcal{E}_n(\mathbf{k})$ as given functions, and says nothing about how to compute them. The aim of the model is to relate the band structure to the transport properties, i.e., the response

[7] If g is appreciable only in a neighborhood of $\mathbf{k}$ small compared with the dimensions of the zone, then $\psi_{n\mathbf{k}}(\mathbf{r}_0)$ will vary little over this range, and as a function of $\mathbf{k}$, $\bar{g}$ will differ little from a constant times g.

[8] Hereafter we shall speak of an electron as having both a position and a wave vector. What we are referring to, of course, is a wave packet, as described above.

of the electrons to applied fields or temperature gradients. One uses the model both to deduce transport properties from a given (calculated) band structure and to deduce features of the band structure from the observed transport properties.

Given the functions $\varepsilon_n(\mathbf{k})$, the semiclassical model associates with each electron a position $\mathbf{r}$, a wave vector $\mathbf{k}$, and a band index n. In the course of time and in the presence of external electric and magnetic fields $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$ the position, wave vector, and band index are taken to evolve according to the following rules:

1. The band index n is a constant of the motion. The semiclassical model ignores the possibility of "interband transitions".
2. The time evolution of the position and wave vector of an electron with band index n are determined by the equations of motion:

$$\dot{\mathbf{r}} = \mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}, \tag{12.6a}$$

$$\hbar\dot{\mathbf{k}} = -e\left[\mathbf{E}(\mathbf{r}, t) + \frac{1}{c}\mathbf{v}_n(\mathbf{k}) \times \mathbf{H}(\mathbf{r}, t)\right]. \tag{12.6b}$$

3. (This rule simply restates those features of the full quantum mechanical Bloch theory that are retained in the semiclassical model.) The wave vector of an electron is only defined to within an additive reciprocal lattice vector $\mathbf{K}$. One cannot have two *distinct* electrons with the same band index n and position $\mathbf{r}$, whose wave vectors $\mathbf{k}$ and $\mathbf{k}'$ differ by a reciprocal lattice vector $\mathbf{K}$; the labels n, $\mathbf{r}$, $\mathbf{k}$ and n, $\mathbf{r}$, $\mathbf{k} + \mathbf{K}$ are completely equivalent ways of describing the *same* electron.[9] All distinct wave vectors for a single band therefore lie in a single primitive cell of the reciprocal lattice. In thermal equilibrium the contribution to the electronic density from those electrons in the nth band with wave vectors in the infinitesimal volume element $d\mathbf{k}$ of k-space is given by the usual Fermi distribution (2.56):[10]

$$f(\varepsilon_n(\mathbf{k}))\frac{d\mathbf{k}}{4\pi^3} = \frac{d\mathbf{k}/4\pi^3}{e^{(\varepsilon_n(\mathbf{k})-\mu)/k_BT} + 1}. \tag{12.7}$$

COMMENTS AND RESTRICTIONS

A Many-Carrier Theory

Because the applied fields are assumed to cause no interband transitions, one can consider each band to contain a fixed number of electrons of a particular type. The properties of these types may differ considerably from band to band, since the kind of motion electrons with band index n can undergo depends on the particular form of $\varepsilon_n(\mathbf{k})$. In (or near) equilibrium, bands with all energies many k_BT above the Fermi energy ε_F will be unoccupied. Thus one need not consider infinitely many carrier

[9] The semiclassical equations of motion (12.6) preserve this equivalence as time evolves. If $\mathbf{r}(t)$, $\mathbf{k}(t)$ give a solution for the nth band, then so will $\mathbf{r}(t)$, $\mathbf{k}(t) + \mathbf{K}$ for any reciprocal lattice vector $\mathbf{K}$, as a consequence of the periodicity of $\varepsilon_n(\mathbf{k})$.

[10] This assumes that interactions of the electron spin with any magnetic fields are of no consequence; if they are, then each spin population makes a contribution to n given by half (12.7) where $\varepsilon_n(\mathbf{k})$ must include the interaction energy of the given spin with the magnetic field.

types, but only those in bands with energies within a few k_BT of, or lower than, ε_F. Furthermore, we shall see below that bands in which all energies are many k_BT less than ε_F—i.e., bands that are completely filled in equilibrium—can also be ignored! As a result, only a small number of bands (or carrier types) need be considered in the description of a real metal or semiconductor.

Crystal Momentum Is Not Momentum

Note that within each band the equations of motion (12.6) are the same as the free electron equations (12.1) except that $\varepsilon_n(\mathbf{k})$ appears instead of the free electron energy $\hbar^2k^2/2m$. Nevertheless, the crystal momentum $\hbar\mathbf{k}$ is *not* the momentum of a Bloch electron, as emphasized in Chapter 8. The rate of change of an electron's momentum is given by the *total* force on the electron, but the rate of change of an electron's crystal momentum is given by Eq. (12.6), in which forces are exerted only by the external fields and not by the periodic field of the lattice.[11]

Limits of Validity

In the limit of zero periodic potential the semiclassical model must break down, for in that limit the electron will be a free electron. In a uniform electric field a free electron can continually increase its kinetic energy at the expense of electrostatic potential energy. However, the semiclassical model forbids interband transitions, and therefore requires that the energy of any electron remains confined within the limits of the band in which the electron originally found itself.[12] Thus there must be some minimum strength to a periodic potential before the semiclassical model can be applied. Such restrictions are not easy to derive, but have a very simple form, which we state here without proof.[13] At a given point in k-space the semiclassical equations will be valid for electrons in the nth band provided that the amplitudes of the slowly varying external electric and magnetic fields satisfy

$$eEa \ll \frac{[\varepsilon_{\text{gap}}(\mathbf{k})]^2}{\varepsilon_F}, \tag{12.8}$$

$$\hbar\omega_c \ll \frac{[\varepsilon_{\text{gap}}(\mathbf{k})]^2}{\varepsilon_F}. \tag{12.9}$$

In these inequalities the length a is of the order of a lattice constant, $\varepsilon_{\text{gap}}(\mathbf{k})$ is the difference between $\varepsilon_n(\mathbf{k})$ and the nearest energy $\varepsilon_{n'}(\mathbf{k})$ at the same point in k-space but in a different band, and ω_c is the angular cyclotron frequency (Eq. (1.18)).

Condition (12.8) is never close to being violated in a metal. Even with a current density as large as 10^2 amp/cm^2 and a resistivity as large as 100 μohm-cm, the field

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11 Although the periodic lattice potential does play a crucial role in the semiclassical equations (through the structure of the function $\varepsilon_n(\mathbf{k})$ determined by that potential), the role cannot be that of a position-dependent force. To probe a force with the periodicity of the lattice one would have to localize an electron within a single primitive cell. Such a localization is inconsistent with the structure of the wave packets underlying the semiclassical model (see Figure 12.1), which are spread over many lattice sites.

12 This requirement is violated every time the free electron wave vector crosses a Bragg plane, since the electron then jumps from the lower free electron band to the higher one.

13 A rough justification is given in Appendix J.

in the metal will only be $E = \rho j = 10^{-2}$ volt/cm. Hence for a on the order of 10^{-8} cm, eEa is of order 10^{-10} eV. Since ε_F is of the order of an electron volt or more, $\varepsilon_{gap}(\mathbf{k})$ must be as small as 10^{-5} eV before condition (12.8) is violated. In practice, gaps this small are never encountered except near points where two bands become degenerate, and then only in an exceedingly small region of k-space about such points. Typical small band gaps are of the order of 10^{-1} eV, and therefore (12.8) is satisfied with a factor of 10^{-8} to spare. The condition is of practical concern only in insulators and in homogeneous semiconductors, where it is possible to establish immense electric fields; when the condition is violated electrons can make an interband transition driven by the field, a phenomenon known as *electric breakdown.*

The condition (12.9) on the magnetic field strength is not as difficult to violate. The energy $\hbar\omega_c$ is of order 10^{-4} eV in a field of 10^4 gauss, in which case (12.9) fails for gaps as large as 10^{-2} eV. Although this is still a small energy gap, such gaps are not at all uncommon, especially when the gap is entirely due to a degeneracy split by spin-orbit coupling. When condition (12.9) fails to hold, electrons may not follow the orbits determined by the semiclassical equations of motion (12.6), a phenomenon known as *magnetic breakthrough* (or "breakdown"). The possibility of magnetic breakthrough must always be kept in mind in interpreting electronic properties in very strong magnetic fields.

In addition to the conditions (12.8) and (12.9) on the amplitude of the applied fields, one must add a low-frequency condition on the fields,

$$\hbar\omega \ll \varepsilon_{gap}, \tag{12.10}$$

or else a single photon could supply enough energy to produce an interband transition. There is also the condition on the wavelength of the applied fields,

$$\lambda \gg a, \tag{12.11}$$

that is necessary if wave packets can be meaningfully introduced at all.[14]

Basis for the Equations of Motion

As discussed above, Eq. (12.6a) is simply the statement that the velocity of a semiclassical electron is the group velocity of the underlying wave packet. Equation (12.6b) is considerably more difficult to justify. It is highly plausible in the presence of a static electric field as the simplest way to guarantee conservation of energy, for if the field is given by $\mathbf{E} = -\nabla\phi$, then we should expect each wave packet to move so that the energy

$$\varepsilon_n(\mathbf{k}(t)) - e\phi(\mathbf{r}(t)) \tag{12.12}$$

remains constant. The time derivative of this energy is

$$\frac{\partial\varepsilon_n}{\partial\mathbf{k}} \cdot \dot{\mathbf{k}} - e\nabla\phi \cdot \dot{\mathbf{r}}, \tag{12.13}$$

[14] It is also sometimes necessary to take into account further quantum effects due to the possibility of closed electronic k-space orbits in a magnetic field. This can be handled by an ingenious extension of the semiclassical model, and is therefore not a limitation in the sense of the restrictions described above. The problem arises in the theory of the de Haas–van Alphen effect and related phenomena, and is described in Chapter 14.

which Eq. (12.6a) permits us to write as

$$\mathbf{v}_n(\mathbf{k}) \cdot [\hbar\dot{\mathbf{k}} - e\nabla\phi]. \tag{12.14}$$

This will vanish if

$$\hbar\dot{\mathbf{k}} = e\nabla\phi = -e\mathbf{E}, \tag{12.15}$$

which is Eq. (12.6b) in the absence of a magnetic field. However, (12.15) is not necessary for energy to be conserved, since (12.14) vanishes if any term perpendicular to $\mathbf{v}_n(\mathbf{k})$ is added to (12.15). To justify with rigor that the only additional term should be $[\mathbf{v}_n(\mathbf{k})/c] \times \mathbf{H}$, and that the resulting equation should hold for time-dependent fields as well, is a most difficult matter, which we shall not pursue further. The dissatisfied reader is referred to Appendix H for a further way of rendering the semiclassical equations more plausible. There it is shown that they can be written in a very compact Hamiltonian form. To find a really compelling set of arguments, however, it is necessary to delve rather deeply into the (still growing) literature on the subject.[15]

CONSEQUENCES OF THE SEMICLASSICAL EQUATIONS OF MOTION

The rest of this chapter surveys some of the fundamental direct consequences of the semiclassical equations of motion. In Chapter 13 we shall turn to a more systematic way of extracting theories of conduction.

In most of the discussions that follow we shall consider a single band at a time, and shall therefore drop reference to the band index except when explicitly comparing the properties of two or more bands. For simplicity we shall also take the electronic equilibrium distribution function to be that appropriate to zero temperature. In metals finite temperature effects will have negligible influence on the properties discussed below. Thermoelectric effects in metals will be discussed in Chapter 13, and semiconductors will be treated in Chapter 28.

The spirit of the analysis that follows is quite similar to that in which we discussed transport properties in Chapters 1 and 2: We shall describe collisions in terms of a simple relaxation-time approximation, and focus most of our attention on the motion of electrons between collisions as determined (in contrast to Chapters 1 and 2) by the *semiclassical* equations of motion (12.6).

Filled Bands Are Inert

A filled band is one in which all the energies lie below[16] ε_F. Electrons in a filled band with wave vectors in a region of k-space of volume $d\mathbf{k}$ contribute $d\mathbf{k}/4\pi^3$ to the total electronic density (Eq. (12.7)). Thus the number of such electrons in a region of position space of volume $d\mathbf{r}$ will be $d\mathbf{r}\, d\mathbf{k}/4\pi^3$. One can therefore characterize a filled band semiclassically by the fact that the density of electrons in a six-dimensional rk-space (called phase space, in analogy to the rp-space of ordinary classical mechanics) is $1/4\pi^3$.

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[15] See, for example, the references given in footnote 1.

[16] More generally, the energies should be so far below the chemical potential μ compared with k_BT that the Fermi function is indistinguishable from unity throughout the band.

The semiclassical equations (12.6) imply that a filled band remains a filled band at all times, even in the presence of space- and time-dependent electric and magnetic fields. This is a direct consequence of the semiclassical analogue of Liouville's theorem, which asserts the following:[17]

Given any region of six-dimensional phase space Ω_t, consider the point $\mathbf{r}', \mathbf{k}'$ into which each point $\mathbf{r}, \mathbf{k}$ in Ω_t is taken by the semiclassical equations of motion between times[18] t and t'. The set of all such points $\mathbf{r}', \mathbf{k}'$ constitutes a new region $\Omega_{t'}$, whose volume is the same as the volume of Ω_t (see Figure 12.2); i.e., phase space volumes are conserved by the semiclassical equations of motion.

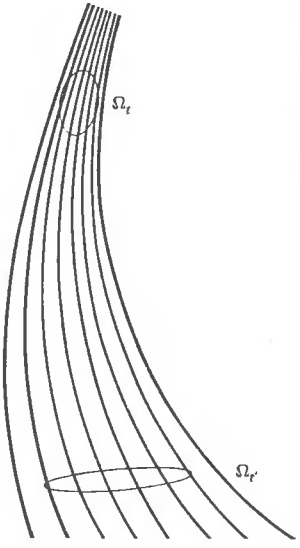

Figure 12.2
Semiclassical trajectories in rk-space. The region $\Omega_{t'}$ contains at time t' just those points that the semiclassical motion has carried from the region Ω_t at time t. Liouville's theorem asserts that Ω_t and $\Omega_{t'}$ have the same volume. (The illustration is for a two-dimensional rk-space lying in the plane of the page, i.e., for semiclassical motion in one dimension.)

This immediately implies that if the phase space density is $1/4\pi^3$ at time zero, it must remain so at all times, for consider any region Ω at time t. The electrons in Ω at time t are just those that were in some other region Ω_0 at time zero where, according to Liouville's theorem, Ω_0 has the same volume as Ω. Since the two regions also have the same number of electrons, they have the same phase space density of electrons. Because that density was $1/4\pi^3$, independent of the region at time 0, it must also be

[17] See Appendix H for a proof that the theorem applies to semiclassical motion. From a quantum mechanical point of view the inertness of filled bands is a simple consequence of the Pauli exclusion principle: The "phase space density" cannot increase if every level contains the maximum number of electrons allowed by the Pauli principle; furthermore, if interband transitions are prohibited, neither can it decrease, for the number of electrons in a level can only be reduced if there are some incompletely filled levels in the band for those electrons to move into. For logical consistency, however, it is necessary to demonstrate that this conclusion also follows directly from the semiclassical equations of motion, without reinvoking the underlying quantum mechanical theory that the model is meant to replace.

[18] The time t' need not be greater than t; i.e., the regions from which Ω_t evolved have the same volume as Ω_t, as well as the regions into which Ω_t will evolve.

$1/4\pi^3$, independent of the region at time t. Thus semiclassical motion between collisions cannot alter the configuration of a filled band, even in the presence of space- and time-dependent external fields.[19]

However, a band with a constant phase space density $1/4\pi^3$ cannot contribute to an electric or thermal current. To see this, note that an infinitesimal phase space volume element $d\mathbf{k}$ about the point $\mathbf{k}$ will contribute $d\mathbf{k}/4\pi^3$ electrons per unit volume, all with velocity $\mathbf{v}(\mathbf{k}) = (1/\hbar)\,\partial\mathcal{E}(\mathbf{k})/\partial\mathbf{k}$ to the current. Summing this over all $\mathbf{k}$ in the Brillouin zone, we find that the total contribution to the electric and energy current densities from a filled band is

$$\mathbf{j} = (-e)\int \frac{d\mathbf{k}}{4\pi^3}\frac{1}{\hbar}\frac{\partial\mathcal{E}}{\partial\mathbf{k}},$$

$$\mathbf{j}_{\mathcal{E}} = \int \frac{d\mathbf{k}}{4\pi^3}\mathcal{E}(\mathbf{k})\frac{1}{\hbar}\frac{\partial\mathcal{E}}{\partial\mathbf{k}} = \frac{1}{2}\int \frac{d\mathbf{k}}{4\pi^3}\frac{1}{\hbar}\frac{\partial}{\partial\mathbf{k}}(\mathcal{E}(\mathbf{k}))^2. \tag{12.16}$$

But both of these vanish as a consequence of the theorem[20] that the integral over any primitive cell of the gradient of a periodic function must vanish.

Thus only partially filled bands need be considered in calculating the electronic properties of a solid. This explains how that mysterious parameter of free electron theory, the number of conduction electrons, is to be arrived at: *Conduction is due only to those electrons that are found in partially filled bands.* The reason Drude's assignment to each atom of a number of conduction electrons equal to its valence is often successful is that in many cases those bands derived from the atomic valence electrons are the only ones that are partially filled.

Evidently a solid in which all bands are completely filled or empty will be an electrical and (at least as far as *electronic* transport of heat is concerned) thermal insulator. Since the number of levels in each band is just twice the number of primitive cells in the crystal, all bands can be filled or empty *only* in solids with an even number of electrons per primitive cell. Note that the converse is not true: Solids with an even number of electrons per primitive cell may be (and frequently are) conductors, since the overlap of band energies can lead to a ground state in which several bands are partially filled (see, for example, Figure 12.3). We have thus derived a necessary, but by no means sufficient, condition for a substance to be an insulator.

It is a reassuring exercise to go through the periodic table looking up the crystal structure of all insulating solid elements. They will all be found to have either even valence or (e.g., the halogens) a crystal structure that can be characterized as a lattice with a basis containing an even number of atoms, thereby confirming this very general rule.

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[19] Collisions cannot alter this stability of filled bands either, provided that we retain our basic assumption (Chapter 1, page 6 and Chapter 13, page 245) that whatever else they do, the collisions cannot alter the distribution of electrons when it has its thermal equilibrium form. For a distribution function with the constant value $1/4\pi^3$ is precisely the zero temperature equilibrium form for any band all of whose energies lie below the Fermi energy.

[20] The theorem is proved in Appendix I. The periodic functions in this case are $\mathcal{E}(\mathbf{k})$ in the case of $\mathbf{j}$, and $\mathcal{E}(\mathbf{k})^2$ in the case of $\mathbf{j}_{\mathcal{E}}$.

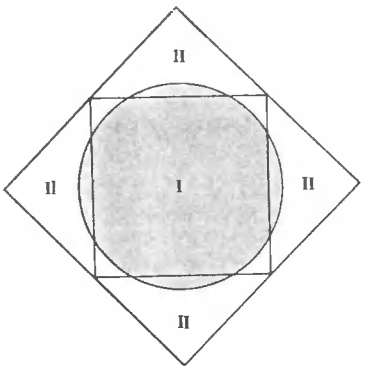

Figure 12.3
A two-dimensional illustration of why a divalent solid can be a conductor. A free electron circle, whose area equals that of the first Brillouin zone (I) of a square Bravais lattice, extends into the second zone (II), thus producing two partially filled bands. Under the influence of a sufficiently strong periodic potential the pockets of first-zone holes and second-zone electrons might shrink to zero. Quite generally, however, a weak periodic potential will always lead to this kind of overlap (except in one dimension).

Semiclassical Motion in an Applied DC Electric Field

In a uniform static electric field the semiclassical equation of motion for $\mathbf{k}$ (Eq. (12.6)) has the general solution

$$\mathbf{k}(t) = \mathbf{k}(0) - \frac{e\mathbf{E}t}{\hbar}. \tag{12.17}$$

Thus in a time t every electron changes its wave vector by the same amount. This is consistent with our observation that applied fields can have no effect on a filled band in the semiclassical model, for a uniform shift in the wave vector of *every* occupied level does not alter the phase space density of electrons when that density is constant, as it is for a filled band. However, it is somewhat jarring to one's classical intuition that by shifting the wave vector of every electron by the same amount we nevertheless fail to bring about a current-carrying configuration.

To understand this, one must remember that the current carried by an electron is proportional to its velocity, which is not proportional to $\mathbf{k}$ in the semiclassical model. The velocity of an electron at time t will be

$$\mathbf{v}(\mathbf{k}(t)) = \mathbf{v}\left(\mathbf{k}(0) - \frac{e\mathbf{E}t}{\hbar}\right). \tag{12.18}$$

Since $\mathbf{v}(\mathbf{k})$ is periodic in the reciprocal lattice, the velocity (12.18) is a bounded function of time and, when the field $\mathbf{E}$ is parallel to a reciprocal lattice vector, oscillatory! This is in striking contrast to the free electron case, where $\mathbf{v}$ is proportional to $\mathbf{k}$ and grows linearly in time.

The $\mathbf{k}$ dependence (and, to within a scale factor, the t dependence) of the velocity is illustrated in Figure 12.4, where both $\varepsilon(k)$ and $v(k)$ are plotted in one dimension. Although the velocity is linear in k near the band minimum, it reaches a maximum as the zone boundary is approached, and then drops back down, going to zero at the zone edge. In the region between the maximum of v and the zone edge the velocity actually decreases with increasing k, so that the acceleration of the electron is opposite to the externally applied electric force!

This extraordinary behavior is a consequence of the additional force exerted by the periodic potential, which, though no longer explicit in the semiclassical model, lies buried in it (through the functional form of $\varepsilon(\mathbf{k})$). As an electron approaches a