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Recent Developments in the Quantum Theory of Transport and Galvanomagnetic Phenomena*

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CONTENTS

I. INTRODUCTORY CONSIDERATIONS

A. General Comments, Scope, and Organization

1. *Introduction*

THIS paper reviews and analyzes the current research in the quantum theory of transport phenomena. Transport processes occur in many areas in physics; included are such different phenomena as electrical conduction, thermal diffusion, paramagnetic relaxation, absorption of sound waves, and many others. In a qualitative way one could say that in transport phenomena one deals with systems which are not in a *strict* thermodynamic equilibrium state. One could distinguish, in a rough manner, two types of transport phenomena; those where the application of outside constraints (such as temperature gradients, alternating fields) prevents the establishment of a strict equilibrium state, others where the initial given state is not an equilibrium state and the system, left to itself, would proceed towards its equilibrium state. The latter would be exemplified by a relaxation process; it should be stressed that under the influence of outside constraints a *steady* state (in this paper distinguished from an equilibrium state; see Sec. C)[1] is generally established. The discussion and description of this state is one of the main concerns in transport theory.

Transport theory, properly speaking, is a special part of nonequilibrium statistical mechanics; one where the deviations from the equilibrium state are usually small.

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[1] Sections and formulas referred to without a part number are those of Part I.

The most fundamental (but also the most difficult) way to approach transport theory would be to obtain it as a special case of the general formalism of nonequilibrium statistical mechanics. Although in principle correct, difficulties of setting up and *utilizing* such a general formalism have severely limited the applicability of this method. (In addition, one attempts to solve a hard problem before an easier one has been solved; this generally is bad tactics.) There also exist many phenomenological descriptions of transport processes. It is of importance to remark that the empirical laws describing these processes always contain empirical constants, such as the electrical conductivity, the thermal conductivity, viscosity coefficients and relaxation times. Within the framework of the phenomenological description, these empirical parameters can be obtained only from experiment. One would hope that a more complete discussion would provide the general form of the empirical laws and relate the experimental parameters in these laws to the atomistic properties of the system. In most theoretical discussions, one adopts neither the completely fundamental nor the completely phenomenological viewpoint. Rather one adds reasonable physical assumptions and experimental information to the basic statistical description. What is reasonable depends strongly on the system and the process under consideration. Since the characteristics of systems and processes vary widely, it is not surprising that the additional assumptions introduced are of a bewildering variety (especially since they often are not explicitly stated). On using this additional information, one can calculate some of the transport properties. In this way expressions are obtained for the empirical parameters in terms of more basic (but generally not yet atomistic) entities. For example, in a purely phenomenological description, thermal and electrical conductivity are empirical parameters. Within the framework of the ordinary kinetic theory of an electron gas, both electrical and thermal conductivity may be *computed* in terms of an *assumed* time τ, the mean time between collisions. This is a typical instance of the use of a statistical procedure, where, because of the special character of the system (a dilute gas), one can make further simplifying assumptions (the existence of a relaxation time) which, strictly speaking, should be proven for the system at hand. Another powerful technique used in the description of transport processes is the application of thermodynamics (either the reversible or irreversible version of thermodynamics) to the process. This does not generally allow the calculation of transport coefficients as such, but it does provide an *interrelation* between different transport coefficients. This procedure again is an interpolation between the purely phenomenological and the completely fundamental approach.

There is a large variety of different assumptions explicit or implicit in the discussions of transport processes. These various assumptions as they pertain to different systems are discussed in detail. Perhaps the most common assumption used in transport theory is that of the existence of a transport equation or rate equation. (Sometimes called a gain-loss equation; the Boltzmann equation in kinetic theory is of this general type.) The physical content of such equations always *appears* self-evident: It states that the time rate of change of the number of particles in a certain state equals the number of particles entering that state minus the number leaving that state. If $n_i(t)$ stands for the number of particles in state i, and if A_{ij} is the probability for a transition per unit time, from i to j, the equation reads

$$dn_i/dt=\sum_j(n_jA_{ji}-n_iA_{ij}). \qquad (1)$$

The mechanics of the process is contained in the coefficients A. In fact, in many circumstances one can compute the coefficients A from the *dynamical* laws which govern the behavior of the system (from the Schrödinger equation, for example). Since an equation of type (1) (often also called a master equation) is so frequently used in the analysis of transport problems, it is important to know its status within physics as well as its domain of validity. This too is discussed in the sequel. But it is well to point out already that in spite of its intuitive appearance, (1) is far from obvious. Certain probability assumptions have made in (1); that a transition probability per unit time A_{ij} exists is by no means self-evident. The states i are presumably eigenstates of some unperturbed Hamiltonian so that the transitions themselves are caused by a perturbation which, however, mixes the eigenstates of that unperturned Hamiltonian (with certain coefficients and *phases*). That the resulting evolution in time can be expressed by (1) should surely depend on the *kind* of perturbation causing the transitions. These brief remarks may indicate that there are subtle but important difficulties connected with the derivation of (1). Finally, if it turns out that (1) has a limited validity only, it would be of great interest if one could point to actual physical situations where refined versions of the master equation (1) would be needed. These points are discussed at great length, but their great importance would appear to justify their inclusion in this introduction.

2. *Purposes of Transport Studies*

The basic purposes of transport studies vary greatly. This gives the field a rather heterogeneous appearance. For this reason, it is of value to list the various motivations for these investigations. Such a list is for systematic purposes only; very few studies have just a single purpose, so generally a given study would contribute information to several classes.

(*a*) *Investigation of transport parameters.* In this class belong all studies designed to obtain the numerical values of transport coefficients. Of special interest is information regarding the variation of these coefficients with changing physical parameters. Examples would be the pressure dependence of viscosity, the magnetic field dependence of conductivity, and the temperature dependence of relaxation times. In some of these situations, knowledge of the actual empirical laws is far from complete. Such information is a prerequisite for further progress.

(*b*) *Correlation of transport parameters and microscopic entities*. The important role played by transport theory derives in part from the circumstance that by using that theory one may relate the experimentally observed transport coefficients to parameters describing the microscopic character of the system. Thus, by studying transport properties one can obtain information about the basic interactions within the system. How easy it is to obtain such information depends on the complexity of the system; in addition, the limitations and assumptions inherent in the statistical treatment must be explicitly recognized. The simplest system traditionally considered is a dilute gas; there the elementary statistical treatment allows one to calculate various entities, such as thermal conductivity and viscosity, in terms of a mean free path λ or, equivalently, an average time between collisions $\tau=\lambda/\bar{v}$ ($\bar{v}$ is some average thermal velocity). (τ is frequently called a relaxation time.) For example, one finds for the viscosity coefficient μ

$$\mu=n\tau kT, \tag{2a}$$

where k is the Boltzmann constant, τ the relaxation time, and n the number of molecules per unit volume. A more complete mathematical analysis, utilizing the Boltzmann transport equation for this process, allows one to refine the expression for the viscosity to

$$\mu=\tfrac{5}{8}(\pi mkT)^{\frac{1}{2}}\left[\int_0^\infty dgg^7\exp(-g^2)Q(g)\left(\frac{4kT}{m}\right)^{\frac{1}{2}}\right]^{-1}. \tag{2b}$$

Here m is the mass and

$$Q(g)=2\pi\int_0^\pi d\theta(\sin\theta)^3 I(g,\theta). \tag{2c}$$

Q is the transport cross section, and $I(g,\theta)$ is the differential cross section for binary (molecule-molecule) collisions. I is completely known once the intermolecular potential is known. The difference between (2a) and (2b) illustrates the difference alluded to before: in the elementary discussion τ is an undetermined parameter; *measurements* of μ as a function of T determine τ as a function of T. However, (2b) allows one to *compute* μ from a knowledge of the intermolecular potential. The basic assumption made in the derivation of (2b) is that only two-body collisions need to be considered. Equations (2a) and (2b) represent different levels of statistical treatment. In (2b) one has a direct relation between a transport quantity and the intermolecular potential. In (2a) the theory leaves τ undetermined; it can be obtained from experiment. Other entities such as the thermal conductivity may be expressed in terms of the same τ. This τ can be obtained from viscosity measurements by using (2a). Thus, by using this value of τ and the computed expression for the thermal conductivity, consistency of the elementary transport treatment may be checked.

A similar but much more involved situation occurs in the study of transport phenomena in solids. The elementary kinetic approach applied to an electron gas yields for the conductivity σ the well-known relation

$$\sigma=ne^2\tau/m, \tag{3}$$

where n is the number of (free) electrons per unit volume, m the mass, τ the already mentioned relaxation time, and e the electronic charge. To compare (3) with experiment with a real solid, one needs to take into account the interaction of the electrons with the periodic lattice. This in some approximate sense can be done by replacing m by m^*, the effective mass. Hence from a measurement of σ in (3) one can determine a combination of m^* and τ. Actually, n, the number of free electrons, is not given by the theory either: it has to be obtained from experiment as well, so that a relation such as (3) serves to obtain relations between parameters describing a solid, rather than as a check on a particular development in the theory. Several types of experiments need to be performed for a given material to determine the various parameters needed for the description of the solid. If the statistical discussion is refined, further details of the structure of the solid, such as the nature of the Fermi surface and the band structure, enter into the expressions for the transport coefficients. To analyze experiments involving, say, the conductivity tensor, one needs information about the Fermi surface; this in turn must be obtained from other experimental information, such as the de Haas-van Alphen effect. Thus, the interpretation of transport experiments in solids is rarely straightforward; it demands the combination of a variety of experimental results together with transport theory and solid-state theory. Even then the results are rarely as immediate as (2a). For instance, a typical result of a conductivity calculation relates the conductivity σ to the effective mass m^*, the Debye temperature Θ, and a number C which can be explicitly written in terms of the (not very well known) wave function of an electron in the particular solid. Therefore, because of the many uncertainties in the calculations, solid-state transport studies are generally not suited for the investigation of the validity of the transport equation. On the other hand, the use of transport theory does provide a method to obtain significant solid state parameters.

In special circumstances one can obtain more definite results. The case of the relaxation of nuclear spins in a metal is again a nonequilibrium situation. On assuming a special form of the coupling between the nuclear spins and the conduction electrons (the hyperfine coupling), one may deduce in perturbation theory the transition probability per unit time [the A's in Eq. (1)]. Application of elementary kinetic theory [just Eq. (1)] provides a relation between the observed relaxation time and the hyperfine coupling which is responsible for the relaxation. This is a direct and simple example of the correlation between a transport and an atomistic quantity.

(*c*) *Connections with irreversible thermodynamics*. The discussion in Sec. (b) shows that it is desirable to perform and analyze a variety of transport-type experiments using the same substance. An obvious way to make such a study would be to obtain a single sample (preferably a single crystal) and subject it to a variety of experimental conditions by introducing electric or magnetic fields or thermal gradients. In the interpretation of these experiments, the characteristics of the material (the solid) would be common to the various experiments. However, when one deals with transport processes in which several irreversible processes may occur simultaneously, new effects occur which in turn require new empirical parameters for their description. For instance, in a pure diffusion process the basic law (Fick's law) states

$$\mathbf{j}_n = -D\nabla n, \tag{4a}$$

where $\mathbf{j}_n$ is the particle current density; ∇n the gradient of the particle density, and D the empirical constant, the diffusivity. Similarly, for thermal conduction (Fourier's law),

$$\mathbf{j}_g = -\kappa\nabla T, \tag{4b}$$

where $\mathbf{j}_g$ is the thermal current density, ∇T the temperature gradient, and κ the thermal conductivity. Now there are circumstances where a temperature gradient causes *both* a particle and a thermal current. This would be a combination of diffusion and thermal conduction. The simplest phenomenological extension of (4a) and (4b) is

$$\mathbf{j}_n = -D\nabla n + F_1\nabla T, \tag{5a}$$

$$\mathbf{j}_g = -\kappa\nabla T + F_2\nabla n. \tag{5b}$$

Equations (5) contain two new constants which should be determined from experiment. A similar situation pertains when both electrical and thermal conduction processes can occur. The appropriate phenomenological relations are

$$\mathbf{j}_{\mathrm{el}} = L_{11}\mathbf{E} + L_{12}\nabla T, \tag{6a}$$

$$\mathbf{j}_g = L_{21}\mathbf{E} + L_{22}\nabla T, \tag{6b}$$

where $\mathbf{j}_{\mathrm{el}}$ is the electric current density and $\mathbf{E}$ the applied electric field; the L's are again empirical parameters. (Clearly $L_{11} = \sigma =$ the conductivity.) Basic in the interpretation of experiments of this type are the symmetry relations first obtained by Onsager. Applied to this case they state that there exists a relation between L_{12} and L_{21}, so that the combined effects require only one additional independent parameter. In general, there are a number of such relations between the transport coefficients characterizing different transport processes. This circumstance enables one in principle to obtain from experiments done on a transport process of one type, results for other types. Other symmetry relations are of importance in connection with anisotropic crystals. The conductivity tensor σ_{ij} of a crystal is defined by

$$j_{e,i} = \sum_{j=1}^{3} \sigma_{ij}E_j \quad i = 1, 2, 3. \tag{7}$$

If the crystal is placed in a magnetic field H, the σ_{ij} becomes a function of H [the same would apply to L_{ij} in (6)]. The Onsager relations would state in this case that

$$\sigma_{ij}(\mathbf{H}) = \sigma_{ji}(-\mathbf{H}). \tag{8}$$

This result is independent of the crystal structure. Anisotropic materials give rise to a variety of new effects. For instance, a thermal gradient in one direction may produce a thermal current in another. The symmetry relations are essential in interpreting these experiments. The use of transport studies in connection with these relations lies in part in the experimental check they provide for relations such as (8), and more significantly in the interrelations they yield between the different processes.

If one actually calculates transport coefficients, the symmetry relations are of no special use. The computed results must agree with the general symmetry principles. The derivation of the Onsager relations is based on an extension of equilibrium thermodynamics to include small deviations from equilibrium. It indeed appears that for many transport processes this description in terms of irreversible thermodynamics is sufficiently general. In these instances one does not need to use the formalism of nonequilibrium theory; the description of these processes in terms of irreversible thermodynamics has the same validity that the description of equilibrium thermodynamics has for equilibrium situations. The question of the validity of these symmetry relations (and therefore of the empirical correlations based on them) can be discussed only if one is able to obtain the laws of irreversible thermodynamics as a result of more general, more *a priori* considerations.

(*d*) *Fundamental theoretical interests*. The fundamental problem of statistical mechanics is to describe the macroscopic behavior of a many particle system in terms of the given mechanical properties (the given interactions) of the constituents of the system. A complete description includes equilibrium as well as transport processes and, in addition, still more general nonequilibrium situations. Consequently, any attempt based on first principles to obtain a complete description of a many-body system must, at least in principle, contain results which are relevant for transport theory. The indirect way in which most basic theories are connected with observable transport quantities makes a direct test of the theory with experiment difficult.

Sometimes, however, a theory predicts general symmetries or particular interrelations between observable quantities. Relations of this type may be checked advantageously through transport-type experiments. It is generally correct that the comparison of transport properties with experiment gives a more sensitive and detailed check of a theory than does a similar comparison of equilibrium properties. (This applies only if the transport coefficients can be obtained from the theory without too many additional assumptions. Unfortunately, this is not often the case.)

Although there are many experimental and theoretical studies concerned with transport processes which do not fit within the division (a)–(d) just given, this division is a fairly natural one. It might be of some help in classifying and organizing the large amount of published material in this field. It is used for this purpose in this paper.

3. Characteristics of the Current Developments

Transport studies of the type outlined in Secs. A.1 and A.2 have been carried out for many years. In the last few years a number of separate developments have taken place which have caused profound changes in the approach to these problems. The basic program of this paper is to summarize and analyze these recent advances. Although many factors have contributed to this development, it is possible to single out a few features which appear characteristic of the newer methods.

(a) The tremendous improvement in experimental techniques allows measurement of many finer details of the transport phenomena. This in turn requires a more careful investigation of the validity of the theoretical treatment used to describe these processes. Of particular importance in this connection are experiments measuring the variation of resistance in high magnetic fields. It is shown later that under these conditions (the high magnetic fields) quantum effects become particularly important, which is a significant new feature.

(b) It was pointed out in Sec. A.2(b) that a knowledge of transport coefficients in solids usually yields a combination of parameters such as effective mass and number of free electrons. Recently, several new methods have been employed which either yield new relations between these parameters or which in some circumstances yield these parameters directly. One may, for example, use cyclotron resonance experiments to determine effective masses directly. (Cyclotron resonance is a typical steady-state process proceeding under the influence of an impressed field.) A knowledge of the effective masses is needed for the interpretation of magnetoresistance experiments. Knowledge of the Fermi surface (also required for the interpretation of these experiments) can in principle be obtained from the de Haas-van Alphen effect. The combined use of a variety of these methods enables a much more detailed analysis of transport processes to be made than was possible heretofore.

(c) One of the striking new features noticeable in recent work is a more critical atitude towards the basic transport equation. This attitude manifested itself in a number of studies devoted to the rigorous derivation of the transport equation. In addition, there are investigations which attempt to circumscribe more precisely under just what conditions a transport equation may be used.

(d) Since serious doubts exist about the *universal* applicability of the transport equation, it is necessary to start (in certain circumstances in any case) from more basic notions of statistical mechanics. In situations demanding a quantum description, the appropriate method is provided by the density matrix method. This indeed is the procedure used in most of the current discussions of transport theory. It is one of the major *technical* changes in the subject; one of the important contributing factors in its changing character.

(e) The use of density matrix techniques, as applied to transport phenomena, gives rise to formal manipulations which are similar to those used in field theory. This is one of the reasons that field theoretic methods are finding more use in solid-state and transport considerations. Other allied techniques, such as a diagrammatic analysis of successive approximation schemes and utilization of the formalism of second quantization, are also finding extensive application in equilibrium and nonequilibrium statistical mechanics. These procedures have the great advantage of formal simplicity, and allow compact expressions for the various transport coefficients. Their use so far has been restricted to the calculation of formal results. It would, however, be unwise to underestimate the potential significance of these methods for transport theory. Field theoretic procedures provide by far the most direct way of obtaining formal expressions for the transport coefficients, and it may well be that starting from these expressions one can devise approximation procedures which will cast these formal expressions into useable forms. In addition, the general interrelations between the various coefficients and processes become most transparent within the context of the field theoretic formalism.

This paper is devoted to the elaboration and discussion of these newer aspects of transport theory.

4. Organization and Outline

The paper is divided into seven parts designated by Roman numerals; each part is divided into a number of sections, denoted by capital letters; finally, each section is divided into subsections. The subsections are numbered consecutively throughout the paper; this section is I.A.4. Formulas are indicated by numbers such as (I.5); within a given *part* the formulas are numbered consecutively and the number I is omitted.

The remainder of Part I contains two further sections, B and C, which describe the conceptual framework of the solid-state and statistical-mechanical considerations needed for the subsequent discussion. Special results and techniques are discussed there for reference purposes.

Part II is devoted to a general discussion of the relations between observed transport coefficients and parameters in transport theory. In fact, Part II contains a quantitative treatment of the material mentioned previously in a general fashion in Sec. A.2. The method of treatment is based on the transport equations. Much of this material exists in book or review form. It seemed, however, worthwhile to review these recent studies in a systematic fashion, for it is against the background of these recent but traditional treatments that one must view the value of the newer ones. To clarify and analyze this relationship it appeared essential to outline the assumptions, successes, and failures of the earlier methods, even though this meant repetition of certain reasonably well-known results. In addition, investigations based on the older transport methods are still current and they are perfectly valid in certain situations. Hence, it is perhaps useful for reference and comparison to have a review of the salient ideas of the Boltzmann-type transport theory.

Part II is divided in two sections. Section A summarizes the assumptions of a conductivity calculation and gives the outline of a typical conductivity calculation with outside fields present. The structure of conductivity theory and an analysis of the assumptions involved are contained in Sec. B. It is hoped that Parts I and II are sufficiently detailed so that the newer developments can be appreciated after a study of these parts.

Part III is concerned with a basic and profound question: the precise status of the transport equation in nonequilibrium statistical mechanics. This general problem has been discussed in a variety of ways. Part III summarizes and reviews some of the different treatments. Sections A–G describe the various methods used to study this question. One of the reasons for the variety of approaches originates from the fact that different authors employ quite different mathematical techniques. In addition, different physical assumptions are used, the equivalence of which is not always transparent; in fact, it is not always true. These features make a unified treatment difficult, but perhaps the methods reviewed will give a representative picture of this active and interesting field. Part III is the most abstract portion of the paper. (A person who is interested in results exclusively could skip it.)

In Part IV the methods outlined in Part III are applied to a derivation of the *formal* expression for the conductivity tensor. The development for the transport properties is carried to a point comparable to the formal expressions for thermodynamic quantities in equilibrium statistical mechanics. In equilibrium theory all quantities may be obtained from the partition function which can be expressed in terms of known characteristics of the system, such as energy levels and wave functions. A similar result is obtained here for the conductivity tensor. The explicit evaluation, however, is even more difficult here than in the equilibrium situation (see Part V). Several such formal results are presented in Part IV, together with a discussion of the relation of these results, to previously obtained expressions.

In Part V the general formal results are applied to specific systems. Of particular concern are the applications to galvanomagnetic effects. Thus, the general results of Part IV are to be specialized to a solid in an outside magnetic field. Unfortunately, it is rarely possible to specialize the general formalism to a particular system in such a way as to obtain tractable results. Instead, one must make additional "opportunistic" assumptions suggested by the special character of the system or invoke empirical results so as to utilize the results of the formal theory. This severely limits the use of the general theory. In fact, different authors derive results of importance for the interpretation of experiments starting from quite different levels of sophistication in the general development. It is not at all uncommon that such different treatments differ not only in mathematical details, but also in the specific experimental results they predict. Consequently, a careful investigation of the mathematical approximations combined with the physical assumptions is of great importance. For this reason the "opportunistic" assumptions, as they occur in the various studies, have been analyzed in detail in Part V. The validity of a specific assumption depends very strongly on the purpose of the investigation. It is possible for an assumption to be incorrect in general, but valid for a particular situation. Examples of this occur in the various sections of Part V.

In Part VI, applications of the general scheme to other problems are given. Among these are a derivation of the susceptibility tensor (Sec. B). Although *thermal* transport properties do not fit in too natural a fashion in the general formal scheme outlined in Parts IV and V, it is possible to relate thermal transport coefficients to time correlations functions (Sec. C). This again is a typical expression of a transport quantity in microscopic terms. In addition, these considerations are closely connected with, and provide examples of, the general discussion of Part III. A number of studies have stressed the close analogy existing between the transport situation (a system in an outside field) and the general theory of the linear response of systems subject to external forces. By exploiting this similarity, one can obtain new formal relations between transport coefficients as well as a different view of transport processes. These formal relations, which have the general character of dispersion relations, yield symmetry properties which are intimately connected with

TABLE I. Subdivisions of statistical mechanics.

1. Equilibrium classical statistical mechanics	2. Nonequilibrium classical statistical mechanics
Basic tools: Distribution function, Maxwell distribution Partition function Canonical, grand ensembles	*Basic tools:* Boltzmann transport equation Master equation Liouville equation Hierarchy of distribution functions
Applications: Classical theory of specific heats, equation of state, virial development, molecular distribution functions, scattering of light by liquids Phase transitions	*Applications:* Calculation of thermal conductivity Electrical conductivity Viscosity Equations of hydrodynamics Diffusion coefficients
3. Equilibrium quantum statistical mechanics	
Basic tools: Distribution functions $\left\{\begin{array}{l}\text{Fermi-Dirac}\\ \text{Einstein-Bose}\end{array}\right.$ Quantum-mechanical partition function Canonical, grand ensemble Density matrix	*Basic tools:* Quantum forms of a transport equation Liouville equation for the density matrix Wigner phase-space functions
Applications: Quantum theory of specific heats of solids Specific heat of an electron gas Magnetic properties of an electron gas Hard-sphere Bose gas (liquid He) Phase transitions	*Applications:* Quantum theory of electrical conductivity Nuclear spin relaxation Thermal conductivity of solids Magnetoresistance Oscillatory Hall effect Line broadening in solids

the Onsager relations. The general theory of the linear response provides a connection between transport phenomena and irreversible thermodynamics. These questions are studied in Part IV, Secs. A and D. It is seen there, too, that although different in detail, these considerations are similar to the other treatments previously discussed. They help to elucidate the status of formal transport theory within statistical mechanics.

Part VII contains a summary of the main results. It is hoped that this summary is presented in such a way that after reading Parts I and II one could look up specific results in VII without having to wade through all the details discussed in the other parts. In addition, Part VII contains a discussion of some questions and problems which are as yet unsettled or only partially settled. There is a large variety of such problems. Some are concerned with basic theoretical questions; others are computational in character; still others refer to incomplete agreement (or disagreement) with experiment. This part too should be understandable after reading Parts I and II.

Even though it is hoped that the discussion is reasonably complete in certain areas, it is clear that other significant areas within transport theory are simply omitted. Nothing is said about the anomalous skin effect; practically nothing about thermoelectric power. There is no compelling reason for the choice of subject discussed. It was clear from the start that not all subjects could be included. It is believed, however, that the material discussed here has indeed been in the center of interest of transport studies. This perhaps is as good a justification as any.

In references to the literature, a few comments about the paper quoted are usually included. To know where this work fits in the general scheme, whether it is superseded (or contradicted) by later work, is probably helpful as an orientation for the reader who is interested in obtaining a view of this sprawling, fascinating field. Finally, it is hoped that the excessive length of this paper is balanced in part by the ease with which it can be read. This paper contains only Parts I and II. The remainder will appear in a later issue.

B. Framework of Statistical Mechanics

In this section, various formulas of statistical mechanics as they pertain to the present discussion are collected. Since most of this material is well known, it may suffice to make a few remarks in conjunction with Table I which contains the various subdivisions of statistical mechanics (equilibrium, nonequilibrium, classical, quantum). Some of the techniques used in these areas and some representative phenomena whose description belongs in these areas are collected as well. The following remarks are meant as an amplification of the table. They are labeled in accordance with the labeling of the subdivisions in the table.

1. Classical Equilibrium Statistical Mechanism

The subject of equilibrium classical statistical is so well known that it would appear sufficient to set the notation and refer to the literature. The Boltzmann distribution function is indicated by $f(\mathbf{x},\mathbf{v})$, $f(\mathbf{p})$, or just f; $f(\mathbf{x},\mathbf{v},t)d^3xd^3v$ is the (probable) number of particles in the positional range d^3x and the velocity range d^3v; $\mathbf{v}$ is the velocity vector, $\mathbf{p}$ the momentum vector, and $\mathbf{x}$ the position vector. The canonical partition function is written as Z (or Z_{el} to distinguish it from Z_Q, the quantum-mechanical partition function). The absolute temperature is written as T, and k is the Boltzmann constant; $\beta = 1/kT$ is often used. The Helmholtz free energy is F. In this notation the basic connection between the partition function and the free energy is given by

$$F = -kT \log Z. \tag{9a}$$

The partition function for a system of N particles, described by a Hamiltonian H (which is a function of N coordinate and momentum vectors $\mathbf{x}_1\cdots\mathbf{x}_N$, $\mathbf{p}_1\cdots\mathbf{p}_N$) is

$$Z_N = \frac{1}{N!(h)^{3N}} \int\cdots\int d^3x_1\cdots d^3x_N d^3p_1\cdots d^3p_N \times e^{-\beta H(\mathbf{p}_1\cdots\mathbf{x}_N)}, \tag{9b}$$

where h is the *Planck* constant; its presence in a classical expression stems from the fact that the quantum-mechanical partition function as usually defined is in a limiting sense connected with (9b) [see [4], p. 82].[2]

Extensive discussions of this subject can be found in many of the standard works on statistical mechanics, such as Tolman [1], de Boer [2], Fowler [3], Hill [4], and ter Haar [5].

2. *Nonequilibrium Classical Statistical Mechanics*

(*a*) *The Boltzmann and the master equation.* Classical nonequilibrium statistical mechanics is discussed much less frequently than equilibrium statistical mechanics. (In the treatises of Tolman [1] and Fowler [3], the topic is hardly mentioned.) Even so, there are many places in the standard literature where the subject is treated in detail, so that for the present purposes it should be sufficient to note some basic equations and give appropriate references to the literature. Just the logical interrelations between various approaches are described in some detail. The fundamental Boltzmann transport equation for the distribution function $f(\mathbf{x},\mathbf{v},t)$ is

$$(\partial f/\partial t) + v_\alpha(\partial f/\partial x_\alpha) + X_\alpha(\partial f/\partial v_\alpha) = C(f) \equiv (\partial f/\partial t)_{\mathrm{coll}}. \tag{10}$$

$\mathbf{X}$ is the outside force per unit mass, $v_\alpha(\partial f/\partial x_\alpha)$ could be written as $\mathbf{v}\cdot\nabla f$; as written in (10), one sums over α from 1 to 3. The terms on the left-hand side of (10) are often called streaming terms. $C(f) \equiv (\partial f/\partial t)_{\mathrm{coll}}$ describes the change (per unit time) in the distribution function due to collisions. These collisions can be between the constituents of the systems (as in the case of gas molecules), or $C(f)$ could describe the effect of collisions of the constituents on one system with those of another system (as in the case of electrons interacting with ions). In the former case, the collision term contains products of f's—the Boltzmann equation is nonlinear; in the latter, both systems would be described by a Boltzmann equation, the collision term in each one would depend on products of the respective distribution functions. It is not at all uncommon to use a discrete notation for f, $fd^3xd^3v = n_i$; one thinks of the positional and velocity ranges as defining a finite cell; n_i gives the number of particles in that cell. For a spatially homogeneous system (no x dependence) and no outside forces ($X=0$), one may write (10) in this notation

$$dn_i/dt = C(n_i), \tag{11}$$

which describes just the effect of collisions. The form of the collision term depends on the interaction. One usually *assumes* that there exists a mechanism which yields a (transition) probability per second for a particle to go from cell i to j.[3] If one assumes the existence of such a probability for just a single particle, (11) assumes the form

$$dn_i/dt = \textstyle\sum_j (n_j A_{ji} - n_i A_{ij}). \tag{11a}$$

[One recognizes (11a) as identical with (1).] Equation (11a) would be appropriate if an outside agency caused the redistribution of the particles over the cells. If, however, collisions *between* particles are the only possible mechanism of changes over the cells, one would need the existence of $A_{ij\to kl}$, the probability of a collision between the particles per unit time, where i and j are the states before collision, k and l those after collision. Equation (11) then would read

$$\frac{dn_i}{dt} = \sum_{j,k,l} (n_k n_l A_{kl\to ij} - n_i n_j A_{ij\to kl}). \tag{11b}$$

The nonlinear character referred to previously is indeed obvious in (11b). Finally, if one describes a mixture of two types of particles indicated by n_i and m_α, and if again the collisions between them are the exclusive mechanism of change, one needs the existence of $A_{i\alpha\to j\beta}$ (defined as the probability per second of an $i\alpha \to j\beta$ collision).

Equation (11) then becomes

$$\begin{aligned} \frac{dn_i}{dt} &= \sum_{j,\alpha,\beta} (n_j m_\alpha A_{j\alpha\to i\beta} - n_i m_\alpha A_{i\alpha\to j\beta}), \\ \frac{dm_\alpha}{dt} &= \sum_{i,j,\beta} (n_i m_\beta A_{i\beta\to j\alpha} - n_i m_\alpha A_{i\alpha\to j\beta}). \end{aligned} \tag{11c}$$

In actual applications all three situations (sometimes

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[2] Bracketed numbers refer to references listed in the Literature Survey at the end of Part I.

[3] In a quantum-mechanical situation one would have a transition from *state i* to *state j* with this interpretation. The discrete notation can be taken over directly to the quantum-mechanical situation.

combined) occur. Even though the collision term is sometimes written slightly differently, often using a continuous notation, its basic structure as given by (11a)–(11c) is always clearly recognizable [6, 7]. It is worthwhile to stress again that the A's are determined by the dynamics, so that they specifically *do not depend* on the numbers n_i. As an example of an equation of type (11a), one may give the Boltzmann equation for electrons in a solid if the electrons scatter from fixed ions. (This is basically the Lorentz model.) In that case, there exists a quantity $I(\mathbf{v},\mathbf{v}')$, the probability per second that in a collision an electron changes its velocity (vector) from $\mathbf{v}$ to $\mathbf{v}'$. The full Boltzmann equation is then

$$\frac{\partial f}{\partial t}+v_\alpha\frac{\partial f}{\partial x_\alpha}+X_\alpha\frac{\partial f}{\partial v_\alpha}=\int d^3v'[f(\mathbf{x},\mathbf{v}')I(\mathbf{v}',\mathbf{v})-f(\mathbf{x},\mathbf{v})I(\mathbf{v},\mathbf{v}')]. \tag{11d}$$

An example of a nonlinear Boltzmann equation is the Boltzmann equation used in kinetic theory of gases. If one calls $\mathbf{g}=\mathbf{v}-\mathbf{v}_1$, if one describes a collision as $\mathbf{v}$, $\mathbf{v}_1\rightarrow\mathbf{v}'$, $\mathbf{v}_1'$, and if $I(g,\theta)$ is the differential cross section for such a collision, the equation reads

$$\frac{\partial f}{\partial t}+v_\alpha\frac{\partial f}{\partial x_\alpha}+X_\alpha\frac{\partial f}{\partial v_\alpha}=\int d^3v_1\int d\Omega gI(g,\theta)(f_1'\,f'-f_1\,f). \tag{11e}$$

The forms (11d) and (11e) are the ones most often used in applications. Once the transport equation (11) is obtained, it is a fairly straightforward matter to show that the system described by the transport equation exhibits an irreversible behavior; it approaches an equilibrium state. Actually, the explanation of the irreversible behavior of a mechanical system on the basis of reversible mechanics demands the use of probability notions. In a crude way these probability ideas are contained in the *existence* of the probabilities A in Eqs. (11). The traditional treatment of transport equations, describing the dynamics through the A's in a probabilistic fashion but treating the variables n_i as well-defined (nonprobabilistic) variables, leads to the well-known paradoxes of statistical mechanics [8]. Uhlenbeck [9] first pointed out that the proper way to describe the physical significance of the transport equation is to retain the interpretation of the A's as probabilities, but introduce instead of the variables $n_i(t)$ a probability function $P(n_1\cdots n_i,\ \cdots,\ t)$ which gives the probability that at time t there are n_i particles in cell i, $i=1\cdots N_w$ (N_w is the number of the cells). The n's therefore become *independent* variables rather than dependent ones as in (11). If one considers a situation where collision between particles cause the changes in the physical situation as in (11b) so that there exists an $A_{ij\rightarrow kl}$, the equation describing the change of P with time would be

$$\frac{\partial P(n_1\cdots n_1\cdots)}{\partial t}=\tfrac{1}{2}\sum_{j,k,l}[(n_k+1)(n_l+1)A_{kl\rightarrow ij}\times P(\cdots n_k+1\cdots n_l+1\cdots n_i-1\cdots n_j-1\cdots)-n_in_jA_{ij\rightarrow kl}P(\cdots n_k\cdots n_l\cdots n_i\cdots n_j\cdots)]. \tag{12}$$

One deduces that

$$\frac{d}{dt}\sum_{n_1}\cdots\sum_{n_i}\cdots\sum{}'\,P(n_1\cdots n_1\cdots,\,t)=0, \tag{13}$$

and the function P may be normalized to unity.

Equation (12) is called the "master equation." Uhlenbeck [9] first introduced it in connection with problems in cosmic-ray showers. In (12) one has a completely probabilistic problem: the propagation of the probability function P in time is determined by the fundamental (given) transition probability A. One may still introduce the average number of particles

$$\bar{n}_i(t)=\sum_{n_1}\cdots\sum_{n_i}\cdots\sum{}'\,n_iP(n_1\cdots n_i\cdots t). \tag{14}$$

The summations in (12)–(14) are all subject to the auxiliary condition

$$\textstyle\sum_i n_i=N \tag{15}$$

which expresses the conservation of the number of particles. The average number $\bar{n}_i(t)$ depends on time through the dependence of the master function on time. From (14) and (12) one may straightforwardly compute $d\bar{n}_i/dt$. If one assumes the usual symmetries of the A's ($A_{ij\rightarrow kl}=A_{kl\rightarrow ij}$, $A_{ij\rightarrow kl}=A_{ji\rightarrow kl}$), one obtains

$$\frac{d\bar{n}_i}{dt}=\sum_{j,k,l}A_{kl\rightarrow ij}(\langle n_kn_l\rangle-\langle n_in_j\rangle), \tag{16}$$

$$\langle n_in_j\rangle\equiv\sum_{n_1}\cdots\sum_{n_i}\sum{}'\,n_in_jP(n_1\cdots n_i\cdots,\,t). \tag{16a}$$

If only $\langle n_in_j\rangle$ were equal to $\bar{n}_i\bar{n}_j$, Eq. (16) would be identical with the traditional Boltzmann equation (11b). However, generally $\langle n_in_j\rangle$ is not equal to $\bar{n}_i\bar{n}_j$. This is due to the correlations between the occupation numbers n_i and the fact that $\sum_i n_i=N$. It is just the neglect of the correlations in (11b) which leads to the paradoxial results. The n_i occurring in the Boltzmann equation (11) are, in fact, an *average* $\bar{n}_i$, defined precisely only by (14). In spite of the approximate character of equations such as (11), they still form the starting point for all applications. Apart from some fundamental considerations [10], there appear to be no computational applications of the master equation formalism. As long as $\langle n_in_j\rangle=\bar{n}_i\bar{n}_j$ (which is the case if the numbers n_i are large), one would expect *physically* that the use of (11) is not likely to lead to serious difficulties. *Mathe-*

matically, one changes from a linear system to a nonlinear one. This is a nontrivial change. It is well to stress that so far a master equation approach has been formulated only for spatially homogeneous systems not under the influence of outside forces. One sees that (16) is similar in structure to (11) but not to (10). Inasmuch as in applications, say in conductivity theory, the influence of outside fields is essential, it follows that to have the analog of a master equation approach one must start with an appropriate generalization of (12). No such generalization appears to exist at present [11]. It is of interest to keep the approximate status of (11), (8), and (10) within the master equation formalism in mind. The master equation approach appears to provide a framework within which one can sensibly discuss transport problems as well as the problems connected with the approach to equilibrium of physical systems. The relation of the master equation to the underlying mechanics describing the system is a completely separate and important question.

(*b*) *The Liouville equation.* A different development—more directly connected with ensemble theory—starts from the Liouville equation for the phase-space density function; $W_N(\mathbf{x}_1\cdots\mathbf{x}_N,\ \mathbf{p}_1\cdots\mathbf{p}_N,\ t)$. For a system described by a Hamiltonian

$$H=\sum_{\alpha=1}^{3}\sum_{i=1}^{N}\frac{p_{i,\alpha}^{2}}{2m}+\sum_{i=1}^{N}V_0(\mathbf{x}_i)+V(\mathbf{x}_1\cdots\mathbf{x}_N), \tag{17}$$

the Liouville equation assumes the form

$$\frac{\partial W_N}{\partial t}=-\{W_N,H\}\equiv-\sum_{i,\alpha}\left(\frac{\partial W_N}{\partial x_{i,\alpha}}\frac{\partial H}{\partial p_{i,\alpha}}-\frac{\partial W_N}{\partial p_{i,\alpha}}\frac{\partial H}{\partial x_{i,\alpha}}\right) \tag{18}$$

or, written explicitly,

$$\frac{\partial W_N}{\partial t}+\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\frac{p_{i,\alpha}}{m}\frac{\partial W_N}{\partial x_{i,\alpha}}+\sum_{i,\alpha}X_{i,\alpha}\frac{\partial W_N}{\partial p_{i,\alpha}}-\sum_{i,\alpha}\frac{\partial V}{\partial x_{i,\alpha}}\frac{\partial W_N}{\partial p_{i,\alpha}}=0. \tag{18a}$$

In (18),

$$X_{i,\alpha}=-\partial V_0/\partial x_{i,\alpha}=\text{the outside force};$$

$V(x_1\cdots x_N)$ represents the interaction potential between the particles. Through the V the dynamics of the system is explicitly contained in (18). From W_N one may construct a hierarchy of functions f_s defined by integrating W_N:

$$f_s(\mathbf{p}_1\cdots\mathbf{p}_s,\ \mathbf{x}_1\cdots\mathbf{x}_s,\ t)=\Omega^s\int\cdots\int d^3p_{s+1}\cdots d^3p_N d^3x_{s+1}\cdots d^3x_N\times W_N(\mathbf{p}_1\cdots\mathbf{x}_N,\ t). \tag{19}$$

The integrals over the space coordinates are over a volume Ω. One can obtain equations for these contracted functions by integrating (17). One obtains, for example, for $f_1(\mathbf{p},\mathbf{x},t)$ if one assumes an *additive* potential

$$V=\textstyle\sum_{i,j}V(\mathbf{x}_i-\mathbf{x}_j),$$

$$\frac{\partial f_1}{\partial t}+\frac{p_\alpha}{m}\frac{\partial f_1}{\partial x_\alpha}+X_\alpha\frac{\partial f_1}{\partial p_\alpha}=\frac{N}{\Omega}\int d^3p_1\int d^3x_1\frac{\partial V(\mathbf{x}-\mathbf{x}_1)}{\partial x_\alpha}\frac{\partial f_2(\mathbf{x}\mathbf{p}\mathbf{x}_1\mathbf{p}_1t)}{\partial p_\alpha}. \tag{20}$$

[One has also assumed in the derivation of (20) that one takes the limit $N\rightarrow\infty$, $\Omega\rightarrow\infty$, but $n=N/\Omega$ fixed.]

The equation for f_2 which is analogous to (20) would involve f_3 and so on. This system of equation is a hierarchy of coupled equations. Even though the structure of (20) is strikingly similar to that of (10), it is not legitimate to just identify the function f_1 occurring in (20) with the function f occurring in (10). The quantity f, the Boltzmann distribution function which occurs in (10), is, roughly speaking, the average number of particles in a cell in the x-v space (the μ space). f refers to a single system. A more precise definition of f can be obtained through the use of the master function P [cf. (14)]. W_N, however, refers to the number density of *ensemble* systems in phase space. As is well known, one *postulates* a connection between the macroscopically observable behavior of a single system and the *average* behavior of the representative ensemble [12, 13]. For *equilibrium* situations the observed values of physical quantities are identified with the ensemble averages of these quantities:

$$Q_{\text{obs}}=\int\cdots\int d^3x_1\cdots d^3x_N d^3p_1\cdots d^3p_N Q W_N. \tag{21}$$

For nonequilibrium situations, however, this is not a feasible procedure. A striking illustration of this failure is afforded by the attempts made to define the analog of a Boltzmann H function, which itself is directly related to the entropy. Recall

$$H=\int\int d^3x\, d^3v\, f\log f. \tag{22}$$

Actually, Gibbs defined a quantity suggested by (22),

$$H_{\text{Gibbs}}=\int\cdots\int d^3x_1\cdots d^3p_N W_N\log W_N. \tag{23}$$

There is, however, no possibility of identifying or relating H_{Gibbs} to the macroscopic entropy, for one proves directly from (23) and (18) that H_{Gibbs} is constant in time, whereas the macroscopic entropy always increases in a nonequilibrium situation. Another illustration, demonstrating that in the Liouville equation *no* statistical assumptions are contained, is the fact that if one solves the Liouville equation with the initial condition

$$W_N(\mathbf{x}_1\cdots\mathbf{p}_N,0)=\prod_{i=1}^{N}\delta(\mathbf{x}_i-\mathbf{x}_i^0)\delta(\mathbf{p}_i-\mathbf{p}_i^0),$$

the solution $W_N(\mathbf{x}_1\cdots\mathbf{p}_N, t)$ remains a δ function along the trajectory of a single system. Physically this is quite obvious; if all ensemble systems start out in the same phase, each one evolves in time in the identical fashion; ensemble members do not influence one another. (The one trajectory contains all the dynamical information.) This behavior is to be contrasted with that of the master equation; if one gives

$$P(n_1\cdots n_i,\ \cdots 0)=\prod\nolimits_i\delta(n_i-n_i^0)$$

as an initial condition for Eq. (12), one finds for any time $t\neq 0$ a nonsingular probability P; the evolution in time proceeds in the typical fashion of a probability process.

Thus, if it is desirable to relate a function f_1 [defined by (19) and (20)] to a Boltzmann function f, or, more generally, if one wants to establish a relationship between the Liouville equation for W_N and the master equation for P, one needs to adjoin probability or statistical notions to the Liouville equation. Several such procedures have been suggested, mainly in connection with the appropriate definition of an H function. One can invoke a "coarse grained" probability distribution in phase space [14, 15]. It is also possible to use an additional time smoothing as suggested by Kirkwood [16] and Hill [17]. The general problem, namely, the precise conditions under which one can derive a master equation from a Liouville equation, has been the subject of many studies [18–20]. It would appear that at the present time the interrelation is at least partially understood for the special case of not too dense, spatially homogeneous gases. One interesting and perhaps unexpected feature is the occurrence and existence of characteristic times and appropriate time scales. (These provide natural times over which to perform averages.) These studies are at present the most basic ones for nonequilibrium statistical mechanics. The significance of these developments for transport theory depends on the following facts:

(a) In transport theory one always works with the Boltzmann equation with outside forces—its status is only partially elucidated by these discussions. For instance, no such equation has been obtained within the framework of the master equation, although one has reproduced the Boltzmann equation, using the Liouville hierarchy, by additional time smoothing (for dilute gases only).

(b) The introduction of outside influences (magnetic fields, high-frequency sound, microwaves) may very well alter the basic time scales (new characteristic times would be introduced) and, as such, change the relationship between the master and the Liouville functions. (It is unreasonable to expect that the relation between these functions would be independent of the nature of the system.) Consequently, in certain transport phenomena one has in principle a possibility to confront

TABLE II. Relations between probability functions.

Linear Liouville equation for W_N		*Linear* master equation for P
(Contains dynamics through Hamiltonian equations)	---------- → ---------- Brout[c] Green[d]	(Contains specific probability assumptions; dynamics is contained in the transition probability
↓	using:	↓
Liouville hierarchy for the contracted functions f_s	(a) time scales (b) finite interaction radius ↗ (c) dilute system	Coupled transport equations for $\bar{n}_i(t)$, $\langle n_in_j\rangle$, etc.
↓	(d) asymptotic time limit	
A truncation procedure relates f_2 to f_1 and f_1 or f_s to f_1 to f_2 ↘	(e) infinite system (f) Stoszahl Ansatz	Product conditions $\langle n_in_j\rangle\cong\bar{n}_i\bar{n}_j$
Relation obtained[a] using: (a) time smoothing (b) binary collisions (c) near equilibrium (d) time scale ↘	(Superposition approximation) Validity studied for equilibrium (20% *error in 4th virial coefficient*,[e] also near equilibrium situations[f] not valid for the relaxation of a chain of oscillators ↙	Boltzmann equation *without* streaming terms ?
Bogoliubov procedure,[b] use: (a) time scales (b) $f_s(\cdots t)=f_s(\cdots,f_1)$ independent of the initial state (c) correlations vanish outside some action volume (d) low-density expansion ↗	The "useful" Boltzmann equation with outside forces and streaming terms	
	↓	
	The *linearized* Boltzmann equation used in solid state theory	
	↓	
	Computation of transport quantities	

[a] See references 16 and 20.
[b] See references 23 and 24.
[c] See reference 18.
[d] See reference 19.
[e] See reference 21.
[f] See reference 22.

these general considerations with experiment. Conversely, there is also the possiblity that there are physical situations in which the variety of assumptions needed to obtain a "useful" Boltzmann equation are not satisfied, so that one would need to use a description at a different level. The status of the Boltzmann equation, as well as the logical interrelations of the various approaches, is summarized in Table II. Most of the results collected in the table have been described already; arrows indicate proven (or partially proven) realtionships, the salient assumptions within these proofs have been listed near the arrows. (This kind of scheme was first used by Uhlenbeck [9].) Table II also refers to the derivation of the Boltzmann equation from the Liouville hierarchy using the ideas of Bogoliubov [23]. This procedure, especially as used by Uhlenbeck [24], provides an organized procedure to study the Liouville hierarchy. The new physical idea in this approach is that one argues that for times large compared to the duration of a collision, the Liouville functions f_s depend on the time only through f_1 irrespective of the initial situation:

$$f_s(p_1x_1\cdots p_Nx_N,\, t)=f_s(p_1x_1\cdots p_sx_s,\, f_1(p_1x_1,\, t).$$

It should be stressed that this property is not *proved*; rather, one seeks solutions of the hierarchy possessing it. If coupled with an expansion in inverse densities (as in the Mayer-Ursell development), one may indeed reproduce the Boltzmann equation. In Table II reference is also made to the linearized Boltzmann equation. This equation is obtained from (10) and (11b) by considering small deviations from the equilibrium distributions:

$$f=f^{(0)}+f^{(1)}, \tag{24}$$

where $f^{(0)}$ is the equilibrium distribution; one neglects all powers of $f^{(1)}$ higher than the first. This linearized equation for $f^{(1)}$ is the one used most frequently in the computation of transport coefficients. The various procedures (Brout and Green, Kirkwood, and Bogoliubov) which attempt to relate the basic dynamics to the general transport theory are all in some sense arbitrary. They are certainly *not* mathematical consequences of, say, the Liouville equation. Rather, certain additional assumptions which are plausible on physical grounds (at least for certain classes of physical systems) have been used as well. So far, all that has been demonstrated is that these methods do reproduce results already known (the Boltzmann equation for dilute gases).[4] The real test of these procedures (and also a possible choice between them) will be provided by the extension of these ideas to new physical situations, where one has *no* previous knowledge. Unfortunately, as Table II shows, the relation between computed transport entities (which are also the experimentally observed quantities) and the basic assumptions and procedures is quite indirect. It appears (at the present time) that certain transport phenomena in solids, where quantum effects also play a role, might provide tests for the validity of these different procedures. This circumstance makes these abstract considerations on the foundations of statistical mechanics particularly pertinent for the discussion of transport phenomena in solids (and conversely). Even though the discussion so far presented is classical, it is seen later that many of the problems, such as the relation between the master and Liouville equations, are basically the same in the quantum-mechanical discussion.

3. *Equilibrium Quantum Statistical Mechanics.*

The Density Matrix Technique.

The formalism of quantum equilibrium statistical mechanics is the one which is most often used in applications. It is discussed at length in many of the works already quoted. In this section a few remarks especially pertaining to currently popular techniques are made.

The transcription from the Maxwell-Boltzmann distribution function to the quantum-mechanical Fermi-Dirac (or Einstein-Bose) distribution is well known [26, 27]. These distribution functions are also denoted by f. In a quantum-mechanical situation, one cannot, strictly speaking, define $f(\mathbf{x},\mathbf{p},t)$ and $f(\mathbf{x},\mathbf{v},t)$; the uncertainty principle precludes the possibility of even making a precise probability statement about positions and momenta simultaneously. Stated differently, if one insists that the wave function of a particle vanishes outside some finite region (the particle is localized), there is a finite probability that the momentum has an arbitrarily high value, so that one cannot require that the momentum values of the particle are contained within a finite range as well. This makes it impossible to define cells in the μ space; in addition, one cannot (rigorously) define phase-space density functions. One usually considers situations in which $f=f(\mathbf{p})$ alone. In applications one often uses the energy ϵ as an independent variable rather than the momentum p. This clearly demands a knowledge of the dispersion law $\epsilon=\epsilon(\mathbf{p})$.

The ensemble description, which is a powerful tool in classical statistical mechanics, can be transcribed to quantum theory as well [28–30]. It appears worthwhile to describe some of these methods, since the techniques developed there are the main ones used here. (See especially Parts III–VI, the discussion of the general transport theory.)

Consider an ensemble of system all described by the identical Hamiltonian operator H.[5] Let α denote a

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[4] All the methods used employ a variety of limiting procedures. It is hard to assess the precise mathematical validity of these limiting processes. For a review of these points, as well as a general summary, see Grad [25].

[5] Both the Hamiltonian and the Boltzmann H function are denoted by H. This should (hopefully) not lead to any confusion.

system in the ensemble; N_e is the number of ensemble systems.

Let $\psi^\alpha(q,t)$ be a normalized time-dependent wave function of ensemble system α. q stands for all position variables $x\cdots x_N$. Call E_n the energy eigenstates of H, and $u_n(q)$ the eigenfunctions so that[6]

$$H\psi^\alpha = -(\hbar/i)(\partial\psi^\alpha/\partial t) \tag{25a}$$

$$Hu_n = E_n u_n. \tag{25b}$$

Finally let $\varphi_n(q)$ be an *arbitrary* complete orthonormal set; $\psi^\alpha(q,t)$ may be developed in such a set,

$$\psi^\alpha(q,t) = \textstyle\sum_n a_n{}^\alpha(t)\varphi_n(q). \tag{26}$$

One knows that $|a_n{}^\alpha(t)|^2$ is the probability to find ensemble member α in state n at time t. The equations of motion of the coefficients a are well known from (25a) and (26):

$$i\hbar\frac{da_n{}^\alpha}{dt} = \sum_m \langle n|H|m\rangle a_m{}^\alpha \equiv \sum_m H_{nm}a_m{}^\alpha, \tag{26a}$$

$$H_{nm} \equiv \langle n|H|m\rangle = \int dq\,\varphi_n{}^*H\varphi_m. \tag{26b}$$

One *defines* the matrix elements of the density matrix ρ_{mn} *relative* to the base $\varphi_n(q)$ as

$$\rho_{mn} = \frac{1}{N_e}\sum_\alpha a_m{}^\alpha(a_n{}^\alpha)^*. \tag{27}$$

Clearly, ρ depends on the *time* as well as on the character of the ensemble. From the assumed normalization of the wave functions ψ, one proves immediately that

$$\mathrm{Tr}\,\rho \equiv \sum_n \rho_{nn} = \frac{1}{N_e}\sum_\alpha\sum_n |a_n{}^\alpha|^2 = \frac{1}{N_e}\sum_\alpha 1 = 1. \tag{27a}$$

Further, $\rho_{nn} = (1/N_e)\cdot\sum_\alpha |a_n{}^\alpha|^2$ is the probability to find an ensemble member at time t in state n; thus the diagonal elements of ρ have a direct physical interpretation.

From (27) and (26) one shows that

$$i\hbar(d\rho_{mn}/dt) = [H,\rho]_{mn}, \qquad i\hbar\dot{\rho} = [H,\rho]. \tag{28}$$

One is working throughout in the Schrödinger picture. In (28), as in the sequel, $[A,B] \equiv (AB-BA)$ the commutator; matrix indices are usually suppressed; (28) is the analog of the Liouville equation (18). In the classical situation, macroscopically observable entities were identified with ensemble averages; in quantum mechanics, when dealing with a single system, experimental results are related to the expectation value of an operator. The expectation value of an operator Q for ensemble member α is

$$\langle Q^\alpha(t)\rangle = \int \psi^\alpha(q,t)^* Q\psi^\alpha(q,t)dq. \tag{29}$$

The basic postulate of quantum statistical mechanics is that the macroscopic observable value of Q is the ensemble average of $\langle Q^\alpha(t)\rangle$;

$$Q_{\mathrm{obs}} = \langle\langle Q(t)\rangle\rangle = \frac{1}{N_e}\sum_\alpha\langle Q^\alpha(t)\rangle. \tag{30}$$

(Ensemble averages are denoted by double angular brackets, quantum-mechanical averages by single angular brackets.) If one were to maintain the precise analogy with the classical postulates, one should actually perform a time average over $\langle Q^\alpha(t)\rangle$ before performing the ensemble average. For equilibrium or near-equilibrium situations one may use (30), but is well to keep this limitation in mind.[7] It is now easy to understand the importance of the density matrix ρ_{nm} for statistical problems. The significant observable entity is Q_{obs}, which by straightforward substitution of (26) in (29) and (30) becomes, using (27),

$$Q_{\mathrm{obs}} = \sum_{n,m}\rho_{nm}Q_{mn} = \mathrm{Tr}(\rho Q)$$

$$Q_{mn} = \langle m|Q|n\rangle. \tag{31}$$

Since traces occur very frequently in the discussion, one should note these important properties:

$$\mathrm{Tr}(AB) = \mathrm{Tr}(BA). \tag{32a}$$

This follows immediately from the definition. If one now calls $BA = C$ so that $A = B^{-1}C$ (if B^{-1} exists), then (32a) becomes

$$\mathrm{Tr}(B^{-1}CB) = \mathrm{Tr}C. \tag{32b}$$

From (32a) follows

$$\mathrm{Tr}(ABC) = \mathrm{Tr}(BCA) = \mathrm{Tr}(CAB), \tag{32c}$$

the cyclic property. From (31) it follows that observed values can be written as a trace in terms of the density matrix. Even though the density matrix was defined relative to a set of functions $\{\varphi\}$, any other choice of such a set, say φ', would lead to the same observable results. This follows: if $\varphi' = B\varphi$ is another orthonormal set (the matrix B is unitary), the density matrix in this new representation becomes by the usual transformation $\rho' = B^{-1}\rho B$, and the matrix Q becomes $Q' = B^{-1}QB$. Therefore, $\mathrm{Tr}(\rho'Q') = \mathrm{Tr}(B^{-1}\rho QB)$, and this by (32b) reduces to $\mathrm{Tr}(\rho Q)$. Hence, one can give the density matrix in terms of *any* orthogonal set.

This freedom of choice of the set of basic functions for a density matrix calculation is a very useful technical trick.

The density matrix appears in the literature in a

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[6] $\hbar$ is the Planck constant divide by 2π. *None* of the fundamental constants are put equal to unity in this paper.

[7] As already pointed out in the discussion of the classical situation, coarse graining or time averaging is necessary only in nonequilibrium situations.

variety of forms all intimately related to (27). One often introduces a density *operator* ρ_{op} (usually written as ρ). The simplest way to define ρ_{op} from (27) is to define the action of ρ_{op} on the members of the set $\{\varphi\}$, namely,

$$\rho_{\mathrm{op}}\varphi_n(q)=\sum\nolimits_m \rho_{mn}\varphi_m(q). \tag{33}$$

Since the ρ_{mn} are known, (33) indeed defines the effect of the density operator on any member of the set φ. Inasmuch as *any* function can be expanded in terms of the set φ, the action of ρ on any function is defined by (33). An important, somewhat singular special case arises when one picks the set $\varphi_n(q)$ as eigenfunctions of the position operator q. In that case one has for the set φ, $\varphi_{q'}(q)=\delta(q-q')$. One then finds from (26) that $a_{q'}{}^{\alpha}(t)=\psi^{\alpha}(q',t)$. Therefore, (27) becomes

$$\rho(q',q'',t)\equiv\langle q''|\rho|q'\rangle=\frac{1}{N_e}\sum_{\alpha}\psi^{\alpha}(q',t)[\psi^{\alpha}(q'',t)]^*. \tag{34}$$

Quite often (34) is also called the density matrix; it is actually the density matrix in the "q representation." Use of (26), (27), and (33) gives alternate forms for (34):

$$\begin{aligned}\rho(q',q'',t)&=\sum_{n,m}\varphi_n(q')\rho_{nm}\varphi_n{}^*(q'')\\&=\sum_m \varphi_m{}^*(q'')\rho_{\mathrm{ob}}\varphi_m(q')=\langle q''|\rho|q'\rangle.\end{aligned} \tag{34a}$$

From (34a) it follows that ρ_{nm} can be expressed in terms of $\rho(q',q'',t)$:

$$\rho_{nm}=\int\int dq'dq''\,\varphi_n{}^*(q')\rho(q',q'',t)\,\varphi_m(q''), \tag{34b}$$

which in turn may be used to transcribe any observable quantity Q_{obs} in terms of $\rho(q',q'',t)$. One only needs to substitute (34b) and the expression for Q_{mn} into (31) to obtain (via closure) the explicit relation

$$\begin{aligned}Q_{\mathrm{obs}}&=\sum_{n,m}\rho_{nm}Q_{mn}\\&=\int\int dq'dq''\rho(q',q'',t)\sum_n \varphi_n{}^*(q')Q_{\mathrm{op}}\varphi_n(q'').\end{aligned} \tag{35}$$

(The sum over n gives the operator Q in the q representation.) From (34) it is clear that $\rho(q',q'',t)$ as an ensemble average is indeed independent of the choice of the set φ. This can be verified by direct calculation on using (34a), for example. In (34), as in (27), the sum over α is over the ensemble members, so that α runs from 1 to N_e. One sometimes finds the density matrix in the x representation written as a sum, not over the ensemble members, but over the *states* over the members of the ensemble. If, say, ensemble member α is in state j, there may be other ensemble members in this same state. Suppose in all there are N_j such ensemble members. Each one of these contributes the same term in the sum over α in (34). Hence (34) may be rewritten as

$$\begin{aligned}\rho(q',q'',t)&=\sum_j \frac{N_j}{N_e}\psi^j(q',t)[\psi^j(q'',t)]^*\\&=\sum_j p_j\psi^j(q',t)[\psi^j(q'',t)]^*;\end{aligned} \tag{34c}$$

$p_j=N_j/N_e=$ the probability to pick an ensemble member in state j. The states $\psi^j(q',t)$ are, in general, time-dependent states; they are not eigenfunctions of H. Equation (34c) is often used instead of (34); it is important to keep the difference in the nature of the sum index in mind. (For a careful discussion of this and related questions, see [4], Chap. IV.) One recognizes that $\rho(q,q,t)$ is the ensemble average of the probability density $|\psi(q,t)|^2$. Consequently, $\rho(q,q,t)$ is the probability that a system (represented by the ensemble) at time t has its constituent particles at positions $\mathbf{x}_1\cdots\mathbf{x}_N(\equiv q)$. As such, $\rho(q,q,t)$ is the counterpart of the classical configuration probability given by the expression $\int dp W_N(p,q,t)$. The classical operation of integration over N momenta is replaced by taking the diagonal elements of the density matrix. The expression for Q_{obs} can be cast in still other forms. To obtain a simple one, define in analogy with (34a) a matrix element of the operator ρQ in the q representation by

$$\langle q''|\rho Q|q'\rangle=\sum\nolimits_m \varphi_m{}^*(q'')\rho_{\mathrm{op}}Q_{\mathrm{op}}\varphi_m(q'). \tag{36}$$

One can now expand the function $\rho_{\mathrm{op}}Q_{\mathrm{op}}\varphi_m(q)$ in the set φ; on using (33), one obtains

$$\langle q''|\rho Q|q'\rangle=\sum_{m,n,n'}\varphi_m{}^*(q'')Q_{nm}\rho_{n'n}\varphi_{n'}(q'). \tag{36a}$$

From (36a) one sees by inspection that

$$\int dq\langle q|\rho Q|q\rangle=\sum_{n,m}Q_{nm}\rho_{mn}=Q_{\mathrm{obs}}. \tag{36b}$$

The ensemble average appears again as an integration over the diagonal elements of the density matrix (this time in the q representation). The appropriate ensemble which represents a particular system is (as in classical statistical mechanics) postulated. In equilibrium one knows that the density matrix and H commute [see (28)][8]; hence, ρ can depend only on the integrals of the motion. For an isothermal system one assumes the *canonical* ensemble

$$\rho=e^{(F-H)\beta},\quad\text{when}\quad \beta=1/kT. \tag{37}$$

F is not an operator, it is to be identified with the Helmholtz free energy. (See [31] for an extensive discussion of the choice of the appropriate ensemble.) From the normalization condition, one has

$$e^{-\beta F}=Z=\mathrm{Tr}(e^{-\beta H}). \tag{38}$$

This is the starting point for practically all applications.

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[8] H, throughout, denotes the Hamiltonian operator.

From a knowledge of the partition function Z, the free energy F follows *trivially*, as do all other thermodynamic entities. The calculation of Z for general systems is a formidable problem. Much of statistical mechanics is devoted to devising special techniques for handling the expression (38). A few results, needed later, are noted here. If one uses the functions φ to compute the trace in (38), one has

$$Z=\mathrm{Tr}(e^{-\beta H})=\sum_n\langle\varphi_n|e^{-\beta H}|\varphi_n\rangle$$
$$=\sum_n\int\varphi_n^*(q)e^{-\beta H}\varphi_n(q). \quad (39)$$

If, however, one picks the set of eigenfunctions of H, u_n, (39) simplifies to

$$Z=\sum_n\langle u_n|e^{-\beta H}|u_n\rangle=\sum_n e^{-\beta E_n} \quad (39a)$$

[from (25b)], a very important relation. One can now use the general formulas given previously to obtain for this special case explicit expressions for the density matrix in the various representations. For instance, straightforward application of (37) in (34a) gives

$$\rho(q',q'')\equiv\langle q''|\rho|q'\rangle$$
$$=Z^{-1}\sum_m\varphi_m^*(q'')e^{-\beta H}\varphi_m(q'). \quad (40)$$

If one specializes to the set u_n, and considers diagonal elements only, one obtains the configuration probability[9]

$$\rho(q,q)=Z^{-1}\sum_m|u_m(q)|^2e^{-\beta E_m}. \quad (40a)$$

Use of (33), on the other hand, yields

$$\rho_{mn}=Z^{-1}\int\varphi_m^*(q)e^{-\beta H}\varphi_n(q). \quad (41a)$$

For the special choice of eigenfunctions u_n, the density matrix is diagonal,

$$\rho_{mn}=Z^{-1}e^{-\beta E_n}\delta_{mn}. \quad (41b)$$

Even though the manner in which the density matrix has been defined here is a fairly standard one, one occasionally sees other definitions. Consider, for example, a function $Z(q',q'',\beta)$ defined by[10]

$$Z(q',q'',\beta)=\sum_n\varphi_n^*(q'')e^{-\beta H}\varphi_n(q') \quad (42)$$

[its similarity to (40) is obvious]. Sometimes $Z(q',q'',\beta)$ is called the density matrix [33, 34] and has the following important properties:

$$\partial Z(q',q'',\beta)/\partial\beta=-H(q')Z(q',q'',\beta) \quad (43a)$$
$$Z(q',q'',0)=\sum_n\varphi_n^*(q'')\varphi_n(q')=\delta(q'-q''). \quad (43b)$$

Equation (43a) is the Bloch equation. Its similarity to the Schrödinger equation is evident; this is the basic reason why formal procedures useful in quantum mechanics may be transcribed to statistical mechanics. The closure relation (43b) serves as an initial condition for the Bloch equation. From (42) and (39), one sees that

$$\int dqZ(q,q,\beta)=Z(\beta). \quad (43c)$$

Thus a knowledge of the Bloch function $Z(q',q'',\beta)$ leads directly to the partition function. This is a very powerful method. It finds especially significant applications for systems of electrons in external magnetic fields. The difficulty of obtaining exact expressions for Z has stimulated the search for approximate methods. Many such methods exist, most of which are based on a perturbation-type development: One assumes that

$$H=H_0+\epsilon H_1, \quad (44)$$

where ϵ is assumed to be small. In order to exploit this fact, one attempts to obtain a development of the free energy F as

$$F=F^{(0)}+\epsilon F^{(1)}+\epsilon^2F^{(2)}+\cdots. \quad (45)$$

H^0 presumably is simple so that $F^{(0)}$ may be obtained; the other terms in (45) are corrections to the free energy. The purpose of the development is to obtain $F^{(1)}$, $F^{(2)}$ in terms of *known* entities. In this connection, the eigenvalues of H_0, $E_n^{(0)}$ and the eigenfunctions $u_n^{(0)}$ are considered known. As an example of a useful expansion and as an illustration of the techniques needed later, one such method is described [35].[11] It is clear from (45) that Z can be expanded in powers of ϵ. Hence, to obtain $F^{(1)}$, etc., one must expand $\mathrm{Tr}(e^{-\beta H})$ in powers of ϵ as well. It is convenient for this purpose to introduce $R(\beta)=e^{-\beta H}$.[12] One wants a series expansion for $\mathrm{Tr}R(\beta)$. The first step invariably consists of writing an integral equation for $R(\beta)$:

$$R(\beta)=e^{-\beta H_0}-\epsilon e^{-\beta H_0}\int_0^\beta d\lambda H_1(\lambda)e^{\lambda H_0}R(\lambda), \quad (46)$$

where $H_1(\lambda)$ is defined by

$$H_1(\lambda)\equiv e^{\lambda H_0}H_1e^{-\lambda H_0}. \quad (46a)$$

In (46) one has achieved a separation of $R(\beta)$ into an unperturbed part ($e^{-\beta H_0}$) and a part proportional to ϵ. The proof of relations such as (46) always proceeds by guessing[13] a function $g(\lambda)$ of the operators, differentiating it with respect to λ, and integrating back. For

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[9] Although the diagonal matrix elements $\rho(q,q)$ are the most important ones, the off-diagonal ones $\rho(q',q'')$, using the set $\{u\}$, do not vanish as might be inferred from de Boer [32].

[10] The partition function is denoted by Z or $Z(\beta)$. $Z(q',q'',\beta)$ written explicitly denotes the function defined by (42).

[11] It may well be that the following description is too detailed; since, however, this kind of method is used so frequently, it was felt worthwhile to include *one* perhaps overly detailed treatment. This degree of detail is not repeated in later evaluations, but the reader is referred to the present discussion for similar calculations.

[12] In some studies $R(\beta)$ is again called density operator; in this paper only ρ defined by (37) is so designated; $\rho=R/Z$.

[13] One could also say: attempt to find an operator $g(\lambda)$ such that $R(\lambda)=e^{-\lambda H_0}g(\lambda)$. Clearly $g(0)=1$; differentiation of this relation leads to (47a); then one proceeds as in the text.

example, defining $g(\lambda)$:

$$g(\lambda)=e^{\lambda H_0}R(\lambda)=e^{\lambda H_0}e^{-\lambda H}. \qquad (47)$$

Clearly $g(0)=1$. Now, differentiate g,

$$dg/d\lambda=-\epsilon H_1(\lambda)e^{\lambda H_0}R(\lambda); \qquad (47a)$$

integrate (47a) over λ from 0 to β:

$$g(\beta)-1=-\epsilon\int_0^\beta d\lambda H_1(\lambda)e^{\lambda H_0}R(\lambda). \qquad (47b)$$

If one now substitutes (47) back for $g(\beta)$ and operates from the left with $e^{-\beta H_0}$, one obtains (46). By iterating (46) one obtains an expansion of $R(\beta)$ in terms of ϵ:

$$R(\beta)=e^{-\beta H_0}-\epsilon e^{-\beta H_0}\int_0^\beta d\lambda H_1(\lambda)$$
$$+\epsilon^2 e^{-\beta H_0}\int_0^\beta d\lambda H_1(\lambda)\int_0^\lambda d\lambda_1 H_1(\lambda_1)+\cdots. \qquad (48)$$

[The fact that integral equations of the type (46) can be iterated so simply is the main reason for their popularity.] One needs $\mathrm{Tr}R(\beta)$. Instead of taking the trace of (48) directly, it is simpler to note the following identity[14]:

$$\frac{\partial}{\partial\epsilon}\mathrm{Tr}(e^{-\beta H})\equiv\frac{\partial}{\partial\epsilon}\mathrm{Tr}(e^{-\beta(H_0+\epsilon H_1)})=-\beta\,\mathrm{Tr}(e^{-\beta H}H_1), \qquad (49)$$

which is trivial only if one forgets that the two parts of H, namely, H_0 and ϵH_1, *do not* commute. For the proof, the trace property is essential [(49) is incorrect if one omits the traces]. To show (49), note

$$\frac{\partial}{\partial\epsilon}\mathrm{Tr}(e^{-\beta H})=\sum_n\frac{(-1)^n\beta^n}{n!}\mathrm{Tr}\left(\frac{\partial}{\partial\epsilon}H^n\right)$$
$$=\sum_n\frac{(-1)^n\beta^n}{n!}\mathrm{Tr}\left(\frac{\partial H}{\partial\epsilon}H^{n-1}\right.$$
$$\left.+H\frac{\partial H}{\partial\epsilon}H^{n-2}+\cdots H^{n-1}\frac{\partial H}{\partial\epsilon}\right).$$

In general, H and $\partial H/\partial\epsilon$ do not commute, but one may use the cyclic property of the trace (32c) to write this expression as

$$\sum[(-1)^n\beta^n/n!]n\,\mathrm{Tr}(H^{n-1}H_1)=-\beta\,\mathrm{Tr}(e^{-\beta H}H_1),$$

proving (49). If (49) is integrated over ϵ between 0 and ϵ, noting that $(e^{-\beta H})_{\epsilon=0}=(e^{-\beta H_0})$, one obtains

$$\mathrm{Tr}(e^{-\beta H})=\mathrm{Tr}(e^{-\beta H_0})-\beta\,\mathrm{Tr}\int_0^\epsilon e^{-\beta(H_0+\eta H_1)}H_1 d\eta, \qquad (50)$$

which is an expression for the trace but not yet a development in ϵ. However, if one now uses for $e^{-\beta(H_1+\eta H_1)}$ in (50) the expansion in η as given by (48), one can perform all the η integrals. [The dependence on ϵ of (48) is only through powers, neither H_0, H_1, nor $H_1(\lambda)$ depend on ϵ.] Thus, one obtains

$$\mathrm{Tr}(e^{-\beta H})=\mathrm{Tr}(e^{-\beta H_0})-\beta\epsilon\,\mathrm{Tr}(e^{-\beta H_0}H_1)$$
$$+\beta\frac{\epsilon^2}{2}\mathrm{Tr}(e^{-\beta H_0})\int_0^\beta d\lambda_1 H_1(\lambda_1)H_1$$
$$-\beta\frac{\epsilon^2}{3}\mathrm{Tr}(e^{-\beta H_0})\int_0^\beta d\lambda\int_0^\lambda d\lambda_1$$
$$\times H_1(\lambda)H_1(\lambda_1)H_1+\cdots. \qquad (51)$$

It is now straightforward to obtain the corrections to the free energy; (45) combined with (38) yields

$$\exp(-\beta F)=\exp(-\beta F^{(0)})\{1-\beta\epsilon F^{(1)}$$
$$+(\epsilon^2/2)[\beta^2(F^{(1)})^2-2\beta F^{(2)}]+\cdots\}. \qquad (51a)$$

One can now compare successive powers of ϵ in (51) and (41a) to obtain

$$F^{(1)}=\mathrm{Tr}(e^{-\beta H_0}H_1)/\mathrm{Tr}(e^{-\beta H_0}) \qquad (52a)$$

$$F^{(2)}=\tfrac{1}{2}\left\{\beta(F^{(1)})^2-\left[\mathrm{Tr}\left(\int_0^\beta d\lambda e^{-\beta H_0}H_1(\lambda)H_1\right)\Big/\right.\right.$$
$$\left.\left.\mathrm{Tr}(e^{-\beta H_0})\right]\right\}. \qquad (52b)$$

Thus, one has a completely definite expression for the free energy as a power series in ϵ. To be useful, one must still be able to analyze the expressions (52). If the unperturbed partition function is known, say Z_0, one sees that

$$F^{(1)}=\frac{1}{Z_0}\mathrm{Tr}(e^{-\beta H_0}H_1)=\frac{1}{Z_0}\sum_n\langle u_n^0|H_1e^{-\beta H_0}|u_n^0\rangle$$
$$F^0=\frac{1}{Z_0}\sum_n\langle u_n^0|H_1|u_n^0\rangle\exp(-\beta E_n^0). \qquad (53)$$

One notices that one has picked eigenfunctions of H^0, namely u_n^0, for the trace calculation, so that

$$\exp(-\beta H_0)|u_n^0\rangle=\exp(-\beta E_n^0)|u_n^0\rangle.$$

Equation (53) is an explicit expression for the first-order free energy correction. The trace term of (52b) is evaluated similarly:

$$\mathrm{Tr}\int_0^\beta d\lambda e^{-\beta H_0}H_1(\lambda)H_1$$
$$=\sum_n\left\langle n\left|\int_0^\beta d\lambda H_1(\lambda)H_1e^{-\beta H_0}\right|n\right\rangle. \qquad (54)$$

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[14] In [35] there is a misprint in the identity corresponding to (49); there is also a mistake in sign in the expression corresponding to (46).

The explicit evaluation of a term such as (54) always makes use of the known action of operators on state vectors $|n\rangle$,[15] namely,

$$\exp(-\beta H_0)|n\rangle=\exp(-\beta E_n^0)|n\rangle \qquad (55a)$$

$$H_1|n\rangle=\sum_m|m\rangle\langle m|H_1|n\rangle. \qquad (55b)$$

On using these expressions, and the expression (46a) for $H_1(\lambda)$, one obtains for the integrand in (54)

$$H_1(\lambda)H_1e^{-\beta H_0}|n\rangle$$
$$=\sum_{m,m'}|m'\rangle\langle m'|H_1|m\rangle\langle m|H_1|n\rangle$$
$$\times\exp(-\lambda E_m^0+\lambda E_{m'}^0-\beta E_n^0).$$

The λ integration is now trivial; in addition, $\langle n|m'\rangle=\delta_{nm'}$ by orthogonality, so one finally obtains

$$\mathrm{Tr}\int_0^\beta d\lambda e^{-\beta H_0}H_1(\lambda)H_1=\sum_{n,m}\langle n|H_1|m\rangle\langle m|H_1|n\rangle$$
$$\times\exp(-\beta E_m^0)-\exp(-\beta F_n^0)/(E_n^0-E_m^0). \qquad (56)$$

This therefore gives again an explicit expression for $F^{(2)}$. It is important to observe that if $E_n^0=E_m^0$, the terms still remain finite because of the Boltzmann factors; in fact, the sum may be written as

$$\sum_n|\langle n|H_1|n\rangle|^2\beta+\sum_{n\neq m}\langle n|H_1|m\rangle\langle m|H_1|n\rangle$$
$$\times\exp(-\beta E_m^0)-\exp(-\beta E_n^0)/(E_n^0-E_m^0). \qquad (56a)$$

[At low temperatures ($\beta\rightarrow\infty$) the first term is the dominant one.] Many other methods are used in the evaluation of the partition function and the density matrix, but the example given contains the basic techniques. The procedure outlined works equally well in a second quantized theory. Indeed, in the derivation one made use only of general properties of operators in quantum mechanics, and these are the same in first and second quantized versions of the theory. Finally, it is much easier to write a development such as (45) than to assess its validity. In actual situations, the decisions as to what can be included in H_0 and how fast the series converges (if it does so at all) remain difficult questions, which can be discussed only for each system individually.

4. *Nonequilibrium Quantum Statistical Mechanics*

The physical basis of the bulk of the work in the quantum theory of transport properties was (until the last few years) provided by an appropriate quantum adaptation of the classical Boltzmann equation (11d) or (11e). The specific modifications introduced by Uhlenbeck and Uehling [36] were, first: to replace the classical collision cross section by its quantum-mechanical counterpart—this is already suggested by the notation in (11e); second, to incorporate the effect of Bose-Einstein or Fermi-Dirac statistics explicitly in the collision term $C(n_i)$ of (11). Whereas the classical collision term originates from the assumption that the number of collisions from $ij\rightarrow kl$ per second is given by $n_in_jA_{ij\rightarrow kl}$ [see (11b)], in the quantum-mechanical situation one assumes instead that this number is given by

$$n_in_j(1-n_k)(1-n_l)A_{ij\rightarrow kl} \qquad (57)$$

for Fermi statistics. With this assumption the collision term becomes, in the notations of (11e) (for a gas),

$$C(f)=\int d^3v_1\int d\Omega gI(g,\theta)[f_1'f'(1-f_1)(1-f)$$
$$-ff_1(1-f')(1-f_1')]. \qquad (58)$$

Actually, one may in some sense *prove* that the expression for the number of collisions for a Fermi system is given by (57). This is done by making a time-dependent perturbation calculation and performing an average over all initial phase. {In a typical time-dependent perturbation approach, one develops the wave function $\psi(q,t)=\sum a_n(t)u_n(q)$ and computes (approximately) the coefficients a_n. One gives the initial situation, hence one gives the coefficients $a_n(0)$, but only up to a phase; these are the phases one needs to average over in order to obtain (57) [37].} Apart from these modifications, quantum transport theory is very similar to the classical theory described in Sec. B.2. Actually, it is often easier to calculate the transition probabilities in the quantum theory than in the classical one. Many problems separate naturally into two parts; a quantum-mechanical one, in which for the process at hand one must obtain the transition probabilities, and a statistical one, in which one studies an *assumed* Boltzmann-type equation for the process which contains the computed transition probabilities. This procedure is standard in many fields, notably, the conductivity theory of metals. In the classical theory the precise status of the Boltzmann equation, within the framework of classical mechanics, demanded careful study (its derivation from the master equation, the relation to the Liouville hierarchy, the introduction of probability notions). The derivation of the quantum-mechanical rate equations from the basic ideas of quantum theory requires similar detailed investigations. These are just the investigations of special current interest. Several of these studies are analyzed in Part III. One of the basic new notions of quantum-statistical mechanics, the density matrix, was already discussed [see (27)]. The further formal development is very similar to the classical one. This basic formal similarity between the quantum and classical situations can be summarized best by a comparison as given in Table III. A glance at this table shows that the parallelism between the quantum and classical situations is very close indeed, so a detailed discussion can be omitted. It is clear, for example, that from the density matrix in the x representation (34), one can construct *reduced* density

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[15] Eigenstates of H_0 are from now on denoted by $|n\rangle$.

TABLE III. Comparison between classical and quantum situations.

Classical nonequilibrium statistical mechanics	Quantum nonequilibrium statistical mechanics	
Phase space density: $W_N(p,x,t)$	Density matrix $\rho(q',q'',t)$ or $[\rho_{nm}(t)]$:	Wigner function $W_Q(x,p,t)$:
Liouville equation:		
$\partial W_N/\partial t+\{W_N,H\}=0$ (18)	$ihd\rho/dt+[\rho,H]=0$ (28)	$\frac{\partial W_Q}{\partial t}+\Sigma\frac{p_{1,\alpha}}{m}\frac{\partial W_Q}{\partial x_{1,\alpha}}+\Omega W_Q=0$ (66)
Observed averages:	Observed quantities:	Observed quantities:
$Q_{\text{obs}}=\int\int dpdxQ(p,x)W_N$ (21)	$Q_{\text{obs}}=\text{Tr}(\rho Q)$ (31)	$Q_{\text{obs}}=\int\int dpdxQ(p,x)W_Q(p,x,t)$ (64)
Additional time smoothing:	Additional time smoothing:	Additional time smoothing:
$\tilde{W}_N=(1/\tau)\int^{\tau}W_N(x,p,t+s)ds$	$\tilde{\rho}_{nm}=(1/\tau)\int_0^{\tau}\rho_{nm}(t+s)ds$	$W_Q=(1/\tau)\int_0^{\tau}W_Q(p,x,t+s)ds$
$\tilde{Q}_{\text{obs}}=\int\int dpdx\tilde{W}_N(Q)$	$\tilde{Q}_{\text{obs}}=\text{Tr}(\tilde{\rho}Q)$	$\tilde{Q}_{\text{obs}}=\int\int dpdxQ(p,x)W_Q(p,x,t)$
Reduced distribution functions:	Reduced density matrices:	Reduced distribution functions:
$f_s(p_1\cdots p_s,x_1\cdots x_s,t)$	$\rho(x_1\cdots x_s,x_1'\cdots x_s')$	$f_s^Q(p_1\cdots p_s,x_1\cdots x_s,t)$
$=\int\cdots\int W_N(p_1\cdots x_N)dp_{s+1}\cdots dx_N$	$=\int\cdots\int\rho(x_1\cdots x_s,x_{s+1}\cdots x_N,$ $\times x_1'\cdots x_s',x_{s+1}\cdots x_N)dx_{s+1}\cdots dx_N$ (59)	$=\int\cdots\int dp_{s+1}\cdots dx_NW_Q(x_1\cdots p_N,t)$
Liouville hierarchy: (19)		
Master function: $P(n_1\cdots n_s,\cdots t)$	Master function for probabilities	Master equation
Master equation: (12)	Master equation	
Boltzmann equation: (11d) or (11e)	Uhlenbeck-Uhling equation	

matrices defined by

$$\rho(\mathbf{x}_1\cdots\mathbf{x}_3,\mathbf{x}_1'\cdots\mathbf{x}_s')$$

$$=\int\cdots\int d^3x_{s+1}\cdots d^3x_N$$

$$\times\rho(\mathbf{x}_1\cdots\mathbf{x}_s,\mathbf{x}_{s+1}\cdots\mathbf{x}_N,\mathbf{x}_1'\cdots\mathbf{x}_s',\mathbf{x}_{s+1}\cdots\mathbf{x}_N).\quad(59)$$

The diagonal elements of these reduced density matrices $\rho(x_1\cdots x_s,x\cdots x_s)$ are, apart from a possible normalization, the counterpart of the classical configurational probabilities $\int\cdots\int d^3p_1\cdots d^3p_sf_s(x_1\cdots x_s,p_1\cdots p_s)$. By successive integrations of the quantum Liouville equation (28), one obtains a hierarchy of equations for the reduced density matrices (59), which are similar in structure to the classical hierarchy [38]. Even though the similarity between the classical and quantum approaches is striking, it is possible to make the correspondence yet closer, so that even the quantum trace calculations may be replaced by an integration over the phase space. It was already pointed out that no quantum-mechanical phase-space distribution function can exist. Wigner [39], however, has constructed a function which can be *used* to compute *correct* averages, although the function itself cannot be interpreted as a probability function. (It can assume negative values.) In the present notation the Wigner function (written as W_Q to distinguish it from the classical phase-space density) is defined by

$$W_Q(x,p,t)=\left(\frac{1}{\pi\hbar}\right)^{3N}\int dye^{(2i/\hbar)py}\rho(x-y,x+y,t),\quad(60)$$

where x stands for N position vectors $\mathbf{x}_1\cdots\mathbf{x}_N$; similarly, p stands for $\mathbf{p}_1\cdots\mathbf{p}_N$. The term (py) in the exponential is

$$\sum_{i=1}^{N}\mathbf{p}_i\mathbf{y}_i;$$

the integration is over $3N$ variables $d^3y_1\cdots d^3y_N$. ρ is the density matrix in the q representation, as given by (34):

$$\rho(x-y,x+y,t)=\frac{1}{N_e}\sum_{\alpha}\psi^{\alpha}(x-y)[\psi^{\alpha}(x+y)]^*.\quad(61)$$

It is clear that W_Q, the Wigner function, is known when ρ is known, and conversely. Thus, the use of the Wigner function is a matter of convenience rather than principle. Its main utility stems from these properties:

$$\int W_Q(x,p,t)dp=\rho(x,x,t).\quad(62)$$

This follows by integration of (60); integration of W_Q over the momenta yields the configurational probability. Integration of (60) over the coordinates x leads directly to the result

$$\int W_Q(x,p,t)dx=\rho(p,p,t).\quad(63)$$

Here $\rho(p,p,t)$ is defined as the diagonal element of the density matrix

$$\rho(p',p,t)=\frac{1}{N_e}\sum_\alpha \psi^\alpha(p',t)[\psi^*(p'',t)]^*, \qquad (63a)$$

and the $\psi^\alpha(p,t)$ are the momentum space wave functions of the ensemble members (Fourier transforms of the configuration space wave functions). Hence $\rho(p,p,t)$ is the momentum space probability density function. Since the integral over x gives the momentum probability function and the integral over p yields the configurational probability, W_Q has at least some of the properties of a classical distribution function. In fact, if one has any *classical* quantity $Q(p,x)$, its quantum-mechanical ensemble average (called Q_{obs} before) can be computed by

$$Q_{\text{obs}}=\int\int dxdpQ(p,x)W_Q(p,x). \qquad (64)$$

For a proof, see Irving and Zwanzig [40]. It follows on the basis of this result that one may develop quantum statistical mechanics in exact correspondence to classical statistical mechanics—one just needs to replace the classical W_N by the quantum mechanical W_Q. Once this is done, further operator or trace calculations are not necessary. The equation W_Q satisfies can be obtained from (60). This can be done most simply by observing that $\partial\rho/\partial t$ can be calculated immediately from (61), since the $\partial\psi^\alpha/\partial t$ is given by the Schrödinger equation

$$(\partial/\partial t)\rho(q',q'',t)=(i/\hbar)[H(q'')\rho-H(q')\rho]. \qquad (65)$$

$H(q')$ means that the Hamiltonian operator must be written in terms of q'. Equation (65) combined with (60) yields the equation for the Wigner function $W_Q(x,p,t)$ as

$$\frac{\partial W_Q}{\partial t}+\sum_{\alpha=1}^{3}\sum_{i=1}^{N}\frac{p_{i,\alpha}}{m}\frac{\partial W_Q}{\partial x_{i,\alpha}}+\Omega W_Q=0. \qquad (66)$$

Ω may be written in many forms; for a Hamiltonian containing a potential energy V, one could write

$$\Omega W_Q(x,p,t)=\frac{i}{\hbar}\left(\frac{1}{\pi\hbar}\right)^{3N}\int\int dydp'e^{(2i/h)(2-y)p'}$$
$$\times[W_Q(x,\,p-p')-W_Q(x,\,p+p')]. \qquad (66a)$$

From this point, one can imitate the classical development. One can again introduce a hierarchy of functions and obtain the equations they satisfy. Procedures such as time smoothing can now be applied to W_Q, as indicated in Table III. It is perhaps well to stress again that the use of the Wigner function is only a formal device; no new physics is introduced by its use. Also, the transport equations of actual use are always equations on the "Boltzmann level" belonging to the general class of master equations. The basic question, the relation between the master equation, describing a stochastic process, and the mechanical Schrödinger equation is in no way elucidated by the Wigner function formalism. It is, however, sometimes easier to incorporate physical ideas within this formalism. If, for example, one attempts to go over from the Liouville-type description to the master equation-type description by a time-smoothing operation, this can be done most conveniently within the Wigner function formalism. One would first define

$$\int\cdots\int d^3p_2\cdots d^3x_N W_Q(\mathbf{p}_1\cdots\mathbf{p}_N,\,\mathbf{x}_1\cdots\mathbf{x}_N,\,t)$$
$$=f_1{}^Q(\mathbf{p}_1\mathbf{x},t). \qquad (67)$$

This is the first function of the quantum-mechanical Liouville hierarchy; it is *not* to be identified, however, with the function in the Uhlenbeck-Uehling equation. Rather one defines a time-smoothed Wigner function

$$\tilde{W}_Q=\frac{1}{\tau}\int_0^\tau W_Q(p,\,x,\,t+s)ds, \qquad (68)$$

and the function in the transport equation "the physical distribution function" is obtained by a contraction of W;

$$\tilde{f}_{1Q}(p_1x_1,t)=\int\cdots\int d^3p_2\cdots d^3x_N\tilde{W}_Q. \qquad (68a)$$

Kirkwood and Ross [41] have shown that the function $\tilde{f}_{1Q}$, for the case of a dilute gas, satisfies the Uhlenbeck-Uehling equation. For this proof the time averaging defined by (68) was essential; this in turn can be discussed most conveniently by using the Wigner function formalism. However, as in the classical case, the real physical problem consists of deriving the Boltzmann equation on the basis of a dynamical description. Great progress has been made during the last few years. Since this is the subject matter of Part III, a discussion of a summarizing table similar to Table II is postponed. It is hoped that, with the background provided so far, one should be able to follow the arguments presented in Part III in detail. A similar summary concerning solid-state matters is given in Sec. B to provide the background for Parts II and IV.

C. Framework of Solid-State Theory

In this section the main ideas of solid-state theory, as they pertain to transport theory, are briefly summarized. Thus the discussion here parallels the one given in Sec. B for statistical mechanics. The combination of the ideas of statistical mechanics and solid-state theory which occurs in transport problems is discussed in Part II. Many books and survey articles cover this general material. These should be consulted for more detailed descriptions. The purpose of the present ex-

TABLE IV. Assumptions in solid-state theory. General Hamiltonian, nuclei, and electrons in interaction; neglect of spin and magnetic interactions; adiabatic approximation; separation philosophy; Taylor development.

Electronic problems	Lattice problems	Interactions
(a) Many-electron problem in a periodic force field	(a) Harmonic approximation	(a) Character of the electron-ion interactions
(b) "Equivalent" one-electron problem in a periodic field. Band structure. Effective mass notion	(b) Theories attempting to calculate $N(w)dw$; frequency distribution (or the level density)	(b) Various assumptions about the behavior of ions (rigid, deformed)
(c) One-electron treatment with an *assumed* dispersion law $\epsilon=\epsilon(k)$	(c) Importance of anharmonic terms: thermal expansion	(c) Calculation of (self-consistent) screened interaction potentials and frequencies
(d) Introduction of external magnetic and electric fields	(d) Equilibrium between phonons. Umklapp processes	(d) Perturbation treatment
(e) Alternate (and better) formulation: Collective description of the many-electron problem		(e) Conductivity calculations (electrical and thermal)

position is to exhibit the relationships between the assumptions *of* the theory and the quantities computed *by* the theory. In addition, the presentation here might in some sense interpolate between the current literature and the existing textbooks. Finally, one might observe that in the interpretation of transport experiments, the transport theory and the solid-state theory are inextricably mixed up. Thus one needs a thorough understanding of the solid-state effects before anything can be deduced about the validity or lack of validity of the transport theory. The logical interrelations of those parts of solid-state physics most relevant for transport theory are shown in Table IV. The remainder of this section consists of a number of somewhat disconnected comments in connection with this table.

1. Systematization of the Assumptions of Solid-State Theory

The most fundamental way in which one could describe a solid is in terms of the nuclei and electrons of which it consists. If one denotes the positions of the electrons by $\mathbf{r}_i(i=1\cdots N)$ and those of the nuclei by $\mathbf{R}_\alpha(\alpha=1\cdots N')$, the nonrelativistic Hamiltonian is given by

$$H=-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\Delta_i-\frac{\hbar^2}{2M}\sum_{\alpha=1}^{N'}\Delta_\alpha+V_{ee}+V_{Ne}+V_{NN}. \tag{69}$$

Here m is the electron mass; M the mass of a nucleus; Δ_i and Δ_α the Laplacian operators with respect to the electronic and nuclear positions. The interaction energies between electrons V_{ee}, as well as those between nuclei V_{NN}, and those between electrons and nuclei could depend on the positions as well as the spins and momenta of the particles involved. In most (but not all) applications, the dependence of these interaction energies on spins and momenta is neglected, so that the various V's represent essentially electrostatic interactions.

The Hamiltonian is written as

$$H=-\sum_i\frac{\hbar^2}{2m}\Delta_i-\frac{\hbar^2}{2M}\sum_\alpha\Delta_\alpha+\tfrac{1}{2}\sum_{i,j}v(\mathbf{r}_1-\mathbf{r}_j)+\sum_{i,\alpha}V(\mathbf{r}_i-\mathbf{R}_\alpha)+\tfrac{1}{2}\sum_{\alpha,\beta}U(\mathbf{R}_\alpha-\mathbf{R}_\beta), \tag{70}$$

$$H\Psi=E\Psi. \tag{70a}$$

Even in this form the problem of determining the eigenstates and eigenvalues of H is both too hard and too general. This Hamiltonian describes *any* nonrelativistic system of interacting particles, not just a solid. Thus, additional information has to be added to the Hamiltonian (70) before detailed results can be expected. By writing (70) in terms of the nuclear and electronic coordinates, one has lost whatever physical information one had about the atomic structure of the atoms which make up the solid. If, for example, one wants to study the properties of solid Na, it is reasonable that one should utilize the known properties of the Na wave functions and atoms. In the description as given by (70) one would make use only of the fact that a Na atom has 11 electrons and the nuclear charge (occurring in U and V) is 11. Use of a formulation such as (70) requires one to solve both the atomic structure problem and the solid-state problem. It would be desirable to introduce existing knowledge about atoms into the formalism. Two other qualitative ideas which allow the construction of a usable theory are the small mass ratio of electrons and nuclei, and the fact that one must associate a well-defined periodic structure (as revealed, for example, in x-ray studies) with a solid. The combination of these qualitative ideas with the Hamiltonian (70) leads to a more usable formalism.

(*a*) *Mass ratio.* The Schrödinger wave function $\Psi(\mathbf{r}_1\cdots\mathbf{r}_N,\mathbf{R}_1\cdots\mathbf{R}_{N'},t)$ in (70a) is abbreviated as $\Psi(r,R,t)$. The procedure customarily followed to obtain solutions is to introduce an auxiliary function $\psi_n(r,R)$ which satisfies

$$\left\{-\frac{\hbar^2}{2m}\sum_i\Delta_i+\tfrac{1}{2}\sum v(\mathbf{r}_i-\mathbf{r}_j)+\sum_{i,\alpha}V(\mathbf{r}_i-\mathbf{R}_\alpha)\right\}\psi_n(r,R)=\epsilon_n(R)\psi_n(r,R). \tag{71}$$

This is the Schrödinger problem for the electrons of the solid for *fixed* nuclear positions. The wave function ψ_n and the energy ϵ_n depend parametrically on the nuclear configuration. On having found such eigenfunctions $\psi_n(r,R)$ and eigenvalues $\epsilon_n(R)$, one attempts to construct eigenfunctions of (70) by writing

$$\Psi(r,R)\cong\varphi(R)\psi_n(r,R). \tag{72}$$

Changes in the nuclear configuration affect the electronic wave function only insofar as these changes alter the coordinates R. This so-called adiabatic approximation is used in practically all applications [42,43]. It is possible to formulate the basis of the adiabatic approximation somewhat more precisely. Since the approximation is so commonly made, it is important to outline how this can be done. Define, as in (71), auxiliary electronic wave functions $\psi_n(r,R)$. Assume that for given R these functions form an orthogonal set. A solution of (70a), $H\Psi=-(\hbar/i)(\partial\Psi/\partial t)$, can be constructed as

$$\Psi(r,R,t)=\textstyle\sum_m \varphi_m(R,t)\psi_m(r,R), \tag{73}$$

which, in constrast to (72), is exact. The equation which $\varphi_m(R,t)$ satisfies can be obtained straightforwardly by substituting (73) into (70), using (71). One obtains

$$\begin{aligned}-\frac{\hbar}{i}\frac{\partial\varphi_n}{\partial t}=-\frac{\hbar^2}{2M}\sum_\alpha \Delta_\alpha\varphi_n(R,t)+\tfrac{1}{2}\sum_{\alpha,\beta} U(R_\alpha-R_\beta)\varphi_n\\ +\epsilon_n(R)\varphi_n+\textstyle\sum_{n'} A_{nn'}\varphi_{n'}(R,t)\\ +\textstyle\sum_{n'}(\nabla_{\alpha'}\varphi_{n'})\cdot\mathbf{B}_{nn'},\end{aligned} \tag{74}$$

with

$$A_{nn'}=-\frac{\hbar^2}{2M}\int dr\psi_n^*(r,R)\textstyle\sum_\alpha \Delta_\alpha\psi_{n'}(r,R), \tag{75a}$$

$$\mathbf{B}_{nn'}=-\frac{\hbar^2}{2M}\int dr\cdot 2\psi_n^*(r,R)\textstyle\sum_\alpha \nabla_\alpha\psi_{n'}(r,R). \tag{75b}$$

∇_α is the gradient operator with respect to R_α. Equation (73), as well as (74), is still exact. {It is amusing that equations such as (75) were first obtained by Pauli [44].} A look at (71) and (74) shows that the electronic problem described by ψ_n and the lattice problem described by φ_n are coupled through the A and B terms. The justification of the adiabatic approximation consists precisely in showing that the contributions to matrix elements and energies due to these terms are small. To demonstrate this, one has to make use of the properties of ψ_n, and these properties depend on the character of V in (71). If one assumes that V is periodic, the solutions $\psi_n(r,R)$ must have a form demanded by Bloch's theorem. So a reasonable form of $\psi_n(r,R)$ would be[16] [45]

$$\psi_n(r,R)=u_n(R-r)e^{ikr}, \tag{76}$$

where u is periodic with the periodicity of the lattice. On substituting (76) into (75a) and using the fact that an operator such as Δ_α may be rewritten as Δ_i [since u depends on $(R_\alpha-r_i)$ only], one obtains for A_{nn} an expression of the type

$$\sim\frac{m}{M}\int u_n^*(r-R)\left(-\frac{\hbar^2}{2m}\Delta_i\right)u_n(r-R)dr. \tag{76a}$$

Equation (76a) represents a small quantity; it is m/M times the electronic kinetic energy. Equation (76a) is also independent of R, for the main contribution to the integral (irrespective of the location of R) comes from r values near the nucleus, and this is independent of the position of the nucleus. One may similarly show that the off-diagonal elements of A are very small.

Making specific assumptions about ψ allows an estimate of the expressions involving A and B. For a further discussion of the adiabatic approximation see Ziman [46] and Haug [47]. (For a slightly different but equivalent formulation see the note in connection with Haug's paper.) If one assumes the validity of this approximation, one can see that it is sensible to study the electronic problem and the lattice problem separately. The coupling between the two may be treated as a perturbation characterized by A and B in (75). Thus the unperturbed state is actually of the form assumed before in (72); in addition, φ satisfies (74) without the A and B terms. The procedure is therefore a systematic perturbation development in terms of A and B. As such, it is the logical extension of the intuitive assumption (72). It is still well to recall that the electronic problem and the lattice problem, in addition to the coupling through the A and B terms, are also coupled through the occurrence of $\epsilon_n(R)$ in (71) and (74). It is also wise to remark that the solution of the electronic problem and the determination of $\epsilon_n(R)$ is far from a trivial task, but still easier than the solution of the combined nuclear-electronic problem. It would be correct to say that the adiabatic approximation is a semiquantitative expression of the small value of the mass ratio of electrons and nuclei. Even so, the approximation is not always valid; as already mentioned, the A and B terms depend on ψ_n. It is of some interest to develop qualitative criteria for the validity of the adiabatic approximation. Physically, one wants to say that the kinetic energy of the nuclei is much smaller than the separation $\Delta\epsilon$ between the electronic levels for a given nuclear configuration. For in that case the motion of the nuclei cannot materially affect the electronic level structure, so that the electronic wave function changes adiabatically [i.e., according to (72)] with the nuclear coordinates. If l is a measure of the location of a nucleus (over a distance l the nuclear wave function is pretty constant), one has from the uncertainty relation $\Delta p\cdot l\sim\hbar$; if v_N is an average nuclear velocity,

$$\tfrac{1}{2}Mv_N^2\cong\hbar v_N/l.$$

Thus the condition for the validity of the approximation

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[16] For this estimate one is using one-electron Bloch wave functions.

is [43]

$$\hbar v_N/l \ll \Delta\epsilon. \tag{77}$$

Another way to arrive at the same estimate is this: An electron in the adiabatic description must make many revolutions around a nucleus during the time that a nucleus travels a distance of order l. If a nucleus travels that distance, the nuclear wave function is badly distorted. Consequently, to be able to talk about an electronic wave function $\psi_n(r,R)$ at a configuration R demands that the distance traveled by the nucleus during the time of a revolution of an electron be much less than l. If the electronic energy level separation is of order $\Delta\epsilon$, the frequency of the radiation emitted is $\sim\Delta\epsilon/\hbar$, and the time associated with a classical revolution is of order $\hbar/\Delta\epsilon$. Thus, the condition just mentioned reads $(\hbar/\Delta\epsilon)v_N \ll l$. This is (77) again. One can therefore check whether or not (77) holds. The validity, as one might anticipate, depends on the details of the electronic spectrum. If there are many electronic levels very narrowly spaced, (77) probably does not hold, whereas for a widely separated energy spectrum it does hold. Use of (77) requires again knowledge of the energy spectrum of $\epsilon(R)$. In point of fact, (77) is numerically satisfied for solids composed of chemically saturated units such as a solid inert gas or an ionic lattice. It is usually satisfied for the K electrons. In metals, (77) is never true for all electrons. However, one may verify that the electrons belonging to closed atomic shells in a metal usually satisfy (77). One may therefore describe ions, consisting of a nucleus and a closed shell of electrons, as a well defined unit: the electrons in the ion move adiabatically with the nucleus. The remaining valence electrons must be separately described. Since basically the distinction between the validity or lack of validity of the adiabatic approximation is a quantitative one, it is generally not possible to decide *a priori* whether the adiabatic approximation is valid for all electrons in an (atomic) closed shell. Stated differently, the distinction between core electrons and valency electrons (defined as electrons for which the adiabatic approximation holds or does not hold) becomes ambiguous. It is this circumstance which causes the "number of free electrons" participating, say, in a conduction process to be an adjustable parameter rather than a theoretically given quantity. The number N occurring in (69) is the total number of electrons, certainly not an adjustable constant. By virtue of the adiabatic approximation, one does not need to describe all N of them; most electrons can be combined with the nuclei to ions. But the precise number is a quantitative matter dependent on the details of the interaction.

Even though, with the introduction of ions in the description of the solid, one has utilized information about the atomic structure of the constituents of the solid, this is not an unmixed blessing. When these ions interact and move, one has to be concerned about the nature of their interactions with electrons and their deformation. This kind of problem does not occur when one considers only bare nuclei and electrons. But then one cannot use the available information about their atomic structure.

(*b*) *Taylor expansion.* The fact that the ions or nuclei (these terms are now used interchangeably) do not move large distances from their equilibrium positions allows a far reaching simplification of the solid-state framework.[17] Define the displacements $\mathbf{y}_\alpha$:

$$\mathbf{y}_\alpha = \mathbf{R}_\alpha - \mathbf{R}_\alpha{}^0. \tag{78}$$

The y's are assumed to be small compared to the distance a between neighbors. Here $\mathbf{R}_\alpha{}^0$ are lattice sites, geometrical locations which express the periodic structure of the solid [48, 49]. A common way to characterize the symmetry character of the crystal is by the three basic lattice vectors $\boldsymbol{\tau}_1$, $\boldsymbol{\tau}_2$, $\boldsymbol{\tau}_3$ (also called primative translations of the lattice). Any lattice point can be reached from any other by a translation vector of the form $n_1\boldsymbol{\tau}_1+n_2\boldsymbol{\tau}_2+n_3\boldsymbol{\tau}_3$, with n_1 n_2 n_3 integers. The equation

$$(\boldsymbol{\tau}_i{}^* \cdot \boldsymbol{\tau}_j) = \delta_{ij} \qquad i,j=1,2,3 \tag{79}$$

defines the reciprocal lattice system $\boldsymbol{\tau}_i{}^*$ [49]. The assumption that $|y_\alpha| \ll a$ suggests that it is sensible to make a Taylor series development of the potentials V and U (also ϵ) as they occur in (71) and (74). For instance,

$$\sum_{i,\alpha} V(\mathbf{r}_i - \mathbf{R}_\alpha) = \sum_{i,\alpha} [V(\mathbf{r}_i - \mathbf{R}_\alpha{}^0) - \mathbf{y}_\alpha \cdot \nabla_i V(\mathbf{r}_i - \mathbf{R}_\alpha{}^0) \cdots]. \tag{80}$$

Similar expansions can be made for U. It is well known that the expansions of U up to quadratic terms in the displacements as applied to (74) (without A and B) yield the Schrödinger equation of the lattice vibrations. It is still of interest to observe that the use of the Taylor expansion (80) in (71) decouples the electrons and the lattice even further. If one uses only the first term of (80), then (71) describes a system of electrons in a periodic field $V_{\text{eff}}(\mathbf{r}_i) = \sum_\alpha V(\mathbf{r}_i - R_\alpha{}^0)$. [The periodicity follows by noting that

$$V_{\text{eff}}(\mathbf{r}_i + \boldsymbol{\tau}) = \sum_\alpha V(\mathbf{r}_i - \mathbf{R}_\alpha{}^0 + \boldsymbol{\tau}) = \sum_\beta V(\mathbf{r}_i - \mathbf{R}_\beta{}^0) = V_{\text{eff}}(\mathbf{r}_i);$$

for if $\mathbf{R}_\alpha{}^0$ runs through all lattice sites in the sum, so does $\mathbf{R}_\alpha{}^0 - \boldsymbol{\tau}$.] The equation becomes

$$\left[-\frac{\hbar^2}{2m} \sum_i \Delta_i + \tfrac{1}{2} \sum_{i,j} v(\mathbf{r}_i - \mathbf{r}_j) + \sum_i V_{\text{eff}}(\mathbf{r}_i) \right] \times \psi(\mathbf{r}, \mathbf{R}^0) = \epsilon_n(\mathbf{R}^0) \psi_n(\mathbf{r}, \mathbf{R}^0), \tag{81}$$

where both ψ and ϵ have been developed in a Taylor

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[17] This fact was also used in the adiabatic approximation. When one solves the electronic problem for a given nuclear configuration, one definitely has a "reasonable" nuclear configuration in mind; i.e., one near the equilibrium sites of the ions. Otherwise a function such as $\epsilon_n(R)$ has no smooth dependence on R at all.

series. Since the $\mathbf{R}_\alpha^0$ are not dynamical variables, (81) describes the behavior of an electron gas in a fixed periodic field uncoupled from the lattice. It is the starting point for all considerations involving band structure.

It is possible to make the indicated Taylor development of the potentials directly in the initial Hamiltonian, (70), which gives formally very similar results. The resulting Hamiltonian splits up into three terms, which may be written as

$$H=H_{\text{el}}+H_{\text{latt}}+H_{\text{int}}, \tag{82}$$

$$H_{\text{el}}=-\sum_{i=1}^{N}\frac{\hbar^2}{2m}\Delta_i+\tfrac{1}{2}\sum v(\mathbf{r}_i-\mathbf{r}_j)+\sum_{i,\alpha}V(\mathbf{r}_i-\mathbf{R}_\alpha^0), \tag{82a}$$

$$H_{\text{latt}}=-\sum_{\alpha}\frac{\hbar^2}{2M}\Delta_\alpha+\tfrac{1}{2}\sum_{\alpha,\beta}U(\mathbf{R}_{\alpha\beta}^0)+\tfrac{1}{4}\sum_{\alpha,\beta,ss'}y_{\alpha\beta,s}y_{\alpha\beta,s'}U_{\alpha\beta,ss'}{}^0, \tag{82b}$$

$$H_{\text{int}}=-\sum_{i,\alpha,s}y_{\alpha,s}V_{i,\alpha,s}{}^0+\tfrac{1}{2}\sum_{i,\alpha,s,s'}y_{\alpha,s}y_{\alpha,s'}V_{i\alpha,ss'}{}^{(0)}. \tag{82c}$$

Here s denotes a Cartesian component of a vector; s runs from 1 to 3. $\mathbf{R}_{\alpha\beta}$ is defined by $\mathbf{R}_{\alpha\beta}=\mathbf{R}_\alpha-\mathbf{R}_\beta$, similarly for $\mathbf{y}_{\alpha\beta}$. A superscript in a quantity, such as $U_{\alpha\beta,ss'}{}^0$, indicates that the quantity is to be evaluated at $y_{\alpha\beta}=0$:

$$U_{\alpha\beta,ss'}{}^{(0)}=\left(\frac{\partial^2U}{\partial R_{\alpha\beta,s}\partial R_{\alpha\beta,s'}}\right)_{y_{\alpha\beta}=0}, \tag{83a}$$

$$V_{i,\alpha,s}{}^0=\left(\frac{\partial V(r_i-R_\alpha)}{\partial r_{i,s}}\right)_{y_\alpha=0},\qquad V_{i,\alpha,ss'}{}^0=\left(\frac{\partial^2V(r_i-R_\alpha)}{\partial r_{i,s}\partial r_{i,s'}}\right)_{y_\alpha=0}. \tag{83b}$$

Quantities such as $U_{\alpha\beta,ss'}{}^0$ depend only on the lattice sites; on the other hand, $V_{i,\alpha,s}{}^0$ does depend on $\mathbf{r}_i$, the position vector of the ith electron. Equation (82) appears to separate the general problem in a natural fashion into an electronic, a lattice, and an interaction problem. Indeed, this development is often used for such purposes; one observes that the electronic part of the Hamiltonian (82a) is identical with (81) obtained by using the adiabatic hypothesis *and* the Taylor expansion. The basic idea in the separation philosophy is the possibility of treating H_{el} and H_{latt} as independent of one another. One may then refine the description by consideration of the effect of the interaction H_{int}. In fact, (82c) is the usual perturbation term from which one computes electron-lattice interactions. Even though this is similar to the separation achieved through the use of the adiabatic hypotheses, it is well to note that in H_{latt} one describes the lattice oscillations of nuclei, including only the repulsive forces (as given by U) between the ions. In order to have a physically sensible situation, one should think of a compensating term in H_{latt}, so as to describe a set of positive ions immersed in a uniform sea of negative charge. Similarly, one should think of H_{el} as having a compensating positive uniform charge density which maintains the electrical neutrality of the system. But now it is clear that the vibrational frequency spectrum, using forces between ions only [as given by (82b)] in a uniform negative charge, may show very little resemblance to the actual vibrational frequency spectrum of a lattice of ions (as experimentally obtained from the lattice specific heat of a metal). For in the latter case the electron distribution is profoundly influenced by the lattice oscillations and in turn affects (through the lattice electron interaction) the vibrational spectrum. The electrons generally follow the lattice vibrations; they tend to screen the lattice electron interactions. In a sense it is therefore a little misleading to refer to (82) as accomplishing a separation of the interactions in a solid. To be sure, (82b) describes lattice oscillations of frequencies Ω (in a uniform electrostatic background); the frequencies depend on U only, as one can see from (82b). However (as already mentioned), the actual lattice oscillations, as observed, are not those of a lattice immersed in a static charge distribution, but rather those of a lattice surrounded by a moving electron distribution. Its eigenfrequencies ω are related to the purely ionic oscillation frequencies Ω by expressions depending on the electron-phonon matrix elements [50].

The calculations attempting to obtain these relations always are of a self-consistent type. It is also possible to develop such calculations directly from the original Hamiltonian (70). Let $\Psi(r,R)$ as before be a wave function satisfying (70a). One observes that

$$\rho(\mathbf{r})=\sum_{i=1}^{N}\int\int dR_\alpha dr_i|\Psi(\mathbf{r}_i,\mathbf{R}_\alpha)|^2\delta(r_i-r) \tag{84}$$

is the electron density at $\mathbf{r}$. (One integrates over all electronic and nuclear coordinates.) It is clear that ρ depends on the exact wave function Ψ. Define next

$$\bar{V}(\mathbf{R}_\alpha)=N^{-1}\int V(\mathbf{r}-\mathbf{R}_\alpha)\rho(\mathbf{r})d^3r. \tag{84a}$$

This is the average interaction energy of an ion at $\mathbf{R}_\alpha$ with the average charge distribution $\rho(r)$. Rewrite H as

$$H=-\frac{\hbar^2}{2m}\sum_i\Delta_i+\tfrac{1}{2}\sum v(\mathbf{r}_i-\mathbf{r}_j)+\sum_{i,\alpha}[V(\mathbf{r}_i-\mathbf{R}_\alpha)-\bar{V}(\mathbf{R}_\alpha)]-\frac{\hbar^2}{2M}\sum_\alpha\Delta_\alpha+\sum_\alpha N\bar{V}(\mathbf{R}_\alpha)+\sum_{\alpha,\beta}U(\mathbf{R}_\alpha-\mathbf{R}_\beta). \tag{85}$$

[H as written is a curious Hamiltonian, the term $\bar{V}$ depends through (84) and (84a) on one of its eigenstates; this corresponds to the self-consistent feature in the calculations.] One can now expand U, V, $\bar{V}$, in a Taylor series around the equilibrium position $\mathbf{R}_\alpha{}^0$. The further Taylor development yields much the same results as before; one, however, does not need to introduce the compensating charges. One can again discuss the electronic and lattice problems separately. Treatment of ρ as a *time*-independent charge density again means that one does not obtain the lattice vibrations of physical interest, just those of an ionic lattice immersed in a static charge. It is possible, however, through a series of canonical transformations to obtain the relations between Ω and ω [51]. These somewhat general observations had as their purpose to stress once again how indirect are the comparisons between experiment and fundamental theory. As an example [52], an experimental check of the relation obtained between ω and Ω involves the following points:

(a) A relation between elastic constants (which are measured) and the actual lattice frequencies ω.

(b) A sum rule relating the Ω frequencies to a plasma frequency (exact relation) which is known.

(c) An approximate calculation of the phonon-electron matrix element which occurs in the derived relation (using a Wigner-Seitz calculation in the process).

It takes a combination of these three pieces of information to verify the relation in question to about 10%.

Actually, in the applications of the theory to experimental situations, one uses equations which are simplified much beyond the stage of those given by (82). The next section discusses some of these further simplifications.

2. *Further Simplifications. One-Electron Picture*

(*a*) *Remarks about the one-electron picture.* In spite of the approximations made in obtaining the Hamiltonian (82) for electrons in a perfect crystal, it is still impossible to obtain solutions of this Schrödinger problem. More serious is the circumstance that it does not even provide a physical framework in terms of which one can describe the results of experiments. Indeed, practically all the new concepts which have been introduced in physics through solid-state theory, such as energy bands, effective mass, and Brillouin zones, have been obtained via the *one*-electron description of solids. In this description one attempts to represent all the various forces acting on a single electron by a single static field acting independently on each electron. This one field incorporates both the interactions between electrons and those between ions. The one-electron Schrödinger equation [a further simplification of (82a)] becomes, therefore,

$$[-(\hbar^2/2m)\Delta+V_\beta(\mathbf{k},\mathbf{r})]\psi_\beta(\mathbf{k},\mathbf{r})=E_\beta(\mathbf{k})\psi_\beta(\mathbf{k},\mathbf{r}). \quad (86)$$

With the successive simplifications in the equations or Hamiltonians, the significance of the potentials in these equations becomes gradually more obscure. Whereas in the original Hamiltonian the significance of an electrostatic potential between electrons and nuclei is unambiguous and the potential itself is known, this is not the case for the potential $V_\beta(\mathbf{k},\mathbf{r})$ which is neither known nor unambiguous. More precisely, one assumes the existence of such an average potential acting on each electron. From the fact that the interaction potential V_{eff} in (81) has the periodicity of the lattice, one infers that V_β has this same periodicity. It is reasonable that if an average static V_β exists at all, it should have the periodicity of the lattice. Most of the well-established portions of solid-state theory, the existence of energy bands, Brillouin zones, and many of the approximation procedures (weak and tight binding), are based directly on a study of equations of the general type (86) [53,54].[18] It should be reiterated, however, that the average potential now is not known, but the determination of this potential is the central problem of this part of solid theory. Many different methods exist; they are reviewed by Reitz [55]; see also Herman [56]. For present purposes the following points are pertinent:

(a) Since in these calculations, one wants to determine both the wave functions of the electrons as well as the periodic field in which they move, one should perform a self-consistent calculation. Unfortunately, the computational difficulties preclude a systematic approach of this type, so one actually picks a physically plausible potential for each state, and then solves the one-electron problem for this potential. This common approach immediately suggests two further points.

(b) Just how sensitive is the computed band structure to the assumed potential? If one picks a V_β, in an *ad hoc* fashion, it is clear that only those results which are reasonably insensitive to the choice can be trusted.

(c) It is common to assume the same potential V in (86) for all states. How accurate this is is not known at present.

It is unfortunate that even the most careful calculations done to date still do not produce good agreement with experiment. Even though the qualitative features of the band scheme seem to be reproduced fairly well, it appears that the details of the band structure are remarkably sensitive to the details of the form of V_β. (An extensive comparison between theory and experiment is given by Ziman [57].) This quantitative failure is even stronger in the light of the success of all the qualitative notions introduced by the one electron description of solids. Concepts such as reduced wave vectors, effective masses, and Brillouin zones, all obtained within the one-electron picture, have been most effective

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[18] Some of the results of these studies, the state of an electron in a periodic potential is determined by a band index β and a wave vector $\mathbf{k}$, the energy for given β is a continuous function of $\mathbf{k}$, have been anticipated by the notation used in Eq. (86).

in the description of experimental results. Very likely these concepts have a validity much beyond the one-electron approach. For this reason any attempt to obtain such ideas from a many-particle viewpoint [cf. Eq. (81)] is of unusual interest. Section C.5 contains some remarks related to current attempts in this direction. For the discussion of conductivity problems, the questions raised here concerning the one electron potential and its influence on the band structure are of lesser importance. In these phenomena only the electrons near the Fermi surface play a significant role. Hence only that portion of the band structure affects the transport properties. For metals in particular a knowledge of the band structure near the Fermi surface is the only relevant part of the band structure. It is a fortunate circumstance for conductivity theory that there are separate and independent experimental procedures which allow one to obtain information about the Fermi surface (de Haas-van Alphen effect, see Part II). This information can then be used in the interpretation of transport properties, so that an appeal to an incomplete theory can be avoided.

(*b*) *Fermi statistics*. The great computational power of the one-electron formulation of solid-state theory stems from the fact that one may apply Fermi statistics to the system of electrons. This is possible since all electrons possess the identical energy spectrum. This therefore yields a description of the complete electronic system. The *number* of electrons in an energy interval dE (per unit volume) is written as $n(E)dE$. The density of states in an energy range dE (of *one* spin direction) is written $g(E)dE$.[19] This entity may be defined by

$$g(E)\Delta E=\frac{1}{8\pi^3}\int_E^{E+\Delta E} d^3k. \tag{87}$$

The integration in (87) is over a region in k space between two surfaces of constant energy. In the special case where E is a function of the magnitude of the vector $\mathbf{k}$ (written as k) only, one sees from (87) that the density of states may be written as

$$g(E)=\tfrac{1}{2}(k/\pi)^2(dk/dE). \tag{87a}$$

It is clear from either (87) or (87a) that $g(E)$ depends explicitly on the structure of the solid through the dependence of the energy on the wave number. Thus $E_\beta(\mathbf{k})$ in (86) must be known, in order to *calculate* $g(E)$. For *free* electrons $g(E)$ is given by

$$g(E)=2\pi(2m)^{\frac{3}{2}}h^{-3}E^{\frac{1}{2}} \tag{87b}$$

(h is the Planck constant). In other cases, (87b) is still often used but with an effective mass m^*, treated as an empirical parameter, rather than m. The number of electrons $n(E)$ is given by[20]

$$n(E)dE=2g(E)dE/e^{(E-\zeta)/kT}+1\equiv 2g(E)f_0(E). \tag{88}$$

The factor 2 in (88) comes from the two spin directions; (88) defines f_0, the Fermi distribution. The temperature-dependent parameter ζ is determined by the total number of electrons per unit volume n:

$$\int_0^\infty 2g(E)f_0(E)dE=n. \tag{89}$$

It is of some interest to distinguish ζ, determined by (89), from the Fermi energy E_F, defined by

$$\int_0^{E_F} 2g(E)dE=n. \tag{89a}$$

E_F is independent of the temperature. The evaluation of the integrals defining ζ and E_F is reasonably simple for free electrons [58]. For other systems g can become quite complicated and the evaluation becomes very involved. The point of recalling these well-known relations is to stress that if the energy spectrum of a system is changed, say by putting the system in a magnetic field, the function $g(E)$ is altered and so is the relation between E_F and ζ. The usual situation (without magnetic field) encountered in most metals is that ζ and E_F are approximately equal. The altered relation between ζ and E_F in a magnetic field is important later. A number of physical phenomena depend on the character of the solid, just through $g(E)$, not through the complete energy band picture. For example, the complete theory of the electronic specific heat is contained in the average energy:

$$2\int_0^\infty f_0(E)g(E)EdE=\langle E\rangle.$$

Clearly, if $E(k)$, hence $g(E)$, were precisely known, the discussion of the specific heat would be reduced to an exercise in integration, for $c(T)=d\langle E\rangle/dT$. Actually, neither $E(k)$ nor $g(E)$ is usually known *a priori*, so one inverts the procedure and employs the experimental information about the specific heat to learn something about $g(E)$. Since other experiments, the intensities of x-ray emission and absorption of metals, depend on the same $g(E)$, one may relate different experimental results to one another. In a theoretical vein, it is possible to relate the density of states g to the previously mentioned partition function Z [see formulas (38) and (39)]. Let E_i be the energy eigenstates of a system, and $N(E)$ the number of states whose energy is *less* than E. It is clear that the number of states in the range ΔE is given by

$$N(E+\Delta E)-N(E)=(dN/dE)\Delta E=g(E)\Delta E. \tag{90}$$

$N(E)$ may be simply expressed in terms of a function

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[19] The density of states in many books is denoted by some form of the letter N (script N in [53] and [57]). In Wannier [45], $g(E)$ is used.

[20] No effort is made to distinguish the absolute value of the wave number k from the Boltzmann constant k.

$\theta(x)$ defined by

$$\begin{aligned} \theta(x)&=0 \qquad & x<0 \\ \theta(x)&=\tfrac{1}{2} & x=0 \\ \theta(x)&=1 & x>0. \end{aligned} \tag{91}$$

One has (just using the definition)

$$N(E)=\textstyle\sum_i \theta(E-E_i) E\neq E_i. \tag{92}$$

It is known[21] that $\theta(x)$ has the integral representation

$$\theta(x)=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{dz}{z}e^{zx}. \tag{93}$$

The integral in the complex z plane is parallel to the imaginary axis; γ is a positive (real) number. From (93) and (92) one obtains

$$\begin{aligned} N(E)&=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{dz}{z}e^{zE}\sum_i e^{-zE_i} \\ &=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{dz}{z}e^{zE}Z(z). \end{aligned} \tag{94}$$

$\sum_i e^{-zE_i}=Z(z)$ is the partition function previously defined, (39).[22] By (90) one finds for the density of states

$$g(E)=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty} dz e^{zE}Z(z), \tag{95}$$

which expresses the interesting relation that $g(E)$, the density of states, is the inverse Laplace transform of the partition function Z. By inverting this relation one obtains the partition function as the Laplace transform of the density of states:

$$Z(z)=\int_0^\infty dE e^{-zE}g(E). \tag{95a}$$

Apart from the interesting formal connection which these relations demonstrate, the complex-variables method provides a powerful technique for the handling of practical problems. Consider, for example, the calculation of the free energy (per unit volume) of a Fermi-Dirac system. This is given by [59]

$$F-n\zeta=-(2/\beta)\sum\log(1+e^{\beta(\zeta-E_i)}), \tag{96}$$

where F is the free energy per unit volume, n the number of electrons per unit volume, β^{-1} as always is kT, and ζ is defined by (89). The evaluation of sums of this type is more difficult than the calculation of $Z(\beta)$ as given by (39). By using the technique just outlined, one shows that $F-n\zeta$ can always be obtained once $Z(\beta)$ is known. To illustrate the method, suppose one wants to evaluate a sum S,

$$S=\textstyle\sum_i B(E_i). \tag{97}$$

$B(E)$ is some given functions of E. One verifies immediately [using the fact that the derivative of $\theta(x)$, with respect to x is a δ function] that

$$S=-\int_0^\infty dE\frac{\partial B}{\partial E}N(E). \tag{98}$$

Now define a function M, so that

$$N(E)=dM/dE \tag{99a}$$

or

$$\begin{aligned} M(E)&=\int_{-\infty}^{E}N(E')dE' \\ &=\int_{-\infty}^{E}dE'\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{dz}{z}e^{zE'}Z(z) \\ &=\frac{1}{2\pi i}\int_{\gamma-i\infty}^{\gamma+i\infty}\frac{dz}{z^2}e^{zE}Z(z). \end{aligned} \tag{99b}$$

Here one has used (94). It is clear that if the partition function $Z(\beta)$ [actually its continuation $Z(z)$] is known, $M(E)$ can be found by performing just one complex integration. If one now substitutes dM/dE for N in (98) and performs a partial integration (assuming appropriate behavior at the boundaries 0 and ∞), one obtains for S

$$S=\int_0^\infty dE\frac{\partial^2 B}{\partial E^2}M(E). \tag{100}$$

The point of this development was to show that a knowledge of the partition function $Z(\beta)$ yields M and S. In the case of actual interest, (96),

$$B(E)=-\beta^{-1}\log(1+e^{\beta(\zeta-E)}),$$

In that case, (100) simplifies to

$$F-n\zeta=2\int_0^\infty dE\frac{\partial f_0}{\partial E}M(E)\cong -2M(E_F). \tag{101}$$

The last step in (101) utilized the well-known (approximate) δ-function character of the derivative of the Fermi function f_0 defined by (88). This technique is of particular importance in the discussion of the behavior of electrons in magnetic fields [34].[23] Considering the intimate connection between the partition function and

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[21] One could consult G. Doetsch, *Theorie and Auwendung der Laplace Transformation* (Dover Publications, New York, 1943), p. 105, but it is probably simpler and faster to apply the Cauchy theorem to (93) and verify the required properties of θ from the integral representation.

[22] More precisely, the partition function $Z(\beta)=\sum_i e^{-\beta E_i}$ is defined for real β, hence $Z(z)$ is the analytic continuation of the partition function.

[23] The use of this technique enabled these authors to obtain an *exact* expression for the partition function of a system of (free) electrons in a magnetic field.

the density of states just demonstrated, it is not surprising that the approximation procedures developed in connection with the evaluation of the partition function (see Sec. B.3) have corresponding counterparts in the discussion of the density of states [60]. This connection is of great use in obtaining the magnetic properties of an electron gas.

(*c*) *Singularities in $g(E)$*. Inasmuch as the function $g(E)$, the density of states, determines many of the quantities of physical importance, any procedure yielding *a priori* information about this function is of great interest. A similar situation exists in the theory of the lattice vibrations, where a similar distribution function $g(\omega^2)$, the number of lattice oscillations per unit frequency interval, determines the thermodynamic behavior of the lattice (in particular the lattice specific heat). The frequencies of the lattice are determined by a secular equation which depends on the force constants of the lattice. In simple crystals one obtains three frequencies and three polarization directions for a given phonon wave vector $\mathbf{q}$ [61]. The reason for referring to the problem of determining the frequency spectrum $g(\omega^2)$ of the lattice vibrations, apart from its obvious relevance to conductivity theory, originates from the fact that recent advances in this field have a direct bearing on the problem of determining the nature of $g(E)$. It was first shown by van Hove [62] that the function $g(\omega^2)$ possesses of necessity a number of singularities. The existence of these singularities can be traced back directly to the existence of critical points, i.e., points where $\nabla_q\omega(q)=0$. The existence of these critical points in turn follows (via a nontrivial mathematical theorem of Morse, see Rosenstock [63]) *exclusively* from the periodic character of the frequency ω as a function of the wave vector $\mathbf{q}$. The only *physical* statement used in reaching the conclusion about the singularities in $g(\omega^2)$ is the periodicity of ω. Exactly the same situation applies to the electronic energy E_β as a function of the wave number $\mathbf{k}$. In fact, $E_\beta(\mathbf{k})$ in (86) possesses the well-known periodicity $E_\beta(\mathbf{k}+\boldsymbol{\tau}^*)=E_\beta(\mathbf{k})$, where $\boldsymbol{\tau}^*$ is a general lattice vector in the reciprocal lattice. Hence, via Morse's theorem the existence of critical points $\nabla_kE=0$ follows, and by van Hove's analysis, singularities in $g(E)$. The existence of this last relation may be inferred by writing the density of states $g(E)$ instead of (87) as[24]

$$g(E)=\int\frac{dS}{(|\nabla_kE|^2)^{\frac{1}{2}}}. \tag{102}$$

This reformulation of (87) is a purely mathematical one; it is essentially a change of variables in the integral (87). S is a surface of constant energy in k space. From (102) one can immediately appreciate the close relationship between critical points in E and singularities of g. The van Hove result, which is of the character of a mathematical existence theorem, has been effectively applied by Rosenstock [63], to enumerate and locate the critical points of the function $g(\omega^2)$ for various crystal lattices. Once one has obtained *all* the singularities one knows a considerable amount about the qualitative features of the spectrum. Still, a knowledge of the critical points determines the spectrum *just* near the critical frequencies. In between such frequencies one needs some kind of interpolation scheme to obtain $g(\omega)^2$. Actually, a more severe limitation comes from the lack of a systematic procedure which obtains and classifies *all* the critical points, and it is just this information which is needed for a complete description of the spectrum. Attempts in this direction have been made by Rosenstock [64] and Rosenstock and Phillips [65], but so far the problem remains unsolved. In two-dimensional situations (as usual) the situation is simpler, and in that case one has [63] obtained detailed results. In obtaining these it was necessary to combine the information about the critical points with information provided by the secular equation of the lattice vibrations. It is also necessary to assume numerical values for the force constants occurring in the secular equation to obtain specific results. In spite of these limitations, the method provides a remarkable amount of qualitative information; it would seem profitable to pursue this kind of investigation. Detailed applications to the electronic density of state functions seem to be called for, especially since the critical energies [where $g(E)$ is its derivative] are singular—correspond to band edges—and the physical parameters near these edges are well known in the band scheme [66].

3. *Introduction of External Fields*

(*a*) *General remarks.* In the development of the ideas of solid-state theory so far presented, only the interaction of the constituents of the system with one another (electron-ion, electron-electron) was taken into account. In actual physical situations, the interaction between the electrons and external fields is of major importance. Most of the phenomena mentioned before as yielding significant solid-state parameters— de Haas-van Alphen effect and cyclotron resonance—involve such external fields explicitly. In principle it ought to be straightforward to introduce such fields. One could start from the initial Hamiltonian (69) for electrons and nuclei, and replace the electronic momenta $\mathbf{p}_i$ by $\mathbf{p}_i-(e/c)\mathbf{A}(\mathbf{r}_i)$ and the nuclear momenta $\mathbf{P}_\alpha$ by $\mathbf{P}_\alpha-(e/c)\mathbf{A}(\mathbf{R}_\alpha)$, where $\mathbf{A}$ is the vector potential of the external magnetic field. The interactions with an electric field could be described as always by adding a term $e\Phi(\mathbf{x},t)$ for each particle at position $\mathbf{x}$ and change e to the Hamiltonian. One then could go through the reduction again, the adiabatic theorem, Taylor develop-

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[24] Actually (102) is written for just a single band. It should contain some constants as well as a summation over the various branches of the multiple-valued function $E(\mathbf{k})$. Equation (102) was given just to suggest the close relationship between critical points and possible singularities of $g(E)$.

ment, separation, equivalent one-electron problem. In practice one never does this. The general approach is much the same as in atomic structure problems. In studying the Zeeman effect of a hydrogen atom, one does not start out with an electron and a proton in a magnetic field and then perform a separation of variables (although this is actually the proper way to do it). Rather one introduces the field directly in the already separated equation. The physical basis of this procedure is the conviction that the energy level scheme of the system is but slightly affected by the introduction of the outside fields. Similarly in solid-state consideration, it is usually assumed that the band structure is essentially unaffected by the introduction of such fields. In atomic problems, one would expect this procedure to be valid for fields such that a typical energy level separation is large compared to the interaction energy per particle. The effect of a perturbing potential such as a magnetic field on the eigenfunctions in a band scheme is extremely profound. Free electrons in a magnetic field are highly degenerate. The introduction of a perturbing periodic potential spreads these levels into bands. This much is sure. But it is hard to obtain even qualitative information about the details of that band structure. The main difficulty which occurs under various guises over and over again concerns the circumstance that the perturbed Hamiltonian has nonvanishing matrix elements between unperturbed wave functions of *different* bands. If β indicates the band index, $\langle\beta|H_{\text{total}}|\beta'\rangle$ is generally different from zero. Thus one generally cannot restrict oneself to the discussion of a single band. The new energy spectrum (with the field) is not always just a trivial shift or displacement of the old one (without a field), but it may well show qualitatively different features.

(*b*) *Electric fields*. The introduction of an electric field in the one-electron picture, as described by (86), may be obtained by adding a term H' to the Hamiltonian of (86). The total (time-dependent) problem would be described by a Schrödinger equation[25]

$$\left(-\frac{\hbar^2}{2m}\Delta+V_\beta+H'\right)\Psi(\mathbf{r},t)=-\frac{\hbar}{i}\frac{\partial\Psi}{\partial t}. \tag{103}$$

(H' is some function of $\mathbf{r}$, perhaps of t, but does not contain operators.)

It is interesting to observe the following alternate form of this Schrödinger problem. As before let $E_\beta(\mathbf{k})$ be the energy eigenvalue of $[-(\hbar^2/2m)\Delta+V_\beta]$. One knows that E_β is periodic:

$$E_\beta(\mathbf{k}+\boldsymbol{\tau}^*)=E_\beta(\mathbf{k}). \tag{104}$$

Construct from $E_\beta(\mathbf{k})$ an operator $E_\beta(-i\nabla)$. ∇ is a gradient operation with respect to the electronic coordinates. One then has

$$E_\beta(-i\nabla)\psi_\beta(\mathbf{r})=E_\beta(\mathbf{k})\psi_\beta(\mathbf{r}). \tag{105}$$

In other words, $E_\beta(-i\nabla)$ has as eigenvalues $E_\beta(\mathbf{k})$, and as eigenfunctions $\psi_\beta(\mathbf{k},\mathbf{r})$. These Bloch functions have the known periodicity properties [67]

$$\psi_\beta(\mathbf{r}+\boldsymbol{\tau})=\exp(i\mathbf{k}\boldsymbol{\tau})\psi_\beta(\mathbf{r}) \tag{106}$$

($\boldsymbol{\tau}$ as always stands for a general lattice vector, $\mathbf{R}_\alpha{}^0$ for a lattice point) or

$$\psi_\beta(\mathbf{r})=e^{i\mathbf{kr}}u_{\mathbf{k},\beta}(\mathbf{r}),\quad u_{\mathbf{k},\beta}(\mathbf{r}+\boldsymbol{\tau})=u_{\mathbf{k},\beta}(\mathbf{r}). \tag{106a}$$

From these properties one proves (105) very easily. From the periodicity of E_β in the reciprocal lattice space, it follows that E_β may be developed in terms of *lattice* vectors $\mathbf{R}_\alpha{}^0$:

$$E_\beta(\mathbf{k})=\sum_{R_\alpha{}^0}E_{\beta\alpha}\exp(i\mathbf{k}\mathbf{R}_\alpha{}^0). \tag{107}$$

The operator $E_\beta(-i\nabla)$ may now be written as

$$E_\beta(-i\nabla)=\sum_{R_\alpha{}^0}E_{\beta\alpha}\exp(\mathbf{R}_\alpha{}^0\cdot\nabla). \tag{107a}$$

Hence

$$\begin{aligned}E_\beta(-i\nabla)\psi_\beta(\mathbf{k},\mathbf{r})&=\sum_{R_\alpha{}^0}E_{\beta\alpha}\exp(\mathbf{R}_\alpha{}^0\cdot\nabla)\psi_\beta(\mathbf{k},\mathbf{r})\\&=\sum_{R_\alpha{}^0}E_{\beta\alpha}\psi_\beta(\mathbf{k},\,\mathbf{r}+\mathbf{R}_\alpha{}^0).\end{aligned} \tag{107b}$$

(This follows by expanding the exponential and using the Taylor expansion of ψ.) If one now uses the property (106) for $\psi(\mathbf{k},\mathbf{r}+\mathbf{R}_\alpha{}^0)$ in conjunction with (107), one just obtains (105) [68].

Now suppose it were possible to construct a solution of (103) in the form

$$\Psi'(\mathbf{r},t)=\sum\nolimits_{\mathbf{k}}a(\mathbf{k},t)\psi_\beta(\mathbf{k},\mathbf{r}). \tag{108}$$

Note that in (108) no *sum* over β is performed. Then

$$\begin{aligned}\left(-\frac{\hbar^2}{2m}\Delta+V\right)\Psi'(\mathbf{r},t)&=\sum\nolimits_k a(\mathbf{k},t)E_\beta(\mathbf{k})\psi_\beta(\mathbf{k},\mathbf{r})\\&=\sum\nolimits_k a(\mathbf{k},t)E_\beta(-i\nabla)\psi_\beta(\mathbf{r})=E_\beta(-i\nabla)\Psi'.\end{aligned} \tag{108a}$$

The crucial point is the possibility to exchange the operator $E_\beta(-i\nabla)$ with the summation over k. One also used (86) and (105). Then Ψ' satisfies the so-called *equivalent* Schrödinger equation [via (108a) and (103)]:

$$[E_\beta(-i\nabla)+H']\Psi'(\mathbf{r},t)=-(\hbar/i)(\partial\Psi'/\partial t). \tag{109}$$

This in a way is a surprising result; that the Bloch energy plays the role of an equivalent kinetic energy operator is certainly not obvious. Once one knows $E_\beta(\mathbf{k})$, one has in (109) an equation which can describe this solid in a variety of external fields. For quasi-free electrons where $E_\beta(\mathbf{k})=\hbar^2k^2/2m^*$, the operator $E_\beta(-i\nabla)$ becomes just the kinetic energy operator but with an effective mass m^*. For a semiconductor where $E(k)$

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[25] The β in $V_\beta(\mathbf{k})$ is kept as much for identification of the (periodic) effective one-electron potential as to indicate an explicit dependence on the band index. A similar remark applies to $E_\beta(\mathbf{k})$ occurring in (86) and later on as well.

$=b_{ij}k_ik_j+b_0$ (with measured effective masses related to b_{ij}), the appropriate equation becomes

$$\left(-b_{ij}\frac{\partial^2}{\partial r_i\partial r_j}+b_0+H'\right)\Psi'=-\frac{\hbar}{i}\frac{\partial\Psi'}{\partial t}.$$

The effect of the lattice is completely contained in the operator $E_\beta(-i\nabla)$. Actually (109) is only approximately valid (a good approximation for semiconductors), for one *cannot* develop a solution of (103) in a set of functions $\psi_\beta(\mathbf{k},\mathbf{r})$ belonging to a given *band* only. The $\psi_\beta(\mathbf{k},\mathbf{r})$ for given β *do not* form a complete set. Physically, one expects the approximation to be a good one if one can expect the electrons to remain in the band in question under the influence of the perturbation. Whereas one generally would expect this to be so, the derivation given does not provide any clues as to when this would or would not be the case. Another point of physical interest to bear in mind is that if one chooses an incomplete set of functions (the Bloch functions in *one* band) in which the electronic wave function is developed, the resultant wave packet can provide only an incomplete localization (in space). At times it is advantageous to describe the effect of fields in a classical or semiclassical vein. In order to accomplish this, one must describe the electron by a very narrow wave packet, and such a wave packet cannot be constructed from the wave functions of just a single band. This situation occurs in describing the helical motion of an electron (in a lattice) in a magnetic field. The radius of the helix becomes smaller for increasing fields. It is clear that if this radius becomes smaller than the degree of localization obtainable (by using wave functions of one band), one cannot use both a semiclassical picture and this incomplete set of wave functions. Mathematically, one could develop Ψ, the solution of (103), in any complete set of states. Since one hopes to devise approximation procedures which yield as a first approximation a description in terms of an equivalent Hamiltonian, and which allow successive refinements, the choice of the set must be tailored to the physical situation. In fact, existing different procedures differ exactly in their choice of the proper set. The other ideas in the derivations are already contained in the discussion of the proof of (105), namely, the possibility of expanding the Bloch energy (107a) and the use of the operator $\exp(\mathbf{R}_\alpha\cdot\nabla)$ as a shift operator (107b).

As an illustration, introduce a set of Wannier functions expressed in terms of Bloch functions by[26]

$$\chi_\alpha(\mathbf{r}-\mathbf{R}_\alpha{}^0)=\textstyle\sum_{\mathbf{k}}\exp(-i\mathbf{k}\mathbf{R}_\alpha{}^0)\psi_k(\mathbf{r}) \qquad (110a)$$

with the inversion

$$\psi_k(\mathbf{r})=\textstyle\sum_\alpha\exp(i\mathbf{k}\mathbf{R}_\alpha{}^0)\chi_\alpha(\mathbf{r}-\mathbf{R}_\alpha{}^0). \qquad (110b)$$

[The band index β is dropped; the summation is over the wave numbers in one band; ψ satisfied (86).] These functions have the important property that they drop off very rapidly as $|\mathbf{r}-\mathbf{R}_\alpha{}^0|\gg a$. [One sees this directly by using the "periodic" representation (106b) for ψ; the exponential in the sum becomes $\exp[-i\mathbf{k}(R_\alpha{}^0-r)]$ when $|R_\alpha{}^0r|a\gg1$; this term oscillates very rapidly.] It is this feature which makes the Wannier functions especially useful in the description of perturbed periodic lattices. Therefore a development of Ψ, (103), in Wannier functions is called for. Write

$$\Psi(\mathbf{r},t)=\textstyle\sum_\alpha c_\alpha(t)\chi_\alpha. \qquad (111)$$

Note that c_α stands for $c(\mathbf{R}_\alpha{}^0,t)$, and χ_α for $\chi_\alpha(\mathbf{r}-\mathbf{R}_\alpha{}^0)$.

The problem is now to determine the equation which the c_α satisfy. Since the χ_α's are given, and the equation for Ψ is known, it is necessary only to substitute (111) into (103). Consider first the term $H'\Psi=\sum_\alpha c_\alpha H'(\mathbf{r})\chi_\alpha$. Now H' represents the external field; since χ_α drops to zero in a few lattice distances, one may write, if the external field does not vary much over such distances,

$$H'\Psi\cong\textstyle\sum_\alpha c_\alpha H'(\mathbf{R}_\alpha{}^0)\chi_\alpha. \qquad (112)$$

Next study the action of $-(\hbar^2/2m)\Delta+V_\beta$ on Ψ, using (110a):

$$\left(-\frac{\hbar^2}{2m}\Delta+V_\beta\right)\Psi=\sum_{\alpha,k}c_\alpha(t)\exp(-i\mathbf{k}\mathbf{R}_\alpha{}^0)E(\mathbf{k})\psi_k(\mathbf{r}).$$

Apply the development of $E(\mathbf{k})$ as given by (107) (remember that the band index is still omitted) and resubstitute $\psi_k(\mathbf{r})$ in terms of χ, (110b); then

$$\begin{aligned}\left(-\frac{\hbar^2}{2m}\Delta+V_\beta)\Psi\right)&=\sum_{\alpha,k,\mu,\lambda}c_\alpha(t)\exp[i\mathbf{k}(\mathbf{R}_\mu{}^0+\mathbf{R}_\lambda{}^0-\mathbf{R}_\alpha{}^0)]E_\mu\chi_\lambda\\&=\sum_{\alpha,\mu}c_{\alpha+\mu}E_\mu\chi_\alpha. \qquad (113a)\end{aligned}$$

The only point remaining is to recall that

$$c_{\alpha+\mu}=c(\mathbf{R}_\alpha{}^0+\mathbf{R}_\mu{}^0);$$

thus one may write formally

$$c_{\alpha+\mu}=\exp(+\mathbf{R}_\mu{}^0\cdot\nabla_\alpha)c_\alpha. \qquad (113b)$$

Note particularly that ∇_α is a gradient operator with respect to a lattice point. The sum over μ in (113a) combines, using (113b) and (107a), to $E(-i\nabla)$. Thus the substitution of (111) in (103) yields

$$\sum_\alpha[E(-i\nabla_\alpha)c_\alpha+c_\alpha H'(R_\alpha{}')]\chi_\alpha=-\frac{\hbar}{i}\sum_\alpha\frac{\partial c_\alpha}{\partial t}\chi_\alpha. \qquad (114)$$

From the linear independence of the χ_α, one obtains the Schrödinger equation for the development coefficients c [69, 70]:

$$E(-i\nabla_\alpha)c_\alpha+H'(\alpha)c_\alpha=-(\hbar/i)(\partial c_\alpha/\partial t). \qquad (115)$$

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[26] A normalization factor has been omitted from (110). One can show that the functions χ are orthogonal to one another.

As before in (109), one has obtained an equation which looks very much like a Schrödinger equation, with the Bloch energy taking over the role of a kinetic energy. The important conclusion to be drawn from this derivation is that to the extent that the approximations made are valid, the eigenvalue spectrum of the energy operator $H_{\text{total}}=(-\hbar^2/2m)\Delta+V_\beta+H'$ is identical with that of $E(-i\nabla)+H'$.[27] Thus one may obtain (approximate) eigenvalues of H_{total} by studing those of $E(-i\nabla)+H'$, and this is an important practical use of (115). It is also clear from this derivation how the derivatives with respect to lattice vectors arise [71].

(*c*) *Introduction of magnetic fields.* It is also possible to construct equivalent Hamiltonians for systems which are subject to magnetic fields. If one has an electron in both a periodic field [called $V(\mathbf{r})$ or $V_\beta(\mathbf{r})$] and a magnetic field characterized by a vector potential $\mathbf{A}$, the appropriate Hamiltonian is

$$H_M=\frac{1}{2m}\left(\mathbf{p}-\frac{e}{c}\mathbf{A}\right)^2+V_\beta(\mathbf{r}) \tag{116}$$

[the operator $\mathbf{p}=(\hbar/i)\nabla$]. The existence of an equivalent Hamiltonian means that the eigenvalues of the Hamiltonian (116) are (in an approximate sense) given by the eigenvalues of the operator

$$E[-i\nabla-(e/\hbar c)\mathbf{A}]. \tag{116a}$$

$E(\mathbf{k})$ as before is the Bloch energy, in terms of the wave number $\mathbf{k}$, of an electron in the periodic field V_β. A proof of this approximate equivalence follows the pattern of the one just given for an electric field. The main difference consists in the fact that one develops the wave functions not just in Wannier functions as before (110b), but rather as

$$\Psi=\sum_\alpha c_\alpha(t)\exp\left(\frac{ie}{\hbar c}\int_{R_\alpha{}^0}^{\mathbf{r}}A(\xi)d\xi\right)\chi_\alpha. \tag{117}$$

The integral is along a straight line joining $\mathbf{R}_\alpha{}^0$ and $\mathbf{r}$. With this expansion the argument is basically identical to that given before [69]. Hence an approximate equivalent Hamiltonian exists in the magnetic case as well. It is of interest not only to have an equivalent Hamiltonian, but to see how one in principle could continue and improve the development. For such purposes one must start from the Hamiltonian (116). There are a few *exact* consequences of that Hamiltonian, which follow just from the periodicity of V [72]. If one calls the eigenvalues of H_M, W and the eigenfunctions Ψ_M,[28] one has as the basic eigenvalue equation

$$H_M\Psi_M=W\Psi_M. \tag{118}$$

From (118) one may deduce in the case where $\mathbf{A}$ is a linear function of $\mathbf{r}$ (the magnetic field is constant):

$$\Psi_{\mathbf{k}}(\mathbf{r}+\boldsymbol{\tau})=\exp\{i[\mathbf{k}\boldsymbol{\tau}+(e/\hbar c)\mathbf{r}\cdot\mathbf{A}(\boldsymbol{\tau})]\}\times\Psi_{\mathbf{k}-(e/\hbar c)\mathbf{A}(\tau)}(\mathbf{r}), \tag{119a}$$

$$W[\mathbf{k}-(e/\hbar c)\mathbf{A}(\boldsymbol{\tau})]=W(\mathbf{k}). \tag{119b}$$

$\boldsymbol{\tau}$ can be any one of the primitive translations of the lattice; $\mathbf{A}(\boldsymbol{\tau})$ denotes $\mathbf{A}$ evaluated at the value $\boldsymbol{\tau}$. These relations which are obvious generalizations of (106a) are due to Harper [72]. Just as the Bloch wave function may be written in the form (106b), one may deduce from (119a) that Ψ may be written as

$$\Psi_\alpha(r)=e^{i\mathbf{k}\mathbf{r}}U[\mathbf{k}-(e/\hbar c)\mathbf{A}(\mathbf{r});\mathbf{r};\mathbf{k}]. \tag{120}$$

U is a function of three variables; it has the periodicity properties

$$U[\mathbf{k}-(e/\hbar c)\mathbf{A}(\mathbf{r}),\mathbf{r}+\tau,\mathbf{k}]=U[\mathbf{k}-(e/\hbar c)\mathbf{A}(\mathbf{r}),\mathbf{r},\mathbf{k}], \tag{120a}$$

$$U[\mathbf{k}-(e/\hbar c)A(\mathbf{r}),\mathbf{r},\mathbf{k}+(e/\hbar c)\mathbf{A}(\tau)]=U(\mathbf{k}-(e/\hbar c)\mathbf{A}(\mathbf{r}),\mathbf{r},\mathbf{k}). \tag{120b}$$

Use of the linearity of $\mathbf{A}$, $A(\mathbf{r}+\boldsymbol{\tau})=A(\mathbf{r})+\mathbf{A}(\boldsymbol{\tau})$, allows one to verify the property (119a) by straight substitution from (120). Since the relations (119) are the only exact consequences of (118), and their derivation is elegant and short, it seems worthwhile to give it here. From the translational invariance of (116), it follows that[29]

$$\Psi_\lambda(\mathbf{r}+\boldsymbol{\tau}_i)=\exp[(ie/\hbar c)\mathbf{A}(\boldsymbol{\tau}_i)\mathbf{r}]\sum_{\lambda'}C_{\lambda'\lambda}{}^i\Psi_{\lambda'}(\mathbf{r}). \tag{121}$$

One could also obtain (121) by verifying by differentiation that if $\Psi(\mathbf{r})$ satisfies (118) for a given W, so does $\Psi(\mathbf{r})\exp-(ie/\hbar c)\mathbf{r}\mathbf{A}(\boldsymbol{\tau}_i)]$. This function must therefore be a linear combination of the eigenfunctions of H_M for a given W. This linear combination is what is written down in (121); the coefficients $C_{\lambda'\lambda}{}^i$ are just numbers; C^i is a matrix (it depends on the specific translation made). From the fact that $\Psi_\lambda(\mathbf{r}+\boldsymbol{\tau}_i+\boldsymbol{\tau}_j)=\Psi_\lambda(\mathbf{r}+\boldsymbol{\tau}_j+\boldsymbol{\tau}_i)$, one obtains, by applying (121) twice,

$$C^jC^i=C^iC^j\exp\{(ie/\hbar c)[\mathbf{A}(\boldsymbol{\tau}_j)\cdot\boldsymbol{\tau}_i-\mathbf{A})\boldsymbol{\tau}_i)\boldsymbol{\tau}_j]\}. \tag{122}$$

A change in labeling of the eigenfunctions Ψ_λ belonging to the given W changes the representation of the C's. One checks by substitution that a representation of C's

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[27] This is probably obvious from what has been said before; in detail, let λ^μ be the eigenvalues of $E(-i\nabla_\alpha)+H'(R_\alpha{}^0)$, $c_\alpha{}^\mu$ the eigenvectors. Then

$$H_{\text{total}}\Psi^\mu=H_{\text{total}}\sum c_\alpha{}^\mu\chi_\alpha=\sum\nolimits_\alpha[E(-i\nabla_\alpha)+H'(\alpha)]c_\alpha{}^\mu\chi_\alpha=\lambda^\mu\sum\nolimits_\alpha c_\alpha{}^\mu\chi=\lambda^\mu\Psi^\mu.$$

It is clear that the *eigenvalues* of the operator $E(-i\nabla_\alpha)+H'(R_\alpha{}^0)$ are independent of α; $\mathbf{R}_\alpha{}^0$ is just an independent variable in terms of which the operator may be expressed.

[28] It is obvious that Ψ is a much overused designation; an attempt has been made to distinguish between wave functions referring to different physical situations. Still, in the following discussion, M is often dropped.

[29] The sum is over all wave functions $\Psi_{\lambda'}$ belonging to a given energy W.

defined by

$$\langle \mathbf{k}|C^j|\mathbf{k}\rangle = \exp(i\mathbf{k}\boldsymbol{\tau}_j)\delta[\mathbf{k}'-\mathbf{k}+(e/\hbar c)\mathbf{A}(\boldsymbol{\tau}^j)] \tag{123}$$

satisfies (122). Use of this representation in (121) and the δ-function character yields (119a) directly. Since all the λ's refer to a definite energy, the different $\mathbf{k}$'s do likewise; $W_k = W_{k'}$. This in conjunction with the δ function in (123) yields (119b).

The further discussion of the function U is a good deal more complicated. It is certainly reasonable to exploit the known periodicity of this function and expand U in the Bloch functions $\psi_{\mathbf{k}}$, or alternately one could use an expansion in plane waves in terms of the reciprocal lattice vectors. On using the original Schrödinger equation (118), one obtains an infinite set of equations for the development coefficients. One has now arrived at the same point where the previous discussion [see Eq. (110), for example] started.[30] The results (119a) extract the exact information. Further developments are concerned with a discussion of the coupled equations satisfied by the development coefficients; one recognizes that transitions between bands again play a significant role; the development as a whole is hard to survey however. Recently Kohn [73] succeeded in giving a prescription (not a unique one) which may yield a systematic development. The starting point is again (116), H_M. Kohn succeeded in constructing an operator $\bar{H}_\beta = \bar{H}_\beta[\mathbf{p}-(e/c)\mathbf{A}]$ and a set of states $\bar{\varphi}_{\beta\mathbf{k}}$, which have the property that

$$H_M\bar{\varphi}_{\beta k} = \sum_{k'} \langle k'|\bar{H}_\beta|k\rangle\bar{\varphi}_{\beta k}. \tag{124}$$

No mixing of the bands. (Even though this result is approximate, the sense in which it is approximate is well defined.)

The functions $\bar{\varphi}_{\beta k}$ have again symmetry characteristics

$$\bar{\varphi}_\beta(\mathbf{k}+\boldsymbol{\tau}^*) = \pm\varphi_\beta(\mathbf{k}). \tag{125}$$

The operators $\bar{H}_\beta$ depend on the operator $[\mathbf{p}-(e/c)\mathbf{A}]$; they can be expanded in terms of the external field H_0[31]:

$$\bar{H}_\beta = \bar{H}_{\beta,0} + H_0\bar{H}_{\beta,1} + H_0^2\bar{H}_{\beta,2} + \cdots. \tag{126}$$

In this sense this is a weak-field development. The operators $\bar{H}_\beta$ have the important periodicity property that

$$\bar{H}_\beta[\mathbf{p}-(e/c)\mathbf{A}+\boldsymbol{\tau}^*] = \bar{H}_\beta[\mathbf{p}-(e/c)\mathbf{A}], \tag{127}$$

which is reminiscent of (104). Also, $\bar{H}_{\beta,0}$ is indeed the one-band Hamilton $E_\beta(-i\nabla)$. Thus, with the construction of the functions $\bar{\varphi}$ and the operators $\bar{H}_\beta$, one appears to have a systematic development. For some reason the actual implementation of this sound and sensible program is extremely complicated; points which one would expect to be of technical difficulty become major obstacles; one can but join Kohn [73][32] in hoping that more transparent methods to obtain these important results will in time be found.

4. *Semiclassical Description. Dispersion Law*

(*a*) *General remarks.* In the preceding sections the various assumptions and simplifications underlying the treatment of electrons in solids have been discussed. It is true that the behavior of electrons must necessarily be governed by quantum-mechanical laws; the band scheme itself is of quantum-mechanical origin. Within a band one deals with a continuum of energy levels; the wave functions of a single band allow localization of a particle of the order of lattice distances a. In dealing with phenomena where the localization is not that precise (larger than a), one could construct wave packets consisting of wave functions all in one band, which would describe the situation with sufficient accuracy. Such a wave packet, however, might well be described classically. Another argument suggesting that a pseudoclassical description might be useful is that once the Bloch energies E_β are known as a function of the wave number $\mathbf{k}$, many classical relations appear to hold; for example, the relation between (average) velocity and energy:

$$\mathbf{v} = \hbar^{-1}\nabla_k E. \tag{128}$$

[Quantum mechanically one proves that $\bar{v}_i = \hbar^{-1}\nabla_i E$; one could define a $\mathbf{v}$ by (128).] Finally, one can also think of a more fundamental approach to the whole question of the behavior of electrons in a solid. In the treatment so far the electron-electron interactions were neglected altogether. One believes that the introduction of these interactions does not affect the qualitative features of the one-electron model. In the discussion of the low-lying states of the many-body problem, it is found that the excitation spectrum of the system may be described in terms of "single-particle type" excitations. These excitations, quasi-particles, have a well-defined but not simple relation between energy and momentum. This understanding would lead one to study the classical and quantum mechanics of (quasi) particles with a given relation between E and $\mathbf{k}$, a given dispersion law, without bothering further about the origin of the dispersion law. Hence one can study a system of particles (actually quasi-particles) with a given relation between E and $\mathbf{k}$; $E_\beta = E_\beta(\mathbf{k})$ possessing the basic periodicity

$$E_\beta(\mathbf{k}+\boldsymbol{\tau}^*) = E_\beta(\mathbf{k}) \tag{129}$$

satisfying Fermi statistics. The purpose[33] of such a

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[30] One could for instance construct a solution of (118) by writing $\Psi_M = \Sigma_{k\beta}\, c_{\mathbf{k},\beta}\psi_{\mathbf{k},\beta}$ (sum over both $\mathbf{k}$ and band index). This yields an intractable set of equations for $c_{\mathbf{k},\beta}$. By expanding U, (120), one makes better use of the periodicity character of the problem.

[31] H_0 is a dimensionless parameter proportional to the external magnetic field.

[32] It is a pleasure to see an author refer to his own results as "shockingly complicated" rather than as results obviously to be anticipated.

[33] A very beautiful account of this approach is given by Lifshitz and Kaganov [74]. The discussion in this section is largely based on their presentation.

study is to find out just how macroscopic observable quantities may be expressed in terms of the attributes of the quasi-particles. The surfaces in **k** space, where $E_\beta(\mathbf{k})$ is a constant, play a significant role in the analysis. Because of the periodicity condition (129), these surfaces are repeated periodically in **k** space. The analysis of these surfaces again depends on the location of critical points [where $\nabla_k E=0$; see Sec. C.2(c)]. Near such a critical point k_0, one may expand E in a Taylor expression

$$E_\beta(\mathbf{k})=E_\beta(\mathbf{k}_0)+\tfrac{1}{2}\frac{\partial^2 E_\beta}{\partial k_\mu \partial k_\nu}(k_\mu-k_{\mu,0})(k_\nu-k_{\nu,0}). \quad (130)$$

The character of this critical point is determined by the reciprocal mass tensor

$$M_{\mu\nu}^{-1}=\hbar^{-2}(\partial^2 E/\partial k_\mu \partial k_2), \quad \mu,\nu=1,2,3. \quad (130a)$$

The constant energy surfaces even for simple dispersion laws can be extremely complicated. The purpose of many experiments is to obtain information about three surfaces. Among these, the study of the Fermi surface $E(\mathbf{k})=E_F$ is especially significant.

(*b*) *The Hamiltonian.* Consider a particle of quasi-momentum $p=\hbar k$ in an external magnetic field H_{ext}; it describes a helix of radius $r=pc/eH_{\text{ext}}$. To allow one to have a semiclassical description, certain conditions have to be satisfied:

(1) The de Broglie wavelength of the particle must be much less than r. This allows one to localize the particle among its orbit. Formally,

$$pc/eH_{\text{ext}}\gg\hbar/p. \quad (131a)$$

(2) The radius r must be much larger than the lattice constant a. [If r were smaller than a, one would need the detailed description of the periodic part $u_k(\mathbf{r})$ of the Bloch function $\psi_\beta(\mathbf{k},\mathbf{r})=e^{i\mathbf{kr}}u_k(\mathbf{r})$, for if $r\ll a$, $\psi_\beta(\mathbf{k},\mathbf{r})\cong u_k(\mathbf{r})$.]

Hence

$$pc/eH_{\text{ext}}\gg a. \quad (131b)$$

(3) The energy level separation of the levels in the field H_{ext} should be small compared to the energy of the electrons; this corresponds to the fact that the external fields produce a small perturbation of the band scheme. Formally,

$$\hbar\omega_H=\hbar(eH_{\text{ext}}/mc)\ll E_F=\text{Fermi energy}. \quad (131c)$$

These three conditions all produce a restriction on H: H should be less than $\sim 10^8$ oe. Since this is a condition which can be met (in many experimental situations) one can sensibly attempt to construct such a classical theory. The dynamics are specified by a classical Hamiltonian

$$H_{\text{cl}}=E_\beta[\hbar^{-1}\mathbf{P}-(e/\hbar c)\mathbf{A}]+e\Phi. \quad (132)$$

Here **A** and Φ are the vector and scalar potential of the external field; **P** is defined by

$$\mathbf{k}=\hbar^{-1}[\mathbf{P}-(e/c)\mathbf{A}(\mathbf{r})]; \quad (132a)$$

k is the wave vector in the Bloch theory ($\hbar\mathbf{k}$ is the crystal momentum). One further specifies that **P** and **r** are conjugate variables, and $E_\beta(k)$ is a given function satisfying the periodicity condition (129). For given **A** and Φ, the Hamiltonian equations yield, in principle, **P** and **r** as functions of the time; hence both the motion of the electron in ordinary space and that in **k** space [obtained from **P** via (134a)] are determined.

From (132) one obtains

$$d\mathbf{r}/dt=\hbar^{-1}\nabla_k E_\beta(\mathbf{k})=\mathbf{v}, \quad (133a)$$

$$\hbar\frac{d\mathbf{k}}{dt}=e\left(\mathbf{E}_{\text{ext}}+\frac{1}{c}\frac{d\mathbf{r}}{dt}\times\mathbf{H}_{\text{ext}}\right)$$
$$=e\left[\mathbf{E}_{\text{ext}}+\frac{1}{c}(\mathbf{v}\times\mathbf{H}_{\text{ext}})\right]. \quad (133b)$$

Even though these equations appear seductively similar to the Lorentz force equation, it is well to remind oneself that writing **v** in (133b) makes the formula look familiar, but it is of no help in solving the problem. To do that one must use the complicated dependence of E_β on **k** in both (133a) and (133b). With Eqs. (132) and (132a) [and (133a) and (133b)] one has a complete classical dynamical description for the behavior of electrons (quasi electrons) in crystals of given dispersion law. The character of the crystals is contained in the form of $E_\beta(\mathbf{k})$. This classical system cannot be solved in general for an arbitrary dispersion law. Interesting and important results can be obtained in special cases [75].

Let $\mathbf{H}_{\text{ext}}=0$; $\mathbf{E}_{\text{ext}}=E_x=\text{const}$. Equation (133b) now becomes $\hbar dk_x/dt=eE_x$, $dk_y/dt=dk_z/dt=0$; hence,

$$k_x-(eE_x/\hbar)t=\text{const}. \quad (134a)$$

The x component of (133a) yields $dr_x/dt=\hbar^{-1}\partial E_\beta/\partial x$, or

$$r_x(t)-r_x^0=\frac{1}{\hbar}\int_0^t dt\frac{\partial E_\beta}{\partial k_x}=\frac{1}{\hbar}\int_{k_x^0}^{k_x}\frac{\partial E_\beta}{dx_x}\frac{\quad}{\partial k_x}dk_x$$
$$=\frac{1}{eE_x}[E_\beta(k_xk_yk_z)-E_\beta(k_x^0,k_y,k_z)]. \quad (134b)$$

k_x^0 and r_x^0 are the x components of the initial wave vector and position vector. Equation (134) describes the motion of the electron in k space as well as position space. Assume that the crystal is such that the x direction (field direction) is one of the directions of the reciprocal lattice, let its magnitude be a^*. Then the fundamental periodicity requirement (129) reads

$$E_\beta(k_x+a^*,k_y,k_2)=E_\beta(k_xk_yk^2).$$

From (134a) one sees therefore that in a time T,

$$T=\hbar a^*/eF_x\cong\hbar/eaE_x. \quad (135a)$$

k_k has changed by an amount a^*, hence the energy E_β returns to its initial value; k_x in turn has moved to an equivalent point k_x+a^*; in this sense the motion is periodic in k space. One observes similarly from (134b) that after a time T, because of the periodicity of E_β, $r_x(T)=r_x^0$, the motion is also periodic in position space. The amplitude A of the oscillation may be obtained from (134b) as

$$A=\Delta E_\beta/eE_x, \quad \Delta E_\beta=\text{bandwidth}. \tag{135b}$$

Thus one concludes that the motion of an electron in a crystal in a constant field (in the direction of a reciprocal lattice vector) is periodic with an amplitude given by (135b) and a period given by (135a). This is strikingly different from the behavior usually expected of an electron. One, however, does not see these oscillations; for typical fields E_x, say of 1 v/m, one finds $A\sim 100$ cm, and $T=10^{-5}$ sec. In a normal situation the time between collisions is of the order 10^{-12} sec, hence the oscillatory motion described never gets a chance to be established—the collisions destroy the oscillatory motion. Excessively high fields would be needed to make T sufficiently small so that many oscillations could take place before a collision would destroy the periodic motion. As a second example, consider the case where $\mathbf{H}_{\text{ext}}=\text{constant}$, $\mathbf{E}_{\text{ext}}=0$. This case is of great practical importance. Equation (133b) becomes in this case

$$d\mathbf{k}/dt=(e/\hbar c)[\mathbf{v}\times\mathbf{H}_{\text{ext}}]. \tag{136}$$

From (136) one sees that $\mathbf{v}d\mathbf{k}/dt=0$; hence

$$\int_{t_1}^{t_2}\mathbf{v}\frac{d\mathbf{k}}{dt}dt=0=\int(\nabla_k E_\beta)d\mathbf{k}; \quad (E_\beta)_1=(E_\beta)_2.$$

This implies that the quantity $E_\beta(\mathbf{k})$ remains constant during the motion in k space, or the motion takes place on a constant energy surface. From (136) one observes further that (for constant external fields) $(d/dt)[\mathbf{H}_{\text{ext}}\cdot\mathbf{k}]=0$; during the motion the component of $\mathbf{k}$ in the direction of the field remains constant. Pick $\mathbf{H}_{\text{ext}}=H_z$. One then knows that the trajectory must have constant k_z and constant $E_\beta(\mathbf{k})$; it must be the intersection of a surface of constant energy with a plane parallel to the k_xk_y plane. It is clear that the nature of the intersection depends on the nature of the energy surface. If the energy surface is simply connected, this intersection is closed curve. (This is one of the defining characteristics of a simply connected surface.) In general, one needs a picture of the energy surfaces as they repeat from zone to zone to study the intersections and hence the trajectories in k space. Since the trajectories are in planes perpendicular to the field direction, it follows that by varying the field directions relative to the crystallographic axes, one samples different slices of the energy surface. In so doing, one may obtain closed orbits within a zone, open orbits, or closed orbits extending over several zones. For the case $\mathbf{H}_{\text{ext}}=H_z$, Eq. (136) reduces to

$$dk_x/dt=(e/\hbar c)v_yH_z, \quad dk_y/dt=-(e/\hbar c)v_xH_z, \quad dk_z/dt=0. \tag{137}$$

The element of arc length along this trajectory is given by $(ds)^2=(dk_x)^2+(dk_y)^2$. In the course of time the electron in k space moves along this trajectory (since $k_z=\text{constant}$, this is a plane curve):

$$(ds/dt)=(cH_z/\hbar c)(v_x^2+v_y^2)^{\frac{1}{2}}\equiv(eH_z/\hbar c)v_\perp. \tag{138}$$

If one now knows that the orbit is closed (this is *not* determined by the dynamics but rather by the nature of the dispersion law), the motion is periodic, and (138) yields for the period

$$T_H=\frac{\hbar c}{eH_z}\oint\frac{ds}{v_\perp}=\frac{\hbar^2c}{eH_z}\oint\frac{ds}{[(\partial E/\partial k_x)^2+(\partial E/\partial k_y)^2]^{\frac{1}{2}}}. \tag{139}$$

The integral is along the trajectory. As it stands, (139) is not useful, since $v_\perp$ depends on $\mathbf{k}$ in a complicated manner through the dispersion law and (133a). Equation (139) may be transformed. Suppose one has an ordinary two-dimensional integral to be integrated over a region bounded by a curve C, defined by $f(x,y)=C$. The area $A(C)=\int\int dxdy$. If ds is the element of length of a curve $f(x,y)=\lambda$ (a level curve), the area may be written as

$$A(C)=\int\int dxdy=\int\int d\lambda\frac{ds}{\nabla f}=\int_0^C d\lambda\oint\frac{ds}{[(\partial f/\partial x)^2+(\partial f/\partial y)^2]^{\frac{1}{2}}}, \tag{140}$$

which may be directly applied. Let $S(E_\beta,k_z)$ be the area contained in the closed curve,[34] then applying (140) in a differential form yields

$$\frac{\partial S}{\partial E}=\oint\frac{ds}{v_\perp} \tag{140a}$$

which, when combined with (139), gives

$$T_H=(\hbar^2c/eH_z)(\partial S/\partial E). \tag{141}$$

For free electrons, one has closed orbits; the frequency of the oscillations is given by eH_z/mc; in the present case, oscillations (for certain electrons in any case) again occur. Define, therefore, an effective (cyclotron) mass m^* by

$$\omega_H=2\pi/T_H=eH_z/m^*c, \tag{142}$$

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[34] This closed curve is the intersection of the energy surface $E_\beta(k)=E_\beta$ with the plane k_z is constant.

so that

$$m^* = (\hbar^2/2\pi)(\partial S/\partial E). \tag{142a}$$

Equations (141) and (142) are the basic relations needed for the interpretation of cyclotron resonance experiments. It is clear that with the observation of the resonance frequencies ω, one determines effective masses, and via (142a) one obtains information about the surface of constant energy. In practice, one often gives a dispersion law, say of the type (130), computes $S(k_z)$ (a purely geometrical calculation), and then determines the coefficients m_{ij} by direct comparison with experiment through (142). One should remember that this definition of effective mass works only for *closed* orbits; no analogous definition exists for open orbits. It should also be remembered that m^* depends on E_β and k_z; hence, different electrons carry out different periodic motions. These two cases discussed probably are sufficient to indicate the general character of these semiclassical methods. The basic equations are always (132), and although in principle everything is straightforward, the periodic character of E_β and the resulting involved nature of the energy surfaces give rise to a wealth of unusual situations and unexpected physical phenomena. Angular dependence of resonance frequencies would be in this class. The semiclassical discussion is essential for whatever understanding one has of these complicated effects.

Other effects, notably the various oscillatory effects, also can be treated by similar methods. In most of those phenomena, quantum effects play a predominant role, and hence the semiclassical discussion has to be supplemented by quantum ideas. This can be done; one can graft quantum rules onto the classical formalism outlined so far. For the de Haas-van Alphen effect, this is a powerful method of description. The actual formalism is of a hybrid character; the dispersion law is quantum mechanical in origin. One then constructs a semiclassical theory based on it and applies Sommerfeld-Wilson type quantum rules to that pseudoclassical theory. It is certain that the resulting formalism has considerable heuristic value. Its status within the general solid-state framework is unclear. For the same reason it would appear unclear just what one can expect from a precise quantum-mechanical theory based on an arbitrary dispersion law. For the qualitative features, a classical theory with quantum rules should be sufficient; for finer details one would expect that a theory of more fundamental character is needed. It may well be that from the many-body approach mentioned previously, one may obtain the approximate validity of such a quantum description with arbitrary dispersion law.

5. *Fundamental Considerations*

(*a*) *Many-body approach.* There can be no doubt that the concepts introduced through the one-electron approximation have shown a surprising power to describe experimental situations. It is therefore of great importance to understand these concepts on a more fundamental basis. The first systematic study of this kind was undertaken by Kohn [76]. The purpose of this particular paper was to give a fundamental explanation of the effective mass notion. The precise result proven was the following: Consider a perfect insulating crystal with fixed nuclei. Introduce a point charge q and an additional electron. The assertion is now that all the low-lying energy levels of the complete system are obtained from a one-particle Schrödinger equation,

$$[-(\hbar^2/2m^*)\Delta - (eq/k^*M)]F = EF. \tag{143}$$

Here m^* is the effective mass and k^* the dielectric constant. It is of interest to point out the starting point of these considerations. It is provided by the many-body Hamiltonian

$$H = -\sum_{i=1}^{N+1} \frac{\hbar^2}{2m}\Delta_i - \sum_{\alpha,i} \frac{e^2 Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha^0|} + \tfrac{1}{2}\sum \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - qe\sum_i \frac{1}{r_i} + \sum_\alpha q\frac{Z_\alpha}{R_\alpha^0}. \tag{144}$$

In H one recognizes the kinetic energy of $(N+1)$ electrons, their interaction with fixed nuclei (second term) (Z_α is the nuclear charge number), and their Coulomb interaction. The point charge q causing the perturbation, placed at the origin, contributes the last two terms in (144). One studies the low-lying energy levels of H. There is no effective mass, no dielectric constant in H. One would hope that such type entities arise more or less naturally in the discussion. It is indeed true that these quantities do arise, but their identification with the conventional definition is far from easy (Kohn [77]). The result of Kohn may be generalized still further (Klein [78]). The response of a solid plus one electron, described previously, to an electromagnetic field $A_\mu(\mathbf{r},t)$ may for low-lying excitations be described by a one-particle Schrödinger equation, involving three parameters m^*, k^*, and the magnetic permeability. For this to be true, the external fields must be slowly varying over distances of the order of lattice spacings a, $(1/A_\mu)\nabla A_\mu \ll 1/a$, and slowly varying in time, $(1/A_\mu)(\partial A_\mu/\partial t) \ll \Delta E/\hbar$, where ΔE is some characteristic energy. Low-lying excitation means more precisely that the energy difference between ground state and excited states is less than ΔE. ΔE is of the order of electron volts.

The results of Kohn and Klein are of great interest; that all the complicated interactions exhibited in (144) are digested so as to just yield a one-particle equation with two parameters is surprising and remarkable. This is the basic justification of the one-electron picture. The proofs are rather complicated and as yet not too transparent. But a most promising beginning has been made in the derivation of one-particle properties on a sound basis.

(*b*) *Fermi surface.* The Fermi surface has been mentioned several times. The Fermi level E_F was defined by

$$n=2\int_0^{E_F} g(E)dE; \qquad (145)$$

however, no precise definition of the Fermi surface was given. One usually describes this surface as representing the limit of occupation in $\mathbf{k}$ space of the one-particle quasi-momentum states $\mathbf{k}$ in the ground state of the the system [79]. All states with momenta less than the Fermi momentum are occupied, all others are empty. The question is how to formulate just what is meant by a Fermi surface for a system of interacting fermions. It is known that for noninteracting particles at absolute zero the number of particles as a function of k exhibit a singularity. (This is the well-known graph of f_0 for complete degeneracy.) The effect of a finite temperature is to destroy that discontinuity. To define a Fermi surface generally, for a system of interacting fermions with a Hamiltonian [80]

$$H=H_0+H_1, \qquad (146)$$

one must first state what is meant by "number of particles in a given state." A precise definition of this would be the mean occupation number of the state k, or the ensemble average of the number operator $a_k^\dagger a_k=n_k$,

$$\bar{n}_k=\langle\langle a_k^\dagger a_k\rangle\rangle. \qquad (147)$$

The a's and $a^\dagger$ are the usual annihilation and creation operators of particles in state k, $\bar{n}_k$ depends on the temperature through the ensemble average. Now the Fermi surface is defined as the locus of the discontinuities of $\lim_{T\to 0}\bar{n}_k$ (Luttinger [81]). It was shown by Luttinger that the volume enclosed by this locus is the same as that enclosed by the Fermi sphere for noninteracting electrons. In the case of no interaction, this definition also reduces to the usual one. It is satisfactory that one can give a precise meaning to the Fermi surface even in the case of interacting particles, but perhaps disillusioning that one needs a rather high-brow formalism (grand ensemble in a second quantized theory) to give a precise definition of the Fermi surface.

LITERATURE SURVEY AND BIBLIOGRAPHICAL NOTES

1. R. C. Tolman, *The Principles of Statistical Mechanics* (Clarendon Press, Oxford, England, 1938), Chap. IV. The discussion in this classic work is based on the ensemble (Gibbs) formulation of statistical mechanics. In particular, the treatment of the Maxwell-Boltzmann distribution is based on considerations of the microcanonical ensemble. A leisurely and careful discussion. No applications can be found in this work.
2. J. de Boer, "Molecular distribution and equation of state of gases," Repts. Progr. in Phys. **12**, 325 (1949). An excellent review of the uses of the canonical partition function both classically and quantum mechanically. The calculation of the molecular pair-distribution function and its comparison with experiment as obtained from x-ray scattering is given in detail. Although newer treatments, the use of the grand ensembles and graphical methods, have in some sense replaced this type of discussion, this is still one of the best and most readable treatments of the subject.
3. R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, New York, 1936). A very detailed, meticulous treatment. The partition function is evaluated in detail for a large number of special systems. Comparison with experiment is carried out. Although the book is beginning to show its age (1936), it contains a host of useful analytical techniques and many examples.
4. T. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chaps. I, V, and VI. Distribution functions are discussed in a very complete fashion in Chap. VI. The chapter on condensation treats the by now classical condensation theory of Mayer, Kahn, and Uhlenbeck. Some comments on the recent work of Yang and Lee and van Hove make this chapter a useful introduction to the study of the current literature on condensation theory.
5. D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954). This book gives a straightforward and usable discussion of selected topics in statistical mechanics. Chapter II discusses the Maxwell-Boltzman distribution, part B contains ensemble theory. The discussion of condensation phenomena is quite abbreviated and not as modern as that given in reference 4. The bibliographical notes are interesting and instructive.
6. S. Chapman and T. G. Cowling, *Mathematical Theory of Non-Uniform Gasses* (Cambridge University Press, New York, 1939), Chap. III. One of the few works exclusively devoted to nonequilibrium theory. Great detail is given in the calculation of the distribution function of nonequilibrium states. The Boltzmann equation is given for many different physical situations. The notation used does not make the book easily readable, but many examples and the meticulous detail given make it unique. There is no discussion of any of the conceptual problems of statistical mechanics.
7. Reference 5, Chaps. I and II. Special forms of the Boltzmann equation are given.
8. Reference 5, Appendix I, this is one of the most easily accessible places where the conceptual problems of statistical mechanics are discussed. The discussion given is based to a large extent on the classic work of P. and T. Ehrenfest [*Encyklopadie der Mathematischen Wissenschaften* (Leipzig and Berlin, 1911), Vol. IV, part 32. English translation: M. J. Moravcsik (Cornell University Press, Ithaca, New York, 1959). In addition, a discussion of, and references to, the mathematical problems raised by these statistical questions is presented. Although somewhat sketchy, the general flavor of the questions involved may be appreciated from a reading of this appendix.
9. G. E. Uhlenbeck, Higgins Lectures at Princeton University, Princeton, New Jersey, 1954 (unpublished). This contains the most complete exposition of the ideas underlying the master equation approach. Some general comments are contained in Appendix I of M. Kac, *Probability and Related Topics in Physical Sciences* (Interscience Publishers, Inc., New York, 1959). The use of the master equation is by now quite current, so it is a little unfortunate that there appears to be no systematic exposition available. The earliest formulation of this approach is given by A. Nordsieck, W. E. Lamb, and G. E. Uhlenbeck [Physica **7**, 344 (1940)], in connection with the statistical theory of cosmic-ray showers.
10. A. J. F. Siegert, Phys. Rev. **76**, 1708 (1949). In this paper it was demonstrated that on the basis of Eq. (12) alone, as $t\to\infty$, $P(n_1\ldots n_i\ldots)$ approaches the equilibrium distribution function.
11. M. Kac, "Foundation of kinetic theory," in 3rd Berkeley Symposium on Math. Statist. Univ. of Calif. 171 (1956). The mathematical aspects of a model-type master equation are studied. Especially illuminating is the investigation of the

relationship between the *linear* master equation and the nonlinear Boltzmann equation.

12. Reference 2, pp. 318–321. An extremely readable discussion of this question is given.
13. Reference 4, pp. 15–17.
14. Reference 1, Chap. VI, pp. 165.
15. Reference 5, Appendix I, p. 364.
16. J. Kirkwood, J. Chem. Phys. **14**, 180 (1946). In this paper, Kirkwood first introduced the idea that in time-dependent situations, one should identify Q (obs) *not* with the ensemble average of Q, formula (21) in the text, but rather with the ensemble average of the time average of Q. If Q is written as $Q(p,x)$ and W_N as $W_n(p,x,t)$ (p and x stand for *all* momenta and coordinates), one first defines the time-averaged phase space density
$$\tilde{W}_N(p,x,t)=\frac{1}{\tau}\int_0^\tau W_N(x,p,t+s)ds, \tag{A1}$$
then
$$\tilde{Q}_{\text{obs}}=\int\int dpdxQ(p,x)\tilde{W}_N(p,x,t). \tag{A1a}$$
This time-smoothing operation has played an important role in the subsequent development. In general (say for a function f_s), the time- and ensemble-averaging procedures are *not* commutative.
17. Reference 4, p. 9. Discussion of Kirkwood's [16] averaging procedure.
18. R. Brout, Physica **22**, 509 (1956). A systematic attempt to derive Kac's master equation [11] from the Liouville equation. The main assumptions are listed in Table II. Actually, several limits are involved, $N\rightarrow\infty$ $\Omega\rightarrow\infty$ $N/\Omega=c$, also $c\rightarrow 0$ $t\rightarrow\infty$; ct is fixed. The result is surprising—only for certain initial distributions of the master equation does the Boltzmann equation describe the approach to equilibrium. These special "factorized" distributions are defined by Kac [11]. Roughly speaking, they have the property
$$f_s(\mathbf{x}_1\mathbf{p}_1\cdots\mathbf{x}_s\mathbf{p}_s,0)=\prod_{i=1}^{s}f_1(\mathbf{x}_i\mathbf{p}_i,0). \tag{A2}$$
Whether "most" (in some sense to be defined) initial distributions have this property is not known.
19. M. S. Green, J. Chem. Phys. **25**, 836 (1956). A derivation of the Boltzmann equation is presented, starting from the Liouville hierarchy, for a spatially uniform system. The basic assumption is a product-type decomposition of cluster functions, similar to the well-known product property in equilibrium theory. One then makes an expansion in the concentration.
20. J. Kirkwood and J. Ross, in *Transport Processes in Statistical Mechanics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1958), p. 1. A more detailed derivation of the Boltzmann equation, from the Liouville hierarchy. Time averaging, which is not used in the Brout [18] and Green [19] studies, is explicitly used. The same volume also contains brief résumés of references 18 and 19, as well as interesting discussions (pp. 19–21) concerning the equivalence or lack of equivalence of these various procedures. There does not at this moment appear to be unanimity concerning this point, nor is it clear how these methods can be extended to apply to other systems.
21. Reference 4, p. 213. References to numerical work checking the accuracy of the superposition approximation in equilibrium situations are given. For the case of a hard-sphere gas, the exact value of the virial coefficients is known; computations using the superposition approximation give the second and third virial coefficient exactly; the fourth virial coefficient is off by about 20%.
22. I. Prigogine and M. Klein, Physica **19**, 74 89 (1953). The validity of the superposition approximation is studied for the special case of the relaxation of a linear chain from a variety of initial configurations. It is found that this principle is valid for equilibrium situations [cf. however, (21)], but generally not valid for nonequilibrium situations. Dissipation effects in particular are *not* included in the Liouville hierarchy—even if this hierarchy is supplemented with the superposition assumption.
23. N. Bogoliubov, J. Phys. U.S.S.R. **10**, 265 (1946).
24. Reference 9. An extensive exposition of the ideas of Bogoliubov [23]. A further systematic presentation can be found in Proc. Midwest Conf. Theoret. Phys., Washington Univ., St. Louis, Missouri (1958). Actual use of the procedure outlined by Bogoliubov—such as corrections to the Boltzmann equation due to triple collisions—was made by S. T. Choh (dissertation, University of Michigan, Ann Arbor, Michigan, 1958).
25. H. Grad, in *Handbuch der Physik* edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 12. A very interesting review of many aspects of kinetic theory. The different levels on which one can study the Boltzmann equation are noted. There is (pp. 216–233) a careful study of the mathematical features of the various derivations of the Boltzmann equation. The doubtful character of the various limiting processes is pointed out. This critique appears to indicate (as does the text) that only applications to new physical situations will enable one to decide which one (if any) of the current procedures is the appropriate one.
26. Reference 1, Chap. X. A detailed description of the properties of the Einstein-Bose and Fermi-Dirac distribution laws.
27. Reference 3, Chap. II.
28. Reference 4, Secs. 9 and 10. The treatment given in this book has been used liberally in the discussion in this paper. Although the details are different, the philosophy used in this book and the present paper are certainly similar.
29. Reference 2, pp. 314. A succinct statement of the density matrix ideas. The discussion of the consequences of the canonical density matrix is particularly nice.
30. Reference 1, Chap. XII. A very meticulous discussion of the basis on which one picks an ensemble. The justification of the ensemble is discussed at length.
31. Reference 4, Sec. 11.
32. Reference 2. Choice of the energy eigenfunctions u_n as an orthogonal set yields a diagonal density matrix in an "energy representation" only, see (41b), but in the q representation one obtains
$$\rho(q',q'')=\frac{1}{Z}\sum_n u_n^*(q'')e^{-\beta E_n}u_n(q') \tag{A3}$$
which is *not* diagonal.
33. A. J. F. Siegert, J. Chem. Phys. **20**, 572 (1952). This paper uses the function $Z(q',q'',\beta)$ [cf. (42)] to give an alternate expansion of the partition function. Consider a Hamiltonian $H=H_0+H_1$, and let u_n and u_n^0 be eigenstates of H and H_0, respectively; E_n and E_n^0 are the energy eigenvalues. Define
$$Z(q',q'',\beta)=\sum_n u_n^*(q'')e^{-\beta E_n}u_n(q') \tag{A4a}$$
$$Z^0(q',q'',\beta)=\sum[u_n^0(q'')]^*\exp(-\beta E_n^0)u_n^0(q'). \tag{A4b}$$
Now reference 33 establishes a connection between Z and Z^0:
$$Z(q',q'',\beta)=Z^0(q',q'',\beta)-\int_0^\beta d\lambda\int dqZ^0(q',q,\beta-\lambda)H_1(q)Z^0(q,q'',\lambda). \tag{A5}$$
This integral equation may be iterated and one obtains a development identical to the one described in the text [see (46)], but for $Z(q',q'',\beta)$ rather than for the operator R.
34. E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) **A210**, 173 (1951). In this paper an *exact* expression for the partition function of free electrons in a constant magnetic is obtained. Since $Z(q',q''\beta)$ satisfies Eq. (43a), which is in this case just the Schrödinger equation for a free electron in a constant magnetic field, which can be solved, one can find $Z(q',q'',\beta)$; hence, by (43c), one can obtain $Z(\beta)$.

35. T. Nakajima, Advances in Phys. 4, 363 (1955). A very nice treatment of some of the perturbation procedures current in statistical mechanics. The discussion here is basically a repetition of a part of this paper. There are occasional nontrivial misprints; some have been noted in the text.
36. G. E. Uhlenbeck and Th. Uehling, Phys. Rev. **43**, 552 (1933). In this paper, the collision term in the Boltzmann equation was written in the form (58). The Bose-Einstein case was also discussed. The solution of the equation was obtained as an expansion similar to Chapman and Enskog development (see reference 6, Chap. VII).
37. Reference 1, pp. 436. All the possible details of this perturbation calculation are given.
38. M. Born and H. S. Green, Proc. Roy. Soc. (London) **A192**, 166 (1947). This is one of a series of papers devoted to the study of the Liouville hierarchy. This particular paper is concerned with the quantum-mechanical Liouville hierarchy, using the reduced density matrices. Although generally the method is similar to that sketched in the text, Born and Green do not (at least not explicitly) introduce any time averaging or coarse graining. Since the Liouville hierarchy is equivalent to the dynamical equations, and as such completely reversible, the introduction of irreversibility in their formalism must result from the mathematical approximations made. It would appear preferable to introduce the probability notions needed to obtain irreversibility in a more explicit manner. That different time scales are essential in obtaining rate equations is not at all clear from this formalism.
39. E. Wigner, Phys. Rev. **40**, 749 (1932). The introduction of the function W_Q, the derivation of the equation W_Q satisfies, and the classical limit all are contained in this remarkable paper, which remained unquoted until about 1946.
40. J. H. Irving and R. W. Zwanzig, J. Chem. Phys. **19**, 1173 (1951). This paper contains a proof of the general validity of Eq. (64); the formalism presented in the text is similar to the one developed in this reference. The formal equations of hydrodynamics are also obtained. [The possibility of using the Wigner function for this purpose was pointed out earlier by M. Dresden, Phys. Rev. **71**, 143 (1947).] If one does not invoke any time smoothing, the Wigner function formalism gives the same results as the reduced density matrix method [38].
41. J. Kirkwood and J. Ross, J. Chem. Phys. **22**, 1094 (1954). The Uhlenbeck-Uehling equation is derived from the Wigner function formalism. One first introduces $\tilde{W}_Q$, the time-smoothed Wigner function (68), then one obtains an equation for reduced distribution function $\tilde{f}_{1,Q}$. If one now has a dilute system, and if one is allowed to make a Born approximation to describe the scattering, one may reproduce the Uhlenbeck-Uehling equation. It is unlikely that this equation has a range of validity beyond the Born approximation. So far no explicit calculation of the extra terms expected for dense, strongly interacting systems have been made.
42. F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940). Although the discussion of the adiabatic approximation on p. 470 is rather brief, it is still one of the best discussions available. The fact that a given accuracy of an energy does not imply a comparable accuracy of the wave function is stressed. This is an important point. Apart from the general observation that the validity of the adiabatic approximation is tied to the small value of m/M, no further validity criteria are mentioned.
43. R. E. Peierls, *Quantum Theory of Solids* (Clarendon Press Oxford, England, 1955). A very nice qualitative discussion of the validity of the adiabatic approximation (p. 4). The criterion (77) is mentioned there. Although this is well known, there seem to be very few places where this limitation is explicitly stated. The treatment of the book as a whole is of a rather refined simplicity. No formal aspects of the adiabatic approximation are discussed.
44. W. Pauli, "Prinzipien der Wellenmechanik," in *Handbuch dre Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1934), Vol. 24, p. 163. Pauli obtained these equations to illustrate quantum mechanical problems in which one has a dependence on outside parameters.
45. G. Wannier, *Elements of Solid State Theory* (Cambridge University Press, New York, 1959). The theorem of Bloch referred to is discussed in many solid-state books. This book has both a nice selection of topics as well as an interesting treatment. The Bloch theorem and the tight binding approximation are discussed (pp. 133–136 and 159) in a very straightforward manner.
46. J. R. Ziman, Proc. Cambridge Phil. Soc. **51**, 707 (1955). If one uses the wave function $\Psi(r,R)=\varphi(R)\psi_n(r,R)$, Eq. (72) in the text, with $\psi_n(r,R)$ satisfying (71), one finds an equation φ has to satisfy. There are terms coupling ψ and φ, the A and B terms in (74). It is shown in this paper that if these terms are used in a perturbation calculation, then in first order the matrix elements of transition (or the electron-phonon scattering amplitude) are the same as in the usual theory, using the Bloch perturbation terms, (82c).
47. A. Haug, Z. Physik **146**, 75 (1956). A discussion of the adiabatic approximation. In the notation of the text, the unperturbed states are given by products of ψ_n and $\varphi_{n,\mu}{}^0$:

$$\left(-\frac{\hbar^2}{2m}\sum_i \Delta_i+V_e(r,R)\right)\psi_n=\epsilon_n(R)\psi_n. \tag{A6}$$

Here V_e includes V and U:

$$\left(-\frac{\hbar^2}{2M}\sum_\alpha \Delta_\alpha+\epsilon_n(R)\right)\varphi_{n,\mu}{}^{(0)}=E_{n\mu}\varphi_{n\mu}{}^{(0)}. \tag{A7}$$

Hence unperturbed states are $|n,\mu\rangle=\Psi_{n\mu}{}^{(0)}=\psi_n(r,R)\times\varphi_{n\mu}{}^0(R)$. The terms A and B are again treated as a perturbation. These perturbations couple the electronic states, described by $|n\rangle$ and the lattice states described by $\varphi_{n,\mu}{}^0$. As always, the perturbation causes transitions changing both the electronic and lattice states. A typical transition matrix element would be [see (74)].

$$-\frac{\hbar^2}{2M}\int\int drdR\psi_n{}^*(r,R)[\varphi_{n\mu}{}^0(R)]^* \times\sum_\alpha (2\nabla_\alpha\varphi_{n'\mu'}{}^0\nabla_\alpha\psi_{n'}+\varphi_{n'\mu'}{}^0\Delta_\alpha\psi_{n'}). \tag{A8}$$

This matrix element can be reduced further using (A7) and (A6). If one in particular assumes that $\int dr\psi(r,R)$ is independent of R and if one makes again a Taylor expansion, one can write this matrix element as

$$\int\int drdy\psi_{n'}{}^*(r)\varphi_{n'\mu'}{}^0(y)(\mathbf{y}\cdot\nabla V_e)\psi_n(r,y)\varphi_{n\mu}{}^0(y), \tag{A9}$$

which one recognizes as a matrix element of (82c) between product states of lattice and electrons. Thus references 47 and 46 both show that a consistent application of the adiabatic approximation and the more common Bloch perturbation term (82c) give the same result in first order.
48. Reference 45, Chap. I. A very readable description of the geometric of the periodic lattices.
49. C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1953), Chap. I.
50. J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955). The relation between the frequencies Ω and ω is derived in this paper. The starting Hamiltonian is obtained—it is very similar to (82). The Hamiltonian is written in second quantized form; for the derivation of the relations between ω and Ω and the phonon-electron matrix element, use is made of the transformation to collective coordinates. A significant paper, but not an easy one to read.
51. A. Kitano and H. Nakano, Progr. Theoret. Physics (Kyoto) **9**, 370 (1953). The Taylor development alluded to in the text was carried out in this paper. This is a rather straightforward

matter. The paper calls attention to the difference between ω and Ω in connection with problems in superconductivity. Again a transformation to collective coordinates is made to obtain the relation between ω and Ω. (The paper is full of misprints!)

52. Reference 50. The calculation mentioned in the text is carried out in Appendix A of this paper.
53. A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1958), 2nd ed. Chapter II gives a nice simple yet precise discussion of the results one can obtain from the study of a Schrödinger equation with periodic coefficients such as (86). The treatment here as in later chapters is lucid and to the point.
54. Reference 42, Chap. VIII. A compact and straightforward discussion of the qualitative and quantitative features of the band approximation can be found here. In particular, the connection between zone structure and crystal symmetry alluded to in the text is obtained in a direct manner.
55. J. R. Reitz, "Methods of the one electron theory of solids," in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 1. This is a complete and easily readable exposition of the various methods available for the calculation of electron wave functions in solids. The treatment is sufficiently detailed so that it can be followed by any person who has mastered the material in a typical solid-state textbook.
56. F. Herman, Revs. Modern Phys. **30**, 102 (1958). A thoughtful and interesting discussion of the physical assumptions underlying band theory. The discussion given in the text was influenced to a considerable extent by this reference. The various methods employed are briefly outlined (not in the detail of reference 55. The illustrative examples of band structure are of special interest since they demonstrate how a combination of theoretical and experimental methods may be used to obtain quite definite information about the band structures.
57. J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960). This book appeared while the present paper was in preparation. The general topic is the theory of transport phenomena in solids. It stops short of an application of density matrix techniques to transport processes, which is the main concern of this paper, but treats the theory up till that point in detail. It seemed natural in a way to use this work as a general reference of the pre-density matrix work and base the remainder of this paper in it. Parts I and II of the present paper could then have been eliminated. It became soon apparent that Part I.B, statistical mechanics, would have to be retained in entirety; part of the interest in transport phenomena in solids is based in the unusual problems in statistical mechanics they present. This feature is absent in reference 57. Several sections of Part I.C also would have to be retained. The greatest duplication occurs in Part II, but even there the difference in the discussion of details and the difference in basic philosophy is so large that a separate treatment seemed justified. In spite of these differences, reference 57 is exceedingly useful. Not the least reason for this is the detailed careful comparison made between theory and experiment. Section 2.12 contains a thorough discussion of the electronic properties of the elements. The conclusion substantiates what has been mentioned in the text: the band structure depends to an unfortunate extent in the form of the atomic potential. In this connection the absence of an iterated solution of the Hartree-Fock equation for a solid is noted.
58. Reference 53, Sec. 1.81 and Appendexes A-3 and A-4. The needed properties of the integrals are given.
59. Reference 53, p. 164. The discussion in the text is essentially the same as that contained in this reference.
60. R. C. O'Rourke and A. W. Saentz, Revs. Modern Phys. **27**, 381 (1955). An extensive discussion of formulas such as (94) in the text. The partition function is expanded using the same expansion as given in Sec. B, Eq. (48). The effects of walls are discussed with unusual care. Applications are to free electrons in a constant magnetic field, reproducing the results of reference 34. These results are exact. Applications, using approximation procedures are made to electrons in a periodic field and outside magnetic field.
61. Reference 45, pp. 63–65. A simple discussion of the vibrations of crystal lattices is given.
62. L. van Hove, Phys. Rev. **89**, 1189 (1953). In this fundamental paper the connection between the periodicity of the frequency and the existence of critical points was first explicitly stated, invoking the use of a theorem due to Morse. The relation between the singularities in $g(\omega)$ and the critical points is also pointed out.
63. H. Rosenstock, Phys. Rev. **97**, 290 (1955). A detailed discussion of reference 62; applications of the considerations of reference 62 to specific lattices. A method is proposed for obtaining the critical points, in reference 62 just statements about their existence were made.
64. H. Rosenstock, J. Phys. Chem. Solids **2**, 44 (1957). An attempt is made to relate the number of three-dimensional saddle points, maxima and minima, in a region to the number of two-dimensional critical points on the boundary. See, however reference 65.
65. J. C. Phillips and H. B. Rosenstock, J. Phys. Chem. Solids **5**, 288 (1958). A sequel to the study of reference 64, showing that the results derived therein are not always correct. However, relations of this general type can be shown to exist.
66. A. A. Maradudin, P. Mazur, E. W. Montroll, and G. H. Weiss, Revs. Modern Phys. **30**, 175 (1958). A beautiful discussion of the lattice vibrations of diatomic lattices. Pertinent is a brief but simple exposition of the ideas of reference 62 as well as a two-dimensional illustration of the theorem of Morse (which is the mathematical basis of the whole development).
67. Reference 53, p. 29. Actually, any book on solid-state theory contains the formulas (106).
68. Practically the identical argument is used in reference 57, pp. 93–95. It is stated there that there is no *experimental* evidence for a lack of validity of equations such as (109) or (116a). This indeed is the case. Yet it is of interest to investigate the precise status of such equations within the theory.
69. J. M. Luttinger, Phys. Rev. **84**, 814 (1951). The equivalence proven by Luttinger in this paper is in fact the one between (116) and (116a). The proof given in the text is an adaptation of that method for the simpler situation of just an external electric field.
70. J. C. Slater, Phys. Rev. **76**, 1592 (1949). A theorem equivalent to (115) was first stated and proved in this reference. Wannier functions were used for this purpose for the first time. Actually reference 69 is an extension of the methods of reference 70 to the magnetic case.
71. Reference 45, p. 200.
72. P. G. Harper, Proc. Phys. Soc. (London) **A68**, 879 (1955). The derivation of the relation (119) is copied directly from Harper's paper. The function u is expanded in Fourier plane waves. The equations coupling the Fourier coefficients are studied in detail for the case where the lattice potential is sinusoidal. One of the results obtained is that the lattice forces tend to broaden the magnetic levels. The level separation is also affected by the lattice; it is no longer uniform. Other conclusions such as the effect of the overlap of bands seem to depend on the details of the model chosen. This is a very instructive paper.
73. W. Kohn, Phys. Rev. **115**, 1460 (1959). The main results of this impressive paper were mentioned in the text. As a sample of the strange difficulties encountered, one might mention the choice of a basic set of functions. Let $\psi_\beta(\mathbf{k},\mathbf{r})=e^{i\mathbf{k}\mathbf{r}}u_{\beta k}(\mathbf{r})$ be an ordinary Bloch wave. Then a very useful complete orthogonal set consists of the functions $u_{\beta 0}e^{i\mathbf{k}\mathbf{r}}$, where $\mathbf{k}$ is restricted to the first Brillouin zone. Since one wants to describe Bloch wave packets, which under the influence of the magnetic field travel through many zones, one would not like $\mathbf{k}$ restricted to the first zone. On letting $\mathbf{k}$ vary over many zones, a redundant

set $u_{\beta 0}e^{i\mathbf{kr}}$ is produced. This set is the one picked, but in part because of the redundancy, the calculation is quite unwieldy.

74. I. M. Lifshitz and M. I. Kaganov, Soviet Phys.—Uspekhi **2**, 831 (1960). An extremely well-written summary of the pseudo- or semiclassical description of electrons in metals. The treatment is self-contained and the mathematics simple, although a little tricky at times. In spite of its simplicity the subject is a rather subtle one, not all the conclusions are as obvious as the authors make them appear.
75. The discussion here follows the one given in reference 45, p. 191.
76. W. Kohn, Phys. Rev. **105**, 509 (1957). The relation between (143) and (144) was established in this paper, the method employed is an expansion of the wave functions of H [given by (144)] in those of H^0.
77. W. Kohn, Phys. Rev. **110**, 587 (1958). In this paper the identity of k^* and the conventionally defined static dielectric constant was demonstrated. The proof makes extensive use of the graphical methods of the many-body theory (and field theory).
78. A. Klein, Phys. Rev. **115**, 1136 (1959). The basic theorem concerning the response of a system plus one electron to an outside field conjectured by Kohn in reference 76 is proven here. The methods of second quantization are used throughout. Inasmuch as one needs to compare systems with different number of particles, this is a natural method to use. The proof is lengthy.
79. Reference 58, p. 66. A typical definition of the Fermi surface.
80. J. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960). The purpose of this study is to investigate the ground state of a many-Fermion system. One needs to calculate the grand partition function;
$$Z_g=\mathrm{Tr}(e^{-\beta(H-\mu N)}), \tag{A10}$$
where N is the number operator $\Sigma a_k\dagger a_k$, μ the chemical potential, and
$$H=H^0+H'=\sum_k \epsilon_k a_k\dagger a_k+\tfrac{1}{2}\sum_{\substack{k,l\\k',l'}} a_k\dagger a_l\dagger a_{k'}a_{l'}\langle kl|V|k'l'\rangle, \tag{A11}$$
where ϵ_k is the single-particle energy in state k, and $\langle kl|V|k'l'\rangle$ is an ordinary matrix element of two-body interactions. a_k and $a_k\dagger$ are annihilation and creation operators of particles in state k. The evaluation of Z_g follows a perturbation-type patterns; it may be cast in a diagrammatic development.
81. J. M. Luttinger, Phys. Rev. **119**, 1153 (1960). Define
$$\bar{n}_k=(Z_g)^{-1}\,\mathrm{Tr}a_k\dagger a_k e^{-\beta(H-\mu N)}. \tag{A12}$$
This is the average number of particles in state k. It may be studied using the methods of reference 80. The locus of its singularities in k space as $T\rightarrow 0$ define the Fermi surface.

II. RELATIONSHIP BETWEEN OBSERVED ENTITIES AND THE THEORETICAL PARAMETERS

A. Nature of Conductivity Calculations

Section A applies the various solid-state and statistical mechanical ideas outlined in I[1] to a conductivity calculation. It is intended to carry the development to a point where one obtains relations between observable transport quantities, and the parameters introduced in the theoretical description. An explicit discussion of such relations always demands extensive numerical computations; these are not given in the present work. In this section the emphasis is on the physical ideas and assumptions contained (explicitly or implicitly) in the calculation of the electrical conductivity. There are a few rather scattered remarks about the thermal conductivity. In Sec. A.1 the influence of external magnetic fields on the conductivity is described. There are many detailed treatments of the subject matter at hand. Of these, the books by Wilson [1][2] and Ziman [2] and the review articles by Sondheimer [3], Blatt [4], and McDonald [5] should be especially noted. The purposes of including this reasonably well-known and readily available material are (a) to establish a uniform notation, (b) to collect and analyze the many different assumptions, and (c) to provide an organized framework against which the later development can be presented. Section A is divided into two subsections. In Sec. A.1 the general outline of a typical calculation is presented. New physical situations are encountered when a magnetic field is introduced; in Sec. A.2 a conductivity calculation in the presence of such fields is presented.

1. General Pattern of a Conductivity Calculation

(*a*) *General outline.* The basic physical idea underlying all conductivity calculations is the possibility of describing a solid in terms of the electronic system and the lattice system separately. The interaction between these two systems can be introduced afterwards. The great success of the separate descriptions of the electronic and lattice systems in correlating and organizing experimental information would suggest such a procedure. One therefore describes the systems in terms of their respective unperturbed wave functions—the electrons by Bloch waves, or some refinement thereof, the lattice system by its quantized vibrations as phonons. The effect of the interactions, in the spirit of perturbation theory, consists of producing transitions between these *unperturbed* states. Both the electron and the phonon distributions are affected by the interaction between the two systems. In addition, both electron and phonon distributions are influenced by the interactions with imperfections in the crystal. The presence of external constraints, such as electric and magnetic fields and thermal gradients, also affects the electron and phonon distributions. The computations of the changes which these various interactions produce in the electron and lattice wave functions, a purely quantum-mechanical problem, is the first part of the calculation. The next part of the calculation is statistical in character: By using the computed transition probabilities of the various processes, it is possible to set up a gain-loss Boltzmann-type equation for both the electron and phonon distribution functions. Whereas in principle this is straightforward, the complexity of the problem (the many separate participating processes) makes this a rather untransparent part of the theory. Once the

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[1] For the text, Part I is referred to as I, Part II as II.

[2] The notation in II is generally the same as in I. Bracketed numbers refer to references listed in the Literature Survey at the end of Part II. References to the Literature Survey of I are prefixed by **1**. Formulas and sections referred to without a part number are those of II; those of I are prefixed by I.

Boltzmann equation is set up, the statistical problem is, in principle, solved. The practical problem is all but solved, for one needs the solutions of the Boltzmann equations to obtain results of physical interest. This third part of the problem is, in principle, purely mathematical in character; to obtain the equations and solutions in a manageable form, one needs all kinds of simplifications and approximations. The justifications of these procedures can come only from physical considerations, so even the supposedly purely mathematical manipulations lean heavily on physical considerations.

Once the solution of the Boltzmann equation is obtained, the calculation of the transport coefficients is straightforward. In the absence of any interactions, the electron and phonon distributions are their respective equilibrium distributions. For the electrons this is the Fermi distribution f_0; the equilibrium distribution of the phonons n_q^0 (the lattice vibrations) is not so explicitly available. It depends on the quantity $g(\omega^2)$ discussed in I, Sec. C.3(c). (A common approximation to n_q^0 is the well-known Bose distribution [6].) The following scheme summarizes the different aspects of a typical calculation.

1. Quantum-mechanical part. One starts from unperturbed wave functions which are products of electronic and phonon wave functions. The effect of the various perturbations (electron phonon interactions, impurities, external fields) is calculated. It is clear that the matrix elements of the perturbing operators, between unperturbed states, play a crucial role in this discussion. The operator describing the electron phonon interaction was discussed in I. (See I, Sec. 2.)

2. Statistical part. The effect of these interactions is to cause deviations from the equilibrium electron and phonon distributions. If one assumes that both an electron and phonon distribution function can be defined, it is straightforward to transcribe the effects of the interactions to the distribution functions. It is at this point that one decides just what processes are to be taken into account. Once can now construct gain-loss equations for the distribution functions, which in principle should determine these functions.

3. Technical part. The next task is the solution of these equations. One always seeks stationary solutions; approximate methods have to be used to obtain them. From the electron distribution f,[3] the electrical current $\mathbf{j}$ follows in the usual manner:

$$\mathbf{j}=\frac{e}{4\pi^3}\int \mathbf{v} f d^3k. \tag{1}$$

It should be noted that[4] the "particle" velocity $\mathbf{v}$ is given by

$$\mathbf{v}=\hbar^{-1}\nabla_k E_\beta. \tag{1a}$$

Thus, a knowledge of *both* the dispersion law $E=E(\mathbf{k})$ and the distribution f is required to obtain the current $\mathbf{j}$. The (electronic) thermal current (per unit area) is

$$\mathbf{Q}=\frac{1}{4\pi^3}\int E(\mathbf{k})\mathbf{v} f d^3k. \tag{2}$$

The methods used in obtaining approximate expressions for f depend on the detailed problem at hand. Some examples are given later.

It can be seen from the rough outline just presented that there are many different areas all properly belonging to conductivity theory. The division just given is a useful one [7] to classify the many studies in this field. Before entering upon a more quantitative discussion, the following points should still be noted.

(a) In most of the calculations actually performed, one does not discuss the effect of the interactions on *both* the electron and phonon distribution functions. Most often[5] one assumes a given stationary phonon distribution; just the changes in the electron distribution are considered.

(b) Physically, the exchange of energy and momentum between the electronic systems and the lattice system is the mechanism which is responsible for the resistance of a substance (excluding impurity resistance). Actually, within the outline just presented, there is noting to indicate the *irreversible* character of the exchange of energy between the lattice and the electronic system. Whereas the possibility of the energy transfer between the two parts of the system is clear, the discussion given so far contains no indications of the origin of this irreversibility.[6] The finite conductivity [via (1)] comes from a lack of symmetry of the distribution function f, but the connection of this asymmetry with an irreversible exchange of energy is certainly not transparent.[7]

(c) In the discussion of the lattice Hamiltonian (I.82b), cubic terms in the Taylor expansion were omitted. It is clear that if they were included, they would affect the phonon distribution. If there are temperature ranges in which these terms can be expected to be important, the phonon Boltzmann equation contains additional terms, corresponding processes described by these terms (phonon-phonon scattering). Thus, the actual structure of the transport equations may be different in different ranges of physical parameters. This circumstance causes very considerable complications in the general discussion of transport processes.

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[3] The number of electrons in a volume element d^3r with wave vector d^3k is given by $(1/4\pi^3)f(\mathbf{k},\mathbf{r})d^3rd^3k$.

[4] The notation is the same as in I. The *lattice* Hamiltonian is frequently referred to as the phonon Hamiltonian.

[5] An exception is discussed in Sec. B.

[6] In fact, nothing prohibits an electron from picking up energy from the lattice.

[7] This is connected with the fact that the approximate solutions of the Boltzmann equation are always expansions in which one keeps only the first power of the applied field. The Joule heat, which is the manifestation of the irreversible electron-phonon interaction, depends on the square of the external field.

(*b*) *Electron-phonon interactions*. The electrons are described by Bloch wave functions as given in (I.86), to be denoted by $\psi_{\mathbf{k}}(\mathbf{r})$. The band index β is usually suppressed. The matrix elements for any perturbation are written as $\langle k' | \text{perturbation} | k \rangle$. The lattice vibrations are described by the Hamiltonian H_{latt} given by[8]

$$H_{\text{latt}} = -\frac{\hbar^2}{2M} \sum_{\alpha} \Delta_\alpha + \tfrac{1}{2} \sum_{\alpha,\beta} U(\mathbf{R}_{\alpha\beta}{}^0) + \tfrac{1}{4} \sum_{\alpha,\beta,s,s'} y_{\alpha\beta,s} y_{\alpha\beta,s'} U_{\alpha\beta,ss'}{}^0. \quad (3)$$

The y's are the displacement of the ions, the $U_{\alpha\beta,ss'}{}^0$ are derivatives of forces, $U_{\alpha\beta,ss'}{}^0$ is symmetrical in s and s'; it depends on $\mathbf{R}_\alpha{}^0 - \mathbf{R}_\beta{}^0$ only [see (I. 83a)].

In the usual manner H_{latt} gives rise to equations for the displacements $M\ddot{y}_{\alpha,s} = -\sum U_{\alpha\beta,ss'}{}^0 y_{\beta,s'}$. A special solution of this classical problem may be written as[9]

$$\mathbf{y}_\alpha = \mathbf{B}_q \exp[i(\mathbf{q}\mathbf{R}_\alpha{}^0 - \omega t)], \quad (4)$$

where $\mathbf{q}$ is the wave number of the lattice waves, and the frequency ω is determined via the equation of motion from the secular equation

$$|\textstyle\sum_\alpha U_{ss'}{}^0(\boldsymbol{\alpha}) \exp(i\mathbf{q}\boldsymbol{\alpha}) - \delta_{ss'} M\omega^2| = 0. \quad (5)$$

(The fact that U depends on the difference $\mathbf{R}_\alpha{}^0 - \mathbf{R}_\beta{}^0$ only has been used. Occasionally $\boldsymbol{\alpha}$ is used for $\mathbf{R}_\alpha{}^0$.) Equation (5) gives the dispersion law (the relation between frequency ω and the wave number $\mathbf{q}$) for the lattice waves. From (5), one *concludes:*

(a) For a given wave vector $\mathbf{q}$, there are three real roots for ω, ω_1, ω_2, ω_3 (written as ω_μ, $\mu = 1,2,3$).

(b) The eigenvectors $\mathbf{B}_1$, $\mathbf{B}_2$, $\mathbf{B}_3$ belonging to these roots are mutually perpendicular (written as $\mathbf{B}_\mu$, $\mu = 1,2,3$).

Both (a) and (b) follow from the obvious observation that the ω's and $\mathbf{B}$'s are the eigenvalues and the eigenvectors of a symmetric matrix.

(c) For long waves (meaning $2\pi/|q| \gg$ lattice distance), one can show that one of the eigenvectors $\mathbf{B}$ is parallel to $\mathbf{q}$; the others are perpendicular to $\mathbf{q}$. Thus, for waves of long wavelength, one has an approximate splitting in transversal and longitudinal waves. Further, if $\mathbf{B}_1 || \mathbf{q}$, one has $v_s =$ sound velocity $= \omega_1/|q|$, $\omega_2 = \omega_3 = v_s' q$.

For a given lattice wave vector $\mathbf{q}$, there are three possible frequencies written as $\omega_\mu = 1,2,3$. The normal coordinates $\xi_{q\mu}$ are defined by

$$\mathbf{y}_\alpha = \frac{1}{(NM\Omega)^{\frac{1}{2}}} \sum_{\beta,\mu} \boldsymbol{\varepsilon}_{q,\mu} \xi_{q,\mu} \exp[i(\mathbf{q}\mathbf{R}_\alpha{}^0)], \quad (6)$$

where Ω is the volume of the solid. The $\boldsymbol{\varepsilon}_{q,\mu}$ are unit polarization vectors [proportional to the vectors B in (4)].

The orthogonality of the vectors B, previously noted, may be expressed as

$$(\boldsymbol{\varepsilon}_{q\mu} \cdot \boldsymbol{\varepsilon}_{q\nu}) = \delta_{\mu\nu}. \quad (6a)$$

One may verify directly that the ξ's satisfy

$$\ddot{\xi}_{q,\mu} + \omega_{q,\mu}{}^2 \xi_{q,\mu} = 0. \quad (7)$$

Thus, the lattice oscillations may be described as a set of uncoupled oscillators. The transition to the quantum theory is now obvious. The quanta of these oscillators are the phonons. The state of the lattice may be described by a lattice wave function

$$\Psi_{n_1 \cdots n_q \cdots}(\xi_1 \cdots \xi_q \cdots) = \prod_q \exp\left(-\frac{1}{2} \frac{\omega_q{}^2 \xi_q{}^2}{\hbar^2}\right) H_{n_q}\left[\xi_q \left(\frac{\omega_q}{\hbar}\right)^{\frac{1}{2}}\right]. \quad (8)$$

Ψ is a product (corresponding to the independent oscillators) of harmonic oscillator wave functions, with the characteristic Hermite functions H_{n_q}. Equivalently, the state of the lattice may be described by a set of occupation numbers $\{n_q\}$ giving the number of phonons of momentum $\hbar\mathbf{q}_\mu$ and energy $\hbar\omega_{q,\mu}$. The matrix elements of ξ and $\partial/\partial\xi$ are all familiar; for instance,

$$\langle n_q' | \xi | n_q'' \rangle = \left(\frac{\hbar}{\omega_q}\right)^{\frac{1}{2}} \left[\left(\frac{n_q' + 1}{2}\right)^{\frac{1}{2}} \delta_{n_q'', n_q + 1'} + \left(\frac{n_q'}{2}\right)^{\frac{1}{2}} \delta_{n_q'', n_q' - 1}\right]. \quad (8a)$$

The state of the solid as a whole may therefore be specified by (antisymmetrized) products of Bloch waves (for the electrons) and lattice wave functions such as (8) written compactly as $\langle \mathbf{k}, n_q |$.

When one deals with an infinite solid, both the phonon wave vector $\mathbf{q}$ and the electron wave vector $\mathbf{k}$ have a continuous spectrum. If the lattice altogether consists of $L_1 L_2 L_3$ unit cells, so that it is a parallelepiped having sides $L_1\boldsymbol{\tau}_1$, $L_2\boldsymbol{\tau}_2$, and $L_3\boldsymbol{\tau}_3$, the periodicity conditions allows only values of $\mathbf{q}$ and $\mathbf{k}$ given by[10]

$$\mathbf{k}, \mathbf{q} = 2\pi\left(\frac{l_1}{L_1}\boldsymbol{\tau}_1{}^* + \frac{l_2}{L_2}\boldsymbol{\tau}_2{}^* + \frac{l_3}{L_3}\boldsymbol{\tau}_3{}^*\right); \quad (9)$$

l_1, l_2, l_3 are integers; the $\boldsymbol{\tau}_1{}^*$, $\boldsymbol{\tau}_2{}^*$, $\boldsymbol{\tau}_3{}^*$ are the primitive translation of the reciprocal lattice (I.79). To obtain the effect of the phonon-electron interactions, one has to compute the matrix elements

$$\langle \mathbf{k}, \{n_q\} | H_{\text{int}} | \mathbf{k}_i' \{n_q'\} \rangle. \quad (10)$$

One therefore needs some explicit expression for H_{int}.

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[8] This formula is identical with (I.82b); occasionally, formulas are repeated as an aid in reading. The notation is the same as before; recall in particular that s is a Cartesian index from 1 to 3.

[9] In this discussion one assumes one atom per unit cell.

[10] Compare the remarks made by Ziman [8] in this connection.

In (I.82) the form of this interaction was obtained as

$$H_{\mathrm{int}}=-\sum_{i,\alpha}\mathbf{y}_\alpha\cdot\nabla_\alpha V(\mathbf{r}_i-\mathbf{R}_\alpha{}^0)\equiv-\sum y_{\alpha,s}V_{i,\alpha,s}{}^{(0)}. \quad (11)$$

This form as written assumes a rigid displacement of the ions. In general, it is better to just assume that the potential seen by the electrons is a linear function of the ionic displacments $\mathbf{y}_\alpha$. (This should be thought of as the first term of expansion in y.) The actual form of V, its relation to the atomic potential, and the degree to which it depends on screening by condution electrons should properly be left open. From (11) one obtains the matrix element (10) by direct substitution. The product character of the unperturbed wave function and the perturbation operator results in a matrix element which itself is a product. The form of the matrix element (8a) demonstrates that only transitions in which the phonon occupation number of a given $\mathbf{q}$ changes by one are allowed (in this order). One obtains

$$\langle\mathbf{k}',n_q|H_{\mathrm{int}}|\mathbf{k},n_q+1\rangle$$

$$=-\sum_{i,\alpha,\mu}\epsilon_{q\mu s}\exp(i\mathbf{q}\mathbf{R}_\alpha{}^0)\int d^3r_i\psi_{k'}{}^*(r_i)$$

$$\times V_{i,\alpha,s}{}^0\psi_k(r_i)\frac{1}{(NM\Omega)^{\frac{1}{2}}}\frac{[\hbar(n_q+1)]^{\frac{1}{2}}}{2w_{q,\mu}}. \quad (12)$$

A similar matrix element may be written for $\langle k',n_q|H_{\mathrm{int}}||k,n_q-1\rangle$. There is one signficant general feature these matrix elements possess, independent of the particular form of V and the wave function. It depends on the periodicity of the potential V only. Recall that $V_{i,\alpha}{}^0$ stands for $\nabla_\alpha V(r_i-R_\alpha)$ evaluated at the equilibrium position. If one uses the periodicity of the Bloch functions (I.106a) in the matrix element (12), one obtains (the phonon factors are omitted)

$$\sum_i\int d^3r_i\exp(-i\mathbf{k}'\mathbf{r}_i+i\mathbf{k}\mathbf{r}_i+i\mathbf{q}\mathbf{r}_i)\epsilon_{q,\mu,s}$$

$$\times\textstyle\sum_\alpha u_{k'}{}^*(r_i)u_k(r_i)\nabla_{\alpha,s}\mathrm{V}\exp[(i\mathbf{q}(\mathbf{R}_\alpha{}^0-\mathbf{r}_i)]. \quad (12a)$$

From the periodicity of the functions u_k, and the periodicity of the potential, one infers that the sum is a periodic function of $\mathbf{r}_i$. From this fact one deduces that the integral is different from zero only if

$$\mathbf{k}^1=\mathbf{k}+\mathbf{q}+2\pi\boldsymbol{\tau}^*, \quad (13)$$

where $\boldsymbol{\tau}^*$ is a general vector of the reciprocal lattice.

The proof of this last statement is very simple. Let $F(\mathbf{r})$ be periodic: $F(\mathbf{r})=F(\mathbf{r}+\boldsymbol{\tau})$. Consider

$$\int d^3\mathbf{r}F(\mathbf{r})\exp[i(\mathbf{k}-\mathbf{l})\mathbf{r}]=I_{\mathbf{k}1};$$

change the integration variable to $\mathbf{r}=\mathbf{r}'+\boldsymbol{\tau}$; this does not change the value of the integral. Therefore

$$I_{kl}=\exp[i(\mathbf{k}-\mathbf{l})\boldsymbol{\tau}]I_{kl}.$$

If $\exp[i(\mathbf{k}-\mathbf{l})\boldsymbol{\tau}]\neq1$, it follows that I_{kl} must vanish. On the other hand, for I_{kl} not to vanish, $(\mathbf{k}-\mathbf{l})\boldsymbol{\tau}=$integer $\cdot2\pi$ or $\mathbf{k}-\mathbf{l}=2\pi\boldsymbol{\tau}^*$, where $\boldsymbol{\tau}^*$ is an arbitrary vector of the reciprocal lattice. This is (13).]

The selection rule (13) is of great importance. It is clear that the matrix elements describe physical processes—the matrix element (12) describes the emission of a phonon of wave number $\mathbf{q}$ by an electron of wave number $\mathbf{k}'$. Processes in which $\boldsymbol{\tau}^*=0$ are usually called normal processes; if $\boldsymbol{\tau}^*\neq0$, they are referred to as U or (Umklapp) processes [9]. For normal processes, (13) appears to express a momentum conservation law. However, the very fact that $\boldsymbol{\tau}^*$ need not be zero, shows that this interpretation cannot be strictly valid. It is better to view (13) as a selection rule operating in phonon electron scattering. On using this selection rule, there remains the electronic part of the matrix element which, apart from constants, is given by

$$M=\boldsymbol{\varepsilon}_{q,\mu}\int d^3r\psi_{k'}{}^*(r)\nabla_\alpha V^0\psi_k(r). \quad (14)$$

M depends on the phonon wave number through $\boldsymbol{\varepsilon}_q$, on the polarization index μ, and on $\mathbf{k},\mathbf{k}'$, and $\mathbf{q}$. The calculation of M is just the evaluation of the integral in (14). To study that integral one needs to know *both* the potential V and the wave function $\psi_{\mathbf{k}}$. There are a number of different studies all concerned with the appropriate choice of V.[11] These studies are admirably summarized by Ziman [10]. For present purposes it is pertinent to point out that the detailed choice of V (rigid ion, Bloch approximation, Bardeen self-consistent calculation) has a decided influence on the results obtained, although the results are qualitatively similar. For the further reduction of M given by (14), still other simplifications are necessary. It is, therefore, not so that the matrix element M is an *a priori* given entity, not even for very simple solids. The general features of the matrix element M may be obtained by examining M for special choices of the potential V. It appears that most of the features can be summarized by an expression of the type

$$M=\boldsymbol{\varepsilon}_{q,\mu}(\mathbf{k}-\mathbf{k}')C(|\mathbf{k}-\mathbf{k}'|). \quad (14a)$$

C is a function depending on the choice of potential; it has an explicit dependence on the scattering angle. The specific forms for M, derived on the basis of special assumptions about V [11–13], all have this form (14a). Some results may be inferred from (14a):

(a) One observes from (14a) and (13) that in the

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[11] If one assumes the perturbing potential V to be proportional to the local displacement (as for a continuous medium), M becomes $\sim\int\psi_{k'}{}^*\exp(i\mathbf{q}\mathbf{r}\nabla V\psi_k$; the other extreme, a rigid ion displacement, gives $M\sim\int\psi_{k'}{}^*\nabla V_\alpha\psi_{k'}V$ is the potential of ion α [as written in (14)].

case of normal scattering ($\boldsymbol{\tau}^*=0$) M contains a term ($\boldsymbol{\varepsilon}_\mu \cdot \mathbf{q}$). For long waves, one of the $\boldsymbol{\varepsilon}_{q,\mu}$ is parallel to $\mathbf{q}$. Since $(\boldsymbol{\varepsilon}_{q\mu} \cdot \mathbf{q})=0$ for the transversal modes, the interaction electrons and longitudinal phonons appears to be the main one. It is clear that this argument breaks down for U collisions even for the special form (14a). The term in M becomes $(\boldsymbol{\varepsilon}_{\mu q} \cdot \mathbf{q}+2\pi\boldsymbol{\tau}^*)$, and there is no reason why $\mathbf{q}+2\pi\boldsymbol{\tau}^*$ should be parallel to $\mathbf{q}$; in general, it is not.

(b) The magnitude of C depends [as one can see through (14)] on the exact wave function ψ. C as written has the dimensions of an energy. In the special cases that C has been computed one finds that it is of the order of the Fermi energy. In terms of the factor C, the final expression for the matrix element (12) becomes

$$\langle \mathbf{k}', n_q | H_{\text{int}} | \mathbf{k}, n_q+1\rangle = \frac{-1}{(NM\Omega)^{\frac{1}{2}}} \frac{[\hbar(n_q+1)]^{\frac{1}{2}}}{2\omega_{q,\mu}} \boldsymbol{\varepsilon}_{q,\mu} \cdot (\mathbf{k}'-\mathbf{k}) \times C\delta_{2\pi\boldsymbol{\tau}^*, \mathbf{k}'-\mathbf{k}-\mathbf{q}}. \quad (15a)$$

Similarly,

$$\langle \mathbf{k}', n_q | H_{\text{int}} | \mathbf{k}, n_q-1\rangle = \frac{-1}{(NM\Omega)^{\frac{1}{2}}} \frac{(\hbar n_q)^{\frac{1}{2}}}{2\omega_{q,\mu}} \boldsymbol{\varepsilon}_{q,\mu}(\mathbf{k}'-\mathbf{k}) C\delta_{2\pi\boldsymbol{\tau}^*, \mathbf{k}-\mathbf{k}'-\mathbf{q}}. \quad (15b)$$

The term (15a) corresponds to the emission of a phonon of momentum $\mathbf{q}$ by an electron in state $\mathbf{k}'$; similarly, (15b) corresponds to an absorption process. The Kronecker δ, in (15), expresses the selection rule (13). From the matrix elements the probability of a transition (per unit time) can be obtained directly. Perturbation theory gives for the transition *rate* from i to f:

$$A_{i\to f}=(2\pi/\hbar)|\langle i|H_{\text{int}}|f\rangle|^2 O(E_i-E_f) \quad (16a)$$

$$O(E)=\sin(Et/\hbar)/\pi E. \quad (16b)$$

O has the properties: (a) $O(E_f-E_i)$ has appreciable values only in the range

$$|E_f-E_i|<\hbar/t; \quad (16c)$$

(b) $O(E)$ for large t approaches a δ function; (c) one checks directly that

$$\int_{-\infty}^{+\infty} O(E)dE=1. \quad (16d)$$

In general, $O(E)$ has the characteristics of a δ function. In some studies [14], $O(E)$ is so written.

With the formulas (16) and (15) the number of transitions per second caused by the electron phonon interaction is explicitly given. The characteristics of the solid are largely contained in C. [One could write the same relations without specializing the matrix element M to the form (14a); the expression (14) would work as well. In many applications C is simply taken as a constant and then the form (14a) is preferable.] This is the end of the purely quantum-mechanical considerations; a statistical treatment is needed to obtain the transport coefficients. It is still important to note from (16) that because of the Hermitean character of H_{int} [obvious from (11)], the quantity A possesses the symmetry property

$$A_{if}=A_{fi}. \quad (17)$$

Another mechanism which redistributes the electrons over the energy levels is scattering of the electron waves by static impurities. This process is basically simpler than the one discussed before. Since impurity ions are some 10^4 heavier than electrons, the scattering of electrons may be treated as purely elastic. Furthermore, one usually is not interested in the disposition of the impurity centers, just their effects on the electron and possibly the phonon distribution are of importance. The calculation of the number of electrons scattered from $\mathbf{k}'$ to $\mathbf{k}$ proceeds much the same as the one previously outlined. The perturbing potential is now provided by the impurities which could create a spherically symmetric or a much more complicated potential. In any case one needs the matrix elements of this potential between Bloch states. From these matrix elements the transition probabilities follow again by (16). The transition rates possess the symmetry (17) for the same reason as before. The detailed numerical discussion of the matrix element requires a knowledge of the impurity potential and the Bloch wave function. The statistical discussion can be carried out knowing just that there exists a scattering probability per unit time. For an explicit form of the impurity scattering matrix element, Wilson [15] should be consulted.

(c) *Boltzmann equation.* Let $f_k(t)$ be the number of electrons in state k, at time t; similarly, let $n_q(t)$ represent the number of phonons of wave number q. The changes in these functions due to the electron phonon interaction are obtained through (16) and (15). Substitutions of (15a) and (15b) in (16) yields directly:

Emission of a phonon of wave number[12]: $\mathbf{q}$
Transition from $|k',n_q\rangle \to |k,n_q+1\rangle$

$$A_{k'\to k,q}=\frac{n_q+1}{\Omega NM}\frac{\pi}{\omega_{q,\mu}}[\boldsymbol{\varepsilon}_{q,\mu}(\mathbf{k}'-\mathbf{k})]^2 C^2\delta_{2\pi\boldsymbol{\tau}^*,k'-k-q} \times O(E_{k'}-E_k-\hbar\omega_q)\equiv(n_q+1)B_{k'\to k,q}. \quad (18a)$$

Absorption of a phonon of wave number q:
Transition from $|k',n_q\rangle \to |k,n_q-1\rangle$

$$A_{k',q\to k}=\frac{n_q}{\Omega NM}\frac{\pi}{\omega_{q,\mu}}[\boldsymbol{\varepsilon}_{q,\mu}\cdot(\mathbf{k}'-\mathbf{k})]^2 C^2\delta_{2\pi\boldsymbol{\tau}^*,k-k'-q} \times O(E_{k'}+\hbar\omega_q-E_k)\equiv n_q B_{k',q\to k}. \quad (18b)$$

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[12] The vector signs **k**,**q** are omitted when these entities are needed as subscripts as in n_q, $A_{k'\to k,q}$.

The quantities B defined by (18a) and (18b) depend on $\mathbf{k}$, $\mathbf{k}'$, $\mathbf{q}$, $\boldsymbol{\tau}^*$, and μ, the polarization index; they, however, do not depend on the phonon occupation numbers. On using (18a) and (18b), the changes in the electron distribution function $f_{k'}$ can be obtained directly as

$$\left(\frac{\partial f_{k'}}{\partial t}\right)_c = -\sum_{k'',q} [f_{k'}(1-f_{k''})(n_q+1)B_{k'\to k'',q} + f_{k'}(1-f_{k''})n_q B_{k',q\to k''}] + \sum_{k'',q} [f_{k''}(1-f_{k'})(n_q+1)B_{k''\to k',q} + f_{k''}(1-f_{k'})n_q B_{k'',q\to k'}]. \quad (19)$$

Each one of the terms in (19) has a very transparent interpretation. The first term represents the losses of the electrons in state k', through the emission of a phonon q by an electron in state k'. The second term similarly represents the depletion of the electrons in k' through the absorption of a phonon by these electrons. The factors $(1-f_{k''})$ occuring in (19) express the Pauli principle for the electrons. If k'' is occupied, no transition to k'' can be made. Similarly, factors like (n_q+1) express the Bose statistics of the phonons. The fact that these factors occur "naturally" in the matrix element, while those like $(1-f_{k''})$ for the electrons have to be put in, comes from the fact that in the quantization of the lattice oscillations in the manner described, the Bose statistics is already contained. Indeed, a common way to describe the quantized lattice oscillations is by phonon creation and annihilation operators satisfying the Bose commutation rules. In this way one describes a many-body Bose system. In contrast, the electron system, so far, has been described in terms of a single electron moving in an average field. It is therefore not surprising that in describing *the system* of electrons, as is done in (19), the Fermi statistics must be explicitly introduced.

External electric and magnetic fields also cause a redistribution of the electrons over the energy levels. Their effects can be described through the streaming terms in the Boltzmann equation (I.10). For stationary distributions $(\partial f/\partial t)$, the complete equation reads

$$e(\mathbf{E}_{\text{ext}}+c^{-1}[\mathbf{v}\times\mathbf{H}_{\text{ext}}])\hbar^{-1}\nabla_k f+\mathbf{v}\nabla_r f=(\partial f/\partial t)_c. \quad (20)$$

In (20) $\mathbf{E}_{\text{ext}}$ and $\mathbf{H}_{\text{ext}}$ are the external electric and magnetic fields; $(\partial f/\partial t)_c$ is given by (19). In spite of its obvious appearance, (20) cannot just be taken over from the classical equation (10). One should note that $\mathbf{v}$ in (20) is, in fact, given by (1a) which depends explicitly on the band structure $E_\beta(\mathbf{k})$. The streaming terms describe the succession of states through which an electron in a periodic lattice moves under the influence of outside fields. They can be obtained [as written in (20)] by using standard perturbation theory [16]. The main limitation is that the electric field should be sufficiently weak so that no band-to-band transitions can occur. This is just the limitation required for the validity of the semiclassical discussion of electrons in periodic lattices as given in I, Sec. C.4. The Lorentz force as used in (20) was already given there in (I.133a). The magnetic term in (20) also results from a (time dependent) perturbation development. As a consequence it can be expected to be valid only for small times. In this case this means times small compared to $2mc/eH_{\text{ext}}$ [17]. Equation (20) with $(\partial f_k/\partial t)$ given by (19) is the basic transport equation which must be solved. It is clear by inspection of the collision term (19) that (20), for given $\mathbf{E}_{\text{ext}}$ and $\mathbf{H}_{\text{ext}}$ and a given dispersion law, is still not an equation for f alone. The phonon distribution $n_q(t)$ occurs explicitly in (19). From the transition probabilities for the processes (18a) and (18b), one can set up a "phonon" Boltzmann equation. (See Sec. B2.) This equation also depends on both f and n; one has a pair of coupled Boltzmann equations. [Compare (I.11c.)] As a first (much needed) simplification, the phonons are usually assumed to be in their appropriate thermal equilibrium state,[13] so that the n_q in some sense are known. In any case, (19) becomes a single integral equation rather than one of a pair of coupled equations. Its solution now depends on the *assumed* phonon distribution. The second approximation customarily made is to ignore all U processes, or equivalently one puts $\boldsymbol{\tau}^*=0$ in the expressions (18). This leaves as only possible processes those described by $B_{k+q\to k,q}$ and $B_{k-q,q\to k}$. The δ function also reduces the double summation in (19) to a single one. Substitution of this simplification, using also that $B_{k\to k-q,q}=B_{k-q,q\to k}$ [as may be verified directly from (18a) and (18b)] gives

$$\left(\frac{\partial f_k}{\partial t}\right)_c = \sum_q B_{k-q,q\to k}[n_q f_{k-q}(1-f_k) - (n_q+1)f_k(1-f_{k-q})] + \sum_q B_{k+q\to k,q}[(n_q+1)f_{k+q}(1-f_k) - n_q f_k(1-f_{k+q})]. \quad (21)$$

To obtain this form of the collision term it is necessary only to neglect the U processes in (19); nothing need be assumed about n_q. Equation (21) may be cast in a more transparent form. Note that the summation over the vector $\mathbf{q}$ is over the first Brillouin zone. Call $\mathbf{q}$, $-\mathbf{q}$ in the first term of (21). Then (21), after a trivial rearrangement, reads

$$\left(\frac{\partial f_k}{\partial t}\right)_c = \sum_q f_{k+q}(1-f_k)[B_{k+q,-q\to k}n_{-q} + (n_q+1)B_{k+q\to k,q}] - \sum_q [f_k(1-f_{k+q})[B_{k+q,-q\to k}(n_{-q}+1) + n_q B_{k+q\to k,q}]. \quad (22)$$

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[13] The nature and validity of the assumptions are discussed in detail in Sec. B.

If one now calls $k+q=k'$ a new summation index, one obtains the collision term in the form

$$\left(\frac{\partial f_k}{\partial t}\right)_c=\sum_{k'}[f_{k'}(1-f_k)S_{k'k}-S_{kk'}f_k(1-f_{k'})], \quad (23a)$$

$$S_{k'k}=B_{k',k-k'\rightarrow k}n_{k-k'}+(n_{k'-k}+1)B_{k'\rightarrow k,k'-k}. \quad (23b)$$

That the second terms in (22) may indeed be written as $S_{kk'}$ follows just from the form of (22) (and the properties of B); however, $S_{kk'}\neq S_{k'k}$. One does not need to assume any special properties of the n_q. One has to assume that the phonon energy $\hbar\omega_q$ does not depend on the *sign* of the vector $\mathbf{q}$. Equation (23a) is the kind of formula one usually writes down [18]. In the derivation given here, one has the explicit form of S (in terms of the B's); the dependence of S on the phonon distribution is obvious. For formal manipulations (and also for some practical calculations), (23a) is a more convenient form. However, sooner or later the sum (actually a triple integral) over q in (22) or the sum over k' in (23a) has to be performed. Then it becomes a matter of choosing appropriate integration variables, and either form can have advantages. In an equilibrium situation (both a phonon and electron equilibrium), one knows that the collision term vanishes, so that $V_{k'k}$, defined by

$$V_{k'k}=f_{k'}^{(0)}(1-f_k^0)S_{k'k}=S_{kk'}f_k^0(1-f_{k'}^0)=V_{kk'}, \quad (24)$$

is a symmetrical function of k and k' (although S in general is not).[14] The further discussion of the Boltzmann equation consists of the description of the approximations necessary to obtain tractable solutions of Eq. (20).

(*d*) *Linearized Boltzmann equation.*[15] *Relaxation times.* The Boltzmann equation as it stands is a nonlinear integro-differential equation; the streaming terms [the left-hand side of (20)] contain the derivatives of the distribution function; the collision terms contain the integrals. It is practically always assumed in all transport calculations that the external agencies causing the derivations from the equilibrium are small. The thermal gradients outside fields are such that products or squares of these entities in some sense may be neglected. The nonequilibrium distribution therefore is assumed to be near the equilibrium distribution f^0 (the Fermi distribution):

$$f^0(E)=(e^{(E-\zeta)/kT}+1)^{-1} \quad \text{[see (I.88)].} \quad (25)$$

It is therefore reasonable as a first approximation to use the equilibrium distribution f^0 in the streaming terms of the Boltzmann equation. One then neglects the gradients (∇_r and ∇_k) of the correction to the equilibrium distribution function. Thus, the streaming terms are now known; from (20) and (25) they become, in this approximation,

$$e(\mathbf{E}_{\text{ext}}\cdot\mathbf{v})(\partial f^0/\partial E)+\mathbf{v}\cdot(\partial f^0/\partial T)\nabla_r T. \quad (26)$$

In writing (26) one has assumed that the only dependence on position r of f^0 is through the dependence of the temperature on position. One has a *local* Fermi distribution, but the local temperature may vary from point to point. The $\mathbf{v}$ in the first term of (26) comes from the $\hbar^{-1}\nabla_k E$ term. In this approximation (which is *always* used), the Boltzmann equation becomes an inhomogeneous integral equation. The approximation to the distribution function just described may be written as[16]

$$f_k=f_k^0+f_k^{(1)}=f_k^0-\Phi_k(\partial f^0/\partial E)=f_k^0+\Phi f_k^0(1-f_k^0)(1/k_0T). \quad (27)$$

Φ is now the unknown function, and it is small by assumption. If (27) is substituted in the symmetrical form of the collision term (23a), one obtains, using (24) and keeping linear terms only

$$(\partial f_k/\partial t)=(1/k_0T)\sum_{k'}(\Phi_{k'}-\Phi_k)V_{k'k}. \quad (28)$$

The equation for Φ is now an inhomogeneous linear integral equation:

$$e(\mathbf{E}_{\text{ext}}\cdot\mathbf{v})\frac{\partial f^0}{\partial E}+\mathbf{v}\cdot\frac{\partial f^0}{\partial T}\nabla_{\nu}T=\frac{1}{k_0T}\int d^3k'(\Phi_{k'}-\Phi_k)V_{k'k}. \quad (29)$$

The kernel of the integral equation $V_{k'k}$ is symmetric, (24); in addition, the entities $V_{k'k}$ are all positive [see (24) and the definitions of S and B]. The kernel of the integral equation is known through the relation of V to S [via (24)], the relation of S to B [via (23b)], the form of the matrix element B as given by (18a). The solution of this integral equation is no trivial task either, especially since in general the quantity C [in (18a)] is a complicated function of $\mathbf{k}$ and $\mathbf{k}'$. In the special case that C is treated as a constant or a function or a function of $|\mathbf{k}-\mathbf{k}'|$, one can analyze the equation further. It is best for that purpose to use the form (29) of the collision term. Substitute V back into S, S into B, and reintroduce the phonon wave number as an independent variable. One then ends up with an expression of the form

$$\int d^3q(\Phi_{k+q}-\Phi_k)f_{k+q}^0(1-f_k^0)\times[B_{k+q,-q\rightarrow k}n_{-q}+(n_q+1)B_{k+q\rightarrow k,q}]. \quad (30)$$

Without entering in all the details of the reduction of this integral (which may be found in Wilson [19], Sommerfeld and Bethe [20]), the following observations may be sufficient to round out this part of the

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[14] If one assumes that $n_q+1\cong n_q$ and also that $n_q=n_{-q}$, one can show from (23b) that S does become symmetric.

[15] In this discussion, magnetic fields are not considered; $H_{\text{ext}}=0$.

[16] When the Boltzmann constant k occurs in the same formulas as a wave vector, the Boltzmann constant is written as k_0.

calculation:

(a) It is clear that some assumption must be made regarding the quantities n_q, the phonon occupation numbers. It is customary to replace them by their average value

$$n_q = \bar{n}_q = (e^{\hbar\omega_q/kT} - 1)^{-1}. \tag{31}$$

In so doing one has assumed a separate phonon equilibrium state.

(b) To discuss the integral (30) further, one must know the dispersion law of the lattice waves. ω_q occurs both in the phonon distribution and in the matrix elements B. One usually assumes the dispersion law for long wavelengths,

$$\omega_1 = v_s q \quad q = |\mathbf{q}|. \tag{32}$$

This should explain the presence of the velocity of sound (or the Debye temperature) in the final results.

(c) The integration over $\mathbf{q}$ should include only the first Brillouin zone. If one replaces this first zone by a sphere of equal volume, one has

$$q_{\max} = 2\pi(3/4\pi\Omega_0)^{\frac{1}{3}}, \tag{33}$$

where Ω_0 is the volume of a unit cell. Actually, the limitation to normal processes in which energy is conserved provides another restriction on the phonon wave numbers which may occur in the integral (30). One has for an emission process $\mathbf{k} \to (\mathbf{k}-\mathbf{q})$, $\mathbf{q}$ that

$$E(\mathbf{k}) = E(\mathbf{k}-\mathbf{q}) + \hbar\omega_q. \tag{34a}$$

From this conservation law, one obtains (in the special case that $E_k = \hbar^2 k^2/2m^*$ and $\omega_q = \hbar v_s q$) the inequality

$$\hbar q/2m^* < (\hbar k/m^*) + v_s q_{\max} < 2k_F(1 + v_s/v_F). \tag{34b}$$

[This follows just by noting that the cosine occuring in $(\hbar^2/2m^*)(\mathbf{k}-\mathbf{q})^2$ has to be less than 1].

Since generally the velocity of sound v_s is much less than the Fermi velocity v_F, one has the effective restriction on the phonon wave number $q_{\max} < 2k_F$ (k_F = Fermi wave number). For a discussion of which limitations, (34a) or (34b), should be used, consult Blatt [21] and Wilson [22].

(d) In the actual evaluation of (30) one is helped by the δ function character of the functions O [defined by (16b)]. This can be exploited by introducing $E_{k+q} - E_\kappa - \hbar\omega_q$ as a new variable in (30); then one integration can be performed. There still remain two integrals to be performed. If one assumes further that E_k is a quadratic function of k, and also that

$$\Phi(\mathbf{k}) = k_x \chi(E), \tag{35}$$

one can perform one more integration.[17] The result then is a linear integral equation, involving a single integral only, for the unknown function χ. χ is a function of just one variable. The collision term has the structure (apart from factors)

$$\left(\frac{\partial f}{\partial t}\right)_c = k_x \int_{-\Theta/T}^{+\Theta/T} dz[\alpha(z)\chi(\eta) - \beta(z)\chi(\eta+z)]. \tag{36}$$

Here $Z = \hbar\omega_q/kT$, $\eta = (E-\zeta)/kT$, and α and β are known expressions depending on the integration variable z and the constants in the problem. The occurrence of the Debye temperature Θ in the limit of the integral can be traced back to the limit of integration in the $\mathbf{q}$ space, as exemplified by (33). One feature may be appreciated just from the form (36). At high temperatures $T \gg \Theta$; the range of integration over z is small (from $-\theta/T$ to $+\Theta/T$). One can therefore expand $\chi(\eta+z)$ in terms of z. This means that at high temperatures one has approximately, from (36) [remember $\chi(\eta+z) \cong \chi(\eta) + z\chi'(\eta) + \cdots$],

$$(\partial f/\partial t)_{\text{coll}} = k_x \chi(\eta) \text{ (quantity depending on } \eta, T) \tag{37a}$$

$$= \Phi \text{ (quantity depending on } \eta, T) \tag{37b}$$

and by (27)

$$(\partial f/\partial t)_c = -(f - f^0)/\tau. \tag{38}$$

Here τ is an entity which can depend on E, η, and other constants. The important thing to remember is that in the high-temperature limit, (37) shows that $\partial f/\partial t$ is proportional to the deviation from the equilibrium state as expressed by $\Phi = k_x\chi$. The proportionality constant depends on the form of α and β in (36). The quantity τ is often called a relaxation time. The preceding analysis showed that in the high-temperature limit such a relaxation time actually exists. In fact, a careful expansion of the integrals in (36) yields an explicit form for τ. In many calculations, the existence of a relaxation time τ, defined by (38), is simply assumed. This has the tremendous advantage that the Boltzmann equation becomes extremely simple. For instance, in an external field $\mathbf{E}_{\text{ext}}$ (no thermal gradients), Eq. (20) becomes

$$e(\mathbf{E}_{\text{ext}} \cdot v)(\partial f^{(0)}/\partial E) = -(f - f^{(0)})/\tau. \tag{39}$$

From (39) one obtains a solution

$$f = f^{(0)} - e\tau(\mathbf{E}_{\text{ext}} \cdot \mathbf{v})(\partial f^0/\partial E). \tag{39a}$$

The current given by (1) is just[18]

$$j_\mu = \frac{e}{4\pi^3} \int v_\mu f d^3k = -\frac{e^2}{4\pi^3} \int \tau v_\mu v_\nu E_{\text{ext},\nu} \frac{\partial f^0}{\partial E}. \tag{39b}$$

The conductivity tensor is usually defined[19] by

$$j_\mu = \sigma_{\mu\nu} E_{\nu,\text{ext}}. \tag{39c}$$

From (39b) and the definition (39c), one obtains an

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[17] It is also necessary to neglect terms of order $(\hbar\omega_q/E_F)^2$.

[18] Here and in the sequel, μ, ν, etc., are used as Cartesian indexes running from 1 to 3.

[19] This is an experimental definition; one applies a field $\mathbf{E}$ in some direction and measures the current in another direction.

expression for $\sigma_{\mu\nu}$:

$$\sigma_{\mu\nu}=-\frac{e^2}{4\pi^3}\int d^3k\tau(\mathbf{k})v_\mu v_\nu\frac{\partial f^0}{\partial E}. \tag{39d}$$

Thus, with a few lines of calculation, one has obtained an explicit expression for an experimentally observable quantity, the conductivity tensor. $\sigma_{\mu\nu}$ is not yet *altogether* explicit; one needs to know the band structure, for **v** must be known as a function of **k** to discuss (39d). [**v** is given as always by $\hbar^{-1}\nabla_k E$, hence $E(\mathbf{k})$ must be known.) $\tau(\mathbf{k})$ must be known as well. To utilize the δ function type character of $\partial f^0/\partial E$, it is best to write the volume element in k space as

$$d^3k=dS(dE/\nabla_k E). \tag{40}$$

One then can transform the k integration to one over the energy and the surface. dS is a surface element of a constant energy surface, $\nabla_k E$ is the normal derivative. On using (40), one obtains

$$\sigma_{\mu\nu}=-\frac{e^2}{4\pi^3}\int dE\frac{\partial f^0}{\partial E}\int\frac{\tau v_\mu v_\nu}{\nabla_k E}dS\cong\frac{e^2}{4\pi^3}\int_{E=\zeta}\frac{\tau v_\mu v_\nu}{\nabla_k E}dS,$$
$$\sigma_{\mu\mu}\cong\frac{e^2}{12\pi^3}\int\frac{\tau v^2dS}{\nabla_k E}. \tag{41}$$

The last relation in (41) is valid for cubic crystals only. An exactly similar calculation for the thermal conductivity starts from the Boltzmann equation

$$eE_xv_x(\partial f^0/\partial E)+v_x(\partial f^0/\partial T)(\partial T/\partial x)=-(f-f^0)/\tau. \tag{42}$$

(Both the electric field E_x and the temperature gradient are assumed to be in the x direction only). Equation (42) only needs rearranging to give f. The definitions of the electric current (1a) and thermal current then give again explicit expressions for the thermal conductivity. As is well known, one fixes the field E_x by the requirement that $j_x=0$; the proportionality between $\partial T/\partial x$ and Q_x then gives the thermal conductivity. Use of the same δ-function character of $\partial f^0/\partial E$ (one actually needs one more term in the expansion of these integrals in terms of kT/ζ) yields for the thermal conductivity κ

$$\kappa=\frac{k^2T}{36\pi}\int_{E=\zeta}\frac{\tau v^2dS}{\nabla_k E}. \tag{43}$$

Comparison with (41) shows that

$$L=\kappa/\sigma T=(\pi^2/3)(k^2/e^2)=\text{const}. \tag{44}$$

Note that the constancy of the Lorentz number L depends only on (a) the existence of a relaxation time; (b) the approximation of the streaming terms by their equilibrium values; (c) the validity of the expansions of the integral over the energy. The accuracy of this expansion depends on the degree to which $\partial f^{(0)}/\partial E$ represents a δ function; this in turn depends on the degree of degeneracy of the electron gas.

Experimentally, one finds that the value for L is indeed the expected value for high temperatures and again for very low temperatures. For intermediate values, however, L varies with temperature. This aspect cannot be reproduced by the theoretical discussion described by (41), (43), and (44).

The whole point of this excursion on relaxation time just given was to emphasize the fact that the introduction of a new adjustable parameter in the theory, through τ, is not nearly as serious as the assumption that a relation of the type (38) holds. After all, the integral equation (36) contains, through the matrix elements B, entities such as C, (18a), which are not really given by the theory either. But as demonstrated in the derivation of the Lorentz number, the assumption of a relaxation time has consequences which are independent of the structure of the solid. These therefore test the validity of (38) directly. It was made plausible from (36) that at high temperatures a relaxation indeed does exist. At low temperatures, the solution of (36) is quite trivial, it becomes $\chi(z)=\text{constant}$. Then it is quite easy to see from (36) and the succeeding argument that a relaxation time again exists, although in a trivial sense.

In general, however, a relaxation time does *not* exist for phonon-electron scattering: An assumption of the type (38) cannot hold true. One has to perform the analysis using the Boltzmann integral equation. It is important to emphasize again that the proof of the existence of a relaxation time, always makes use of solutions of the Boltzmann equation of a certain type, those *near* equilibrium $f=f^0-\Phi(\partial f^0/\partial E)$. Even for processes for which a relaxation time can be defined, (38) is not necessarily valid for all states of the system, Usually it applies to just those stages of a nonequilibrium process which are near equilibrium. Relaxation time arguments play an important role in impurity scattering. In Sec. 1(b) it was mentioned that the scattering of electrons by impurities is a separate mechanism for the redistribution of electrons. The description of this process is substantially simpler (the scattering is elastic) than the one given before. If u is a perturbing potential, one has only two scattering processes [compare (18)] transitions from $\mathbf{k}'\rightarrow\mathbf{k}$, and those from $\mathbf{k}\rightarrow\mathbf{k}'$. The number of such processes[20] per second is, by (16),

$$A_{k\rightarrow k'}=(2\pi/\hbar)|\langle\mathbf{k}|u|\mathbf{k}'\rangle|^2\delta(E_k-E_{k'}) \tag{45a}$$

$$A_{k'\rightarrow k}=(2\pi/\hbar)|\langle\mathbf{k}'|u|\mathbf{k}\rangle|^2\delta(E_{k'}-E_k). \tag{45b}$$

One observes that for this case of elastic scattering

$$A_{k'\rightarrow k}=A_{k\rightarrow k'}. \tag{45c}$$

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[20] The function previously called O, which behaves as a δ function, is here written as a δ function. The important symmetry relation (45c) was mentioned in (17). The various A's can be distinguished by their subscripts.

The change in f, due to these collisions, may be written immediately:

$$\left(\frac{\partial f_k}{\partial t}\right)_c = \sum_{k'} [A_{k'k} f_{k'}(1-f_k) - A_{kk'} f_k(1-f_{k'})] = \sum_{k'} A_{k'k'}(f_{k'}-f_k), \quad (46)$$

which is linear as one would expect; the scattering of electrons of fixed impurities should result in a linear equation. If one assumes a distribution function of the form

$$f_k = f_k^{(0)} - k_x(\partial f^0/\partial E)\chi(E) \quad (47)$$

and if $E=E(|k|)$, a relaxation time always exists. To show this, note that in an elastic collision, $E=E'$, $|k|=|k'|$, and $f_k^{(0)}=f_{k'}^{(0)}$, the equilibrium distribution depends on E alone. Use of (47a) in (46) gives

$$\left(\frac{\partial f_k}{\partial t}\right)_c = \sum_{k'} A_{k'k}\left[-k_x'\frac{\partial f^0}{\partial E'}\chi(E') + k_x\frac{\partial f^0}{\partial E}\chi(E)\right] = k_x\frac{\partial f^0}{\partial E}\chi(E)]\sum_{k'}\frac{k_x-k_x'}{k_x}A_{k'k} = -\frac{f_k-f_k^{(0)}}{\tau(k)}. \quad (48)$$

$1/\tau$ has been defined as

$$\frac{1}{\tau(k)} = \sum_{k'}\frac{k_x-k_x'}{k_x}A_{k'k}. \quad (49)$$

It is clear that τ, so defined, depends on k, and on the matrix elements of the perturbation, but *not* on the occupation numbers. In (48), (47) has been applied. From the form of (48), it is clear that for impurity scattering a relaxation time always exists. As stressed before, this must be understood in the sense that *if there* are solutions to the full equation of the form (47), the collision terms for these solutions can be written as (48). The evaluation of is still a separate question; it depends on the details of the scattering mechanism.

2. *Conductivity in an External Magnetic Field*

The general pattern of a conductivity calculation for a solid in a magnetic field is much the same as that outlined previously. There are, however, some technical differences as well as some matters of principle which make a separate discussion worthwhile. In addition, there is a wealth of phenomena associated with the behavior of solids in magnetic fields, which have an intrinsic interest and yield significant solid-state parameters as well. The discussion outlined in this section stops short of the treatment using density matrix techniques. This discussion is on the "Boltzmannian level"; the transport equation in one form or another is still the basis of the discussion. The assumptions made are noted; their limitations are discussed in detail in Sec. B. The limitations of the treatment given here are some of the more compelling reasons for attempting the density matrix approach.

(*a*) *Obvious calculation.* It is clear that the physical *mechanism* which produces electrical resistance should not qualitatively be affected by the presence of a magnetic field. The scattering of electron waves by impurities, the electron-phonon interactions, may in their details be dependent on such fields, but the general features should remain much the same. As a first approximation, it is in fact reasonable to assume that the scattering term in the Boltzmann equation is unaffected by the magnetic field. [See, however, the discussion in Sec. A. 2(e)]. A straight imitation of the procedure used previously would suggest starting from Eq. (20), with a given external field H_{ext} replacing in the usual manner the unknown distribution function f by f^0 (the equilibrium distribution) in the streaming terms. [See the discussion in Sec. A. 1(d).] The magnetic terms would become, in that case,

$$\frac{e}{\hbar c}[\mathbf{v}\times\mathbf{H}_{\text{ext}}]\nabla_k f^{(0)} = \frac{e}{\hbar c}[\mathbf{v}\times\mathbf{H}_{\text{ext}}]\nabla_k E\frac{\partial f^0}{\partial E} = \frac{e}{c}[\mathbf{v}\times\mathbf{H}]\frac{\partial f^0}{\partial E}\cdot\mathbf{v} = 0. \quad (50)$$

Hence, one sees that the magnetic field does not change the streaming terms in the Boltzmann equation in equilibrium. The magnetic field rotates the velocity vectors around the field direction, but this does not result (in equilibrium) in any set steaming in k space.

Write again [compare (27)]

$$f = f^{(0)} + f^{(1)}. \quad (51)$$

$f^{(0)}$ is the Fermi distribution; $f^{(1)}$ is the correction to it. One must retain this correction in the magnetic field term. Hence, the Boltzmann equation for $f^{(1)}$ becomes

$$e(\mathbf{E}_{\text{ext}}\cdot\mathbf{v})\frac{\partial f^{(0)}}{\partial E} + \frac{e}{\hbar c}[\mathbf{v}\times\mathbf{H}_{\text{ext}}]\nabla_k f^{(1)} + \mathbf{v}\nabla_r f^{(0)} = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}}. \quad (52)$$

For the present, the existence of a relaxation time is just assumed. The discussion is based on

$$e(\mathbf{E}_{\text{ext}}\cdot\mathbf{v})\frac{\partial f^{(0)}}{\partial E} + \frac{e}{\hbar c}[\mathbf{v}\times\mathbf{H}_{\text{ext}}]\nabla_k f^{(1)} + \mathbf{v}\frac{\partial f^{(0)}}{\partial T}\nabla_r T = -\frac{f^{(1)}}{\tau}. \quad (53)$$

This equation has been the subject of a large number of investigations [23, 24]. Whereas the solutions of (53), and especially the transport coefficients deduced from them, are frequently difficult to analyze, it should be noted that (53) as it stands is a first-order inhomogeneous partial differential equation— not too complicated a mathematical object. Later a solution applicable in general is given. To appreciate the large variety of phenomena (53) can describe with a minimum of calculation, it is instructive to solve (53) for the case of a spherical band structure $E=\hbar^2\mathbf{k}^2/2m^*$, so that

$$\mathbf{v}=\hbar^{-1}\nabla_k E=\hbar\mathbf{k}/m^*. \tag{54}$$

This simple relation between $\mathbf{v}$ and $\mathbf{k}$ is essential for this method.

Write (51) as[21]

$$f=f^{(0)}+f^{(1)}=f^{(0)}-\boldsymbol{\chi}(E)\cdot\mathbf{k}(\partial f^0/\partial E). \tag{55}$$

χ is now the new unknown function; it depends on E only. One shows directly (by carrying out the gradient operation and frequent use of the orthogonality of $[\mathbf{v}\times\mathbf{H}_{\text{ext}}]$ and $\mathbf{v}$) that

$$[\mathbf{v}\times\mathbf{H}_{\text{ext}}]\hbar^{-1}\nabla_k f=-(e/\hbar c)\mathbf{v}\cdot[\mathbf{H}_{\text{ext}}\times\boldsymbol{\chi}](\partial f^0/\partial E). \tag{55a}$$

If one assumes as before that the only (x,y,z) dependence in f^0 is through the temperature, one checks that

$$\nabla_r f^{(0)}=(\partial f^0/\partial E)T\cdot\nabla_r(E-\zeta/T).$$

Substitution of these results in (53) yields

$$e\mathbf{E}_{\text{ext}}-(e/\hbar c)[\mathbf{H}_{\text{ext}}\times\boldsymbol{\chi}]$$
$$+T\nabla_\nu(E-\zeta/T)-(m^*/\hbar\tau)\boldsymbol{\chi}. \tag{56}$$

This equation can be solved without further approximations. [Take the scalar and vector product of (56) with $\mathbf{H}_{\text{ext}}$ and compare the resulting equations.] One obtains, calling

$$\mathbf{P}=e\mathbf{E}_{\text{ext}}+T\nabla_r(E-\zeta/T), \tag{57}$$

$$\boldsymbol{\chi}=\frac{\hbar}{m^*}\tau\frac{\mathbf{P}-\alpha\tau[\mathbf{H}_{\text{ext}}\times\mathbf{P}]+\alpha^2\tau^2\mathbf{H}_{\text{ext}}(\mathbf{H}_{\text{ext}}\mathbf{P})}{1+(\alpha\tau)^2H_{\text{ext}}^2}, \tag{58}$$

$$\alpha=e/m^*c. \tag{58a}$$

With (58) one has obtained a solution for f, valid for rather general situations and arbitrary orientations of the electric and magnetic fields, with possible thermal gradients. One may see just by inspection that the vector χ may be written as

$$(m^*/\hbar\tau)\chi_\mu=a_1P_\mu+a_2\epsilon_{\mu\nu\rho}H_\nu{}^0p_\rho+a_3H_\mu{}^0H_\rho{}^0P_\rho$$
$$\equiv\textstyle\sum_\rho U_{\mu\rho}P_\rho \tag{59}$$

$$U_{\mu\rho}=a_1\delta_{\mu\rho}+a_2\epsilon_{\mu\nu\rho}H_\nu{}^{(0)}+a_3H_\mu{}^{(0)}H_\rho{}^{(0)}. \tag{59a}$$

In these relations μ, ν, and ρ run from 1 to 3; the summation convention (sums over indices occurring twice) is implied. $\epsilon_{\mu\nu\rho}$ is the Levi-Civita symbol, different from zero only if all indices are different; in that case its value is $+1$ for even, (-1) for odd permutations of the indices. From (58) one sees that the coefficients a in (59) are simple functions of the relaxation time τ and the magnitude of the magnetic field. The components of $\mathbf{H}_{\text{ext}}$ have, in (59), been written as $H_\nu{}^0$. The quantities of experimental interest, the electrical and thermal currents, can now be directly expressed, using (54), (55), (59), and (61), as[22]

$$j_\mu=T_{\mu\rho}{}^{\text{el}}P_\rho,$$

$$T_{\mu\rho}{}^{\text{el}}=-\frac{e}{4\pi^3}\left(\frac{\hbar}{m^*}\right)^2\int d^3k\frac{\partial f^0}{\partial E}k_\mu k_\nu U_{\nu\rho}\tau(k), \tag{60a}$$

$$Q_\mu=T_{\mu\rho}{}^{\text{th}}P_\rho,$$

$$T_{\mu\rho}{}^{\text{th}}=-\frac{e}{4\pi^3}\left(\frac{\hbar}{m^*}\right)^2\int d^3k\frac{\partial f^0}{\partial E}k_\mu k_\nu U_{\nu\rho}\tau(k)E(k). \tag{60b}$$

The linear relation between the currents produced and the impressed outside fields as given by $\mathbf{P}$, (57), is an immediate consequence of the use of the linear approximation. The calculation of the responses produced is reduced to a calculation of the tensors $T_{\mu\rho}$, which are given as integrals. These integrations are straightforward, apart from the fact that they contain $\tau(\mathbf{k})$, the relaxation time, both explicitly and through the coefficients a in U, (59). One needs to say something about $\tau(\mathbf{k})$ before a comparison with experiment can be made. The enormous variety[23] of effects which can occur can be appreciated from these relations. The directions of the currents produced are connected in a rather indirect manner (through T to U) to the direction of the applied magnetic field. It is, in principle, not difficult but in practice rather involved, to analyze any given situation in detail. The tensor U (hence T) is not symmetrical. This asymmetry originates from the vector product term in (58) which produces the term $\epsilon_{\mu\nu\rho}H_\nu{}^{(0)}$ in (59a) and $\epsilon_{\mu\nu\rho}H_\nu{}^{(0)}\neq\epsilon_{\rho\nu\mu}H_\nu{}^{(0)}$. In actual practice one does not deal with the most general orientations of the fields and temperature gradients. In fact, the feasible orientations are often dictated by experiment.

(1) Longitudinal effects. Suppose the external magnetic field $\mathbf{H}_{\text{ext}}$ is parallel to $\mathbf{P}$ (if isothermal conditions prevail, this would mean $\mathbf{E}_{\text{ext}}\|\mathbf{H}_{\text{ext}}$). In that case $\boldsymbol{\chi}$ simplifies appreciably (the vector product term is zero) and one obtains

$$\boldsymbol{\chi}=(\hbar/m^*)\tau\mathbf{P}. \tag{61}$$

This surprising result shows that $\boldsymbol{\chi}$ is independent of the applied magnetic field and so is the current. Hence, for spherical energy surfaces, using only the existence of a relaxation time (the dependence of τ on $\mathbf{k}$ did not

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[21] This is suggested by (27) and (35).

[22] The conductivity tensor is defined by the relation between the current and the applied field

$$j_\mu=\sigma_{\mu\nu}E_\nu{}^{\text{ext}}, \tag{60c}$$

in the absence of any thermal gradients. $T_{\mu\rho}$ in (60) symbolizes a general tensor relation.

[23] For an exhaustive listing of all these effects, see Jan [25]. Blatt [26] also has an interesting discussion of the variety of effects.

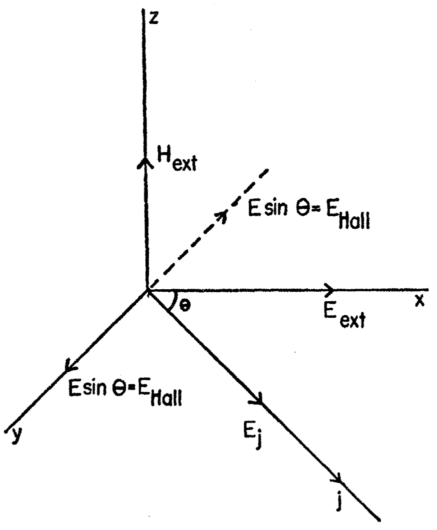

FIG. 1. Directions in the Hall effect.

enter the discussion), this development shows that there can be no longitudinal effects. There is *no* longitudinal magnetoresistance, and no change of resistance in a longitudinal magnetic field. When a relaxation time can be defined at all, the presence of longitudinal effects is generally considered as an indication of more complicated band structures.

(2) Transversal effects. In the transversal situation the electric and magnetic fields are perpendicular to one another: $(\mathbf{E}_{\text{ext}}\cdot\mathbf{H}_{\text{ext}})=0$. On assuming an isothermal situation, $\mathbf{P}=e\mathbf{E}_{\text{ext}}$, Eq. (59) for χ_μ simplifies to

$$\chi_\mu=\frac{\hbar\tau e}{m^*}(a_1E_\mu{}^{\text{ext}}+a_2\epsilon_{\mu\nu\rho}H_\nu{}^{\text{ext}}E_\rho{}^{\text{ext}}). \tag{62}$$

Substitution of this form of χ in the expressions for the current gives

$$j_\mu=-\left(\frac{\hbar}{m^*}\right)^2\frac{e^2}{4\pi^3}\int d^3k\tau(\mathbf{k})k_\mu k_\nu\frac{\partial f^0}{\partial E}\times(a_1E_\nu{}^{\text{ext}}+a_2\epsilon_{\nu\rho\lambda}H_\rho{}^0E_\lambda{}^0). \tag{63}$$

At this point the dependence of τ on the wave vector comes into play. Since it was already assumed that E depends just on the absolute value $|k|$, it is certainly reasonable to make the same assumption for τ. Then both a_1 and a_2, which depend on $\mathbf{k}$ through τ, depend on $|k|$. $f^{(0)}$ depends on E by the same isotropy assumption on $|k|$. Hence, the integrand in (63) has the form $k_\mu k_\nu F(|k|)$; if $\mu\neq\nu$, the integrand is an odd function, hence the integral vanishes. The integral may be written as

$$j_\mu=\sigma_E\delta_{\mu\nu}E_\nu{}^{\text{ext}}+\sigma_H\delta_{\mu\nu}\epsilon_{\nu\rho\lambda}H_\rho{}^{\text{ext}}E_\lambda{}^{\text{ext}} \tag{64a}$$

or, in vector notation,

$$\mathbf{j}=\sigma_E\mathbf{E}_{\text{ext}}+\sigma_H[\mathbf{H}_{\text{ext}}\times\mathbf{E}_{\text{ext}}]. \tag{64b}$$

The relation between the conductivity tensor $\sigma_{\mu\nu}$, (60c), and σ_E and σ_H is given by

$$\sigma_{\mu\nu}=\sigma_E\delta_{\mu\nu}+\sigma_H\epsilon_{\mu\lambda\nu}H_\lambda{}^{\text{ext}}. \tag{64c}$$

The σ_E and σ_H are obtained from the integral expression (63) just by putting $\mu=\nu$, so one has $k_\mu{}^2$ in the integrand which may be replaced by $\frac{1}{3}k^2$. On using the expressions for a_1 and a_2 given by (59) and (58), one obtains the explicit expressions

$$\sigma_E=-\frac{e^2}{12\pi^3}\int d^3k\tau(k)\frac{v^2}{1+(\alpha\tau H_{\text{ext}})^2}\frac{\partial f^0}{\partial E}, \tag{65a}$$

$$\sigma_H=\frac{e^2}{12\pi^3}\int d^3k\tau(k)\frac{v^2\alpha\tau}{1+(\alpha\tau H_{\text{ext}})^2}\frac{\partial f^0}{\partial E}. \tag{65b}$$

One can check that (65a) reduces to (39d) if $H_{\text{ext}}=0$ [and the isotropic case is taken in (39)]. From (64b) one sees immediately that j is perpendicular to the external field H_{ext}. (This is intuitively appealing. The only forces acting on electrons are the electric force and the Lorentz force, and both of these are perpendicular to $\mathbf{H}_{\text{ext}}$; the net current produced $\mathbf{j}$ should be perpendicular to $\mathbf{H}_{\text{ext}}$.)

If τ is known or given, the quantities σ_E and σ_H may be calculated. On the other hand, the entities σ_E and σ_H are directly connected to quantities which can be measured. As written, the current $\mathbf{j}$ has a definite direction in a plane perpendicular to $\mathbf{H}_0$ (see Fig. 1). One can measure the conductivity in the direction of j in a given field $\mathbf{H}_{\text{ext}}$. For this one needs the component of E_{ext} in the j direction, which is $E_j=j^{-1}(\mathbf{E}\cdot\mathbf{j})$. The conductivity is obtained from $\sigma_1E_j=j$; hence, from (64b),

$$\sigma_1=j^2/(\mathbf{j}\cdot\mathbf{E})=(\sigma_E{}^2+\sigma_H{}^2H_{\text{ext}}{}^2)/\sigma_E. \tag{66}$$

It is possible to evaluate this quantity explicitly using (65a) and (65b). The surprising result is that if one evaluates the integrals involving the Fermi function f^0 to zeroth order in kT/ζ, one finds the same value for the conductivity as without the field H_{ext}.

For spherical energy surfaces, with isotropic relaxation time, the transversal magnetoresistance is zero in zeroth order. ($\partial f^0/\partial E$ is used just as a δ function; if one takes higher terms in kT/ζ into account, one gets a nonvanishing value for the transversal magnetoresistance.) The Hall coefficient may also be obtained from σ_E and σ_H. The Hall coefficient R is defined by

$$E_{\text{Hall}}=RjH_{\text{ext}}. \tag{67}$$

Here j is the current, H_{ext} the magnetic field acting on it, which in fact causes a deflection of the electrons from their previous path. E_{Hall} is the electric field perpendicular to the current which just balances the deflection caused by the magnetic field. In the case under discussion, the electric field acting perpendicular to the current[24] is given by $E_{\text{ext}}\sin\theta$. If one imposes a

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[24] It should be kept in mind that E_{ext} and H_{ext} are given and fixed. The current produced is $\mathbf{j}$.

field $E_{\text{ext}}\sin\theta$ perpendicular to j in addition, one has a total electric field of $E_{\text{ext}}\cos\theta$ in the direction of j. This experimental situation is appropriate for a measurement of $\sigma_{\perp}$. Furthermore, the balancing field $E_{\text{ext}}\sin\theta$ equals the Hall field. From (64), one obtains

$$(\mathbf{j}\cdot\mathbf{E}_{\text{ext}})=\sigma_E E_{\text{ext}}^2, \quad \text{also} \quad j^2=\sigma_E{}^2 E_{\text{ext}}^2+\sigma_H H_{\text{ext}}^2 E_{\text{ext}}^2$$

Hence

$$E_{\text{Hall}}=RjH_{\text{ext}}=E_{\text{ext}}\sin\theta=\sigma_H H_{\text{ext}}E_{\text{ext}}^2/j \tag{68}$$
$$R=\sigma_H E_{\text{ext}}^2/j^2=\sigma_H/\sigma_E{}^2+H_{\text{ext}}^2\sigma_H{}^2.$$

Hence the two experimentally observable entities $\sigma_{\perp}$ and R, the transversal magnetoresistance and the Hall coefficient, are expressed in terms of the computed quantities σ_E and σ_H. The discussion so far was based on the linearized equation (53), coupled with the additional assumption that the energy surfaces are spheres. Since the results are surprising (and in conflict with experiment), it is certainly of interest to perform similar calculations for general energy surfaces. The starting equation is again (53); however, instead of writing $f^{(1)}=-\mathbf{k}\chi(E)(\partial f^0/\partial E)$ as was done in (55), assume not that the deviation

$$f^{(1)}=-\Phi\partial f^0/\partial E. \tag{69}$$

Φ, the unknown is now generally a function of $\mathbf{k}$. Φ may be substituted in (53). A first-order differential equation results, which may be solved by standard methods[25] [27]. The result, however, is not in a particularly useful form for the calculation of the currents. One can obtain a simple approximate solution by writing Eq. (53) (for the isothermal case) as

$$-\tau(e\mathbf{E}_{\text{ext}}\cdot\mathbf{v})\frac{\partial f^0}{\partial E}=\left(1+\frac{e\tau}{\hbar c}[\mathbf{v}\times\mathbf{H}_{\text{ext}}]\cdot\nabla_k\right)f^{(1)}$$
$$\equiv(1+\Omega)f^{(1)}. \tag{70}$$

Here (70) defines the operator Ω; it can be written in either vector or tensor notation:

$$\Omega=(e\tau/\hbar c)[\mathbf{v}\times\mathbf{H}_{\text{ext}}]\cdot\nabla_k$$
$$=(e\tau/c)\epsilon_{\mu\nu\rho}v_\nu H_\rho M_{\mu\lambda}{}^{-1}(\partial/\partial v_\mu). \tag{71}$$

The second form of (71) results upon changing the differentiation with respect to k, into one with respect to v, using the definition of the effective mass tensor:

$$M_{\mu\lambda}{}^{-1}=\hbar^{-2}(\partial^2 E/\partial k_\mu\partial k_\lambda). \tag{72}$$

The vector form of the operator Ω is useful to establish such results as $\Omega F(E)=0$. From (70) one obtains the formal solution

$$f^{(1)}=(1+\Omega)^{-1}\left(-\tau\mathbf{E}_{\text{ext}}\mathbf{v}\frac{\partial f^0}{\partial E}\right)$$
$$=(1-\Omega+\Omega^2\cdots)\left(-\tau e\mathbf{E}_{\text{ext}}\mathbf{v}\frac{\partial f^0}{\partial E}\right). \tag{73}$$

From the form of (71) one can see that this is just a development in increasing powers of the magnetic field strength. The electric field strength occurs only as $\mathbf{E}_{\text{ext}}$. The action of the Ω operator on the E_{ext} term is particularly simple if one neglects the v (or k) dependence of the relaxation time, or if τ depends on E only. For in that case the only velocity dependence in the inhomogeneous term is contained in $\mathbf{v}$ (Ω acts on functions of E alone, just as if they were constants). Since $f^{(1)}$ can be written as a power series in H_{ext}, the applied field, the current can be similarly written:

$$j_\mu=\sigma_{\mu\nu}E_\nu{}^{\text{ext}}+\sigma_{\mu\nu\rho}{}^{(1)}E_\nu{}^{\text{ext}}H_\rho{}^{\text{ext}}$$
$$+\sigma_{\mu\nu\rho\tau}{}^{(2)}E_\nu{}^{\text{ext}}H_\rho{}^{\text{ext}}H_\tau{}^{\text{ext}}+\cdots. \tag{74}$$

The expressions for $\sigma_{\mu\nu\rho}{}^{(1)}$, etc., can be directly obtained from (73) and (71) and the definition of the current (1). For instance, in the case that τ depends on E only, one obtains for $\sigma_{\mu\nu\rho}{}^{(1)}$ (using just the linear terms in Ω in 73).

$$\sigma_{\mu\nu\rho}{}^{(1)}=\epsilon_{\rho\lambda\sigma}\frac{e^3}{4\pi^3 c}\int d^3k\tau^2\frac{\partial f^0}{\partial E}v_\mu v_\sigma M_{\nu\lambda}{}^{-1}. \tag{75}$$

The dependence of the conductivity tensor on the effective mass can be seen explicitly.

The use of these and similar expressions is pretty much restricted to energy surfaces, which are quadratic functions of k. In that case the integrals are still manageable. There are also reasons to believe that in certain materials the band structure may be appropriately represented by such surfaces. It is no doubt clear that the expansion described is an expansion valid for small magnetic fields. This should be contrasted with the results obtained before, which were valid for all values of the applied field. The limitations and restrictions of these procedures are discussed in Sec. B.

(*b*) *General features of the conductivity tensor.* So far all considerations were based on the Boltzmann equation (53) in which the existence of a relaxation time was simply assumed. It is possible to deduce some results of a rather general and formal character on the basis of the linearized Boltzman equation without the relaxation time assumption. The distribution function is again written as

$$f=f^{(0)}-\Phi\partial f^{(0)}/\partial E. \tag{76}$$

This is exactly the form used previously in (27); hence, the reduction of the collision term (assuming all the time that the magnetic field does *not* affect the scattering) proceeds as before. If for simplicity an isothermal

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[25] From this exact solution, valid for all values of H_{ext}, one can obtain the "small field expansion," derived in an alternate way in the text, with the same results. One can, however, also obtain a "high-field expansion," which also can be derived in an alternate way (see Sec. C). A careful study of the exact solution might well be worthwhile.

situation is considered, Eq. (52) may be written as

$$e(\mathbf{E}_{\text{ext}}\cdot\mathbf{v})\frac{\partial f^{(0)}}{\partial E}=\frac{1}{k_0T}\int d^3k'(\Phi_{k'}-\Phi_k)V_{k'k}+\frac{e}{\hbar c}[\mathbf{v}\times\mathbf{H}_{\text{ext}}]\cdot\nabla_k\Phi. \qquad (77)$$

It is convenient[26] to introduce the linear operator O by

$$O\Phi\equiv\frac{1}{k_0T}\int d^3k'[\Phi(k')-\Phi(k)]V_{k'k}. \qquad (78)$$

On using (78) and (71) one may write

$$(\partial f^0/\partial E)e(\mathbf{E}_{\text{ext}}\cdot\mathbf{v})=(O+\Omega_H)\Phi. \qquad (77\text{a})$$

[Ω_H differs from Ω (71) by a factor τ. The notation Ω_H shows that the Ω operator depends explicitly on H_{ext}, the operator O does not depend on H_{ext}.)

Note that both O and Ω_H are scalar operators (operating on scalars they again yield scalars). If one writes

$$\Phi=e\mathbf{E}_{\text{ext}}\chi=eE_\mu{}^{\text{ext}}\chi_\mu, \qquad (76\text{a})$$

the unknown vector components χ_μ satisfy the equation

$$v_\mu\partial f^0/\partial E=(O+\Omega_H)\chi_\mu. \qquad (77\text{b})$$

The operators O and Ω both satisfy certain simple symmetry properties: If Φ_1 and Φ_2 are functions of the wave vector $\mathbf{k}$, one has

$$\int d^3k\Phi_1O\Phi_2=\int d^3k\Phi_2O\Phi_1, \qquad (79\text{a})$$

$$\int d^3k\Phi_1\Omega(H)\Phi_2=\int d^3k\Phi_2\Omega(-H)\Phi_1. \qquad (79\text{b})$$

[The proofs of these relations are straightforward. In (79a) one just uses the definition of O, then a renaming of the integration variables in conjunction with the symmetry of V leads to (79a). To verify (79b), one needs to apply Gauss' theorem, together with a few vector identities.] The calculation of the current demands as always

$$j_\mu=\frac{e}{4\pi^3}\int v_\mu fd^3k.$$

Use of (76) gives

$$j_\mu=-\frac{e}{4\pi^3}\int v_\mu\frac{\partial f^0}{\partial E}\Phi. \qquad (80)$$

In the procedures so far presented, one always attempted to calculate Φ. However, to study formal properties it is actually better to eliminate $\partial f^0/\partial E$ by (77b) [28]. If one uses (77b) in (80), one obtains

$$j_\mu=-\frac{e}{4\pi^3}\int d^3k\Phi(O+\Omega_H)\chi_\mu$$
$$=-\frac{e^2}{4\pi^3}\int d^3kE_\nu{}^{\text{ext}}\chi_\nu(O+\Omega_H)\chi_\mu. \qquad (81)$$

From (81) one obtains for the conductivity tensor relating j and E^{ext},

$$j_\mu=\sigma_{\mu\nu}(H)E_\nu{}^{\text{ext}}, \qquad (82\text{a})$$

$$\sigma_{\mu\nu}(H)=-\frac{e^2}{4\pi^3}\int d^3k\chi_\nu(O+\Omega_H)\chi_\mu. \qquad (82\text{b})$$

In contrast to the tensor T written in (60a), this σ as written is not known, since the χ's [the solutions of (77b)] are not known. It is interesting to consider the following symmetry. Let Φ^+, or χ^+, be the solutions of the transport equations for the magnetic field $\mathbf{H}_{\text{ext}}$, so that

$$v_\mu\partial f^0/\partial E=[O+\Omega(H)]\chi_\mu{}^+. \qquad (77\text{b})$$

Now consider a physical situation where the direction of the magnetic field $\mathbf{H}_{\text{ext}}$ is reversed, everything else is the same. The solutions Φ or χ are now different, and are denoted by Φ^- and χ^-. The $\chi_\mu{}^-$ satisfy

$$v_\mu\partial f^0/\partial E=[O+\Omega(-H)]\chi_\mu{}^-. \qquad (77\text{c})$$

Comparison of (77b) and (77c) gives $[O+\Omega(-H)]\chi_\mu{}^-=[O+\Omega(H)]\chi_\mu{}^+$. Substitute this into (82a):

$$\sigma_{\mu\nu}(H)=-\frac{e^2}{4\pi^3}\int d^3k\chi_\nu{}^+[O+\Omega(-H)]\chi_\mu{}^-. \qquad (83)$$

From (83) one sees immediately via the symmetry relations (79) that

$$\sigma_{\mu\nu}(H)=\sigma_{\nu\mu}(-H). \qquad (84)$$

Equation (84) is a general property; it just depends on the linearity of the Boltzmann equation. Results of this type are of general and formal interest. One deduces immediately that the symmetrical part of the conductivity tensor is an even function of H, while the antisymmetrical part of σ is an odd function of H.

In the more general situations, when one has external magnetic and electric fields, as well as thermal gradients present, a very similar argument yields again a tensor relation between the currents produced and the outside agencies producing them. Formally,

$$j_\mu=T_{\mu\nu}{}^{(1)}(H)\left[E_\nu{}^{\text{ext}}-\frac{T}{e}\frac{\partial}{\partial r_\mu}\left(\frac{\zeta}{T}\right)\right]+T_{\mu\nu}{}^{(2)}(H)\frac{1}{T}\frac{\partial T}{\partial r_\nu}, \qquad (85\text{a})$$

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[26] It is actually more than convenient. A thorough knowledge of the operator O, its eigenvalues and eigen vectors, would describe the manner in which the phonon electron equilibrium is approached.

$$Q_\mu = T_{\mu\nu}{}^{(3)}(H)\left[E_\nu{}^{\text{ext}} - \frac{T}{e}\frac{\partial}{\partial r_\nu}\left(\frac{\zeta}{T}\right)\right] + T_{\mu\nu}{}^{(0)}(H)\frac{1}{T}\frac{\partial T}{\partial r_\nu}. \quad (85b)$$

Equations (85) replace Ohm's law (82b); the symmetry relations follow as before from (79a) and (79b). They are

$$T_{\mu\nu}{}^{(1)}(H) = T_{\nu\mu}{}^{(1)}(-H) \quad (86a)$$

$$T_{\mu\nu}{}^{(4)}(H) = T_{\nu\mu}{}^{(4)}(-H), \quad (86b)$$

$$T_{\mu\nu}{}^{(2)}(H) = -T_{\nu\mu}{}^{(3)}(-H). \quad (86c)$$

It should be clear from the preceding discussion that these relations follow from the linearized Boltzmann equation. It was not necessary to construct explicit solutions to obtain the relations (86); rather, all solutions must be in harmony with the symmetry relations. For a detailed comparison with experiment, one needs the explicit form of the tensors T; not just the general symmetry characteristics [29].

(*c*) *Boltzmann equation on the "Fermi surface."* With the formulas (75) and (74), one has obtained formal expressions for the conductivity in external magnetic fields. As was mentioned at that point, the use of these formulas is restricted to relatively small external magnetic fields. In practice, there is also the additional restriction to spherical—or generally quadratic—energy surfaces. Assuming such surfaces one attempts to fit the elements of the mass tensor occurring in (75) with the magneto-resistance data. Reasonable fits can often be obtained and one learns something about the effective masses of the electrons. For many purposes it is necessary to find out something about the character of the constant energy surfaces, the relations given are not suitable for such purposes. There is a considerable difference between showing that an *assumed* form of an energy surface with appropriately adjusted parameters fits the the data and the systematic investigation of the character of such surfaces. For this latter study, the formalism given is not suitable; it is also not sufficient to restrict the investigation to small magnetic fields. What one needs, since one has to start from the transport equation in any case, is a reformulation of the Boltzmann equation which relates the transport equation more intimately to the trajectories of the electrons in the k space. It is reasonably clear that this must be possible. For one has neglected the effect of the external fields in the scattering in any case; the collisions can be treated as before. The effect of the external electric and magnetic fields on the electrons consists of a redistribution of the electrons in k space, according to the equations of motion:

$$\hbar d\mathbf{k}/dt = e(\mathbf{E}_{\text{ext}} + c^{-1}[\mathbf{v}\times\mathbf{H}_{\text{ext}})] \quad (87)$$

$$\mathbf{v} = d\mathbf{r}/dt = \hbar^{-1}\nabla_k E_\beta(\mathbf{k}). \quad (87a)$$

Here one uses the semiclassical description of the electrons in k space. $E_\beta(\mathbf{k})$ is the (given) dispersion law. The effect of external fields on the electrons was described in detail in I, Sec. C.4. From the discussion there one recalls that if an external magnetic field acts on an electron, both its energy and the component of k in the direction of the field are fixed. Thus, the electron describes a trajectory which is the intersection of a plane k_z = constant, with a constant energy surface. If the line element of a trajectory is ds, one has from (I.138)[27]

$$(\hbar c/eH_{\text{ext}})(ds/v_\perp) = dt. \quad (88a)$$

One can introduce an angle measured along the trajectory by

$$d\varphi = \omega_H(c\hbar/eH_{\text{ext}})(ds/v_\perp) = \omega_H dt, \quad (88b)$$

$$\omega_H = eH_{\text{ext}}/m^*c. \quad (88c)$$

Thus, under the influence of a magnetic field alone, just the variable φ would change (and very simply at that, $\dot\varphi = \omega_H$). A distribution function describing the effect of such a field would be just a function of φ. Actually when both an electric and a magnetic field act, the energy, as well as the k_z of an electron, changes in a manner determined by (87). The remarks just made suggest that it might be advantageous to use as independent variables describing the electrons, under the influence of an external field, the energy $E(k)$, k_z, and φ defined by (88b).[28] In terms of these variables the Boltzmann equation becomes [30, 31]

$$(\partial f/\partial\varphi)\dot\varphi + (\partial f/\partial k_z)\dot k_z + (\partial f/\partial E)\dot E = (\partial f/\partial t)_c. \quad (89)$$

$\dot\varphi$, $\dot k_z$, and $\dot E$, must be determined from (87). Assume $\boldsymbol{H} = \boldsymbol{H}_z$ only, then one obtains from (81)

$$\begin{aligned} \dot E &= \nabla_k E\cdot\mathbf{k} = e(\mathbf{v}\cdot\mathbf{E}_{\text{ext}}), \\ \dot k_z &= (e/\hbar)E_z, \\ \dot\varphi &= \omega_H\{1 + (c[\mathbf{E}\times\mathbf{v}_\perp]_z/H_z v_\perp{}^2)\}. \end{aligned} \quad (90)$$

The distribution function depends on all three variables; the trajectory of an electron now does not lie on a constant energy surface. However, the amount of energy an electron picks up from the field is usually small compared to the Fermi energy ζ, and small compared to the thermal energy of the electrons. The electron's trajectory therefore remains quite near the Fermi surface, roughly within a "distance" of kT. It would be a reasonable first approximation to describe the orbit as lying on that surface. Approximately one has then $\dot\varphi \cong \omega_H$. [That approximation gets better as H increases, for the first term of $\dot\varphi$ in (90) is of order H, see (88c); the second is independent of H.] The Boltzmann equation may now be rewritten as

$$\omega_H(\partial f/\partial\varphi) + (\partial f/\partial k_z)(e/\hbar)E_z + e(\mathbf{v}\cdot\mathbf{E}_{\text{ext}})(\partial f/\partial E) = (\partial f/\partial t)_c. \quad (90a)$$

The net result of the preceding analysis was to yield

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[27] The symbols are all defined in connection with (I.138).

[28] In this way one takes the geometry of the constant energy surfaces into account in a more natural fashion.

this much simpler appearing equation for $f=f(k_z,\varphi,E)$. The remaining discussion of (90) is quite similar to the usual discussion of the transport equation. The following brief sketch should describe the situation. As always, one considers states near equilibrium, so one makes an expansion away from the equilibrium state. Write

$$f=f^{(0)}(E)+f^{(1)}(k_z,\varphi,E). \tag{91a}$$

(Note that now, since k_z and E are treated as *independent* variables, $\partial f^0/\partial k_z=0$.)

The equation for $f^{(1)}$ becomes quite simple [neglect as always quadratic terms in E_z; this causes the neglect of $(\partial f^{(1)}/\partial k_z)E_z$]. The equation for $f^{(1)}$ is

$$\omega_H(\partial f^{(1)}/\partial\varphi)+e(\mathbf{v}\cdot\mathbf{E}_{\text{ext}})(\partial f^{(0)}/\partial E)=(\partial f/\partial t)_c, \tag{92}$$

which can be discussed very simply if one assumes a relaxation time

$$(\partial f/\partial t)_c=-(f-f^{(0)})/\tau=-f^{(1)}/\tau. \tag{93}$$

With this assumption, the equation for $f^{(1)}$ becomes trivial and the solution can be written down at once[29]:

$$f^{(1)}=-\frac{e}{\omega_H}\frac{\partial f^{(0)}}{\partial E}\mathbf{E}_{\text{ext}}\cdot\int_0^{\varphi}d\varphi'\mathbf{v}(\varphi',k_z,E)\times\exp[-(\varphi-\varphi')/\omega_H\tau]. \tag{94}$$

Before discussing the application of this formula, it is interesting to point out that a similar solution of the linearized Boltzmann equation exists under rather general circumstances. Let f satisfy the linearized Boltzmann equation

$$\frac{\partial f}{\partial t}+\mathbf{v}\cdot\nabla_r f+\frac{e}{\hbar}\left(\mathbf{E}_{\text{ext}}+\frac{\mathbf{v}\times\mathbf{H}_{\text{ext}}}{c}\right)\nabla_k f=-\frac{f-f^{(0)}}{\tau(\mathbf{k})}. \tag{95}$$

Then $f^{(1)}=f-f^{(0)}$ can always be written as

$$f^{(1)}=-\frac{\partial f^0}{\partial E}\int_{-\infty}^{t}dt'e\mathbf{E}_{\text{ext}}(\mathbf{r}',t')\mathbf{v}(\mathbf{r}',t')\times\exp\left(-\int_{t'}^{t}\frac{dt''}{\tau(t'')}\right). \tag{96}$$

Here $\mathbf{E}_{\text{ext}}$ and $\mathbf{H}_{\text{ext}}$ can be functions of $\mathbf{r}$ and t; τ can depend on $\mathbf{k}$. The integration in (96) is over the time. $\mathbf{r}'$ and t' refer to a place and time along the *trajectory* of an electron, which at time t reaches a position $\mathbf{r}$ and a quasi-momentum $\mathbf{k}$. Both $\mathbf{E}$ and $\mathbf{v}$ in (96) depend on the actual orbit of the electron; $f^{(1)}$ depends implicitly on the magnetic field H_{ext}, *through* the dependence of the orbit on $\mathbf{H}_{\text{ext}}$.

It is reasonably straightforward to verify that $f^{(1)}$ indeed is a solution of (95) [33]. It is also clear that when both $\mathbf{E}_{\text{ex}}$, and τ are constants, (96) reduces to (94). [The connection between φ and the time variable is given by (88b).] The calculation of the current from $f^{(1)}$ follows the familiar pattern. One just needs to apply (1). It should be kept in mind, however, that the independent variables in $\mathbf{v}$ are φ, k_z, and E; hence, d^3k should be expressed in terms of these variables (even if this is not written explicitly). After a change of integration variables, one obtains for the conductivity tensor,

$$\sigma_{\mu\nu}(H)=-\frac{e^2}{4\pi^3\omega_H}\int d^3k\frac{\partial f^0}{\partial E}\int_0^{\infty}d\varphi' v_\mu(\varphi)\times v_\nu(\varphi+\varphi')e^{-\varphi'/\omega_H\tau}. \tag{97}$$

In spite of its simple appearance, (97) is not a particularly transparent expression. Its complexity stems from the integration over φ. Just as in the general case in (96) one has to integrate over the trajectory of the electron. The φ integration is over the trajectory of the electron on a surface of constant energy. With the approximations made to arrive at (94), the orbit is practically located on the Fermi surface. Hence, (97) expresses the conductivity tensor in terms of integrals over the trajectory which an electron describes on the Fermi surface under the influence of an external magnetic field. The nature of this trajectory depends on the nature of the Fermi surface. The simplest situation is that the Fermi surface is a simply connected closed surface completely contained within a zone. The intersections of the surface with planes of constant k_Z (which give the trajectories) are then closed curves. In that case, the variable φ, ranges from 0 to 2π, clearly $v(\varphi)$ is a periodic function. [This is the situation described before. See (I.142).] The more usual situation for metals is that several zones are partly filled. The Fermi surface intersects zone boundaries, and the periodic repetition from cell to cell in the reciprocal lattice space yields a complicated surface. A cross section of such a surface may or may not yield closed curves. It was explained previously that the plane of the trajectory is perpendicular to the field direction. By varying the field direction, relative to the crystal axis, the intersection may change character—from a closed to an open curve. The change by virtue of (97) should be reflected in the conductivity tensor [30]. It is this fact which suggests that the magnetoresistance may vary quite strongly with the magnetic field direction. Actually, the use of (97) is not so trivial either. Knowing the energy as a function of k, one should calculate the vector $\mathbf{v}=\hbar^{-1}\nabla_k E$, as a function $\mathbf{k}$. Then one should transform from $k_xk_yk_z$ to E, φ, k_z; substitute that in $\mathbf{v}$ and integrate, to obtain (97). In the case of closed orbits, the periodicity of v (with period 2π) simplifies matters. The integral from 0 to ∞ can be reduced to an integral from 0 to 2π:

$$\int_0^{\infty}d\varphi' v_\nu(\varphi+\varphi')e^{-\varphi'/\omega_H\tau}=\sum_{n=0}^{\infty}\int_{2\pi n}^{2\pi(n+1)}=\sum_n e^{-2\pi n/\omega_H\tau}\int_0^{2\pi}.$$

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[29] There is a misprint in the sign of the exponential in the corresponding formula of Ziman [32].

On using this, one obtains for (97), by summing the geometric series,

$$\sigma_{\mu\nu}(H)=-\frac{e^2}{4\pi^3}\int d^3k\frac{\partial f^0}{\partial E}\frac{1}{1-e^{-2\pi/\omega_H\tau}} \times\int_0^{2\pi} d\varphi' v_\mu(\varphi)v_\nu(\varphi+\varphi')e^{-\varphi'/\omega_H\tau}.$$

At this point is is possible to expand the exponentials. This is a useful expansion when $\omega_H\tau\ll 1$ is a high-field expansion. The integrals remaining are quite tractable. In this manner one obtains asymptotic values of σ in high magnetic fields. From this brief sketch it can be seen that the Boltzmann equation (90a) or (92) yields specific results for the conductivity tensor. Two points should still be mentioned.

(1) Lifshitz *et al.* [30] have developed these ideas, without the explicit use of a relaxation time; instead, they average Eq. (90a) over a period T; then one obtains (using the periodicity of the motion)

$$\langle\partial f/\partial t\rangle_c=e\langle\mathbf{v}\cdot\mathbf{E}_{\text{ext}}\rangle(\partial f^0/\partial E).$$

This gives a certain amount of information about the collision term. Then, using an expansion of the unknown function in inverse powers of the field, one can construct a successive approximation scheme to determine the distribution function. The lowest order gives the behavior at high fields. That discussion applies to closed orbits only.

(2) The actual behavior predicted at high fields for a given orientation of the crystal is a magnetoresistance which should either saturate or increase as H^2. Both have been reported, as have a variety of other behaviors.

The interpretation of experiments on polycrystalline materials is not always clear cut; the observed behavior is then an average over many directions. The analysis of open orbits can be carried out using similar methods [34]. The qualitative predictions of these theoretical ideas have received striking confirmation.

Detailed experiments of the anisotropy of the magnetoresistance of single crystals show a surprising amount of structure. This tends to confirm the general ideas of the theory; it shows also that the Fermi surfaces are generally quite complicated open surfaces. From a theoretical standpoint, however, the use of the high-field expansion (with $\omega_M\tau>1$), coupled with the use of classical distribution functions and a semiclassical description of the electrons, might well give cause for concern. This particular point is elaborated in Sec. B. It is clear from (97) that no matter what further expansion is employed, there is an immediate connection between the character of the electron trajectories on (or near) the Fermi surface and the conductivity tensor. The method reported here exhibits this connection quite directly. It is to be kept in mind, however, that for the very large fields contemplated here ($\omega_H\tau>1$), other effects, notably quantum effects, would begin to play a significant role so that the predictions made by the theory might well be seriously modified.

Note added in proof. The current experimental situation is summarized in a conference report on *The Fermi Surface* [77].

(*d*) *Effect of strong magnetic fields. de Haas-van Alphen effect.* From the foregoing description it is no doubt clear that the further discussion of the conductivity in high magnetic fields is of great interest. The validity of the statistical basis of the discussion, the linearized Boltzmann equation, has so far not been questioned. Within the framework of the Boltzmann equation, several refinements are still possible, which are particularly pertinent for the description of electrons in high magnetic fields. Since these refinements can have a considerable influence on the expected behavior it is appropriate to describe them briefly.

In many ways the most striking example of the influence of a strong magnetic field on a system of electrons is the de Haas-van Alphen effect; the oscillatory dependence of the magnetic susceptibility on the applied magnetic field. It is generally known that these oscillations are quantum mechanical in origin. They arise from the quantization of the electronic energy levels in a constant magnetic field. The literature on the de Haas-van Alphen effect is extensive [35]; just the aspects which are important for transport theory are summarized here. The starting point of most discussions is the effect of a homogeneous magnetic field H_Z on a system of free electrons. The starting Hamiltonian is

$$H_M=(1/2m)[\mathbf{p}-(e/c)\mathbf{A}]^2. \tag{98}$$

$\mathbf{A}$ is the vector potential in these calculations, usually picked as [36]

$$\mathbf{A}=(0,H_zx,0). \tag{99}$$

[It is to be noted that this starting point is a little embarrassing. One clearly describes a *free* electron (gas). No band structure of any kind is involved. The only possible solid state effect one can introduce is through the use of an effective mass m^* in (98). Yet the results of this analysis are applied to electrons in certain solids, with in fact rather good results.]

The use of the vector potential (99) in the Hamiltonian gives

$$H_M=(1/2m)[p_x{}^2+(p_y-m\omega_Hx)^2+p_z{}^2] \tag{100}$$

with

$$\omega_H=eH/mc. \tag{100a}$$

This Hamiltonian yields the eigenfunctions ψ and eigenvalues E of an electron in a magnetic field (the Schrödinger equation is exactly soluble):

$$\psi_{nk_yk_z}=(L_yL_z)^{-\frac{1}{2}}e^{ik_yy}e^{ik_zz}u_n[x-[\hbar k_y/m\omega_H)], \tag{101a}$$

$$E_{nk_yk_z}=(n+\tfrac{1}{2})\hbar\omega_H+(\hbar^2k_z{}^2/2m). \tag{101b}$$

Here u_n is a normalized harmonic oscillator wave function; the dimensions of the box are $L_xL_y(L_z)$; the k_x, k_y, k_z are the wave numbers of the electron.[30] The wave function and energy should be contrasted with those of free electrons:

$$\psi_{k_xk_yk_z}{}^0=(L_xL_yL_z)^{-\frac{1}{2}}e^{i\mathbf{k}\mathbf{x}}, \tag{102a}$$

$$E_{k_xk_yk_z}{}^0=(\hbar^2/2m)(k_x{}^2+k_y{}^2+k_z{}^2). \tag{102b}$$

It is important to note that the energy (101b) is degenerate; in fact, it is infinitely degenerate (k_y can assume an infinite number of values $k_y=\text{integer }2\pi/L_y$ all for the same energy) in contrast to the free electron, where the only degeneracies are accidental ones. It was explained in I, Sec. C.2(b), that many of the important properties of a system are determined by the density of states $g(E)$ as a function of E. The partition function is given as the Laplace transform of the density of states [see (I.87) and (95a)]. The differences of the expressions for the energy, with and without magnetic fields, (101b) and (102b), lead to strikingly different expressions for the density of states in the two cases. One has from (102b) in the usual manner[31]

$$g^0(k_xk_yk_z)=\text{const }dk_xdk_ydk_z, \tag{103a}$$

$$g^0(E)=\text{const }E^{\frac{1}{2}}dE. \tag{103b}$$

[See also (I.87b); the relationship between (103a) and (103b) depends explicitly on the connection between the energy and the wave number (102b).]

The number of states (with the magnetic field on) with given n lying in a range dk_ydk_z is proportional to dk_ydk_z. The number of states of given n in the range dk_z is (since E does not depend on k_y)

$$\int_{-(m\omega_H/\hbar)L_x}^{+(m\omega_H/\hbar)L_x}dk_y=\text{proportional to }\omega_H;$$

in fact

$$g(n,k_z)dk_z=(1/4\pi^2)(m\omega_H/\hbar). \tag{104a}$$

From (101b), one has

$$dk_z\sim dE/[E-(n+\tfrac{1}{2})\hbar\omega_H]^{\frac{1}{2}}.$$

Thus, on combining these results, one sees that

$$g(E)dE=\frac{\Omega}{4\pi^2}\cdot\tfrac{1}{2}\hbar\omega_H\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\sum_n\frac{dE}{[E-(n+\frac{1}{2})\hbar\omega_H]^{\frac{1}{2}}}, \tag{104b}$$

where Ω is the volume $L_xL_yL_z$. The sum is over all nonnegative integers, which leaves

$$E-(n+\tfrac{1}{2})\hbar\omega_H>0.$$

One can see either from the graph (Fig. 2), or from (104b), that whenever the energy E approaches an oscillator level $(n+\frac{1}{2})\hbar\omega_H$, the number of states $g(E)$ diverges. Certain periodic features of the density of states are also immediately evident. This becomes more obvious by considering $\sum_n[(E/\hbar\omega_H)-(n+\frac{1}{2})]^{\frac{1}{2}}$. (This is actually the quantity which is graphed in Fig. 2.) This quantity is a function of $E/\hbar\omega_H=Emc/\hbar eH\equiv\xi$. In this notation, (104b) reads

$$\frac{g(E)}{\Omega}\frac{4\pi^2}{(\hbar\omega_H)^{\frac{1}{2}}}\left(\frac{\hbar^2}{2m}\right)^{\frac{3}{2}}=\sum_n\frac{1}{[\xi-(n+\frac{1}{2})]^{\frac{1}{2}}}\equiv F(\xi). \tag{104c}$$

The function $F(\xi)$ is approximately periodic in ξ, with period 1. This is precisely true for values of $\xi=\frac{1}{2}$, $\frac{3}{2}$, and approximately true near this value. Consider now ξ, not as a function of E, but as a function of H. The right-hand side of (104c), a function of ξ, is unaffected by this reinterpretation. The left-hand side gives, apart from constants $g(E)/H^{\frac{1}{2}}$, the density of states of a given energy (apart from $H^{\frac{1}{2}}$) as a function of ξ. From the approximate periodicity of F as a function of ξ, one therefore infers that the density of states for a given energy is approximately periodic in ξ, i.e., in the variable $1/H$. [Again, this statement really refers to $g(E)/H^{\frac{1}{2}}$.] The period of the periodicity of the density of states as a function ξ is unity; in terms of $1/H$, it is

$$\Delta(1/H)=e\hbar/Emc. \tag{105}$$

Thus, with the limitation noted, a change of $1/H$ of $e\hbar/Emc$ in the external magnetic field essentially reproduces the density of states of the energy E. For values of E, near $(n+\frac{1}{2})\hbar\omega_H$, the value of $g(E)$ is very nearly reproduced. If phenomena are determined to a considerable extent by the density of states at just one given energy (as most transport properties are determined by the density of states at the Fermi energy), one expects a periodic repetition of these phenomena characterized by a period in the inverse magnetic field strength, given by

$$\Delta(1/H)=e\hbar/E_Fmc. \tag{105a}$$

It is this peridocity in the density of states, contained in (104b) which is the basis for all the oscillatory effects, be they equilibrium processes as the susceptibility oscillations, or oscillations in the magnetoresistance. The oscillatory effects need a much more explicit treatment than that presented here.[32] In the applications to actual solids, the starting Hamiltonian of free electrons is not a very suitable one. Still, it is the

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[30] Strictly speaking, one could use an infinite domain in x for the harmonic oscillator wave function. It is a little simpler to use a finite dimension in the x direction as well. This also limits the values of k_y to $k_y=\pm(m\omega_H/\hbar)L_x$. One thus neglects that part of the oscillator wave function that spills over the boundary. This should not cause any trouble.

[31] g^0 indicates the density of states in the absence of a field. g is used to denote the density of states with a field present.

[32] Even though the method presented here gives the physical reason for the occurrence of the oscillations, the practical applications of the de Haas-van Alphen effect are most interesting for materials with complicated Fermi surfaces. By applying a quantum rule of the type $\oint[\mathbf{p}-(e/c)\mathbf{A}]d\mathbf{s}=(n+\gamma)\hbar$; $0<\gamma<1$, Onsager has been able to relate the period (105a) to the external cross-sectional area of the Fermi surfaces perpendicular to H. A careful investigation of the oscillations would therefore give a considerable amount of information about the geometry of the Fermi surface. These quantum rules are hard to justify *a priori.*

only case which can be rigorously solved. As such and for the qualitative insight it provides, the free electron gas is worth discussing. It is interesting to point out that inasmuch as $g(E)$ in (104b) the density of states, is known, the Laplace transform of $g(E)$, which is also known, gives the partition function (I.95a). From the partition function, the free energy of the system can be obtained using (I.101). Thus, from (104) one is only two complex integrations away from results which can be compared with experiment.

In the further development of these ideas, it is necessary to introduce a Boltzmann distribution function, $f(n,k_y,k_z)$ which replaces the previously used f_k. $f(n,k_yk_z)$ gives (approximately) the probability for an electron to be in a state described by a wave function $\psi_{nk_yk_z}$.

One assumes the Fermi form for such a function:

$$f^{(0)}(n,k_yk_z)=\{\exp[\beta(E_{nk_yk_z}-\zeta^H)]+1\}^{-1}. \tag{106}$$

Here ζ^H actually depends on the external magnetic field, as can be seen from the equation which determines ζ^H:

$$\frac{N}{\Omega}=2\int_{\frac{1}{2}\hbar\omega H}^{\omega} g(E)f^0(E)dE. \tag{107}$$

It is only possible to evaluate the sums and integrals in special cases. The dependence of ζ on H need only be considered in very high fields. In that case the energy ζ^H, shows again an approximate periodic dependence on $1/H$.

(*e*) *Influence of magnetic fields on relaxation time.* It has been assumed throughout the discussion of the transport phenomena in magnetic fields, that the interactions between electrons and phonons, or between electrons and impurities, is unaffected by the external magnetic field. Since the effects of large magnetic fields are interesting and not too transparent, it is of importance to investigate just what effects magnetic fields can be expected to have on the scattering mechanisms. This study amounts to a recalculation of the various scattering matrix elements given before, Eqs. (11) and (12). The general problem is hard, just to study the modifications of the Bloch wave functions in a constant magnetic field is an extremely difficult task. (See I, Sec. C.3). As an orientation, it will help if one studies the effect of a strong magnetic field on the scattering of free electrons by phonons and impurities. The advantage of studying this case, is that through (101) the wave functions and energies of such a system of electrons are explicitly known. Thus, the magnetic field can be taken into account exactly, the various scattering processes are treated as perturbations.[33] The general outline is again the same as usual:

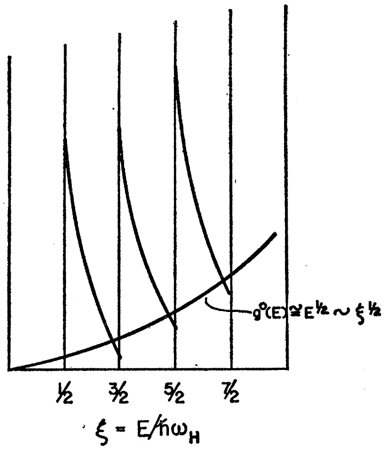

FIG. 2. Density of states in a magnetic field.

$$\begin{tikzcd}
\text{Wave functions} \arrow[d] & \\
\text{Matrix elements of the perturbation} \arrow[d] & \\
\text{Transition rates} \arrow[r] & \text{relaxation time} \arrow[d] \\
& \text{Boltzmann equation} \arrow[r] & \text{conductivity.}
\end{tikzcd}$$

The wave functions of the Hamiltonian (98) have been given; states will be denoted by $|n,k_yk_z\rangle$. It is interesting to observe that the expectation values of the velocity operators are given by

$$\begin{aligned}
\langle v_x\rangle &\equiv\left\langle\frac{\partial H_M}{\partial p_x}\right\rangle=\int\psi^*\frac{p_x}{m}\psi=0,\\
\langle v_y\rangle &\equiv\left\langle\frac{\partial H_M}{\partial p_y}\right\rangle=\int\psi^*\frac{p_y-m\omega_Hx}{m}\psi=0, \qquad (108)\\
\langle v_z\rangle &\equiv\left\langle\frac{\partial H_M}{\partial p_z}\right\rangle=\int\psi^*\frac{p_z}{m}\psi=\frac{\hbar k_z}{m}.
\end{aligned}$$

The current is in the same (z) direction as the magnetic field. One now needs to study the matrix elements of the electron phonon interaction:

$$\langle n'k_x'k_y'|H_{\text{int}}|n,k_xk_y\rangle. \tag{109}$$

This should be compared with the exactly analogous expression (12). Consider the lattice vibrations as the oscillation of a continuum, so that the perturbing potential H_{int} may be written as proportional to the local displacement $\sum e^{i\mathbf{q}\mathbf{x}}$, where $\mathbf{q}$ is the phonon wave number. The matrix element (109) becomes, therefore, $\int d^3x\psi_{n'k_y'k_z'}{}^*e^{i\mathbf{q}\mathbf{x}}\psi_{n,k_y,k_z}$. This matrix element can be calculated. Call the three quantum numbers $n,k_yk_z\equiv\alpha$. One obtains the number of scattering processes from α to α', due to the lattice vibrations as (apart from constants)

$$A_{\alpha\to\alpha'}=\text{const}\textstyle\sum_q|\langle\alpha'|e^{i\mathbf{q}\mathbf{x}}|\alpha\rangle|^2\delta(E_\alpha-E_{\alpha'}). \tag{110}$$

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[33] For this calculation, one should consult the papers of Argyres and Adams [37] and Argyres [38]. The longitudinal case only is treated in these papers.

Actually, (110) contains several assumptions, the most important ones are:

(a) The phonons may be treated as a gas in equilibrium, in contrast with (31).

(b) The collisions between the electrons and phonons are effectively elastic: $\hbar\omega_q \ll E_\alpha$. This is the reason why the structure of (110) is so much simpler than that of (30). It makes the calculation of the matrix element more akin to that of the scattering of electrons by impurities (45a).

From (110) and (101a), one may after a rather tedious calculation [38] obtain the number of transitions per second from $nk_yk_z \rightarrow n'k_z'$:

$$A(nk_yk_z,n'k_z')=\sum_{k_y'} A(n,\, k_yk_z \rightarrow n'k_y'z_z')$$

$$=\delta(E_\alpha'-E_\alpha)\frac{m\omega_H}{\hbar}. \quad (110a)$$

The importance of this relation lies in the fact that it shows the probabilities for transitions from $nk_2 \rightarrow n'k_z'$, are the same as those from $n'k_z' \rightarrow n,k_z$, or the probabilities for forward and backward scattering in the z direction are the same.

Next calculate the loss of momentum of the electrons in the z direction due to the scattering:

$$(\dot{k}_z)_s=\sum_{n'k_y'k_z'} A(n,k_yk_z,n'k_y'k_z')(k_z'-k_z) \quad (111)$$

$$=\sum_{n',k_z'} A(nk_yk_z,n'k_z')(k_z'-k_z), \quad (111b)$$

$$\dot{k}_z=-k_z\sum_{n'k_z'} A(nk_yk_z,n'k_z'). \quad (111a)$$

Because of the symmetry of the $A(nk_yk_z,n'k_z')$, with respect to k_z' and $-k_z'$, and $+k_z'$ terms canceled the $-k_z'$ terms in the summation in (111b). Define the relaxation time of an electron in state n by

$$\frac{1}{\tau_n}=-\frac{\dot{k}_z}{k_z}=\sum_{n',k_z'} A(nk_yk_z,n'k_z'). \quad (112)$$

To obtain an explicit expression for τ, one merely needs to substitute $A(nk_yk_z,\, n',k_z')$ given by (110a), and perform the summations over n' and k_z'. Since A, contains an energy δ function, it is sensible to replace the summation over k_z', for fixed n', by an integration over the energy E'. This brings in the density of states of a given energy; by using the same type argument that yielded (104b), one now obtains

$$\frac{1}{\tau_n}=\mathrm{const}\int g(E')\delta(E'-E)dE'=\mathrm{const}\,g(E)$$

$$=\mathrm{const}\,\hbar\omega_H\sum_{n'}\frac{1}{[E_n-(n'+\frac{1}{2})\hbar\omega_H]^{\frac{1}{2}}}. \quad (113)$$

Expression (104b) has been used to write the explicit form of $1/\tau_n$. Observe that the periodic repetitions of the density of states yields a similar periodicity of the relaxation time. For energy levels where $E_n=(n+\frac{1}{2})\hbar\omega$, the relaxation time vanishes as a result of the infinite density of levels in the immediate proximity of the level in question.

The main results of this study are, therefore:

(a) For free electrons in a strong magnetic field, a relaxation time exists.

(b) The explicit expression for the relaxation time depends on the density of states.

(c) The constant in (113), not explicitly written, contains a temperature factor T. This factor T comes from a factor n_q, the phonon occupation number, which occurs in the expression for the number of phonon electron scattering processes; see (21), for example. One assumed $n_q \cong kT/\hbar\omega_q$, and this factor persists in the expression for τ. A very similar analysis can be given for the scattering of electrons by impurities. The transition probability may be written down immediately [compare (39a)]:

$$A(\alpha \rightarrow \alpha')=(2\pi/\hbar)\sum|\langle\alpha|U(\mathbf{x}-\mathbf{R}_i)|\alpha'\rangle|^2$$

$$\times\delta(E_\alpha'-E_\alpha), \quad (114)$$

where U is the impurity potential. To evaluate A, an explicit form for U must be assumed. The sum in (114) is over all impurities. The computations are rather nastier than those previously given. The results obtained are that:

(a) A relaxation time does exist for impurity scattering.

(b) There is in general no symmetry between backward and forward scattering.

From the preceding discussion, it is now easy to calculate the conductivity. First one has to calculate the collision terms in the Boltzmann equation. From the arguments presented in connection with (46), and from (110), one obtains

$$(\partial f/\partial t)_{\mathrm{coll}}=\sum\nolimits_{\alpha'}(f_{\alpha'}-f_\alpha)A_{\alpha'\alpha}, \quad E_\alpha\cong E_{\alpha'}. \quad (115)$$

(This simple form results only because the scattering was considered as elastic.) Since one contemplates electric fields in the z direction only (longitudinal case), one would write f, the distribution function, as

$$f=f^{(0)}+k_z\Phi, \quad (116)$$

where Φ, the deviation from the equilibrium state, depends on E only; hence, $\Phi(E_\alpha)=\Phi=\Phi(E_{\alpha'})=\Phi'$. Therefore, (115) may be written as

$$(\partial f/\partial t)_{\mathrm{coll}}=\sum_{\alpha'}(k_z'-k_z)\Phi_\alpha A_{\alpha'\alpha}$$

$$=\Phi_\alpha\sum_{n'k_y'k_z'}(k_z'-k_z)A_{\alpha'\alpha}=\Phi_\alpha k_z(\dot{k}_z/k_z)$$

$$=-(f-f^{(0)})/\tau_n. \quad (117)$$

The last two equalities in this chain follow directly from (111), (111a), (112), and (116). Actually, the crucial step is that of equating of Φ_α and $\Phi_{\alpha'}$. For this allows Φ_α to be pulled out of the summation over α' and this establishes the characteristic form of a relaxation time. It is to be noted that the possibility to achieve this depends on the *assumed* form (116) of the distribution function. Both this form and the elastic scattering were essential to derive (117). It is therefore a little misleading to assert that (112) proves the existence of a relaxation time. More precisely, the form (117) in which one uses the relaxation time does not follow just from the validity of (112).

With the assumption of (117), one can now write the transport equation as [see (39)]

$$eE_zv_z(\partial f^{(0)}/\partial E)=-(f-f^{(0)})/\tau \tag{118}$$

with the solution

$$f=f^{(0)}-e\tau E_zv_z(\partial f^{(0)}/\partial E). \tag{118a}$$

The current in the z direction j_z follows[34] from (1) as always:

$$j_z=\frac{2}{4\pi^3}\sum_{n=0}^{\infty}\int_{-\infty}^{+\infty} dx_zg(n,k_z)e\langle v_z\rangle f(n,k_z). \tag{119}$$

Here $g(n,k_z)$ is the number of states with given n in a range between k_z and k_z+dk_z, the factor 2 in (119) comes from the two spin directions. The integration over k_y [which should be present in (119)] has been carried out. Since f in (118a) depends on k_z and E (or n), but not on k_y, it can be carried out trivially. On using (104a) and $\langle v_z\rangle=\hbar k_z/m$ (108), the longitudinal conductivity (σ_{zz}) is

$$\sigma=\text{const}\hbar\omega_H\sum_{n=0}^{\infty}\int k_z^2\tau(E)\frac{\partial f^0}{\partial E}dk_z. \tag{120}$$

This can be transformed in a variety of ways: by introducing E as an integration variable, instead of k_z, using (101b); by introducing τ as given by (113). If this is done, one obtains

$$\sigma(H_z)=\text{const}\int_{\hbar\omega_H/2}^{\infty} dE\frac{\partial f^0}{\partial E}\frac{\sum_n[E-(n+\frac{1}{2})\hbar\omega_H]^{\frac{1}{2}}}{\sum_n[E-(n+\frac{1}{2})\hbar\omega_H]^{-\frac{1}{2}}}. \tag{121}$$

From this point on, detailed integrations need to be done to study the exact dependence of the longitudinal magnetoresistance on the magnetic field. As one might anticipate, there is indeed a periodic dependence of the longitudinal magnetoresistance on H, but only for a degenerate electron gas. The amplitude appears to be smaller than that for the corresponding de Haas-van Alphen oscillations. (Even for the nondegenerate electron gas, there is some effect, but this is no longer oscillatory.)

The general conclusion one can draw from these considerations, is that many different physical mechanisms can influence the magnetoresistance in a profound manner. The discussion just presented indicates that there indeed can be a nonvanishing longitudinal magnetoresistance, even for a solid having only one spherical energy surface. The theory here presented is mainly pertinent for semiconductors, but there one knows one has more complicated energy surfaces. These more complicated surfaces also effect the magnetoresistance. It becomes therefore a real challenge to disentangle the many possible effects. It is probably impossible to decide the significance of these various factors, from just a single experiment. It would seem very appropriate to combine the information obtained here about the field dependence of the relaxation time with the discussion of the Boltzmann equation on the Fermi surface (Sec. C). It is not at all impossible that this field dependence of the relaxation time just deduced would alter the estimates about the high-field asymptotic behavior of the conductivity tensor. This in turn would be important for the comparison with experiment. It is also desirable to start from as fundamental a theoretical framework as possible, so that the simplifications and approximations can be noted in the process of computation. This is better than starting in the middle not knowing just what is assumed, but this latter procedure is often the only one feasible in practice.

B. Structure of Conductivity Theory

In Sec. A, the general pattern of a conductivity calculation was outlined. In the course of this outline, the assumptions made were usually noted. No discussion of the validity was attempted at that time. In this section, the various assumptions are analyzed in detail. This is a useful study; not only is the logical structure of a theory clarified by an explicit discussion of the assumptions, but possible extensions, improved agreement with experiment, can often be obtained through the elimination of unwarranted restrictions. This rather brief section is divided into three subsections. In Sec. 1 the assumptions made are listed, without much comment. The general character of the agreement with experiment is noted. (For detailed comparisons of that type, reviews written for that specific purpose should be consulted [5, 39]. The lack of agreement between theory and experiment is the strongest stimulus for a reconsideration of the assumptions made in the calculation. Section 2 contains a more detailed analysis of some of the assumptions made. Several of the attempts to free the theory from unrealistic restrictions are reported as well. Section 3 contains a discussion of intrinsic difficulties. It is clear that the distinction between an "intrinsic difficulty" and a serious "practical difficulty" is ambiguous. In Sec. 3, those aspects of the theory which appear to

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[34] One should take into account that the n quantum number is discrete. The integral over k_x, k_y, and k_z thus becomes a sum over n, with integrals over k_z and k_y.

require a possible enlargement of the conceptual framework used in conductivity theory are treated. Section 2, on the other hand, contains refinements of the theory, generally within the framework of the Boltzmann transport theory. But it must be admitted that the distinction is tenuous at best, so perhaps it should not be taken too seriously.

1. *Assumptions and Their Consequences*

(*a*) *Summary of the assumptions made* (in order of appearance). As a help in assessing the reliability of the theoretical predictions of conductivity theory, the various assumptions usually made are collected at this point.[35] (Most of the assumptions written here have been noted before. The sections in this paper, most relevant to the assumption in question, are given.)

As a problem in solid-state theory, conductivity theory inherits a large number of the assumptions, as well as the general framework of solid state theory. This was summarized in I, Sec. C; for the present the following points are especially pertinent:

(1) One generally considers lattice waves of long wavelength only, so that the waves can be separated in longitudinal and transversal waves.

(2) In the lattice (phonon) Hamiltonian, cubic terms in the ionic displacements are neglected (no phonon-phonon interaction).

(3) The one-electron picture of a solid (in one form or another) is used. Coulomb, exchange, and correlation effects are usually neglected or introduced as corrections.

(4) The electron phonon interaction is treated by perturbation theory. The form of the perturbing potential itself is not *a priori* given. It depends on the model chosen to describe the electron-phonon interaction.

(5) The electron-phonon interaction matrix element depends on the form of the one-electron wave function. Special simplifying assumptions about the wave function are made in the reduction of the matrix element. One usually assumes that the phonon energy $\hbar\omega_q$ is small compared to the electron energy E_k.

These simplifications usually allow an explicit computation of the matrix element.

(6) It is frequently assumed that C, (14a), is a constant. One of the results obtained in the calculation of the matrix element is the selection rule for the electron and phonon wave numbers $\mathbf{k}'=\mathbf{k}+\mathbf{q}+2\pi\boldsymbol{\tau}^*$, Eq. (13).

(7) In many[36] calculations the restriction $\boldsymbol{\tau}^*=0$ in (13) is used. Only N processes—no U (Umklapp) processes are considered. It is then a *consequence* of the assumptions (4), (5), (7), and (1) that the electrons interact only with the longitudinal lattice modes.

The assumptions (1)–(7) written so far have their origin in the solid-state nature of the conductivity problem. There are assumptions of a rather different character, resulting from the transport nature of the conduction process.

(8) It is almost always assumed that it is possible to define a meaningful distribution function $f_{\mathbf{k}}$, which gives the (probable) number of electrons in state $\mathbf{k}$. A similar assumption (usually less explicit) is made regarding the number of phonons of wave number $\mathbf{q}$.

(9) The existence of a Boltzmann gain loss equation both for $f_{\mathbf{k}}$ and $n_{\mathbf{q}}$ is usually taken for granted.

(10) In the Boltzmann equation, there are terms expressing the effect of external electric and magnetic fields on the distribution function. It is generally supposed that these fields do not materially affect the states of the system. The effects of these external fields are calculated using perturbation theory. Transitions between bands are neglected. Sometimes one uses a semiclassical description for these terms.

(11) The interaction of electrons with lattice imperfections of one kind or another is also treated using perturbation theory.

By using the assumptions (8)–(11) and (4), one can construct a coupled set of equations for f_k and n_q, which express the manner in which these functions change in the course of time.

(12) It is usually assumed that the phonons by themselves are in a thermodynamic equilibrium state. Thus, the electrons are interacting with a phonon gas, which itself is unaffected by the interactions (and the outside gradients).

(13) A variety of assumptions can be made regarding this equilibrium phonon spectrum. One of the more common forms used is the Debye spectrum. Somewhere along the way the relation between ω and $\mathbf{q}$, the dispersion law of the lattice waves, is also required.

A systematic use of the assumptions so far described yields an integral equation for the electron distribution function. The further discussion is concerned with the construction of approximate solutions to that equation. Further approximations and simplifications need be made to obtain usable expressions.

(14) One solves the Boltzmann equations, for states, which are near the equilibrium state. This allows a *linearization* of the Boltzmann equation. Within transport theory there are no examples of the use of the nonlinear equation.

(15) The solutions obtained are always expansions in the outside electric field strength (or the thermal gradients). Just the first term of these expansions is used.

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[35] There are studies where several of the assumptions mentioned here are not made. Some of these are noted later. The purpose of this summary is to provide a reasonably complete list of the usual assumptions as made in a typical calculation [40].

[36] A considerable amount of work has and is being done in removing this quite artificial assumption. See Sec. 2.

(16) A common simplification of the collision term consists of assuming the existence of relaxation times for electron-phonon scattering and electron impurity scattering.

With the assumption of a relaxation time, the integral equation for f becomes a differential equation which can generally be solved. The transport parameters then can be expressed in terms of integrals over the Fermi surface (in which the relaxation times enter). There are known series expansion [41] for such integrals; however, one needs some knowledge of the Fermi surface and the relaxation times to evaluate them.

(17) In the evaluation of the integral expressions for transport quantities, spherical, quadratic, or approximately quadratic, Fermi surfaces are usually assumed. In addition, a simple dependence of τ and E, or $|k|$ only is postulated. (τ is often taken to be a constant.)

In the assumptions given so far, the strength of the outside fields was not explicitly mentioned. From (15) one infers that the electric fields and thermal gradients are taken into account only in the first order, so they in some sense should be small. Nothing of the kind was assumed about the magnetic fields, so presumably they could be of arbitrary strength. It is worth noting that in the discussion of the magnetoresistance given in [Sec. A 2(c)], where limiting values (for high fields) for the conductivity tensor were calculated, assumption (10) is still maintained. In a strong magnetic field, it is no longer appropriate to describe an electron in terms of Bloch waves—even free electrons in such a field are described by nk_yk_z rather than $\mathbf{k}$.

(18) In describing conductivity in very strong fields, assumption (10) is maintained. The existence of a (perhaps modified) distribution function is also assumed.

Assumption (18) is not a new assumption; it is rather an extension of assumptions (10) and (8) to rather extreme circumstances. In high fields, quantum effects may well assume a significant role. It is for that reason that assumption (18), which insists that a classical type distribution can be obtained, should really be examined with care.

A similar situation exists regarding the investigations of the influence of strong magnetic fields on the electron-phonon relaxation time. As stated, the effect of the field was studied for free electrons and applied to electrons and solids. Underlying this and many similar studies is the assumption that:

(19) Qualitative features of the effects of strong fields on electrons in solids, may be studied by considering the electrons as effectively free.

It is clear that if the magnetoconductivity is strongly dependent on the Fermi surface, as was indicated previously (19) may be quite wrong. The assumptions outlined here are the main ones employed. For detailed numerical studies, all kinds of special techniques often approximate in character are used. These special techniques are not included here among the assumptions, although it is not at all uncommon that a procedure is particularly effective in special circumstances only. A discussion of such procedures is essential for the analysis of detailed situations, but no such discussions are contemplated here.

(*b*) *Results; comparison with experiments.* The specific results which are obtained using the assumptions outlined, are collected here [42].

(1) Let σ stand for the conductivity; $\rho=1/\sigma$ is the resistivity. Then in the approximation in which the previous considerations apply, one has

$$\rho=1/\sigma=\rho_r+\rho_i, \tag{122}$$

where ρ_r is the residual resistance, independent of the temperature, varying from sample to sample. ρ_i is the resistivity of the ideal pure metal; it depends on the temperature:

$$\rho_i=4A(T/\Theta)^5J_5(\Theta/T). \tag{123}$$

A is a constant (it contains the C^2, the square of the matrix element), and Θ is the Debye temperature. Equation (122) expresses a physical law, Mathiessen rule; it is certainly valid whenever a separate (constant) relaxation time can be defined for each of the scattering processes separately:

$$J_n(x)=\int_0^x \frac{z^n dz}{(e^2-1)(1-e^{-z})}. \tag{124}$$

(2) There are corresponding results for the thermal resistivity:

$$1/\kappa=1/\kappa_r+1/\kappa_i. \tag{125}$$

Here the thermal and electrical (residual) conductivities are connected by the Franz-Wiedemann law

$$1/\kappa_r=\rho_r/LT, \tag{126}$$

where L is the Lorentz number equal to $\frac{1}{3}(\pi k/e)^2$. [This result can be made plausible without calculation. If the various scattering mechanisms act independently as suggested by (122) and (125), one is allowed to consider just the effect of the impurity scattering. It was shown that for impurity scattering a relaxation time generally exists (49). It was also demonstrated that whenever a relaxation time does exist, the Lorentz number L is constant. This is just the content of (126).]

$$\frac{1}{\kappa_i}=\frac{4A}{LT}\left(\frac{T}{\Theta}\right)^5\left[\left(1+\frac{3}{2^{\frac{3}{2}}\pi^2}N_a^{\frac{3}{2}}\left(\frac{\Theta}{T}\right)^2\right)J_5-\frac{1}{2\pi^2}J_7\right], \tag{127}$$

where N_a is the number of conduction electrons per atom. The comparison of the theory with experiment[37]

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[37] There is also an explicit expression for the thermoelectric power in terms of the same entities. It actually plays a significant

is based on formulas (122)–(127). In general, one finds reasonable agreement between theory and experiment. One would expect that the agreement should be best for alkali metals since they most nearly approximate the type of behavior of the solids which has been assumed. The theoretical calculations generally do not reproduce the degree of variety that the experiments possess. [This is not surprising, assuming, for example, that the dispersion law $E_\beta(\mathbf{k})=\hbar^2k^2/2m^*$ does not allow for the variation in band structure, which solids actually possess.] Even for Na, where the assumptions made are probably most nearly satisfied, the agreement is far from perfect, especially as far as the thermal conductivity is concerned.[38] The other alkali metals follow the qualitative predictions of the theory; for instance, (123) predicts that $\rho_i \rightarrow T^5$ for $T \ll \Theta$. This is indeed found for the alkali metals, but at a temperature much below that computed by the theory. This same pattern of qualitative agreement and quantitative conflict also applies to the thermal conductivities. The agreement there is generally not quite as good as for the electrical conductivities. For elements other than alkali metals, even the qualitative agreement between theory and experiment largely disappears. To make further progress, the theory must take the band structure of the metal into account in considerably greater detail than has been done heretofore.

This detailed study must be carried out before one can draw any further general conclusions regarding the basic agreement or disagreement of the theory and experiment. Two points should still be made in this general connection.

(a) The Debye temperature Θ is used as an adjustable parameter in the comparison with the experiments. In general, the value of Θ obtained from the conductivity data is not the *same* as that obtained from, say, specific heat data. For materials other than Na, it is not always possible to fit the conductivity data with just a single Θ. If $\Theta(T)$ is a rapidly varying function, this means only that (123) does not hold at all.

(b) Whereas the thermal and electrical conductivities show, at least in a general way, the behavior predicted by the simple theory, this is no longer so for the thermoelectric power. Even the sign of the effect is not always predicted correctly; the simplest metals at low temperatures generally show a much larger thermoelectric power than the theory predicts. One of the important assumptions (12) made in the calculation is certain to be violated.

A further detailed comparison of theory and experiment is given by Ziman [43].

The assumptions made in a conductivity calculation in an external field are much the same as those made in calculation without field. Thus, a comparison of those calculated results with experiments is also called for. The basic relations to be compared are of the type (65a) and (65b), or generally (97). The computed quantities result as integrals over the Fermi surface. As pointed out previously, they are extremely sensitive to the character of the trajectories on the Fermi surface. So one actually uses magnetoresistance data to map out the Fermi surface. It is hard to decide that one has agreement or disagreement of magnetoresistance data with a transport theory when one is dealing with a substance whose Fermi surface is unknown. If one has alternate information about the Fermi surface, either by calculation or other experimentation, one may investigate the consistency of these two types of information [44]. An example of the kind of information obtained is contained in an investigation of Olsen and Rodriguez [45] in which the magnetoresistance of Cu was studied (a single crystal). The result obtained is that if the experiment is analyzed *assuming* the Boltzmann transport theory *assuming* a relaxation time, then the data are inconsistent with a Fermi surface, which is a single closed surface within the first Brillouin zone not touching the zone boundary. Hence, one concludes that the Fermi surface does touch the zone boundary. This is a typical example of the type of result obtained. The calculations are made, assuming a particular form; of the surfaces of constant energy this fixes the quantities M of the constant energy surfaces. Then using a low-field expansion (70), one calculates, say $\sigma_{\mu\nu\rho}^{(1)}$, (75); this may be compared with experiment. In the comparison with experiment, the data of most significance are those obtained using single crystals. As expected, the magnetoresistance is extremely anisotropic [46]. It would appear that the theoretical ideas underlying the interpretation of these experiments are generally sound. The situation in very high fields is less clear cut. It has been suggested [30] that the magnetoresistance should either saturate or increase as H^2. Although both have been found, so has a linear behavior of $\Delta\rho/\rho$. This could be due to the fact that this behavior is observed for polycrystalline samples; hence, an average over crystallographic direction is observed [34,47], but it is probably fair to say that the general question of the high-field behavior has not definitely been settled. Detailed experiments of a variety of effects, magnetoresistance and de Haas-van Alphen for example, on a single crystal would be very useful.

Note added in proof. For new significant results consult the recent conference report on *The Fermi Surface* [77].

2. *Discussion, Extensions, and Refinements*

(a) *General remarks.* With as large a number of assumptions involved in a typical calculation, the number of possible and sensible modifications which can be

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role in this comparison. Formulas (122)–(127) are not exact solutions of the Boltzmann equation. For high and low temperature they do go over in the exact expressions; hence, they have the status of interpolation formulas.

[38] Some of the refinements to be discussed later yield substantial improvements for Na.

made is very large. There is no point in just changing assumptions around to see whether an *ad hoc* change here or there produces a better agreement with experiment in some isolated instances. One rather seeks some general viewpoint which would allow one, in a systematic manner, to refine the physical description and obtain successively better agreement with experiment. Many of the assumptions which have been listed are actually quite reasonable, in spite of their *ad hoc* appearance. A number of the assumptions refer to the perturbation treatment of the various interactions. Although this is generally hard to justify rigorously, perturbation theory in solid-state theory usually provides a reliable guide (with some notable exceptions). Assumptions such as (14) and (15) are obviously expressions of what is known experimentally. The known linearity of the experimental relation between the currents produced and the impressed fields is the physical reason that one investigates the solutions of the *linearized* Boltzmann equation. Within the Boltzmannian framework, the most arbitrary assumptions are perhaps those referring to the independent equilibrium of the phonon system (12), and the special character of that system. Before analyzing the basis of these (and other) assumptions, it should be noted that apart from the theoretical ideas, one uses experimental information to obtain the final results for σ or x. Specifically, the dispersion law $E=E_\beta(k)$ of the electrons is used, as is the phonon spectrum. So, before altering any assumptions (using the simplest form of the transport theory), one should investigate the effect of the use of more realistic dispersion laws and a phonon spectra on the transport coefficients. It is not unreasonable to hope that in this manner one can reproduce more variety in the behavior of the transport properties than is obtained from (122)–(124). Certainly this study needs to be undertaken, perhaps even before other generalizations are considered. Occasional investigations of this type have been undertaken. Cornish and McDonald [48] investigated the effect of change in the dependence of ω on $\mathbf{q}$ on the electrical conductivity. Substantial effects were found, but a systematic series of such studies appears to be lacking.

The next most obvious refinement concerns more precise solutions of the transport equation. Use of either numerical methods or a version of the variation principle [49,50] enables one to obtain more accurate solutions to the Boltzmann integral equation (relaxation times need not be assumed). Sometimes the agreement between theory and experiment is somewhat improved by these more precise computations, but generally serious quantitative discrepancies remain. Thus, as one would rather expect, the problem is mainly a physical one. Several refinements can be made in connection with the calculations of the electron phonon scattering matrix element M (14a),

$$M=\boldsymbol{\varepsilon}_{q,\mu}(\mathbf{k}'-\mathbf{k})C(\mathbf{k}'-\mathbf{k}). \tag{128}$$

In the comparison with experiment so far discussed, C was actually taken to be a constant. An obvious improvement should result if one uses for C a more realistic function, for instance, the one obtained from the self-consistent calculation of Bardeen [12]. This type of calculation was made by Ziman [51], who showed that with this form of the matrix element, one can achieve excellent agreement with experiment for Na.[39] It would be worthwhile to have a general study of the dependence of the temperature variation of electrical and thermal conductivity (and thermoelectric power) as they depend on C. Through the recent advances in the fundamental understanding of the relationship of the one- (free) electron picture to the more rigorous many-electron system [52], the assumptions (1)–(6) can all be considered to be on a much firmer footing. The use of the collective description which enables one to take correlation effects into account leads to a modified density of states for the electron system $g(E)$. As one would expect, such a modified density of states leads to changed values of the conductivities and thermoelectric power. The actual magnitudes of the effects are different for different materials [53], but it does not at present appear that an appeal to this modification alone can remove all the discrepancies between theory and experiment.

(*b*) *Coupled phonon-electron system. Steady state of the lattice.* It was shown in Sec. A.1(c) how one can set up a gain-loss Boltzmann equation for the electron in terms of the distribution function of transition probabilities B, defined by (18a) and (18b). The equation for the change of the electron distribution function had the form

$$\begin{aligned}\frac{df_{k'}}{dt}=&-\sum_{k'',q}{}'\,[f_{k'}(1-f_{k''})(n_q+1)B_{k'\to k'',q}\\&+f_{k'}(1-f_{k''})n_qB_{k',q\to k''}]\\&+\sum_{k'',q}{}'\,[f_{k''}(1-f_{k'})(n_q+1)B_{k''\to k',q}\\&+f_{k''}(1-f_{k'})n_qB_{k'',q\to k'}].\end{aligned} \tag{129}$$

These identical processes cause changes in the phonon distribution function. There is, therefore, an equation describing the time rate of change of n_q, which is the exact counterpart of (129), namely,

$$\begin{aligned}\frac{dn_q}{dt}=&\sum_{k,k'}{}'\,[f_k(1-f_{k'})(n_q+1)B_{k\to k',q}\\&+f_{k'}(1-f_k)(n_q+1)B_{k'\to k,q}]\\&-\sum_{k,k'}{}'\,[f_k(1-f_{k'})n_qB_{n,q\to k'}\\&+f_{k'}(1-f_k)n_qB_{k',q\to k}].\end{aligned} \tag{130}$$

In both (129) and (130), the selection rule (13) must be satisfied; i.e., in the summations in (129) and (130)

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[39] One has to invoke U processes to obtain this agreement. See the discussion in Sec. (b).

a relation of the type $-\mathbf{k}'+\mathbf{k}-q=2\pi\boldsymbol{\tau}^*$, must be satisfied. Equation (130) can be written more compactly by combining terms; but (130) shows the connection with (129) most directly. A difference, worth noting in (129) and (130) is that the summations are over different variables: $\mathbf{k}'$ and $\mathbf{q}$ in (129); $\mathbf{k}$ and $\mathbf{k}'$ in (130).

The complete description of the electron-phonon system should be given in terms of two coupled integral equations, (129) and (130). Each equation has appropriate streaming terms, the collision terms are the ones written in (129) and (130). These equations should form the basis for the discussion of the joint electron-phonon system.

One of the important assumptions made in most conductivity calculations is that the phonon distribution may be considered as unaffected by the electron-phonon interaction. Stated differently, the phonons maintain an equilibrium independent of the electron-phonon interactions.

In addition, it is supposed that the transport coefficients depend in an insensitive manner on the phonon distribution [assumptions (12) and (13)]. These assumptions would be sensible only if one could find physical mechanisms which would cause a phonon equilibrium to be established much more rapidly than the electron equilibrium. Equivalently, the phonon relaxation time should be much shorter than the electron relaxation time. It would be interesting if these conclusions could be obtained from the coupled system of equations. There is no evidence that this is the case. The assumption that the lattice may be considered in equilibrium is so far rather arbitrary.[40] States in which *both* the electrons *and* phonons are in equilibrium do exist. In fact, a repetition of the argument which yielded (129) shows that the number of scattering processes of the type $\mathbf{k}'\rightarrow\mathbf{k}\cdot\mathbf{q}$ (k',k, and q have specified values) is given by $(f_{k'})(1-f_k)(n_q+1)B_{k'\rightarrow kq}$. The number of inverse processes ($k,q\rightarrow k'$) is by the same type argument $f_k(1-f_{k'})n_qB_{kq\rightarrow k'}$. In equilibrium, one expects (by the general principles of statistical mechanics) these numbers to be equal so that

$$f_{k'}{}^0(1-f_k{}^0)(n_q{}^0+1)=f_k{}^0(1-f_{k'}{}^0)n_q{}^0 \qquad (131)$$

for all k',k, and q which can be "connected by a scattering process." Hence, (131) has to hold for all k',k, and q which satisfy

$$E(\mathbf{k}')=E(\mathbf{k})+\hbar\omega_{\mathbf{q}}. \qquad (131a)$$

From (131) and (131a) one obtains the equilibrium distributions as

$$f_k{}^{(0)}=(e^{(E_k-\zeta)/kT}+1)^{-1} \qquad (132a)$$

$$n_q{}^0=(e^{\hbar\omega_q/kT}-1)^{-1}. \qquad (132b)$$

This is just what is to be expected for a Fermi and a Bose gas in equilibrium. Substitution of (132) into the transport equation shows that the collision terms do indeed vanish; hence, the equilibrium, once it is reached, persists. These remarks do not help in justifying the use of an equilibrium phonon distribution and a nonequilibrium electron distribution. One might hope to show that any given electron-phonon distribution would evolve in time towards the distributions (132).[41] Even this, though interesting, is irrelevant for the transport problem where one certainly deals with a nonequilibrium electron distribution. How and in what way the equilibrium is reached is closely connected with the kind of scattering processes considered. It is common [assumption (7)] to restrict one's self to N processes, defined by choosing $\boldsymbol{\tau}^*=0$ in (13), so that

$$\mathbf{k}'=\mathbf{k}+\mathbf{q}. \qquad (131b)$$

With this assumption one has introduced another conservation law in the scattering process. Thus, the "stationary distribution" under these conditions is determined by (131), (131a), and (131b). The general equilibrium solution is now

$$f_k{}^{(0)}=(e^{\beta(E_k-\zeta-\mathbf{k}\mathbf{a})}+1)^{-1}, \qquad (133a)$$

$$n_q{}^0=(e^{\beta(\hbar\omega_q-\mathbf{q}\mathbf{a})}-1)^{-1}. \qquad (133b)$$

Here **a** is an arbitrary constant vector, $\beta=1/k_0T$.

It is easy to check and important to observe that, for these distributions, the currents *do not vanish*. There is nothing very unusual about the fact that an additional conservation law affects the form of the distribution function. {In ordinary kinetic theory one deduces from the principle of detailed balancing $f_if_j=f_kf_l$ (f_i = number of molecules in cell i), together with the conservation of energy at collision $\epsilon_i+\epsilon_j=\epsilon_k+\epsilon_l$, *and* the conservation of momentum $\mathbf{p}_i+\mathbf{p}_j=\mathbf{p}_k+\mathbf{p}_l$, that f has the general form $f_i=A\exp[-\beta(\epsilon_i+\mathbf{a}p_i)]$, **a** is arbitrary.} This is a stationary distribution where the system as a whole moves with a momentum proportional to **a**. Equations (133a) and (133b) are the exact counterparts of these distributions [54].

Even though mathematically (133a) and (133b) are perfectly satisfactory (even rigorous) stationary solutions of the coupled transport equations in the absence of external fields, they describe curious physical situations. One has no external fields, but yet from (133) nonvanishing persistent currents. This corresponds to infinite conductivities. Another way to describe these rather startling results is to consider **R**, the total (quasi momentum) defined by

$$\mathbf{R}=\sum_k\mathbf{k}f_k+\sum_q\mathbf{q}n_q. \qquad (134)$$

By virtue of the conservation law (131b), valid for N scattering processes, **R** does not change in the course of time even if f and n do. In equilibrium, R is independent

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[40] It is possible to show that, for temperatures high compared to the Debye temperatures, the collisions between phonons (often omitted) do indeed provide a mechanism which allows the phonon system to remain in or near equilibrium. For this, one has to take the anharmonicity into account explicity. For low temperatures this does not work, the lattice cannot be considered in equilibrium.

[41] In statistical mechanics, this type of statement is proven by using the H theorem.

of the time. Now consider a system in a uniform electron field E_x; then the total change in R_x is

$$\left(\frac{\partial R_x}{\partial t}\right)_{\text{total}}=\left(\frac{\partial R_x}{\partial t}\right)_x+\left(\frac{\partial R_x}{\partial t}\right)_{\text{field}}. \tag{134a}$$

In a stationary state, $(\partial R_x/\partial t)_{\text{total}}$ should be zero. One already knows that $(\partial R_x/\partial t)_{\text{coll}}$ is zero; hence,

$$\left(\frac{\partial R_x}{\partial t}\right)_{\text{total}}=\left(\frac{\partial R_x}{\partial t}\right)_{\text{field}}=\sum_k k_x\left(\frac{\partial f_k}{\partial t}\right)_{\text{field}}$$
$$=-\frac{e}{\hbar}E_x\int d^3k k_x\frac{\partial f}{\partial k_x}=\frac{eE_x}{\hbar}\int d^3k f=\frac{neE_x}{\hbar}. \tag{135}$$

Consequently, $\partial R_x/\partial t\neq 0$; R_x is not time independent. In fact, R_x is increasing linearly with the time—a stationary state is not established. This is a restatement of the result obtained previously which states that finite currents can occur without field. For every given $\mathbf{R}$, one can determine $\mathbf{a}$, in (133a), which in turn determines a current $(\int \mathbf{v} f_k)$. The present result (135) asserts that for a given constant external field the current increases without bound (since $\mathbf{R}$ does). Both formulations have the same physical content; without a field one can have a finite current, with a field, an infinite current. It is now no doubt clear that the common reason for the occurrence of $\mathbf{a}$ in (133a) and the constancy of $\mathbf{R}$ is the restriction of the scattering events by (131b), the omission of U processes. For the establishment of a stationary state for finite values of the transport coefficients, the U processes are essential. From the fundamental significance of the U processes for the electron phonon interactions, it may appear puzzling that their omission (as in the ordinary theory) gives reasonable results. Actually, (131b) is precisely valid for electron interacting with a continuous medium. In that case one is no longer interested in describing the continuous medium and the electrons as part of one dynamical system. The medium rather functions as a heat reservoir affecting the electrons, but not influenced by them. The usual Boltzmann equation for the electrons describes just the stationary state established under the combined influence of the outside fields and the "phonon" reservoir. It appears that under certain circumstances this is not too bad a description.

The moment U processes are taken into account, one so to say acknowledges that the phonons are a part of the total dynamical system. In that case one genuinely discusses a coupled system. Consequently, the various aspects of the phonon system (the phonon spectrum, in particular) have to be taken into account in a much more detailed manner.

In principle, it is easy enough to take the U processes into account. Instead of imposing the restriction (131b) on the summations in the Boltzmann equations (129) and (130), one now uses the proper selection rule (13),

$$\mathbf{k}'-\mathbf{k}-\mathbf{q}=2\pi\boldsymbol{\tau}^*. \tag{136}$$

Since one restricts $\mathbf{k}$ and $\mathbf{k}'$ as well as $\mathbf{q}$ to lie in the first Brillouin zone, it follows that for given $\mathbf{k}$ and $\mathbf{k}'$, there exists a unique value of $\mathbf{q}$. (For a graphical demonstration see Ziman [55].) Actually, the evaluation of the integrals, the detailed investigation of the implications of the transport equations, becomes enormously more difficult.[42] Extensive studies of the effect of *UK* processes on conductivity and thermoelectric power have been made by Ziman [56], Bailyn [57], and many others.

It appears very difficult to make arguments which would allow one to assess the significance of the *UK* processes in general. When *UK* processes are considered, it is no longer true that the phonon-electron interaction is predominantly between the longitudinal modes and the electrons [as can be seen from (14a)]. Thus, with the introduction of U processes, a whole new class of other scattering events (between electrons and transverse phonons) is introduced as well. The results also become (as one might expect) much more dependent on the details of the phonon distribution. Finally, with the *UK* processes taken into account, the matrix element M (14a), or the function C, also enters the calculation, in new ways. The behavior of M as a function of $\mathbf{k}$ and $\mathbf{k}'$, therefore also enters in a different form in the final results. It is practically impossible to estimate the combined effect of these various interrelated factors without detailed calculations.

The general picture which emerges is certainly not clear in all its details, but certain features seem to be standing out as reasonably definite:

1. *UK* processes are significant, down to the very lowest temperatures for both electrical and thermal conductivities.
2. The contribution of the transversal phonons is generally significant; at low temperatures the transversal contributions are the dominant ones.
3. The transport phenomena, at low temperatures in particular, are extremely sensitive to the assumed phonon spectrum.

For a more precise discussion, including the many calculational details on which these results are based, [56] and [57] as representative references should be consulted. The general significance of the *UK* processes, of the coupled Boltzmann equations, can be appreciated from the foregoing discussion.

(*c*) *Relaxation times.* The status of assumption (16), the existence of a relaxation time, is somewhat peculiar. One can actually prove the existence of relaxation times for certain processes as was done in (49) and (112). It was already pointed out that for the phonon-electron scattering there is a relaxation time for high temperature and one for low temperature, but *no* relaxation

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[42] It is clear from (136) that the actual zone structure of the material plays a much more significant role in these calculations than in the previous ones where $\boldsymbol{\tau}^*$ was necessarily zero. This too complicates the explicit discussion.

time in general. The proof of the existence of relaxation times is restricted to solutions of the transport equation of a special form, those near equilibrium. One then investigates the nature of the collision term for solutions of that type. It is often convenient, however, to describe processes by relaxation times. For instance, the interactions between phonons can, in an approximate manner, be taken into account by introducing a phonon-phonon relaxation time. In order to describe the coupled phonon-electron problem in a more realistic way, Hanna and Sondheimer [58] introduce the following refinements in the usual description:

(1) They did not assume that the lattice is in equilibrium.

(2) They assumed that both transverse and longitudinal modes interact with conduction electrons.

The simplest way to introduce these refinements is just to introduce three relaxation times (three separate mean free paths), one for the longitudinal modes, and two for the transversal one. These mean free paths (or relaxation times related to them) can strictly be defined in the high-temperature limit; each one now depends on an appropriate interaction constant C_j. In addition, one has to introduce a number of mean free paths (relaxation times) to schematize the various processes which can scatter *phonons*, such as impurities and anharmonicity of the lattice (phonon-phonon scattering). These relaxation times, corresponding to the efficiency of the processes they represent, are strongly temperature dependent. At low temperatures the main mechanism scattering phonons is impurity scattering, while at high temperatures the phonon-phonon scattering predominates. This kind of information is fed into the formalism through the assumed dependence of the relaxation times on temperature. With these assumptions, one can now explicitly calculate the electrons and phonon distributions, hence, the transport coefficients.

Since this is a well-defined extension of the customary theory, the effects of the lack of the equilibrium of the lattice can be explicitly obtained. On carrying out this program, one finds a reasonable agreement between theory and experiment. (It should be noted that one has also introduced a substantial number of new parameters, so that it is not too easy to judge whether or not the agreement obtained is fortuitous [59].) Whereas these remarks indicate the utility of the relaxation time notion, they are of no help in understanding the question of the existence of a relaxation time in general situations. The basic point of introducing a relaxation time is that it allows the replacement

$$(\partial f/\partial t)_c \cong -(f-f^{(0)})/\tau, \tag{137}$$

where $(\partial f/\partial t)_c$ is usually given as an integral operator. That (137) is a tremendous simplification is evident. Consider, in order to study the general validity of (137), the linearized Boltzmann equation written in the form

$$(\partial f/\partial t) = Of; \tag{138}$$

O is defined by (78). f is assumed to vary only because of collisions described by the operator O. O is a *linear* operator. [In fact, (79a) shows that O is a self-adjoint operator if one restricts one's self to real functions f.] Suppose one knows the eigenfunctions (u_n) and eigenvalues λ_n of the operator O, so that

$$Ou_n = \lambda_n u_n. \tag{139}$$

The u_n are now known functions of k, the λ_n are real numbers. *Any* solution of (138) can be written as

$$f(\mathbf{k}t) = \sum\nolimits_n C_n e^{\lambda_n t} u_n(\mathbf{k}). \tag{140}$$

The C_n are coefficients, independent of $\mathbf{k}$ and t; they are determined by the initial value of f. The possibility of writing (140) depends on the linear character of O. It is now easy to formulate some conditions for the eigenvalues of the collision operator, which in some sense yield the approximate validity of (137).

(1) Suppose that O is one of the eigenvalues.

(2) Suppose all other eigenvalues are negative and distinct. From (140), one sees that in that case

$$\lim\nolimits_{t\to\infty} f(k,t) = C_0 U_0(k)$$

(for all the exponential factors will go zero in that limit). $C_0u_0(k)$ is the limiting distribution for infinite time; this is the equilibrium distribution. In that case, (140) may be rewritten as

$$f(\mathbf{k},t) = C_0u_0 + C_1e^{\lambda_1 t}u_1(\mathbf{k}) + C_2e^{\lambda_2 t}u_2(\mathbf{k}) + \cdots. \tag{141}$$

Assume further that

(3) $\quad |\lambda_1| \ll |\lambda_2| \ll |\lambda_3|.$

This means that for times $1/\lambda_1 \gg t \gg 1/\lambda_2$ the exponentials of all but the first are practically equal to zero. For such times one may write

$$f(\mathbf{k},t) \cong C_0u_0 + C_1e^{\lambda_1 t}u_1(\mathbf{k}). \tag{141a}$$

From (141a), one sees that for such times

$$(\partial f/\partial t) \cong \lambda_1(f-f^0) \qquad f^0 = \text{the equilibrium distribution}). \tag{141b}$$

This indeed is the relation usually employed to define a relaxation time. (Note that the eigenvalues λ were assumed to be negative.) "The" relaxation time is the negative eigenvalue of the collision operator nearest zero.

Whether the collision operator O does indeed possess the characteristics (1)–(3), which allow the approximate definition of a relaxation time, depends on the kernel V of the integral operator. This in turn depends on the character of the interaction.

From this very simple minded argument, one can see that in the approach to the equilibrium, there are certain characteristic times (in fact infinitely many) which describe the various stages of the process. It is interesting that the relaxation times emerge as eigenvalues of the collision operator.

This technique was applied very effectively by Chang and Uhlenbeck [60] in connection with the following problem. A particle, mass m, is under the influence of given forces. It is bound harmonically to a center, as well as acted upon by a periodic external force. It is surrounded by a gas of particles of mass M. The particle m and the molecules M can collide, with a given force law. The problem is to find the power absorbed by the particle from the external field. For the present discussion, the pertinent point is the observation that this problem again reverts to a discussion of the Boltzmann equation, which in this case reads [the notation is the same as in (I.11e)]:

$$\frac{\partial f}{\partial t}+\mathbf{v}\nabla_x f+\mathbf{X}\nabla_\nu f = \int d^3v_1 \int d\Omega g I(g,\theta)[F'f'-Ff] \equiv Of. \quad (142)$$

Here F is the given (Maxwellian) distribution of the gas M.[43] The equation for f is again an integral equation, a linear one. The collision term has the general form assumed in (138). The problem as stated can be solved *exactly* for certain force laws between m and M. This corresponds to certain special forms of the scattering cross section I.[44] The reason the problem can be solved is just that for these special force laws one can obtain the spectrum of the operator O. [One may verify by explicit construction of the eigenvalues that the eigenvalue spectrum does indeed have the properties (1) and (2).]

With an exact solution available one can now test the validity of the approximate expressions of the collision term. Of particular interest here is the question of the validity of the approximation (137). In this special case (the force between m and M is a repulsion proportional to r^{-5}, the external force is an alternating one, $eE_0 \cos\omega t$; m is bound harmonically to the origin with potential $-\frac{1}{2}m\omega_0^2r^2$) the approximation (37) cannot be valid for all values of the mass ratio m/M. This actually can be seen in a reasonably elementary manner by studying the equation for the average velocity and position. These entities are defined by

$$\bar{x}_\mu = \int\int d^3x d^3v x_\mu f, \quad (143a)$$

$$\bar{v}_\mu = \int\int d^3x d^3v v_\mu f. \quad (143b)$$

Now from (142) one may obtain equations for $\bar{x}$ and $\bar{v}$ by multiplication by x_μ and v_μ, respectively, and integration over d^3x and d^3v. On carrying out these operations, one obtains

$$d\bar{x}_\mu/dt = \bar{v}_\mu \quad (144a)$$

$$d\bar{x}_\mu/dt = X_\mu(\bar{x}) - \tau^{-1}\bar{v}_\mu. \quad (144b)$$

Here τ^{-1} is a reasonably complicated but known integral over I, $X_\mu(\bar{x})$ is the external force evaluated at $\bar{x}$. (X depends linearly on x in this case.) Equation (144) is an *exact* consequence of (142). (From these equations one could calculate the time dependence of $\bar{x}$ and $\bar{v}$; hence, the power absorbed by the particle m by taking the time average of $\bar{v}_x E_0 \cos\omega t$.) If one uses instead of (142) the relaxation approximation (137), one can again find the equation of motion for the average values very easily; this time they read[45]

$$d\bar{x}_\mu/dt = \bar{v}_\mu - (\bar{x}_\mu/\tau), \quad (145a)$$

$$d\bar{v}_\mu/dt = X_\mu(\bar{x}) - (\bar{v}_\mu/\tau). \quad (145b)$$

It is evident by inspection that (144) and (145) are not the same. They do indeed lead to different observable results (such as a different power loss). In general, even in this simple case, the relaxation time assumption is not valid. It would be of great interest to have a systematic investigation of the relationship between the character of the intramolecular forces and the degree of validity of a solution obtained by a simple relaxation time. Among other things this would involve the study of the spectra of the collision operator as a function of the intramolecular forces (or the electron phonon interaction). It is worth noting (with regret) that the electron-phonon system is basically a coupled one. It is not so obvious how one should apply techniques of the type described, which are valid for linear operators only, to those situations. Probably some judicious linearization can be performed and perhaps something can be learned about a more precise way of introducing relaxation times in the formalism. No studies of this kind seem to exist at present.

3. *Intrinsic Difficulties*

The refinements discussed in the preceding section were all elaborations of the same underlying framework. The basic notions, the distribution functions, and the equations they were to satisfy, were all on the "Boltzmannian level." (Reverting back to Table II, one can see that they refer to the "useful" Boltzmann equation.) Since even within this framework there are so many additional assumptions which need be made for practical calculations, it might appear unreasonable to discuss an even broader framework as a basis for the computations. There are, however, a number of separate arguments,

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[43] In the solid-state context, (42) describes the Boltzmann equation of electrons of mass m, interacting with an equilibrium phonon distribution which in this case is Maxwellian. The analysis has not been carried out for a Bose distribution for F; this might be amusing.

[44] For the special case considered $gI(g,\theta)$ is a function of θ alone.

[45] It should be noted that the τ, introduced in (145a) is the assumed relaxation time in (137). It seems reasonable to *pick* it as the same entity occurring in (144b).

which all indicate that the Boltzmann level is indeed inadequate to describe several of the physical situations which occur in transport processes. Some of the arguments are more compelling than others and not all of them apply to identical situations, but it would appear that together they provide a strong incentive for basing the investigation of a number of transport phenomena on the density matrix (described in I, Sec. B) rather than on the transport equation.[46] In this section several of the arguments leading to this conclusion are presented. Some brief comments are added to the somewhat disconnected remarks to present a more unified picture.

(*a*) *Difficulties of generalization of the Boltzmann equation.* The classical Boltzmann equation as usually written down [(I.11)] applies to dilute gases. It would appear reasonable to expect that one can, by a fairly straightforward procedure, generalize the equation to dense systems, so that one might take triple and higher collisions into account in a systematic manner. Actually, the generalization to higher densities is not at all straightforward; one has, so to say, to take "the long way around." It is only possible to obtain such a generalization starting from the Liouville hierarchy [(I.20), see also Table II], then integrations and additional smoothing or averaging operations need be performed. (Some of the necessary procedures were described in I.) The method is certainly not direct, but most important is the observation that this generalization (to a reasonable new physical situation: dense gases) can only be performed by enlarging the Boltzmannian framework. It was not until fairly recently that the correction terms for such higher terms were written down correctly [61].

The fact that it is difficult to generalize the Boltzmann equation to dense system, cannot be considered as an objection to the equation as such. It is, however, rather disturbing that the framework on which the Boltzmann equation is based seems incapable of describing a physical situation, which does not appear qualitatively different. One needs a drastic revision instead.

(*b*) *Lack of systematic development.* In all the calculations given, just the first approximation to the distribution function was used. Higher approximations in the external field strength, for example, are rarely considered. In fact, in certain perfectly respectable conductivity theories, one cannot even make a systematic development including terms in E_{ext}^2. [An example is given in Sec. (d).]

In the Lorentz theory of conductivity, the electrons scatter elastically from fixed ions. Thus, no energy can be transferred from the electron system to the lattice. In particular, this means that there can be no Joule heat. Since the Joule heat is proportional to E_{ext}^2, one sees that it is not possible in this theory to have a consistent development as far as E_{ext}^2. In general, the description of the Joule heat would demand the introduction of dissipative terms in the equation for f. This could be done most effectively by introducing a separate phonon equation coupled to the electron equation, as was sketched in Sec. B.2(b). One then should really prove that from these equations the dissipative character follows. Thus, in this case again, a slight refinement of the procedure changes the formalism in a rather decisive manner. One cannot, without making other modifications, extend the development to higher orders *and keep* a physically sensible situation. This is no convincing argument against the use of the Boltzmann equation, it rather serves once again to stress its limited domain of applicability.

(*c*) *Definition of distribution function.* The two points discussed so far referred to the *classical* situation; f, the distribution function, was defined in the μ space ($\mathbf{x}$, $\mathbf{v}$ space). In the conductivity calculation, however, one deals most definitely with a quantum situation. It was stated before (I, Sec. A.3) that in quantum theory, because of the uncertainty principle, one cannot, strictly speaking, define a μ-space distribution function. Thus, it makes no sense to discuss an equation for $f(\mathbf{k},\mathbf{x},t)$. This is a very basic objection; it would seem to destroy the Boltzmann equation as a legitimate means of description of quantum transport processes. In principle this is true. In many applications, however, one considers the distribution function as a function of $\mathbf{k}$ and t only (not of x); the uncertainty principle does not preclude the use of these functions. When a positional dependence is considered at all, it usually occurs through the dependence of the distribution function on the external parameters, such as the dependence of the temperature on x. For example,

$$\partial f^0/\partial x = (\partial f^0/\partial T)(\partial T/\partial x).$$

In order that this expression makes sense, it is only necessary that an electron can be localized over macroscopic distances such as $(T^{-1}\partial T/\partial x)^{-1}$. This can be done using wave packets which contain only a very small range of wave numbers. In this limited and approximate sense, one can use a distribution function which is a function both of $\mathbf{k}$ and $\mathbf{x}$. Even though there is no objection in principle against using a distribution function f_k, it is worth observing that it must be carefully defined when one is dealing with a strongly interacting system of particles. For noninteracting particles, f_k just gives the number of particles in state k, where k labels the free particle states. For *interacting* particles one cannot give individual particle characteristics such as $\mathbf{k}$ and obtain a description of the system as a whole. One seeks in the interacting case a set of variables which describes either the particles, or some combination of particles, or the excitation spectrum of the system in such a way that in first approximation these entities may be considered independent of one another. Just as in the free particle case, the energy is a sum $E=\sum_k E_x$; one now seeks new variables $\boldsymbol{\eta}$, so that the total energy

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[46] In fact, in some instances, one has no choice, but to base the discussion on the density matrix formalism. Transversal magnetoresistance is a case in point.

can be written $E=\sum E_\eta$. Refinements can then be introduced later. A typical example occurs in the collective description of an electron gas [62], where the complicated and strong Coulomb interaction between electrons are replaced by a "collective" energy which is a sum over the separate collective modes. In addition, there is a much smaller screened electron interaction. One could phrase the search for variables η as a search for "good" quantum numbers. The description of the system as a whole consists of the distributions of the "constituents" of the system over the states defined by the "good" quantum numbers. "Constituent" now can stand for an actual particle (as for noninteracting systems) or for a pair of particles (as in superconductivity), an excitation, etc.

In these circumstances, one can again define a distribution function, although its changed meaning should be recognized.

These considerations become a good deal easier to formulate within the context of second quantization [63]. Let $|k\rangle$ stand for a single particle state, a_k and $a_k\dagger$ for annihilation and creation operators. Then $a_k\dagger a_k=n_k$ is *always* the number operator of particles in state k, whatever that state k is. The "state" of the system as a whole can now be described as a superposition of eigenstates of the number operators n_k. The system of a one-particle wave function $|k\rangle$ is arbitrary in this formulation. One set $|k\rangle$ can be more convenient than another, but any complete set can be used [64]. It is no longer true that n_k and the Hamiltonian commute; the interaction generally redistributes the particles. The statistical discussion proceeds straightforwardly; if a Hamiltonian is given, say of the form

$$H=\sum_k \epsilon_k a_k{}^\dagger a_k+\sum_{i,j,k,l} a_k{}^\dagger a_l{}^\dagger V a_i a_j, \tag{146}$$

one may define the grand partition function

$$Z_g=\operatorname{Tr}(e^{-\beta(H-\mu N)});\quad N=\sum a_k{}^\dagger a_k,\quad \beta=1/k_0T. \tag{147}$$

The average number of particles in state k is then

$$\bar{n}_k=\frac{1}{Z_g}\operatorname{Tr}(a_k{}^\dagger a_k e^{-\beta(H-\mu N)}), \tag{148}$$

which is the definition of the distribution function which is *always* valid.

In using *this* definition of a distribution function (so far only defined for equilibrium states), one has gone well beyond the scope of the Boltzmannian description. (If this same level of description is used in nonequilibrium situations, one is just using the density matrix formalism.) Perhaps this brief discussion shows that a consideration of the precise definitions of a distribution function in quantum theory leads rather naturally to a description in terms of occupation numbers (which are just the eigenvalues of the number operators) and hence to a use of a second quantized formalism.

(*d*) *Limitations of Boltzmann equation.* The general idea of the conductivity calculation is to study the changes produced in the electron distribution by the electron-phonon interaction together with the external electric field; however, even assuming that such an electron distribution can be defined, it does not necessarily follow that a Boltzmann equation for that function can be constructed.

The distribution function gives the number of electrons in state **k**, more precisely in an interval d^3k around state **k**. The numbers f_k change rather rapidly (as a function of energy) in a region kT around the Fermi energy $E_F=\zeta$. In order to define a distribution function, it should be possible to give the number of electrons in energy ranges which are small in comparison with kT. When dealing with electrons interacting with phonons, the lifetime of the specific electron state is rather short, of the order of a relaxation time. From the uncertainty relation, one obtains then an intrinsic indefiniteness in the energy of order $\hbar/\tau$. One must demand that the uncertainty in the energy is less than the thermal energy or

$$\hbar/\tau\ll kT. \tag{149}$$

For if $\hbar/\tau>kT$, the basic uncertainty in the electron energy would be larger than the energy width over which the electrons are distributed. To have an electron distribution function at all, one needs an energy discrimination well defined up to fractions of kT. The intrinsic uncertainty $\hbar/\tau$ should be smaller than that. This is the content of (149) [65].

It would appear that (149) is a necessary condition for the possible definition of a distribution function. This same condition reappears in a different connection. The collision term in the Boltzmann equation (always obtained in a perturbation expansion) contains terms of the following type [(16a) and (16b)]:

$$\textstyle\sum_{k'}|\langle k'|U|k\rangle|^2(f_{k'}-f_k|O(E-E'). \tag{150}$$

U is some perturbing potential.[47] The function O has a general δ-function type character, as was mentioned before. If one uses O as a δ function in the sum, one in fact asserts that $O(E)=\sin(Et/\hbar)/\pi E$ is a rapidly varying function compared to the other factors in the integral. O has appreciable values only when $E-E'<\hbar/t$, where t is a measure of the lifetime of state E. However, in the interval kT near the Fermi surface, the functions $f_{k'}$ and f_k may vary appreciably; hence, one cannot generally treat them as a constant or, what is the same, treat O as a δ function. If, however, the range $\hbar/t$, where O is appreciable, is only a small fraction of kT, the variation of O in that region is much larger than the variation of f (which has all of kT to achieve its variation). Hence, if $\hbar/t\ll kT$, O in (150) may be replaced by a δ function. If one identifies the lifetime of a state with t, this condition is again equivalent with (149).

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[47] In (150) one has written the matrix element for the scattering by impurities.

Unfortunately, (149) is not satisfied for many metals. Typical values would be $\hbar/\tau \sim 0.1$ ev; $kT \sim 0.01$ ev. The nature of this severe limitation of the validity of the transport equation has been the subject of several investigations [66–70].

The study by van Wieringen [69] is in many ways the most straightforward. One expands the wave function of the actual system (electrons plus impurities) in terms of unperturbed Bloch wave functions:

$$\Psi(\mathbf{x},t) = \int d^3k \psi_k(x) a_k(x,t) e^{-(i/\hbar)E_k t}. \tag{151}$$

From the Schrödinger equations for Ψ, which contains the scattering potential U, one obtains the usual equations for the development coefficients a_k. One now makes an expansion

$$a_k(t) = a_k{}^{(0)} + a_k{}^{(1)} + \cdots \tag{152a}$$

with the solution

$$a_k{}^n(t) = -\frac{i}{\hbar} \int d^3k' \langle k|U|k'\rangle \times e^{-(i/\hbar)(E_k - E_{k'})t} a^{n-1}(\mathbf{k}',t). \tag{152b}$$

The calculations of a to second order give just the transitions rate (150). One can now carry the development to fourth order. On using the fact that the scattering potential is a sum of *randomly arranged* impurities, one can estimate the various terms and in this way establish that the fourth-order terms are negligible as long as

$$\hbar/\tau - \ll E_F. \tag{153}$$

This inequality is generally satisfied. It is certainly striking that the parameter $\hbar/\tau kT$ does not enter in the calculation at all.

This calculation shows that the perturbation expansion under the restriction (153) is a sensible one. However, the physical reasons for the validity of the expansion are not yet clear, nor has the possibility of defining a distribution function [for which (149) appears essential] been demonstrated. Equation (153) can be given a very intuitive interpretation. Call

$$\Lambda = v_F \tau, \tag{154}$$

where v_F = Fermi velocity, and Λ is the mean free path of an electron, the average distance traveled between collisions. If one wants to talk about a classical orbit at all, with electrons experiencing a well-defined set of collisions, Λ must be larger than the de Broglie wavelength λ of an electron or

$$\Lambda > \lambda, \quad v_F - > \hbar/mv_F, \quad mv_F{}^2 > \hbar/\tau. \tag{155}$$

This one recognizes as (153), which therefore appears as a condition for the semiclassical description of an electron in a lattice.[48] However, neither the intuitive appealing condition (153) nor the wider validity of the perturbation expansion dispose of the inequality (149), which is generally not satisfied.

The most precise discussion of this question has been given by Lewis [67]; there are a few closely related subtle points involved.

(1) It should first be noted that an electron makes generally both elastic and inelastic collisions. That means that one should be extremely careful with the uncritical application of the results of nondegenerate perturbation calculus as in (150). The electronic states to which (16) is applied are either degenerate or very nearly so. So one should analyze the effects of this degeneracy (this is exactly what was done by Lewis [67]).

(2) The energy uncertainty of a state is determined by $\Delta E = \hbar/T$, where T is some characteristic time. This T must be the lifetime for the decay of the state *with* a *change* in energy. Thus, the time which should properly go in (149) is the relaxation time t for inelastic collisions only. For the actual relaxation process, occuring in conductivity and nonequilibrium theory, elastic collisions are every bit as effective as inelastic ones. In the aforementioned Lorentz study theory of conductivity, one has only elastic collisions. Use of $\Delta E = \hbar/\tau$ would, in that case, yield an infinite lifetime, whereas the actual relaxation time is finite. This is due to the "relaxation" effect of the elastic collisions.

It is asserted[49] [66] that the relaxation time for inelastic collision is

$$\tau_{\text{inel}} = (E_F/kT)\tau_{\text{elastic}} \tag{156}$$

Since, by the previous argument, the condition (149) should properly by replaced by $\hbar/\tau_{\text{inel}} \ll kT$, one reobtains, using (156), the condition (153).

The τ which should enter the indefiniteness of the energy of the electrons $\Delta E = \hbar/\tau$; is not necessarily the experimental relaxation time, but a longer time (156). This makes the intrinsic uncertainty ΔE much smaller; this in turn allows the construction of a distribution function. The confusion as to what precise time interval should be used in the uncertainty relation is closely connected with the uncritical use of the nondegenerate perturbation calculation in transport theory. To elucidate this point, one may consider a simple example given by Lewis [67]. Consider the one-dimensional elastic scattering of electrons from impurity centers. Suppose there is also an electric field E_x. The transport equations, in the notation used throughout, is now

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[48] The conditions (155) and (153) guarantee that the electron-phonon interactions can be described as a succession of "collisions" of well-defined duration, while in between the collisions, the electron can be described classically.

[49] In order to obtain this result, one has to estimate the relative efficiency of elastic and inelastic collisions. Although there are many plausible ways to do this [using (16)] just by counting the available states, none seem particularly compelling.

$$\frac{\partial f_k}{\partial t}+\frac{E_x}{\hbar}\frac{\partial f_k}{\partial k}=\int_{-\infty}^{+\infty} dk'[(1-f_k)f_{k'}A_{k'\to k} \\ -f_k(1-f_{k'})A_{k\to k'}]. \quad (157)$$

The A's are [see (18a) and (18b)] the transition *rates*. The A's contain the functions O, which are often replaced by δ functions. It is this point which needs investigation. The A's have the general symmetry noted in (46c),

$$A_{k'k}=A_{kk'}. \quad (158)$$

This symmetry is valid independent of the replacement of the O functions by the δ functions; it follows just from the form of the matrix elements A and the even character of the O functions [Eq. (16)].

The customary treatment of the transport theory can be applied to (157). Note first that because of (158), one can write

$$\frac{\partial f_k}{\partial t}+\frac{E_x}{\hbar}\frac{\partial f}{\partial k}=\int_{-\infty}^{+\infty} dk' A_{k'k}(f_{k'}-f_k)=\left(\frac{\partial f}{\partial t}\right)_{ccll}. \quad (157a)$$

One checks the conservation of particles by integrating (157a):

$$\frac{\partial}{\partial t}\int_{-\infty}^{+\infty} dk f_k=0. \quad (159)$$

Suppose now one replaces the O functions occurring in the transition rates A by strict energy δ functions, (this corresponds to the usual procedure). A can then be written [see (45) again]

$$A_{k'k}=|\langle k'|U|k\rangle|^2\delta(k^2-k'^2). \quad (160)$$

The only transitions which can occur are from $k\to -k$; this is physically sensible in a one-dimensional elastic scattering. The unperturbed states are e^{ikx} and e^{-ikx} for a given energy.[50] On using

$$\delta[k^2-(k')^2]=(1/2|k|)[\delta(k-k')+\delta(k+k')],$$

one may write

$$A_{k'k}=B(k)[\delta(k-k')+\delta(k+k')]. \quad (161)$$

One observes from (160) that since $k'=\pm k$, B_k must be an even function of k. Substitution of (161) into (157a) immediately gives

$$\frac{\partial f_k}{\partial t}+\frac{E_x}{\hbar}\frac{\partial f}{\partial k}=B(k)[f(-k)-f(k)]=\left(\frac{\partial f}{\partial t}\right)_c. \quad (162a)$$

This equation corresponds precisely to the Boltzmann equation (20), which is the starting point for all conductivity calculations. One can now proceed in the usual way, seek stationary solutions of (162a) by expanding the stationary solutions in powers of E_x, keeping only first powers in E_x. Writing

$$f=f^{(0)}+E_x\Phi \quad (163)$$

and carrying out the indicated procedure yields, after a trivial calculation,

$$f\cong f^{(0)}-\frac{E_x}{2\hbar B(k)}\frac{\partial f^0}{\partial k}, \quad (163a)$$

when f^0 is the equilibrium Fermi distribution. The current is found again in the time-honored manner[51]

$$j\sim\int_{-\infty}^{+\infty} vfdk\sim\int_{-\infty}^{+\infty} e\frac{\hbar k}{m}fdk \\ =E_x\int_{-\infty}^{+\infty}\frac{k}{B(k)}\frac{\partial f^0}{\partial k}dk. \quad (164a)$$

The conductivity thus has the familiar form

$$\sigma=-\int\frac{kdk}{B(k)}\frac{\partial f^0}{\partial k}\cong\frac{k_F}{B(k_F)}. \quad (164b)$$

Just how accurate the last approximation in (164b) is depends on the degree of degeneracy of the electron gas. But in any case (164b) yields σ.

The similarity of the development just given [Eqs. (157a)–(164b)] to the typical conductivity calculation is no doubt evident. One special feature of these equations is worth noting; from (162a), one sees that

$$[\partial f(k)/\partial t]_c+[\partial f(-k)/\partial t]_c=0. \quad (165)$$

Hence, the function $[f(k,t)+f(-k,t)]$ is unaffected by collision states which are not equilibrium states, but which are symmetric (are not influenced by collisions). Stated yet differently, symmetric deviations from the equilibrium state do not relax towards equilibrium. Their relaxation time is infinite.

One may now relax the strict δ function character of the matrix element $A_{k'k}$ and yet obtain a similar result. In fact, the perturbation calculations gives not a δ function, but a function having a sharp maximum, near $k=k'$. Transitions from $k\to k'\neq -k$ are possible. So one replaces the δ function by a function which has its values in ranges of k' near $|k|$ such that the corresponding variation of energy $E'-E\sim\hbar/\tau$. One can then apply the integral *mean* value theorem to the integrals over k' in (157a); the equation becomes

$$\frac{\partial f_k}{\partial t}+\frac{E_x}{\hbar}\frac{\partial f}{\partial k}=B(k^*)[f(-k^*)-f(k)]. \quad (166a)$$

Here k^* is some value of k, in the interval Δk. The interval is given by

$$(\hbar^2/2m)[(k^2)-(k')^2]\sim\Delta E=\hbar/\tau.$$

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[50] It is quite evident that one deals with a doubly degenerate system.

[51] Factors 2π, other constants are omitted in this calculation. One also assumed $v=\hbar k/m$.

Equation (166a) is an exact consequence of (157a). One can now follow the general pattern, and obtain an approximate solution to (166a), which again yields a current and a conductivity. The only condition involved for the validity of the procedure is that the energy difference $(\hbar^2/2m)(k^2-k'^2)$ be a small fraction of the Fermi energy. [This in particular allows the approximation in formulas (164b) to be made in this case as well.] It thus appears possible to relax the δ function condition and obtain a next approximation subject only to the restriction

$$(\hbar^2/2m)(k^2-k'^2)\sim\Delta E=\hbar/\tau\ll E_F. \tag{167}$$

This is in harmony with (153). To show the great care one must exercise in using equations in transport theory, it is amusing to show that even though the development starting from (162a) follows the same outline as that in conductivity theory, with formally identical results, the calculation is actually somewhat deceiving. Note that the stationary solution f_k satisfies

$$(E_x/\hbar)(\partial f/\partial k)=B(k)[f(-k)-f(k)]. \tag{162b}$$

It can be shown that rigorously (i.e., without expansion in E_x) Eq. (162b) has no solution at all. One sees from (162b) that $\partial f/\partial k$ is an *odd* function of k; hence (without approximation), $f(k)$ is an *even* function. But this means that the current $j=\int kfdk=0$. Thus, from (162b) one has an identically vanishing current. In fact, since f is even, (162b) becomes $\partial f/\partial k=0$; Eq. (162b) has no sensible solution at all. Yet (163) is (to first order in E) an approximation, which one *feels* has rather more significance than the equation which it solves. But from a formal standpoint the stationary equation (162b) has no nontrivial solutions.[52] Although the one dimensionality of this model causes this example to be rather extreme, the result illustrates a point made before: Equations are valid in limited ranges only; they usually have only *approximate* solutions which are meaningful; improvements, in principle, are impossible. To make refinements one cannot find better approximate solutions to a given equation; one has to start from a *different* equation having a different domain of validity.

(*e*) *Quantum limit.* The basic limitation of the Boltzmannian description is that $\Lambda>\lambda$. (The mean free path of the electron is large compared to the de Broglie wavelength.) Basically, this means that one describes the electrons using wave packets. The condition just given expresses the possibility of localization of the electron within a mean free path as a (physically obvious) condition for the validity of that description. There are other inequalities required for such a description; for instance, λ should be small compared to distances over which the external parameters vary appreciably. This condition is always satisfied. If a magnetic field is applied, altogether new situations may arise. The field causes electrons to spiral around the field direction, with a frequency $\omega_H=eH/mc$. (It should be noted that m is for a real metal or semiconductor, the *effective* mass. Thus m may be as much as a hundred times smaller than the mass of a free electron ,and ω_H a corresponding amount higher). An electron of velocity v describes a circular orbit of radius $r_H=v/\omega_H$. For high fields r_H becomes very small. In the presence of a magnetic field, there are therefore at least three characteristics lengths, r_H the radius of the circular orbit, Λ the mean free path and λ the de Broglie wavelength. The physical situation depends very sensitively on the relative magnitudes of those lengths. (There are three characteristic times, corresponding to these lengths: $1/\omega_H$, the cyclotron resonance period, the relaxation time τ, and the "duration" of a collision λ/v_F.) The presentation of conductivity theory given so far refers to the usual case where $\lambda<\Lambda<r_H$; this is a small field semiclassical situation. As soon as $r_H\sim\Lambda$, or $\omega\tau\sim1$, the situation changes. For then the electron moves for an appreciable time under the influence of a magnetic field with only occasional collisions. In that case one can*not* take the magnetic field into account as a perturbation, one *can* take the collisions into account as a perturbation and treat the magnetic field more precisely. These are quantum phenomena, associated with the motion of electrons in magnetic field, the de Haas-van Alphen effect was a manifestiations of these quantum phenomena. Hence, in fields strong enough so that $\omega_H\tau>1$, the quantization [Sec. B.2(d)] of the individual electrons *must* be taken into account. It is important to note that a typical relaxation time $\tau\sim10^{-14}$; hence, for $\omega_H\tau\sim1$; $\omega_H\cong10^{14}$, the corresponding level separation is $\hbar\omega_H=0.1$ ev. This level separation is much larger than kT (at 10°). (Actually, a frequency $\omega_H\sim10^{14}$ requires a magnetic field of order $H=10^6$; for those electrons having a small effective mass, the necessary field can be much smaller.)

Another consequence of the introduction of a strong field is that $k_xk_yk_z$ are no longer "good" quantum numbers. One cannot use the Bloch scheme to classify the states. One *can* use k_z, E, and n [see (101b)] to characterize states; the distributions over these states with n, a discrete variable, demand a quantum treatment.

The de Haas-van Alphen oscillations have their origin in the quantized energy levels of an electron in a magnetic field (it is a genuine *macroscopic* quantum phenomenon). This same level structure also gives rise to a variety of oscillatory transport effects. Oscillations in the magnetoresistance [71], the Hall effect [72], and the thermal magnetoconductivity [73]. (See [74].) Just as the discussion of the de Haas-van Alphen effect requires the study of the consequences of the energy level scheme, the oscillatory transport phenomena can

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[52] It should be realized that a similar conclusion cannot be obtained if one studies the *time*-dependent equation (162a). This already indicates that one should properly study the *time* evolution of a given deviation from equilibrium. One would also find that the time-dependent solutions behave very differently for different time intervals. The study of the stationary state alone is the crudest possible approach.

be described only by an explicit investigation of the effect of this level structure. This can be done only in a consistent manner by using the density matrix technique.

There is a point of rather formal character which, however, demonstrates clearly that the density matrix method is the proper one to describe certain phenomena. Consider a system of electrons in a constant magnetic field H_z oriented along the z axis. This system was discussed using the Hamiltonian (100). One may recall that the velocity operators were defined by (108):

$$\begin{aligned} v_x &= \partial H_M/\partial p_x = p_x/m, \\ v_y &= \partial H_M/\partial p_y = (p_y - m\omega_H x)/m, \qquad (168) \\ v_z &= \partial H_M/\partial p_z = p_z/m. \end{aligned}$$

The matrix elements of the velocity operators between Landau States[53] can easily be obtained [74, 75]:

$$\begin{aligned} &\langle n,\mathbf{k}|v_x|n',\mathbf{k}'\rangle \\ &\quad = i\left(\frac{\hbar m_H}{2m}\right)^{\frac{1}{2}}\left[-(n+1)^{\frac{1}{2}}\delta_{n',n+1}+n^{\frac{1}{2}}\delta_{n',n-1}\right]\delta_{\mathbf{k}\mathbf{k}'}, \\ &\langle n,\mathbf{k}|v_y|n',\mathbf{k}'\rangle \qquad (169) \\ &\quad = \left(\frac{\hbar\omega_H}{2m}\right)^{\frac{1}{2}}\left[-(n+1)^{\frac{1}{2}}\delta_{n',n+1}+n^{\frac{1}{2}}\delta_{n',n-1}\right]\delta_{\mathbf{k}\mathbf{k}'}, \\ &\qquad \langle n,\mathbf{k}|v_z|n'\mathbf{k}'\rangle = \frac{\hbar k_z}{m}\delta_{n'n}\delta_{\mathbf{k}'\mathbf{k}}. \end{aligned}$$

One sees from (169) that if $n=n'$, both $\langle v_x\rangle$ and $\langle v_y\rangle$ are zero; the transversal components of the current have only off diagonal matrix elements. This causes the vanishing of the quantum average of these operators in any state. A special case of this was noted in (108). v_z, however, does have diagonal matrix elements; its average values does not vanish. One now would be tempted to give a statistical description of this system of electrons using the distribution function $f(n,k_y,k_z)$. Thus, the current in the z direction would be given by (apart from constants) (119) and (108)[54]:

$$j_z = \sum\langle v_x\rangle g(n,k_z)f(n,k_y,k_z). \qquad (170)$$

The discussion of this sum was given previously. In the same way one would obtain the x component of the current:

$$j_x = \sum\langle v_x\rangle g(n,k_z)f(n,k_y,k_z) = 0. \qquad (170a)$$

Thus, one concludes that the transversal current is necessarily zero. It is at this point that the difference between the results of the density matrix technique (which is rigorous) and the distribution function method (which is approximate) becomes quite explicit. According to the density matrix method, the observed current is the ensemble average of v_x or, using (I.31),

$$\begin{aligned} j_z = \langle\langle ev_z\rangle\rangle &= e\sum_{n,n',k,k'}\langle n,k|v_z|n',k'\rangle\langle n'k'|\rho|n,k\rangle \\ &= \sum_{n,k} e\frac{\hbar k_z}{m}\langle n,k|\rho|n,k\rangle \\ &= \sum_{n,k}\langle v_z\rangle g(n,k_z)f(n,k_y,k_z). \qquad (171) \end{aligned}$$

The fact that v_z has diagonal matrix elements (169) has been used. Since only *diagonal* matrix element of the density matrix occur, one can utilize the identity of the diagonal matrix elements of ρ with the function $g(n,k_z)f(n,k_y,k_z)$. The direct relation between diagonal density matrix elements and distribution functions was noted before. Thus, (171), using the density matrix, gives the identical result as (170), using the distribution function. However, consider j_x; next

$$\begin{aligned} j_x = \langle\langle e\bar{v}_x\rangle\rangle &= e\sum_{n,n',k,k'}\langle nk|v_x|n'k'\rangle\langle n'k'|\rho|n,k\rangle \\ &= e\sum_{n,n'}\langle n|v_x|n'\rangle\langle n'|\rho|n\rangle\neq 0. \qquad (171a) \end{aligned}$$

Since $\langle n|v_x|n'\rangle$ is non*zero* only if $n'=n\pm 1$, the nondiagonal matrix elements of ρ, which have *no* distribution function type interpretations, play a crucial role.[55] Equation (171b) is *not* identical with (170b); Eq. (171b) is correct. In this transversal case one *cannot* use a distribution function; the density matrix is required. The use of the Boltzmann distribution function gives indeed qualitatively incorrect results.

An even more extreme quantum-mechanical situation occurs when the radius of curvature r_H, becomes comparable with the de Broglie wavelength λ or, what amounts to the same thing, when $\hbar\omega_H \sim E_F$. This happens in extremely strong fields only (10^7-10^8 gauss); but again for electrons with a small effective mass, this limit may well be within reach. In this case again, a detailed quantum-mechanical treatment is needed.

When one is dealing with systems where the thermal gradients vary very rapidly or, more realistically, when a system is subject to a periodic external perturbation, new characteristic times (or distances) appear, and with them a whole new class of interesting phenomena.

The task of obtaining a firmer basis for the transport equation is thus of both fundamental and practical interest. It is unfortunate that the path from the well-defined starting point, the density matrix, to the actual applications is so tortuous and long. One, however, may take solace from the facts that much of the work presented so far can indeed be justified, so it was worth doing, yet some physical situations require the density

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[53] Landau states, the basis of the Landau representations, are the exact eigenstates of an electron in a constant field given by (101a). They often be abbreviated as $|n,k_xk_z\rangle$.

[54] $\langle v_x\rangle$ stands for the quantum average, an expectation value of v_x.

[55] By using distribution functions, one can take only the diagonal elements of ρ into account. When only off-diagonal elements play a role as in (171b), the Boltzmann approach is bound to give incorrect results.

matrix approach (even the simplification to a master equation is not allowed), this justifies the labor to come.

LITERATURE SURVEY AND BIBLIOGRAPHICAL NOTES

1. A. H. Wilson, reference 153. Chapters VIII and IX contain perhaps the most systematic treatment of conductivity theory available. In Chap. VIII, a relaxation time is assumed: in Chap. IX, the interaction between phonons and electrons is treated in detail. In addition to the general discussion, applications are worked out for solids with given band structures. The computed quantities are then compared with experiment. Much of the discussion in II parallels the discussion in this reference.
2. J. M. Ziman, reference 157. The parts of this reference relevant to the material in II are: Chap. V, "Electron-phonon interaction"; Chap. VII, "Formal transport theory"; Chap. IX, "Electronic conduction in metals." The treatment is detailed and well documented. Especially useful are the comparisons of the various methods to calculate phonon electron interactions in Chap. V. Chapter VII contains a lucid discussion of the variation principle, which compliments the one given in reference 1. Chapter IX contains the most up-to-date and complete conductivity calculations leaving little to the imagination. The involved character of the calculation is evident in spite of the fact that this is one of the more transparent discussions.
3. E. H. Sondheimer, "Electron transport phenomena in metals," in *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. II. An extremely readable summary of the status of transport phenomena in metals. Most attention is given to the comparison of theory and experiment at low temperatures. The theoretical basis is outlined and several of the attempted refinements are given.
4. F. Blatt, "Theory of mobility of electrons in solids," in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 6, p. 200. A complete discussion of the applications of the transport equation to solid-state theory. In addition to some standard material, many specialized topics are discussed in detail. Among these are the applications of transport theory to semiconductors, the conductivity tensor in *n*-type germanium and silicon. The treatment is generally easy to read, occasionally it is quite condensed. The extremely detailed comparisons with experiment are most useful.
5. D. K. C. McDonald, "Resistance of metals at low temperatures," Inst. intern. phys. Solvay, Conseil phys, 10^{e} Conseil, Brussels, 1955 (1956). This is an extremely stimulating report on the experimental status of transport properties in 1955. Special attention is called to the phenomena which are only incompletely understood. Among these are the resistivity minimum, both in simple metals and in alloys. It is in a way unfortunate that this excellent report (and others in the same volume) is contained in a book which is not too easily obtainable.
6. J. M. Ziman, reference 157. In the detailed conductivity calculation presented in this reference, Chap. IX, the Bose distribution for n_q is explicitly used.
7. Reference 3. The general tone of the summary in the text has been influenced strongly by this reference.
8. J. M. Ziman, reference 157, Chap. I, p. 19. The use of the periodic boundary conditions is common place in solid-state discussions. Their purpose is always to avoid a detailed discussion of the surface effects. In addition, one can use plane waves $\exp(i\mathbf{qx})$ which are momentum eigenstates, which simplifies the discussion. One can, if so desired, give a geometrical representation of this boundary condition. In two dimensions this means that one wraps the surface on a torus. In three dimensions one must imagine that points on opposite sides of a parallelepiped are identified. One then obtains a perfectly well-defined manifold. Contrary to Ziman's statement that "for topological reasons" the boundary conditions cannot be satisfied, the parallelepiped with identified opposite sides is a much studied topological manifold. It cannot be imbedded in a three-dimensional Euclidean space, but this is irrevelevant both for the topological study and the utilization of the periodic boundary condition. It is a real problem to demonstrate that as $L_1\, L_2\, L_3$ and N go to infinity, with N/Ω fixed, the entities of physical interest approach a finite well-defined limit. Results of this type are demonstrated in certain studies in statistical mechanics.
9. R. E. Peierls, reference 143, pp. 41 and 138. Practically all standard texts in solid state have a discussion of the Umklapp processes. Whereas reference 157 contains many more applications of U processes than 143, the physical description in the latter is perhaps as clear as any.
10. J. M. Ziman, reference 157, Chap. V. A detailed discussion of the dependence of the matrix element M given by (14a) on the various forms of the assumed electron-phonon interaction. The calculations are given in detail for the rigid-ion approximation (5.4), the deformable ion [the Bloch case (5.5)], and the Bardeen self-consistent calculation (5.7). It was perhaps not stressed sufficiently in the text that the assumed form of the matrix element M and the character of C can be considered appropriate *only* for alkali metals. The treatment given in this reference had a decisive influence in the presentation given in the text.
11. A. H. Wilson, reference 153, Sec. 9.3. A detailed treatment of the calculation of the electron-phonon matrix element for rigid ions. The discussion is as clear and straightforward as possible given the tenuous character of the subject matter.
12. J. Bardeen, Phys. Rev. 52, 688 (1937). This calculation of the electron-phonon interaction is one of the classics of solid-state theory. The electron-phonon interaction is computed by using a self-consistent procedure. It was recognized in this paper that conduction electrons follow the displaced ions very rapidly, with a consequent screening of the scattering potential. It is this fact which makes a self-consistent calculation sensible. This same feature is also the basis for the weak short-range screened electron-electron interactions in metals, rather than the strong long-range Coulomb interaction.
13. J. M. Ziman, reference 157, Chap. V, Sec. 5.8. A valuable summary of the net results of the many studies of the electron-phonon interaction. The only notable omission is the electron-phonon interaction treated by the use of collective coordinates (see reference 150). Although Ziman correctly points out that the calculated results are not materially different from those obtained by more conventional means, the introduction of collective coordinates provides a different viewpoint in the descriptions of electrons in a solid; as such it would appear to be of unusual importance.
14. Reference 4. In Blatt's discussion, the function $O(E_i-E_f)$ in (16b) is written as a δ function. Although it is indeed correct that in many instances O does act like a δ function, there are circumstances where this replacement must be done with care. [See Sec. B 3(d).]
15. A. H. Wilson, reference 153, Sec. 9.4. An explicit calculation of the relaxation time for impurity scattering. A similar and much simplified version of this calculation is given in the text.
16. A. H. Wilson, reference 153, Secs. 2.82, 2.83, and 2.85. Details of a perturbation calculation which shows how a wave function changes under the influence of external electric and magnetic fields are given. Let $\Psi(\mathbf{x},t)$ be the wave function of the electron in the external electric and magnetic field, let $\psi_k(\mathbf{x})$ be Bloch wave functions. If one develops $\Psi(\mathbf{x},t)=\Sigma c_k\psi_k(\mathbf{x})$ so that $|c_k(t)|^2$ is the probability that the electron is in state k at time t, one obtains

$$\frac{\partial}{\partial t}|c_k|^2 = -\frac{e}{\hbar}[\mathbf{v}\times\mathbf{H}_{\mathrm{ext}}]\nabla_k|c_k|^2 - e\mathbf{E}_{\mathrm{ext}}\cdot\nabla_k|c_k|^2. \quad \text{(A13)}$$

This is used to obtain (20) in the text.

17. E. N. Adams and P. N. Argyres, Phys. Rev. **102**, 605 (1956). This paper contains a critique of the customary method of proof of the "effective mass theorem" in solid-state theory. The failure of the theorem to hold (for short times) stems from the mixing of wave functions of different bands. By constructing new wave functions so as to eliminate interband couplings, one may reestablish the theorem in *first* order in the applied fields. (The result applies only to time-independent outside fields.)
18. Reference 4, Eq. (3.4).
19. A. H. Wilson, reference 153. This discussion starts from Eq. (30), with explicit expressions for the transition rates B. One integration can be performed because of the δ function character of B (it contains an "almost δ function" of $E_{k1}-E_k-\hbar\omega_q$). On introducing this as a variable, one integral can be performed. If E_k is a quadratic function of k, and some other simplifications are made: (30) may be reduced to a single integral.
20. A. Sommerfeld and H. Bethe, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1934), Vol. 24, p. 2. This is one of the older references to solid-state theory generally and to transport calculations in particular. In spite of this (or perhaps because of it), the treatment is thoughtful and detailed. The pattern of the conductivity outlined in the text is very similar to the one followed in this reference. The Boltzmann equation [like (30)] is set up, and the reduction of the integral is given in great detail, as are the simplifying assumptions. This treatment is one of the most complete available. No *UK* processes or other refinements are included.
21. Reference 4. To decide which inequality, (34b) or (33), gives a more stringent restriction on q, one need only express the Fermi wave number k_F in terms of the electron density.
22. A. H. Wilson, reference 153. This reference shows that (33) may be rewritten as $\hbar\omega_q < k\theta$: θ is the Debye temperature. Equation (33) applies when $n > \frac{1}{4}N_a$, (34b) applies when $n < \frac{1}{4}N_a$: N_a is the number of atoms per unit volume, n the number density of electrons.
23. A. H. Wilson, reference 153. An *exact* solution to Eq. (53) is given.
24. Reference 4. The treatment given in the text follows the discussion given in this reference rather closely.
25. J. P. Jan, Galvanomagnetic and thermomagnetic effects in metals in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 3. An extensive compilation of the many experimental results in this field. The emphasis is definitely on experiments, theory is introduced only in so far as needed to describe the experiments. Special attention is devoted to the detailed interpretation of specific experiments. There is some discussion of the oscillatory effects.
26. Reference 4. A useful classification of the transport effects in magnetic fields. The discussion is not as extensive as in reference 25, but Table III is very useful.
27. A. H. Wilson, reference 153, Eq. (8.55.5).
28. Max Kohler, Ann. Physik **40**, Ser. 5, 601 (1942). The derivation of the symmetry relations (94), as presented in the text, is taken from this paper. This reference also contains the derivation of the more general results (86), which were mentioned but not proven in the text. In addition, Kohler's paper contains an interesting derivation of the analog of the Franz-Wiedemann law, in the presence of magnetic fields. If one assumes that (a) the collisions which electrons suffer are practically elastic collisions, (b) the solutions χ are slowly varying functions of energy, and (c) the electron gas is degenerate, one can show that the Franz-Wiedemann law holds for the individual tensor elements of the thermal and electrical conductivity tensor. This paper also contains one of the first classifications of the galvanomagnetic and thermomagnetic effects of single crystals. A significant paper.
29. A. H. Wilson, reference 153. Formulas corresponding to Eqs. (85a) and (85b), Eqs. (8.1.9) and (8.1.10) are given without proof. It is correctly stated there that the whole theory of conductivity is contained in the tensors $T_{\mu\nu}$ of (85): however, one might gain the impression from this reference that these tensors are *known*. Actually they are expressed in terms of (unknown) solutions of the Boltzmann equation. This enables one to *deduce* the symmetry properties, but Kohler's argument [28] does not yield the explicit form of the solutions.
30. I. M. Lifshitz, M. Ia. Azbel, and M. I. Kaganov, "Theory of the galvanomagnetic effects in metals," Soviet Phys.—JETP. **4**, 41 (1957). Part 1 of this paper contains a discussion of the behavior of conduction electrons in metals. This part of the discussion is reproduced in the text, in I, Sec. C.4. Much of this same material is reviewed in reference 174. The distinction between open and closed orbits on the Fermi surface is given. Part 2 of this reference deals with Eq. (89) in the text, there referred to as the "kinetic equation." The equation is solved by a power series in $1/H_z$, H_z is the applied field. Very detailed predictions about the high-field behavior of the conductivity tensor are made. The σ_{xy} component can be shown to be given by $\sigma_{xy}=(ec/H)(n_1-n_2)$, where

   n_1 = number of electrons
   n_2 = number of holes. (A14)

   This was one of the first papers which suggested that the magnetoconductivity might show a strong angular dependence, which could be used to obtain the detailed structure of the Fermi surface. The discussion in the text should make it easier to read this paper, but the text provides a beginning only. This paper contains a great deal more than is reported here.
31. J. W. McClure, Phys. Rev. **101**, 1642 (1956). This paper contains a discussion of Eq. (89), more precisely of Eq. (90). The approximation is made that even in the presence of an external field, the trajectory lies on the Fermi surface. This has as a consequence that the motion is periodic, this periodicity is exploited in this paper by expanding f in a Fourier series. The conductivity tensor can be expressed in terms of the Fourier components of the velocity v.
32. J. M. Ziman, reference 157. Equation (94) in the text corresponds to Ziman's formulas 12-7. 11. There is a difference in sign between Ziman's expression and (94). Equation (94) agrees with the sign used by Heine. Ziman starts the discussion from (92), rather then from (89), but the discussion given in the text is in many ways similar to the treatment of Ziman.
33. V. Heine, Phys. Rev. **107**, 431 (1957). It is shown by straightforward substitution (in the Appendix of this paper) that $f^{(1)}$ defined by (96) satisfies (95).
34. I. M. Lifshitz and V. G. Peschanshi, Soviet Phys.—JETP **35**, 875 (1959). This paper is a continuation of reference 30. Most of the analysis there was concerned with closed orbits; this reference is concerned with the extension to open Fermi surfaces.

   The methods are much the same as those in reference 30; the specific predictions are: (a) In some directions the resistivity approaches saturation, in others it rises without limit ($\rho\sim H^2$). (b) In polycrystalline samples there may be a linear increase of the resistivity with H as a consequence of the average over orientations. Special examples are worked out for typical Fermi surfaces.
35. D. Shoenberg, in *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 226; A. B. Pippard, Inst. intern. phys. Solvay, 10$^{\mathrm{e}}$ Conseil, Brussels, 1955, 123 (1956). These two references together provide an excellent description of the theoretical background, the experimental techniques, and the uses of the de Haas-van

Alphen effect. The remarkable degree of structure in the susceptibility oscillations is directly connected to a number of significant parameters; for instance, it was shown by Onsager that the period of oscillations is inversely proportional to extreme cross-sectional area of the Fermi surface. (This is the maximum area cut of the Fermi surface by planes perpendicular to the field direction.) Onsager's result thus allows the calculation of the external areas from observation of the periods as functions of the field directions. It is possible to obtain a great deal of information about this Fermi surface from these extremal areas. Hence, the de Haas-van Alphen effect is a significant tool in studying the Fermi surface. It is in this connection that the de Haas-van Alphen effect is discussed in Pippard's work.

Shoenberg's work contains both the theory and a very lucid discussion of the relationship of finer details of the oscillations, such as their phase, the variations of amplitude with temperature, with the various theoretical quantities, such as the electron velocity on the Fermi surface. Both references are well worth studying in detail. The importance of the de Haas-van Alphen effect for the present is twofold: it shows the importance of quantum phenomena; it provides significant information about the Fermi surface.

36. A. H. Kahn and H. P. R. Frederikse, "Oscillatory behavior of magnetic susceptibility and electronic conductivity," in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1959), Vol. 9, p. 257. Many of the phenomena to be described in the text are contained in this interesting summary. The discussion is shorter than in the text but quite lucid. The notation used in the text is very similar to that used in this reference. (The *sign* of the electric charge is opposite.) Specific references to this paper are given many times at appropriate places. The choice of material in Sec. (d) has been influenced by the presentation in this reference.
37. P. N. Argyres and E. N. Adams, Phys. Rev. **104**, 900 (1956). The calculation presented in the text [Sec. 2(d)] is taken directly from this paper and reference 38.
38. P. N. Argyres, J. Phys. Chem. Solids 4, 19 (1958). The papers referred to in references 37 and 38 treat the same problem: the influence of magnetic fields on the relaxation times of electron phonon and electrons impurity scattering. Reference 38 contains only a discussion of the electron-phonon relaxation time; reference 37 discusses the electron impurity scattering as well. The methods and the formal results are sketched in the text; the main result is (113). In these papers the formal expressions and the various sums are evaluated for degenerate electron gases. Actually, references 37 and 38 are extraordinarily similar; in reference 37, it is assumed that the n quantum number [in (109), for example] is zero and remains zero. This is the extreme quantum limit. This restriction is dropped in reference 38; this causes some computational complications, but the general character of the calculation is much the same.
39. Reference 3, Sec. 2.
40. A. H. Wilson, reference 153. "A typical" calculation can be exemplified by the discussion given: the assumptions are given in Chap. IX of this reference.
41. A. H. Wilson, reference 153, Appendexes A4 and A5. Detailed series expansions as well as numerical values of the integrals in question are given.
42. Reference 3. The discussion given in the text follows that of this reference very closely.
43. J. M. Ziman, reference 157. All of Chap. IX is devoted to the electronic conduction in metals; substantial parts of this chapter analyze the agreement between theory and experiment. Several phenomena are discussed: the resistance minimum in alloys, lattice resistance, and the electrical resistance of transition metals. This is at present probably the most up-to-date and complete comparison available.
44. Garcia Moliner, Proc. Phys. Soc. (London) **A72**, 996, 111 (1958).

    This is a typical calculation of the kind mentioned in the text: (a) a specific form of the Fermi surface was assumed; (b) a single relaxation time was assumed. On this basis one can thus compute the magnetoresistance which comes out in terms of the assumed asymmetry parameters of the Fermi surface. (One uses the iterative solution of the Boltzmann equation for this calculation.) Then one can perform an average over-all directions so as to obtain results valid for a polycrystal. These results can be compared with experiment. The consistency of assumed forms of the Fermi surface may be tested in this manner. For Na only does one find that the Fermi surface can be approximately spherical.
45. R. Olson and S. Rodriguez, Phys. Rev. **108**, 1212 (1957). The result of the experiments on the magnetoresistance of single Cu crystals lead to the conclusion mentioned in the text, that the Fermi surface of Cu in all probability intersects the boundary of the first Brillouin zone. Certain assumptions (such as the existence of isotropic relaxation times) are always contained in the analysis.
46. N. E. Alekseevski and Yu. P. Gaidnkov, Soviet Phys.—JETP **10**, 481 (1960). The experiments measuring the fractional change of the resistivity as a function of angle, for fixed field, show a remarkable amount of structure. (In harmony with the general predictions of Lifshitz, *et al.*, reference 30, and Lifshitz and Peschanski, reference 34.) If for fixed field one averages at each H over all angles, a linear behavior as a function of H results (in harmony with older measurements).
47. J. M. Ziman, reference **157**, Chap. XII. An outline of the reference 30. Some of the arguments are perhaps a little easier to follow, but reference 30 is much more complete than Ziman's review. In Chap. XII it is also suggested the linear behavior of the fractional change in resistivity with H is due to the polycrystalline nature of the sample. [For similar views see references 30 and 34.]
48. R. A. Cornish and D. K. C. McDonald, Phil. Mag. **42**, 1406 (1951). In this study a rather different phonon spectrum was assumed. The spectrum was supposed to consist of a number of linear portions. This has an effect on the resistivity calculated with this new phonon spectrum. The agreement with experiment was definitely improved.
49. E. H. Sondheimer, Proc. Roy. Soc. (London) **A203**, 75 (1950). In this paper higher order terms are included in the variational solutions of the integral equations of transport theory. The correction terms introduced by this improved calculation are small. They do not materially improve the agreement with experiment.
50. J. M. Ziman, reference 157, Sec. 7.7. A simple exposition of the variational principle. It is perhaps well to point out that one of the weaknesses of a variational procedure is the fact that it is hard to assess the accuracy of a solution. Also one cannot make a *systematic* improvement of the solutions one obtains. Even so the variational procedure is a powerful tool in the numerical analysis of the Boltzmann equation.
51. J. M. Ziman, reference 157, formula 9.7.5.

    The numerical work in connection with this calculation is contained in J. M. Ziman, Proc. Roy. Soc. (London) **A226**, 436 (1954).
52. J. Bardeen and D. Pines, reference 150. This paper contains many references to earlier work on the collective description. There is also a very clear summarizing discussion by Pines of the collective description of an electron gas in the proceedings of the 10th Solvay Congress, which was referred to in reference 5. A similar review is D. Pines, in *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1, p. 368.
53. Reference 4. A short discussion of the effect which the modifications of the dispersion law $E=E(k)$, demanded by the collective description, have on the transport properties of alkali metals is given. The calculations were made by R. Barrie [Phys. Rev. **103**, 1581 (1956).] For Li, the changes are

largest; but even for Na, the correction in the conductivities is far from negligible.

54. S. Chapman and T. G. Cowling, reference **16**; D. ter Haar, reference **15**.
55. J. M. Ziman, reference **157**, Fig. 112.
56. J. M. Ziman, reference **157**. In the discussion of the electronic conduction, the contribution of the U processes is considered in detail (Chap. 9.5). The calculation becomes involved, and a variety of approximations dealing with the specific geometry of the U processes, need be made to obtain tractable results. The results as they refer to conductivity are quoted
57. M. Bailyn Phys. Rev. **112**, 1587 (1958). "Transport in metals I," "Transport in metals II" (this second paper was in preprint form when this review was written). These papers contain perhaps the most organized studies of the effect of UK processes (in I), and the effect of the detailed form of the phonon spectrum on the calculated transport properties. In addition, a more precise calculation of the electrons phonon matrix element is given (this is quite similar to the results obtained by J. Bardeen and D. Pines, reference **150**). In this reference the coupled integral equations for the electron phonon systems are written down. A relaxation time is assumed for the electron-electron interactions, as well as for the phonon-phonon interactions but *not* for the electron phonon interactions. This study is the most refined which can be made within the Boltzmannian framework.

    Solutions of the coupled systems are constructed by means of the variational principle. (It is pointed out in this paper that the variational trial functions are always of the form for an electric field in the x direction.)

    $$f=f^0-(\partial f^0/\partial E)(\nabla E)_x E_{\text{ext}}\chi(E). \qquad \text{(A15)}$$

    Here $\chi(E)$ is written as a power series, whose coefficients are to be determined. The restriction that χ is a function of E alone is a severe limitation whose validity is hard to judge. This situation is inherent in any use of a variational procedure. See also the remark made in connection with reference 50. The qualitative results of the calculations are quoted in the text. The quantitative results are still not very satisfactory. It is suggested by Bailyn that this may be due to an unrealistic phonon spectrum. This type study is certainly of great interest: further detailed work of this character is most necessary. The papers are not easy to read.
58. I. I. Hanna and E. H. Sondheimer, Proc. Roy. Soc. (London) **A239**, 247 (1957). The discussion in the text is directly based on this paper.
59. J. M. Ziman, reference **157**, Chap. IX. This reference objects to the manner in which the phonon mean free path for impurity scattering was fixed by Hanna and Sondheimer in their calculation. This is in harmony with the remark made in the text. The large number of free parameters in such theories (as Hanna and Sondheimer) make a crucial confrontation of theory and experiment quite difficult.
60. W. Chang and G. E. Uhlenbeck, "Kinetic theory of a gas in alternating outside force fields," University of Michigan, Ann Arbor, Michigan, Tech. Rept. 2457-3-T. The discussion in the text is based on this work. It is a pity that this very interesting paper is not generally available. A summary is contained in reference 120.
61. S. T. Choh and G. E. Uhlenbeck, "Kinetic theory of phenomena in dense gases," U. S. Navy theoretical physics contract. An extensive and detailed discussion of the applications of the ideas of Bogolinbov, to the study of dense gases. The Triple collision terms are explicitly written down. See also reference 124.
62. D. Bohm and D. Pines, see reference 150.
63. L. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), Sec. 46.
64. R. Gatto, Nuovo cimento **10**, 592 (1955). There are many formulations of statistical mechanics using the second quantized formalism. This reference is one of the earlier and simpler papers on this subject. It is mainly devoted to equilibrium statistics. There are a large number of such formulations for nonequilibrium situations, which are especially pertinent in connection with the problem of the approach to equilibrium. This will be discussed in Part III and appropriate references will be given at that time.
65. R. E. Peierls, reference **143**, p. 124. Actually Peierls derives this relation from the well-known fact that a time-dependent perturbation calculation is a short-time expansion. If the time during which it can be valid is t; $t<\tau$. Since the time of the validity is of order $\hbar/kT$, one must have $\hbar/kT<\tau$, or $\hbar/\tau<kT$. (It is not obvious that the time during which the perturbation expansion can be expected to be valid is indeed given by $t\sim\hbar/kT$.)
66. Reference 4. A discussion of this question is given. It is recognized in this reference that one must be very careful about the interpretation of the time, which should be used in the uncertainty relation. Many of the comments made are based on the work of H. W. Lewis, reference 67.
67. H. W. Lewis, "Wave packets and transport of electrons in metals," in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 7, p. 353. The main concern of this paper is with the nature of the inequality (149). The discussion is extremely lucid. The underlying physical reasons for the validity of the transport equation, even when (149) is not satisfied are discussed. The treatment in the text, is to a large extent based on this reference. Two related points are stressed. One cannot neglect the fact that one deals with a degenerate situation (in electron impurity scattering), this affects the way in which the entities entering the uncertainty relation must be interpreted. The one-dimensional model mentioned in the text is directly copied from this reference. The general physical interpretation is again that expressed by Lewis.
68. D. A. Greenwood, Proc. Phys. Soc. (London) **A71**, 585 (1958). This paper is devoted to the inequality (149). The method of showing that this can be replaced by the weaker condition (153), is based on the density matrix. This will be discussed further in Part III.
69. J. S. van Wieringen, Proc. Phys. Soc. (London) **A67**, 206 (1954). The discussion given is an outline of this paper. Although the conclusions are easy to phrase, the calculations are quite annoying. It is worth noting, that in all these discussions of the validity of the Boltzmann equation, one always treats the case of the scattering of electrons of randomly distributed impurities (or of a stationary phonon distribution with random phases). No comparable discussion appears to exist for the system of coupled Boltzmann equations.
70. R. E. Peierls, reference **143**, pp. 140–142. An argument is given which indicates that the correct conditions for the validity of the transport equation are (153) not (149). The argument is perhaps not as convincing as one might hope. The crucial point appears to be the form (155) of the inequality (149), i.e., the possibility of defining collisions which are localized events.
71. P. B. Alers and R. T. Webber, Phys. Rev. **91**, 1060 (1953). Experimental observation of oscillations in the magnetoresistance.
72. J. M. Reynolds, H. W. Hemstreet, T. E. Leinhardt, and D. D. Triantas, Phys. Rev. **96**, 1203 (1954). Observations of the oscillations in the Hall effect.
73. P. B. Alers, Phys. Rev. **101**, 41 (1956). Observation of the oscillations in the thermal magnetoresistance. (The effect of a magnetic field on the thermal conductivity.)
74. Reference 36. An up-to-date summary of the oscillatory transport properties can be found in this reference (most of the detailed discussion refers to bismuth).
75. Reference 38. The wave functions and the necessary recursion relations are given.

76. P. N. Argyres and L. M. Roth, J. Phys. Chem. Solids **12**, 89 (1959). The matrix elements of the velocity operator (169) are given in many places. This reference is one of them.

77. *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb, proceedings of an international conference held at Cooperstown, New York, August 22–24, 1960 (John Wiley & Sons, Inc., New York, 1961). This conference report appeared when this review was already in print. Many of the general conclusions mentioned in the text appear to be substantiated by the recent results. From the theoretical side, the intrusion of many-body perturbation theory techniques into solid-state physics seems to continue at an accelerated pace. On the experimental side, the variety and richness of solid-state phenomena such as magnetoresistance, the anomalous skin effect, and ultrasonic attenuation continues to grow at an even greater pace. The relationship between the fundamental theory and the experiments appears to be getting less direct. Indeed, one needs a separate "theory for the experiments." This naturally leads to the construction of special models and several such models are suggested and discussed in this reference. The summarizing reports, as well as the discussions, are extremely invaluable; they give a vivid picture of the tremendous amount of detailed work going on and the tenuous character of the interpretation of the effects.