Quantum Theory of Electrical Transport Phenomena*

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The usual theories of electrical conductivity suffer from a number of weaknesses. This paper attempts, on the basis of a simple model, to put the theory on as rigorous a basis as possible. A technique is developed which gives the entire density matrix of the system of charge carriers in the steady state. Our model consists of noninteracting free (or Bloch) electrons being scattered by "random" rigid impurity centers. The density matrix is developed in ascending powers of the strength of the scattering potential. The familiar Boltzmann transport equation represents an approximation valid in the limiting cases of very weak or very dilute scatterers. Higher order corrections are given.

I. INTRODUCTION

IN this paper we shall be concerned with the problem of calculating the electrical conductivity of a somewhat simplified model of a real substance, on as rigorous a basis as possible. The problem of electrical conductivity is usually treated on the basis of a *transport equation*.[1] This is an equation for a distribution function f, which describes the probability of a particle being in any given state. The equation is determined by the requirement that in the *steady state* the total rate of change of the distribution function must vanish. This is in turn a sum of the change due to the acceleration by the electric field, and a term due to collisions, which limit this acceleration. Thus the usual transport equation has the form

$$(\partial f/\partial t)_{\text{field}} + (\partial f/\partial t)_{\text{collisions}} = 0. \qquad (1)$$

Equation (1) is incomplete in several respects. First, it is well known that in quantum mechanics if we wish to find the average of a physical quantity we need in general not only the probabilities of different states being occupied, but the entire density matrix (see below). Now the occupation probabilities of some complete set of states are just the diagonal elements of the density matrix in this representation. Therefore for (1) to contain all necessary information we have to assume that we can find a "natural representation" for our system, and that for this representation the density matrix may be considered as diagonal at all times. This so-called "random phase" assumption must also be made in the derivation of (1), and is a serious weakness of the derivation. Further, it is not always clear just what "natural representation" should be chosen, and

one can obtain different answers by making different choices.[2]

Recently considerable progress in the question of removing this random-phase assumption has been made by Van Hove,[3] who studied the question of the approach to equilibrium rather than the steady state in the presence of an external electric field. He was able to show that the random-phase assumption could be replaced by certain properties of the interaction causing collisions, and that these properties could be verified in particular problems. The method we shall use to avoid the random-phase assumption is formally rather different from that of Van Hove but rests, very likely, on similar properties of the interaction.

Another weakness of Eq. (1) in its usual form is that it treats the collision interaction by the lowest order of perturbation theory. The question of what exactly occurs in higher order seems never to have been investigated carefully. We shall extend the theory in this direction also, and show that in the higher orders terms of the usual form appear but, in addition, there are some characteristic deviations from the standard transport equation. Some of these new terms would seem to play a role in the theory of the Hall effect in ferromagnetic substances.[2]

The general technique is the following. We shall imagine a *closed* system in the presence of an external electric field which is gradually being turned on. The sample is taken to be cubical in shape and periodic boundary conditions are imposed. These boundary conditions allow the existence of a steady current and are justified in detail in Appendix A. The density matrix of this system then has a well-defined equation of motion. We study this density matrix for a given electric field in the limit where the rate of turning on becomes

[1] See, for example, A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Edwards Brothers, Ann Arbor, 1943), Vol. 24, Part 2, pp. 499–554.

[2] This situation arises in practice when considering the problem of the Hall effect in ferromagnetic substances. Differing results were obtained by R. Karplus and J. M. Luttinger [Phys. Rev. **95**, 1154 (1954)] and J. Smit [Physica **21**, 1 (1955)], with different assumptions. In fact, the desire to settle this controversy was the starting point of this paper. We hope to return to the application of our results to the Hall effect question in a later publication.

[3] L. Van Hove, Physica **21**, 517 (1955).

very slow. The solution is obtained in the form of a power series in a parameter λ, which measures the strength of the interaction causing collisions. To the lowest order in λ the standard transport equation is obtained; in higher order there are deviations.

In Sec. II we shall consider a collection of electrons so dilute that we can neglect their interaction with each other and can also neglect the effect of Fermi-Dirac statistics on their behavior. Then every electron may be treated as completely independent of all the others, and we have essentially to deal with a single-electron problem. The collision mechanism is provided by a set of fixed impurities distributed at "random" throughout the volume occupied by the electrons. (The precise meaning of "random" in this problem will be made clear in the discussion below.) The electrons are treated as completely free except for their interaction with the impurities and with the external electric field. The impurities are allowed to be anywhere in the volume under consideration. In this section we limit ourselves to the lowest order effects in the strength of the interaction of the electrons with the impurities. In Sec. III, the generalization to higher orders in the strength of the interaction is considered. In Sec. IV, we generalize the discussion to the case where there is also a periodic potential present.

In the Appendices we deal with a number of related questions. In treating the acceleration of electrons by an external homogeneous electric field there are certain well known technical difficulties, associated with the limitation of the current by the walls of the container. In Appendix A a ring-shaped sample is discussed in detail leading to an unambiguous prescription for dealing with these difficulties. In Appendices B and C some of the details of the derivations omitted in the text are given. In Appendix D the approach to the steady state and the effect of time-dependent external fields are considered. In the main body of the text we have limited ourselves to effects linear in the external field; in Appendix E we show that the quadratic effects give rise to the Joule heating. Finally, Appendix F generalizes these results to the case of Fermi-Dirac statistics.

We hope to return to the treatment of electron-electron and electron-phonon interaction by these techniques in a later publication.

II. MATHEMATICAL FORMULATION OF THE PROBLEM

The total Hamiltonian, H_T, for each electron in our problem may be written

$$H_T = H_0 + H' + H_F, \tag{2}$$

where H_0 is the Hamiltonian of the free electrons, H' the interaction with the impurity centers and H_F the interaction with the external electric field. We have[4]

$$H_0 = p^2/2m, \tag{3}$$

$$H' = \sum_{i=1}^{N} \phi(r - r_i) = \lambda V, \tag{4}$$

$$H_F = -eE_\alpha x_\alpha. \tag{5}$$

In (4), λ is some dimensionless measure of the strength of the interaction of the impurity with the electron, $\phi(r)$ is the interaction energy with a single impurity center, and the r_i are the locations of the N impurity centers. In (5), e is the (algebraic) charge of the electron, the E_α ($\alpha = 1, 2, 3$) are the x, y, and z components of the external field, respectively, and the repeated index α implies a summation over it. We shall sometimes write

$$H \equiv H_0 + H', \tag{6}$$

the total Hamiltonian in the absence of an external field.

We now consider a collection of ν electrons moving under the action of the same H_T and introduce the density matrix ρ_T for this collection. We denote the wave functions of the electrons by $\psi^i(r,t)$ and expand them in a complete set of time-independent functions $\psi_n(r)$:

$$\psi^i(r,t) = \sum_n a_n{}^i(t) \psi_n(r).$$

Then the Hermitian matrix $\rho_T(t)$, with elements

$$(\rho_T)_{mn} = \frac{1}{\nu} \sum_{i=1}^{\nu} a_m{}^i(t) a_n{}^{i*}(t)$$

in the ψ_n representation, is the density matrix.[5] The expectation value of any observable quantity A at time t is given by

$$\bar{A}(t) = \mathrm{Tr}[\rho_T(t)A]. \tag{7}$$

Further, $\rho_T(t)$ varies with time according to

$$i(\partial\rho_T/\partial t) = [H_T, \rho_T]. \tag{8}$$

(Units are chosen such that $\hbar = 1$.)

The diagonal elements $(\rho_T)_{nn}$ give the probability of finding an electron in the state ψ_n. The sum of all these probabilities is of course unity for a wave function normalized to unity. If we can find ρ_T from (8) we can calculate the observed value of any quantity (for example, the current) by means of (7).

We shall use (8) in the following way. Imagine that in the very remote past ($t = -\infty$) we have a collection of electrons in equilibrium with a heat bath at temperature T. There is no external field present. Then at this time contact with the heat bath is broken and the electric field is very slowly turned on. It is convenient to turn the field on according to the formula

$$E_\alpha = E_\alpha{}^0 e^{st}, \tag{9}$$

so that E_α is zero at $t = -\infty$ and reaches its full value

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[4] We shall not indicate explicitly the vector character of k or r. Thus $e^{ik\cdot r}$ means $e^{i\mathbf{k}\cdot\mathbf{r}}$ and $k \neq k'$ means $\mathbf{k} \neq \mathbf{k}'$ throughout.

[5] See, for example, R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, New York, 1930), pp. 327 ff.

E_α^0 at $t=0$. We shall see later that the results do not depend on s as long as it is chosen "reasonably." [See discussion following Eq. (47).] The collection of electrons is now described by a single-particle density matrix ρ_T, whose time development is given by (8). We shall be interested in the solution for $t=0$ when the field has reached its full value.

Since the entire system is isolated, the conductivity which we calculate in this way will be an "adiabatic" conductivity. In general we would expect this to be equal to the more usual "isothermal" conductivity. We shall not, however, enter into a discussion of this point here.

With this in mind, our problem is now to find a solution of (8), E_α given by (9), which reduces at $t=-\infty$ to the equilibrium distribution, say ρ. This is just the usual Maxwell-Boltzmann distribution

$$\rho = Ke^{-\beta H}, \tag{10}$$

where

$$\beta = 1/kT$$

and

$$K^{-1} = \text{Tr}(e^{-\beta H}). \tag{11}$$

We must use H (instead of H_0) here, since at $t=-\infty$ the electrons are not free but are interacting with the impurities.

We shall limit ourselves here to calculating ρ_T correct to terms to the first order in the electric field. This is of course all we need if we want to compute the current to terms linear in the field, i.e., in the ohmic region. One might however raise the following objection to our procedure. Since our system is closed, properly speaking it cannot reach a steady state since the Joule heat keeps its energy steadily increasing. However, the Joule heat is quadratic in the external electric field. Therefore, there exists a time of action of the electric field such that the Joule heating is negligible but after which the steady state has set in. The conductivity we calculate in this way will then correspond to the original temperature. By limiting ourselves to terms linear in E_α we *automatically* eliminate any such difficulty, since the heating effects are of second order in E_α. In Appendix F, we shall actually show that the quadratic terms in E_α do give rise to exactly the Joule heating of the whole sample.

We write the total density matrix as

$$\rho_T = \rho + \rho_F, \tag{12}$$

where ρ_F is linear in E_α. Since the density matrix would stay equal to the equilibrium one if the E_α were zero, the ρ in (12) is simply the equilibrium value given by (10). Inserting this into (8), we get

$$i(\partial\rho_F/\partial t) = [H+H_F, \rho+\rho_F]$$
$$= [H_F,\rho] + [H,\rho_F], \tag{13}$$

neglecting terms of the second order in E_α. The quan-

tity ρ_F must satisfy the initial condition

$$\rho_F(t=-\infty)=0. \tag{14}$$

Now since H_F may be written as

$$H_F = H_1 e^{st},$$
$$H_1 = -eE_\alpha^0 x_\alpha, \tag{15}$$

Eqs. (13) and (14) can be satisfied with the Ansatz

$$\rho_F = fe^{st}, \tag{16}$$

where f is independent of time. The quantity f is the correction to the density matrix at $t\equiv 0$, which is what we want. Inserting (15) and (16) into (13), we obtain

$$isf = [H_1,\rho] + [H,f]. \tag{17}$$

To solve (17)—which is valid for any representation—we shall choose the representation for which H_0 is diagonal, i.e., plane waves with periodic boundary conditions. The normalized eigenfunctions are

$$\psi_k = e^{ik\cdot r}/\sqrt{\Omega}, \tag{18}$$

where Ω is the volume of the container. The allowed k_α are given by

$$k_\alpha = (2\pi/L)n_\alpha, \tag{19}$$

where

$$n_\alpha = 0, \pm 1, \pm 2, \cdots \pm \infty$$

and

$$\Omega = L^3.$$

We also have

$$H_0\psi_k = \epsilon_k^0\psi_k, \tag{20}$$

where $\epsilon_k^0 = k^2/2m$. In this representation, (17) becomes

$$(\omega_{kk'}^0 - is)f_{kk'} = C_{kk'} + \sum_{k''}(f_{kk''}H'_{k''k'} - H'_{kk''}f_{k''k'}), \tag{21}$$

where $\omega_{kk'}^0 = \epsilon_k^0 - \epsilon_{k'}^0$, and $C = [\rho,H_1]$. The commutator C is a known matrix in principle, since ρ and H_1 are. The matrix elements of H' are easily obtained:

$$H'_{kk'} = \frac{1}{\Omega}\int_\Omega e^{-i(k-k')\cdot r}\sum_i \phi(r-r_i)dr$$
$$= \frac{1}{\Omega}\sum_i e^{-i(k-k')\cdot r_i}\int_\Omega e^{-i(k-k')\cdot r}\phi(r)dr.$$

For simplicity we take ϕ to be a potential of finite range so that we can extend the r integration over all space. Then

$$H'_{kk'} = \frac{\phi_{kk'}}{\Omega}\sum_i e^{-i(k-k')\cdot r_i}, \tag{22}$$

where

$$\phi_{kk'} \equiv \int e^{-i(k-k')\cdot r}\phi(r)dr. \tag{23}$$

The diagonal element of H' is clearly

$$H'_{kk} = N\phi_{kk}/\Omega,$$

and is independent of the location of the impurities. If there is no particular order in their location then there is no particular connection between the phases of the N terms in (22). In this case $H'_{kk'}$ $(k \neq k')$ is in general of order $\sqrt{N}$ rather than N. Here we see the sort of sharp distinction which the randomness in the positions of the impurities produces between diagonal and non-diagonal matrix elements in the k-representation. This suggests that we split (21) into diagonal and non-diagonal parts. We may write

$$(\omega_{kk'}{}^0 - is)f_{kk'}$$
$$= C_{kk'} + (f_k - f_{k'})H'_{kk'} + f_{kk'}(H'_{k'k'} - H'_{kk})$$
$$+ \sum_{k''(k''\neq k, k')} (f_{kk''}H'_{k''k'} - H'_{kk''}f_{k''k'}), \quad (24)$$

for $k \neq k'$, and

$$-isf_k = C_k + \sum_{k'(k'\neq k)} (f_{kk'}H'_{k'k} - H'_{kk'}f_{k'k}). \quad (25)$$

Here $f_k \equiv f_{kk}$ and $C_k \equiv C_{kk}$. The function f_k is just the usual distribution function dealt with in transport theory. In (24) we have separated out the individual terms in the k'' sum where k'' is equal to k or k'. The only reason that these terms give contributions comparable to the entire sum is that, as we shall see later, they are of larger order of magnitude in N owing to the randomness of the impurity positions. We can deal at once with the third term on the right-hand side of (24). Defining $\epsilon_k = \epsilon_k{}^0 + H'_{kk}$ and $\omega_{kk'} = \epsilon_k - \epsilon_{k'}$, we rewrite (24) as

$$(\omega_{kk'} - is)f_{kk'} = C_{kk'} + (f_k - f_{k'})H'_{kk'}$$
$$+ \sum_{k''(k''\neq k, k')} (f_{kk''}H'_{k''k'} - H'_{kk''}f_{k''k'}). \quad (26)$$

That is, the only effect the diagonal elements of H' have is to shift the unperturbed energies $\epsilon_k{}^0$ by H'_{kk}. Since we want there to be a finite density of impurities present, N/Ω will be finite, and this energy correction will stay finite for an infinite sample. Actually, by (23), H'_{kk} is independent of k, so that this energy shift is the same for all k. By resetting the zero of energy we may remove this constant (which is the same as choosing $H'_{kk} = 0$, throughout the calculation), and we shall for simplicity imagine that this has been done.

So far everything is quite general. We shall now try to obtain a solution of (26) in a power series in λ. To do this we must first get some idea of how we can expect the different terms in (26) to depend on λ for small λ. We begin with the commutator

$$C_{kk'} = -eE_\alpha{}^0[\rho(H_0 + H'), x_\alpha]_{kk'}. \quad (27)$$

Now we may expand ρ in powers of H' (taking into account its noncommutativity with H_0) and this gives for ρ a power series in λ. Therefore in general we will have

$$C_{kk'} = C_{kk'}{}^{(0)} + C_{kk'}{}^{(1)} + C_{kk'}{}^{(2)} + \cdots, \quad (28)$$

$C_{kk'}{}^{(n)}$ being proportional to λ^n. We shall limit ourselves here to the evaluation of $C_{kk'}{}^{(0)}$, the higher order terms being left to Appendix C.

In the lowest order,

$$\rho = \rho_0 = K_0 e^{-\beta H_0}$$
$$= K_0 \exp(-\beta p^2/2m). \quad (29)$$

Using the commutation rules (or $x_\alpha = i\partial/\partial p_\alpha$), we obtain the operator relationship

$$(\rho_0, x_\alpha) = \frac{1}{i}\frac{\partial \rho_0}{\partial p_\alpha} = -\frac{1}{i}K_0\frac{\beta p_\alpha}{m}e^{-\beta H_0}. \quad (30)$$

(For a justification of the formal use of these commutation rules, see Appendix A.) Therefore

$$C_{kk'}{}^{(0)} = ieE_\alpha{}^0\left(-\frac{\beta k_\alpha}{m}K_0 e^{-\beta\epsilon_k}\right)\delta_{kk'}. \quad (31)$$

Defining

$$\rho_k = K_0 e^{-\beta\epsilon_k}, \quad (32)$$

we may write

$$C_{kk'}{}^{(0)} = ieE_\alpha{}^{(0)}(\partial\rho_k/\partial k_\alpha)\delta_{kk'}. \quad (33)$$

It is important to realize that the derivative occurring in (33) is the *formal derivative* and (33) is meant to be identical with (31), the question of whether the allowed values of k are discrete or continuous playing no role.

Thus the diagonal terms of C begin with the zeroth order in λ while the off-diagonal ones are of the first order in λ. We shall see later that f_k is of order λ^{-2}. This is also the result in usual transport theory, the f_k being inversely proportional to the transition probabilities. If we assume this, then it follows at once from (26) and (33) that $f_{kk'}$ $(k \neq k')$ is of order λ^{-1}. Thus (26) can be solved by an iterative procedure. Let us first obtain the lowest order result. From the orders in λ discussed above, we see at once that on the right-hand side of (26) the second term dominates and we obtain

$$f_{kk'} = \frac{(f_k - f_{k'})H'_{kk'}}{\omega_{kk'} - is} \quad (34)$$

in lowest order. If we insert this in (25), again retaining only the lowest order, we obtain

$$-isf_k = ieE_\alpha{}^{(0)}\frac{\partial\rho_k}{\partial k_\alpha} + \sum_{k'(k'\neq k)} |H'_{kk'}|^2$$
$$\times\left[(f_k - f_{k'})\left(\frac{1}{\omega_{kk'} - is} - \frac{1}{\omega_{kk'} + is}\right)\right]. \quad (35)$$

We shall now show that (35) is just the usual transport equation. Inserting for $H'_{kk'}$ its value from (22), we have

$$|H'_{kk'}|^2 = \frac{|\phi_{kk'}|^2}{\Omega^2}\sum_{i,j}e^{-i(r_i - r_j)\cdot q}, \quad (36)$$

where $q \equiv k - k' \neq 0$.

This quantity depends in general on the positions of all the impurities. We shall now show, however, that the summation over k' in (35) has the effect of "washing out" these fluctuations. In fact, if there are no correlations between the positions of the impurities, (35) becomes a well-defined equation independent of these positions. The general method of proof is the following. Suppose we have any quantity M which is a function of the positions of all the impurities. For each arrangement of impurities, M will have some definite value. Let us define the *ensemble average* of M, say $\langle M \rangle$, as the average of M over all the different arrangements of the impurities, without any correlation between the impurities. That is,

$$\langle M \rangle = \int_\Omega \cdots \int_\Omega \frac{dr_1}{\Omega} \frac{dr_2}{\Omega} \cdots \frac{dr_N}{\Omega} M(r_1 \cdots r_N). \quad (37)$$

(In assuming that the impurities are truly independent we are of course allowing two or more to occupy the same position. We adopt this model for the sake of simplicity, although it is not realistic for high impurity concentrations.)

For a specific system the value of M will in general deviate from $\langle M \rangle$, the deviation depending on the positions of the impurities. However, it *might* be that as $N \to \infty$ the fraction of arrangements which satisfy the inequality

$$|(M/\langle M \rangle) - 1| < \delta \quad (38)$$

for δ arbitrarily small, approaches 1. In other words, we could take $M = \langle M \rangle$ for all but a negligible number of arrangements. A sufficient condition for this to be true is that

$$\lim_{N \to \infty} \frac{\langle (M - \langle M \rangle)^2 \rangle}{\langle M \rangle^2} = \lim_{N \to \infty} \frac{\langle M^2 \rangle - \langle M \rangle^2}{\langle M \rangle^2} = 0. \quad (39)$$

Now direct calculation shows that for $|H'_{kk'}|^2$ this is *not* true. In fact,

$$\langle |H'_{kk'}|^2 \rangle = (|\phi_{kk'}|^2/\Omega^2) N \quad (40)$$

and

$$\langle (|H'_{kk'}|^2)^2 \rangle = (|\phi_{kk'}|^2/\Omega^2)^2 (2N^2 + N), \quad (41)$$

so that the right-hand side of (39) actually approaches unity rather than zero.

On the other hand, since $\omega_{kk'}$ is a smooth function of k', and the same will be shown for $f_{k'}$, the summation over k' in (35) may be broken up into regions of momentum space in which $\omega_{kk'}$ and $f_{k'}$ do not vary appreciably, but $|H'_{kk'}|^2$ may. Let the number of states in such a region be ν. In general ν will be of the order N, i.e.,

$$\nu = aN, \quad (42)$$

where a is some very small number independent of N.[6] Therefore we consider instead of $|H'_{kk'}|^2$ the quantity

$$M = \frac{1}{\nu} \sum_{k' \text{ in } \nu} |H'_{kk'}|^2. \quad (43)$$

We assert that whereas (39) is not satisfied for $|H'_{kk'}|^2$, it is for M given by (43). Direct calculation gives

$$\langle M \rangle = (|\phi_{kk'}|^2/\Omega^2) N, \quad (44)$$

and

$$\langle M^2 \rangle = \left(\frac{|\phi_{kk'}|^2}{\Omega^2} \right)^2$$
$$\times \left[N^2 + \frac{1}{\nu^2} N(N-1) \sum_{k',k'' \text{ in } \nu} (\delta_{k',k''} + \delta_{2k,k'+k''}) \right]. \quad (45)$$

The N^2 term is the one we want, the rest being of lower order in N. The $\delta_{k',k''}$ gives a contribution of $N(N-1)/\nu$, which is only of order N since ν is. The $\delta_{2k,k'+k''}$ only yields a result if the region ν surrounds k, and even in this case the contribution is at most $N(N-1)/\nu$, which is only of order N. Therefore we see that M defined by (43) does satisfy (39), and is a well-defined quantity equal to its ensemble average for all but a negligible fraction of possible arrangements of the impurities. (An example of an exceptional arrangement where M can deviate substantially from $\langle M \rangle$ is a periodic-impurity lattice. In that case M is sometimes of order N^2 rather than N. Such exceptional arrangements form a negligible fraction of all possible arrangements.) The entire result of this discussion is therefore that without any loss of rigor we may replace $|H'_{kk'}|^2$ in (35) by its ensemble average. (The generalization of this result to higher order terms is found in Appendix B.) This gives

$$is f_k = ie E_\alpha^0 \frac{\partial \rho_k}{\partial k_\alpha} + \sum_{k'(k' \neq k)} \left(N \frac{|\phi_{kk'}|^2}{\Omega^2} \right)$$
$$\times (f_k - f_{k'}) \left(\frac{1}{\omega_{kk'} - is} - \frac{1}{\omega_{kk'} + is} \right). \quad (46)$$

The solution of (46) depends in general on the value of s. However, there is a tremendous range of s (including the physically interesting rates with which we could turn on the field) for which the solution is practically independent of s. This range is given by the

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[6] The number of states in a little region of k space Δ is given by $\nu = [\Omega/(2\pi)^3]\Delta$. Since $N \sim \Omega$, we may write this as

$$\nu = \left[\frac{\Omega}{N} \frac{\Delta}{(2\pi)^3} \right] N,$$

so that a is determined by the volume per impurity and the volume of k space over which ϵ_k and f_k do not vary appreciably.

following conditions. First,

$$s \ll 1/t_r, \quad 1/t_a,$$

where t_r is of the order of the relaxation time, and t_a is an "atomic time." That is, t_a is a time associated with the dynamics of the electron and has nothing to do with t_r. In our problem t_a would be of the order of $\hbar/\bar{\epsilon}$ or $r_0/\bar{v}$, where $\bar{\epsilon}$ is a typical energy of the electron, r_0 the size of an impurity, and $\bar{v}$ a typical electron velocity. When this condition is satisfied we may drop the left-hand side of (46), which is of the order of st_r times the second term on the right-hand side. Further, if $s \gg \Delta E/\hbar$ (where ΔE is of the order of the spacing of the translational electronic levels), the sum in (46) may be replaced by an integral according to

$$\sum_{k'} = \frac{\Omega}{(2\pi)^3} \int dk'. \qquad (47)$$

Once we have done this, the condition $s \ll t_a^{-1}$ enables us to use the well-known result

$$\lim_{s \to 0^+} \left(\frac{1}{x - is} \right) = P(1/x) + i\pi\delta(x), \qquad (48)$$

where $P(1/x)$ is the principal value of $1/x$ and $\delta(x)$ is the ordinary Dirac δ function. Therefore (46) becomes

$$0 = eE_\alpha^{(0)} \frac{\partial \rho_k}{\partial k_\alpha} + 2\pi \sum_{k'} \frac{N |\phi_{kk'}|^2}{\Omega^2} \delta(\omega_{kk'})(f_k - f_{k'}). \quad (49)$$

Now the transition probability $w_{kk'}^{(0)}$ per unit time from a plane-wave state k' to k due to a *single* impurity may be written, in lowest Born approximation, as

$$w_{kk'}^{(0)} = 2\pi \frac{|\phi_{kk'}|^2}{\Omega^2} \delta(\omega_{kk'}). \qquad (50)$$

If we define the total transition probability $W_{kk'}^{(0)}$ as the sum of those occurring due to each of the impurities, then we have

$$0 = eE_\alpha^{(0)} \frac{\partial \rho_k}{\partial k_\alpha} + \sum_{k'(k' \neq k)} (W_{k'k}^{(0)} f_k - W_{kk'}^{(0)} f_{k'}), \quad (51)$$

which is the customary transport equation used in the theory of impurity conductivity. The first term is the acceleration due to the external electric field, the second is just the rate of change of the distribution function due to collisions.

In this theory we now have a rigorous meaning for the distribution function f_k, namely as diagonal elements of the density matrix in the plane-wave representation. The expectation value of any operator A is given, by (7), as

$$\bar{A} = \mathrm{Tr}(\rho A) + \mathrm{Tr}(fA)$$
$$= \bar{A}_0 + \bar{A}_F. \qquad (52)$$

The first term $\bar{A}_0$ is just the equilibrium value of A, and will not interest us further here. The second term $\bar{A}_F$ is the correction due to the presence of the electric field. In the k-representation we have

$$\bar{A}_F = \sum_{k,k'} f_{kk'} A_{k'k}$$
$$= \sum_k f_k A_{kk} + \sum_{k,k'(k \neq k')} f_{kk'} A_{k'k}. \qquad (53)$$

In general, both terms of (53) will be necessary.

For calculating the current we need the average velocity. The velocity operator is, as usual,

$$v_\beta = i[H_T, x_\beta]$$
$$= p_\beta/m. \qquad (54)$$

The matrix elements of v_β are

$$(v_\beta)_{kk'} = k_\beta \delta_{kk'}/m. \qquad (55)$$

Therefore, for the velocity the off-diagonal elements of f automatically play no role, and

$$\bar{v}_F = \sum_k k_\beta f_k/m. \qquad (56)$$

We see that for calculating the conductivity only the diagonal elements of f play a role, and these satisfy (to the lowest order) the ordinary transport equation. Therefore under these circumstances the "random phase" assumption is justified in this representation.

As an example of an operator for which the off-diagonal terms play a vital role, we consider the acceleration. The acceleration operator is given by

$$a_\beta = i[H_T, v_\beta] = \{eE_\beta + i[H', p_\beta]\}/m, \qquad (57)$$

which has the matrix elements

$$(a_\beta)_{k'k} = [eE_\beta \delta_{kk'} + i(k_\beta - k_\beta')H'_{k'k}]/m. \qquad (58)$$

Therefore, at $t = 0$,

$$\bar{a}_\beta = \left[\frac{1}{m} eE_\beta^{(0)} + i \sum_{k,k'(k \neq k')} (k_\beta - k_\beta') f_{kk'} H'_{k'k} \right]. \qquad (59)$$

If we dropped the off-diagonal elements of f, we would obtain only the first term $eE_\beta^{(0)}/m$, which is certainly not correct. Since to terms linear in the electric field there is a stationary state, to this order in E_α^0 the acceleration must vanish. However, the off-diagonal contribution is easily evaluated. We have, to the order we are working in,

$$i \sum_{k,k'} (k_\beta - k_\beta') f_{kk'} H'_{k'k} = i \sum_{k,k'} (k_\beta - k_\beta') \frac{f_k - f_{k'}}{\omega_{kk'} - is} |H'_{kk'}|^2$$

$$= i \sum_{k,k'} k_\beta (f_k - f_{k'}) |H'_{kk'}|^2 \left(\frac{1}{\omega_{kk'} - is} - \frac{1}{\omega_{kk'} + is} \right). \qquad (60)$$

By means of (35), with very small s, (60) becomes

$$i \sum_{k,k'} (k_\beta - k_\beta') f_{kk'} H'_{k'k}$$

$$= eE_\alpha^{(0)} \sum_k k_\beta \frac{\partial \rho_k}{\partial k_\alpha} = -eE_\alpha^{(0)} \delta_{\alpha\beta} = -eE_\beta^{(0)}. \qquad (61)$$

Inserting (61) in (59) we see that $\bar{a}_\beta = 0$, as we expected. Thus for the calculation of the acceleration the off-diagonal elements are essential.

III. HIGHER APPROXIMATIONS

We now consider the problem of finding the higher approximations to the transport equation (51). To do this we need only continue the iterative process begun in the last section. We shall only push this process two orders (in λ) further, since it is there that new phenomena begin to occur. Since f_k begins with λ^{-2} we need it to order λ^0, and since $f_{kk'}$ ($k \neq k'$) begins with λ^{-1} we need it to order λ. To this order, (26) and (25) become, for very small s,

$$(\omega_{kk'} - is)f_{kk'} = C_{kk'}{}^{(1)} + (f_k - f_{k'})H'_{kk'} + \sum_{k''}{}' (f_{kk''}H'_{k''k'} - H'_{kk''}f_{k''k'}), \quad (62)$$

and

$$0 = C_k{}^{(0)} + C_k{}^{(2)} + \sum_{k'}{}' (f_{kk'}H'_{k'k} - H'_{kk'}f_{k'k}), \quad (63)$$

respectively. The prime on the summation means that the summation is taken in such a way that all index equalities are avoided. [In (62) this means $k'' \neq k, k'$, in (63) $k' \neq k$.] Further, in (63) we have left out $C_k{}^{(1)}$ since it vanished with our choice of $H'_{kk} = 0$ (see Appendix C).

The lowest order solution of (62) is given by (34). If we insert this in the last term of (63), and solve again for $f_{kk'}$, we get the first correction. Continuing this process indefinitely would give $f_{kk'}$ as a power series in λ, the terms increasing very rapidly in complexity for higher powers. To terms linear in λ we obtain

$$f_{kk'} = f_{kk'}{}^{(0)} + f_{kk'}{}^{(1)} + f_{kk'}{}^{(2)}, \quad (64)$$

where $f_{kk'}{}^{(0)}$ is given by (34) and

$$f_{kk'}{}^{(1)} = \frac{1}{\omega_{kk'} - is} \sum_{k''}{}' (kk''k')$$
$$\times \left(\frac{f_k - f_{k''}}{\omega_{kk''} - is} - \frac{f_{k''} - f_{k'}}{\omega_{k''k'} - is} \right), \quad (65)$$

$$f_{kk'}{}^{(2)} = \frac{1}{\omega_{kk'} - is} \left[\sum_{\substack{k'',k''' \\ k'' \neq k, k' \\ k''' \neq k, k''}} \frac{(kk'''k''k')}{\omega_{kk''} - is} \right.$$
$$\times \left(\frac{f_k - f_{k'''}}{\omega_{kk'''} - is} - \frac{f_{k'''} - f_{k''}}{\omega_{k'''k''} - is} \right)$$
$$- \sum_{\substack{k'',k''' \\ k'' \neq k, k' \\ k''' \neq k'', k'}} \frac{(kk''k'''k')}{\omega_{k''k'} - is}$$
$$\times \left. \left(\frac{f_{k''} - f_{k'''}}{\omega_{k''k'''} - is} - \frac{f_{k'''} - f_{k'}}{\omega_{k'''k'} - is} \right) + C_{kk'}{}^{(1)} \right]. \quad (66)$$

Here we have introduced the notation

$$(kk''k') \equiv H'_{kk''}H'_{k''k'},$$
$$(kk'''k''k') \equiv H'_{kk'''}H'_{k'''k''}H'_{k''k'}, \text{ etc.} \quad (67)$$

If we insert (64) in (63) we obtain, for very small s, the "transport equation"

$$0 = T_k{}^{(0)} + T_k{}^{(1)} + T_k{}^{(2)}, \quad (68)$$

where $T_k{}^{(0)}$ is just the right-hand side of (35) which we have already discussed, and

$$T_k{}^{(1)} = \sum_{k'(k' \neq k)} (f_{kk'}{}^{(1)}H'_{k'k} - \text{c.c.}), \quad (69)$$

$$T_k{}^{(2)} = \sum_{k'(k' \neq k)} (f_{kk'}{}^{(2)}H'_{k'k} - \text{c.c.}) + C_k{}^{(2)}. \quad (70)$$

First let us consider (69). Regrouping the terms somewhat, interchanging the indices k and k' here and there and making use of the fact that $(kk''k'k)^* = (kk'k''k)$, we obtain

$$T_k{}^{(1)} = A_k{}^{(1)}f_k - \sum_{k'} B_{kk'}{}^{(1)}f_{k'}, \quad (71)$$

with

$$A_k{}^{(1)} = \sum_{k',k''}{}' (kk''k'k) \left(\frac{1}{d_{kk'}{}^- d_{kk''}{}^-} - \text{c.c.} \right), \quad (72)$$

and

$$B_{kk'}{}^{(1)} = \sum_{k''}{}' (kk''k'k)$$
$$\times \left(\frac{1}{d_{kk''}{}^+ d_{k''k'}{}^-} - \frac{1}{d_{kk'}{}^- d_{k''k'}{}^-} - \frac{1}{d_{kk'}{}^+ d_{kk''}{}^+} \right) - \text{c.c.} \quad (73)$$

We have introduced the notation

$$d_{kk'}{}^+ = \frac{1}{\omega_{kk'} + is},$$
$$d_{kk'}{}^- = \frac{1}{\omega_{kk'} - is} = -(d_{k'k}{}^+)^*. \quad (74)$$

Now once again the summation over k' and k'' which occur in (72) and (73) have the effect of replacing $(kk'k''k)$ by its ensemble average (see Appendix B). This is easily seen to be

$$\langle (kk'k''k) \rangle = \frac{\phi_{kk'}\phi_{k'k''}\phi_{k''k}}{\Omega^3} N. \quad (75)$$

The resulting summands in (72) and (73) are smooth functions of k' and k'' and therefore may be replaced by integrations according to (47). Now making use of (48), (72) becomes

$$A_k{}^{(1)} = \sum_{k',k''}{}' \langle (kk''k'k) \rangle 2\pi i$$

$$\times \left[\delta(\omega_{kk'}) P\left(\frac{1}{\omega_{kk''}}\right) + \delta(\omega_{kk''}) P\left(\frac{1}{\omega_{kk'}}\right) \right]$$

$$= 2\pi i \sum_{k',k''}{}' \delta(\omega_{kk'}) \left\{ P\left[\frac{\langle (kk''k'k) \rangle}{\omega_{kk''}}\right] + P\left[\frac{\langle (kk'k''k) \rangle}{\omega_{kk''}}\right] \right\}$$

$$= 2\pi i \sum_{k',k''}{}' \delta(\omega_{kk'}) \left[\frac{\langle (kk''k'k) \rangle}{d_{kk''}{}^-} + \frac{\langle (kk'k''k) \rangle}{d_{kk''}{}^+} \right]. \quad (76)$$

again using the symmetry in k' and k''. The reason for writing $A_k{}^{(1)}$ in this form will become clear when we discuss (73). We may rewrite the coefficient of $\langle (kk''k'k) \rangle$ in (73) as

$$\frac{1}{d_{kk'}{}^- d_{kk''}{}^+} - \frac{1}{d_{kk'}{}^+ d_{kk''}{}^+} - \frac{is}{d_{kk'}{}^- d_{kk''}{}^- d_{k''k'}{}^-},$$

by direct algebraic transformation. All the integrals which arise from the last term are regular, and approach zero as s does. Therefore

$$B_{kk'}{}^{(1)} = \sum_{k''} \langle (kk''k'k) \rangle \left(\frac{1}{d_{kk'}{}^- d_{kk''}{}^+} - \frac{1}{d_{kk'}{}^+ d_{kk''}{}^+} \right) - \text{c.c.}$$

$$= 2\pi i \sum_{k''}{}' \delta(\omega_{kk'}) \left[\frac{\langle (kk''k'k) \rangle}{d_{kk''}{}^+} + \frac{\langle (kk'k''k) \rangle}{d_{kk''}{}^-} \right]. \quad (77)$$

Making use of (75), (76), and (77), and defining

$$w_{kk'}{}^{(1)} = \frac{2\pi \delta(\omega_{kk'})}{\Omega^3}$$

$$\times \sum_{k''} \left(\frac{\phi_{kk''}\phi_{k''k'}\phi_{k'k}}{d_{kk''}{}^+} + \frac{\phi_{kk'}\phi_{k'k''}\phi_{k''k}}{d_{kk''}{}^-} \right), \quad (78)$$

we easily see that

$$T_k{}^{(1)} = iN \sum_{k'} (w_{k'k}{}^{(1)} f_k - w_{kk'}{}^{(1)} f_{k'}). \quad (79)$$

The interpretation of this result is immediate. The quantity $w_{kk'}{}^{(1)}$ is just the first correction to the Born approximation for the scattering from plane wave state k' to k by a single impurity. $Nw_{kk'}{}^{(1)} \equiv W_{kk'}{}^{(1)}$ is just the correction due to all N impurities.[7] Therefore the only effect of $T_k{}^{(1)}$ is to replace the transition probabilities $W_{kk'}{}^{(0)}$ in (51) by $W_{kk'}{}^{(0)} + W_{kk'}{}^{(1)}$, i.e., to use the correct transition probabilities to the order in question.

We now turn to the discussion of (70). There are two terms, those from the commutator, say $T_k{}^{(2)}(C)$, and those linear in f_k, say $T_k{}^{(2)}(f)$. That is, we write

$$T_k{}^{(2)} = T_k{}^{(2)}(C) + T_k{}^{(2)}(f), \quad (80)$$

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[7] See, for example, W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, New York, 1954), third edition, pp. 168 ff. For the scattering on a single impurity there is of course no question of an energy shift.

where

$$T_k{}^{(2)}(C) = C_k{}^{(2)} + \sum_{k'} \left[\frac{C_{kk'}{}^{(1)} H'_{k'k}}{d_{kk'}{}^-} - \text{c.c.} \right], \quad (81)$$

and

$$T_k{}^{(2)}(f) = [T_k{}^{(2)}(f)]' + [T_k{}^{(2)}(f)]'', \quad (82)$$

with

$$[T_k{}^{(2)}(f)]' = \sum_{k',k'',k'''}{}' \frac{1}{d_{kk'}{}^-}$$

$$\times \left[\frac{(kk'''k''k)}{d_{kk''}{}^-}\left(\frac{f_k - f_{k'''}}{d_{kk'''}{}^-} - \frac{f_{k'''} - f_{k''}}{d_{k'''k'}{}^-} \right) \right.$$

$$\left. - \frac{(kk''k'''k)}{d_{k''k'}{}^-}\left(\frac{f_{k''} - f_{k'''}}{d_{k''k'''}{}^-} - \frac{f_{k'''} - f_{k'}}{d_{k'''k'}{}^-} \right) \right] - \text{c.c.}, \quad (83)$$

$$[T_k{}^{(2)}(f)]'' = \sum_{k',k''}{}' \frac{1}{d_{kk'}{}^-}$$

$$\times \left[\frac{(kk'k''k)}{d_{kk''}{}^-}\left(\frac{f_k - f_{k'}}{d_{kk'}{}^-} - \frac{f_{k'} - f_{k''}}{d_{k'k''}{}^-} \right) \right.$$

$$\left. - \frac{(kk''kk'k)}{d_{k''k'}{}^-}\left(\frac{f_{k''} - f_k}{d_{k''k}{}^-} - \frac{f_k - f_{k'}}{d_{kk'}{}^-} \right) \right] - \text{c.c.} \quad (84)$$

The division of $T_k{}^{(2)}(f)$ given in (82) comes about by eliminating from (83) those terms where any of the indices k, k', k'', k''' are equal.

The calculation of $T_k{}^{(2)}(C)$ is very straightforward, using the results of Appendix C. $C_k{}^{(2)}$ is already given by (C.11). The other term is

$$\sum_{k'}{}' \left(\frac{C_{kk'}{}^{(1)} H'_{k'k}}{\omega_{kk'} - is} - \text{c.c.} \right) = 2ieE_\alpha{}^{(0)} \sum_{k'}{}' P$$

$$\times \frac{|H'_{kk'}|^2}{\omega_{kk'}} \left(\frac{\partial}{\partial k_\alpha} + \frac{\partial}{\partial k_{\alpha}'} \right) \frac{\rho_k - \rho_{k'}}{\omega_{kk'}} \quad (85)$$

making use of (C.9). The usual argument now replaces $|H'_{kk'}|^2$ by its ensemble average, so that (85) becomes

$$2ieE_\alpha{}^0 \frac{n}{(2\pi)^3} \int dk' P \frac{|\phi_{kk'}|^2}{\omega_{kk'}} \left(\frac{\partial}{\partial k_\alpha} + \frac{\partial}{\partial k_{\alpha}'} \right) \frac{\rho_k - \rho_{k'}}{\omega_{kk'}}, \quad (86)$$

where n is the number of impurities per unit volume. Putting these results together, we have

$$T_k{}^{(2)}(C) = ieE_\alpha{}^{(0)} \left\{ \frac{\partial}{\partial k_\alpha}\left[\gamma\rho_k - \frac{n}{(2\pi)^3}\int dk' |\phi_{kk'}|^2 \right.\right.$$

$$\left. \times \frac{1}{\omega_{kk'}}\left(\frac{\rho_k - \rho_{k'}}{\omega_{kk'}} + \beta\rho_k \right) \right] + \frac{2n}{(2\pi)^3}\int dk' P$$

$$\left. \times \frac{|\phi_{kk'}|^2}{\omega_{kk'}}\left(\frac{\partial}{\partial k_\alpha} + \frac{\partial}{\partial k_{\alpha}'} \right) \frac{\rho_k - \rho_{k'}}{\omega_{kk'}} \right\}. \quad (87)$$

A word may be said about the significance of the two terms which enter into $T_k{}^{(2)}(C)$. The $C_k{}^{(2)}$ term is just the correction which arises because the equilibrium distribution function is not that of the free electrons, but that of the free electrons in the presence of impurities. The other term, (85), arises from the combined effects (or interference) between the change in the distribution function due to the electric field, and the change due to the collisions with the impurities.

We next consider $[T_k{}^{(2)}(f)]'$. This may be written

$$[T_k{}^{(2)}(f)]' = A_k{}^{(2)}f_k - \sum_{k'}{}' B_{kk'}{}^{(2)}f_{k'}, \qquad (88)$$

with

$$A_k{}^{(2)} = \sum_{k'k''k'''}{}' \left(\frac{\langle(kk'''k''k'k)\rangle}{d_{kk'}{}^{-}d_{kk''}{}^{-}d_{kk'''}{}^{-}} - \text{c.c.} \right), \qquad (89)$$

and

$$B_{kk'}{}^{(2)} = \sum_{k''k'''}{}' \left[\langle(kk''k'''k'k)\rangle \left(\frac{1}{d_{kk'}{}^{-}d_{k''k'}{}^{-}d_{k'''k'}{}^{-}} - \frac{1}{d_{kk'}{}^{+}d_{kk''}{}^{+}d_{kk'''}{}^{+}} + \frac{1}{d_{kk'}{}^{+}d_{k'''k'}{}^{-}d_{kk'''}{}^{+}} - \frac{1}{d_{kk'}{}^{+}d_{k'k''}{}^{-}d_{k'''k'}{}^{-}} \right) \right.$$

$$+ \langle(kk'k''k'''k)\rangle \left(\frac{1}{d_{kk'}{}^{-}d_{kk''}{}^{-}d_{kk'''}{}^{-}} - \frac{1}{d_{k''k'}{}^{+}d_{kk''}{}^{-}d_{kk'''}{}^{-}} + \frac{1}{d_{k'''k'}{}^{+}d_{k''k'}{}^{+}d_{kk''}{}^{-}} - \frac{1}{d_{kk'}{}^{+}d_{k''k'}{}^{+}d_{k'''k'}{}^{+}} \right)$$

$$+ \langle(kk''k'k'''k)\rangle \left(\frac{1}{d_{kk'''}{}^{+}d_{k'''k'}{}^{+}d_{k'''k'}{}^{+}} + \frac{1}{d_{kk''}{}^{+}d_{k'''k'}{}^{+}d_{k'k''}{}^{+}} + \frac{1}{d_{kk''}{}^{+}d_{kk''}{}^{+}d_{k'''k'}{}^{+}} - \frac{1}{d_{kk'''}{}^{-}d_{k''k'''}{}^{-}d_{k'k''}{}^{-}} \right.$$

$$\left. \left. - \frac{1}{d_{kk'''}{}^{-}d_{k''k'''}{}^{-}d_{k'k''}{}^{-}} - \frac{1}{d_{kk'''}{}^{-}d_{kk'}{}^{-}d_{k''k'}{}^{-}} \right) \right], \qquad (90)$$

where as usual the matrix elements have been replaced without any loss of rigor by their ensemble averages. By interchanging a few summation indices, we may easily rewrite $A_k{}^{(2)}$ in the following form:

$$A_k{}^{(2)} = 2\pi i \sum_{k'k''k'''}{}' \delta(\omega_{kk'}) \left[\frac{\langle(kk'k''k'''k)\rangle}{d_{kk'}{}^{+}d_{kk'''}{}^{+}} + \frac{\langle(kk'''k''k'k)\rangle}{d_{kk'}{}^{-}d_{kk'''}{}^{-}} + \frac{\langle(kk'''k'k''k)\rangle}{d_{kk'}{}^{+}d_{kk'''}{}^{-}} \right]. \qquad (91)$$

The reduction of $B_{kk'}{}^{(2)}$ is rather tedious but straightforward. Just as in (73), we can show by direct algebraic transformation that up to terms proportional to s, which vanish in the limit, we have

$$B_{kk'}{}^{(2)} = 2\pi i \sum_{k''k'''}{}' \delta(\omega_{kk'}) \left[\frac{\langle(kk'k''k'''k)\rangle}{d_{kk'}{}^{-}d_{kk'''}{}^{-}} + \frac{\langle(kk'''k''k'k)\rangle}{d_{kk'}{}^{+}d_{kk'''}{}^{+}} + \frac{\langle(kk'''k'k''k)\rangle}{d_{kk'}{}^{-}d_{kk'''}{}^{+}} \right]. \qquad (92)$$

The ensemble averages are easily seen to be given by

$$\langle(kk'k''k'''k)\rangle = \frac{A_{k'k''k'''}}{\Omega^4} [N + N(N-1)\delta_{k+k'', k'+k'''}], \qquad (93)$$

where

$$A_{k'k''k'''} \equiv \phi_{kk'}\phi_{k'k''}\phi_{k''k'''}\phi_{k'''k}. \qquad (94)$$

Now let us make the following definitions. Put

$$w_{kk'}{}^{(2)} = 2\pi\delta(\omega_{kk'}) \frac{1}{\Omega^4} \sum_{k'',k'''}{}' \left[\frac{A_{k'k''k'''}}{d_{kk'}{}^{-}d_{kk'''}{}^{-}} + \frac{A_{k'''k''k'}}{d_{kk'}{}^{+}d_{kk'''}{}^{+}} + \frac{A_{k'''k'k''}}{d_{kk'}{}^{-}d_{kk'''}{}^{+}} \right], \qquad (95)$$

and

$$u_{kk'} = 2\pi\delta(\omega_{kk'}) \frac{N}{\Omega^4} \sum_{k'',k'''}{}' \left[\frac{A_{k'k''k'''}\delta_{k+k'', k'+k'''}}{d_{kk'}{}^{-}d_{kk'''}{}^{-}} + \frac{A_{k''k'''k'}\delta_{k+k'', k'+k'''}}{d_{kk'}{}^{+}d_{kk'''}{}^{+}} + \frac{A_{k'''k'k''}\delta_{k+k', k''+k'''}}{d_{kk'}{}^{-}d_{kk'''}{}^{+}} \right]. \qquad (96)$$

Then $[T_k{}^{(2)}(f)]'$ becomes

$$[T_k{}^{(2)}(f)]' = iN \sum_{k'}{}' (w_{k'k}{}^{(2)} + u_{k'k})f_k - (w_{kk'}{}^{(2)} + u_{kk'})f_{k'}. \qquad (97)$$

The interpretation of the $w_{kk'}{}^{(2)}$ terms is very simple. Just as in (79), $w_{kk'}{}^{(2)}$ is the *second* correction to the Born approximation for the scattering of plane wave states k' into state k by a *single* impurity.[7] $Nw_{kk'}{}^{(2)} \equiv W_{kk'}{}^{(2)}$ is just the correction due to all N impurities. Therefore the only effect of the w terms in (97) on the transport equa-

tion is to replace the transition probabilities $W_{kk'}{}^{(0)}+W_{kk'}{}^{(1)}$ by $W_{kk'}{}^{(0)}+W_{kk'}{}^{(1)}+W_{kk'}{}^{(2)}$, i.e., to use the correct transition probabilities to the order in question.

The u terms in (97) also have a very simple meaning. They represent the effect on the transition probability of *interference* between scattering from two impurities, averaged over all possible configurations of the pair. The fourth order (the one studied here) is the first order in which such effects occur. In higher orders of course we would find interference effects between scattering from three impurities, etc.

As is easily seen by replacing the sums by integrals in (95), (96), and (97), the w terms are proportional to n while the u terms are proportional to n^2, as they must be.

Finally we must consider $[T_k{}^{(2)}(f)]''$. This may easily be simplified by a little algebra into the following form:

$$[T_k{}^{(2)}(f)]''=\sum_{k',k''}{}'(f_k-f_{k'})\left[-\frac{\langle|H'_{kk'}|^2{}_k\rangle}{(d_{kk'}{}^-)^2}\left(\frac{\langle|H'_{kk''}|^2\rangle}{d_{kk''}{}^+}-\frac{\langle|H'_{k'k''}|^2\rangle}{d_{k'k''}{}^-}\right)+\frac{\langle|H'_{kk''}|^2\rangle\langle|H'_{k''k'}|^2\rangle}{d_{kk'}{}^-d_{kk''}{}^-d_{k'k''}{}^+}\right]-\text{c.c.} \quad (98)$$

In (98) we have once more replaced the matrix elements by their ensemble averages, as may be shown to be rigorous. In addition, we have written ensemble averages like $\langle|H_{kk'}|^2|H_{k'k''}|^2\rangle$ as $\langle|H_{kk'}|^2\rangle\langle|H_{k'k''}|^2\rangle$. It is easy to show that the difference is of the order of $1/N$ smaller than the matrix elements themselves.

In (98) the first two terms have a very simple physical meaning. Let us define

$$\epsilon_k{}^{(2)}\equiv\Delta_k-i\tfrac{1}{2}\gamma_k=\sum_{k''}\frac{\langle|H'_{kk''}|^2\rangle}{\epsilon_k-\epsilon_{k''}+is}=\sum_{k''}\frac{|H'_{kk''}|^2}{d_{kk''}{}^+}. \quad (99)$$

From (99) and (48),

$$\Delta_k=\sum_{k''}P\frac{\langle|H'_{kk''}|^2\rangle}{\omega_{kk''}}, \quad (100)$$

$$\gamma_k=2\pi\sum_{k'}\langle|H'_{kk''}|^2\rangle\delta(\omega_{kk''}). \quad (101)$$

The quantity Δ_k represents an energy shift for the state k, the principal value being necessary since we are in the continuous spectrum. The quantity γ_k is just the total transition probability per unit time (to lowest order) from the state k to any other state. Thus it is the reciprocal of the lifetime of a plane wave state k.

With (99) we may write for the first two terms of (98)

$$\sum_{k'}(f_k-f_{k'})\left[-\frac{\langle|H'_{kk'}|^2\rangle}{(d_{kk'}{}^-)^2}(\epsilon_k{}^{(2)}-\epsilon_k{}^{(2)*})\right]-\text{c.c.}=\sum_{k'}\left[\frac{|H'_{kk'}|^2(f_k-f_{k'})}{(\epsilon_k+\epsilon_k{}^{(2)})-(\epsilon_{k'}+\epsilon_{k'}{}^{(2)*})-is}-\frac{|H'_{kk'}|^2(f_k-f_{k'})}{\epsilon_k-\epsilon_{k'}-is}\right]-\text{c.c.} \quad (102)$$

to the order in question. If we combine this with (46), we see that what these terms do is replace denominators $\epsilon_k-\epsilon_{k'}-is$ by

$$(\epsilon_k+\epsilon_k{}^{(2)})-(\epsilon_{k'}+\epsilon_{k'}{}^{(2)*})-is$$
$$=(\epsilon_k+\Delta_k)-(\epsilon_{k'}+\Delta_{k'})-i\left(\frac{\gamma_k+\gamma_{k'}}{2}+s\right). \quad (103)$$

Since γ_k is positive, these denominators now represent delta functions of argument $(\epsilon_k+\Delta_k)-(\epsilon_{k'}+\Delta_{k'})$ with a "natural width," $(\gamma_k+\gamma_{k'})/2$. That is, the transitions take place between the states of the same *corrected* energy $\epsilon_k+\Delta_k$ but even this energy is not *exactly* conserved. It is conserved up to an energy of the order average reciprocal lifetime of the states in question. To this order we may replace every denominator occurring in (68) by these corrected denominators, so that if we wish we may drop the first two terms of (98) and remember that the corrected denominators (103) are always to be used.

For the last term in (98) we have not obtained a simple and clear physical interpretation.

This completes the discussion of the transport equa-

tion up to and including terms in λ^4. To obtain f_k to this order, we expand the solution of (68) in powers of λ and break it off at λ^0. That is, we can obtain f_k from $f_k{}^{(0)}$ by a perturbation technique.

As far as the calculation of expectation values goes, all the comments following (53) are still valid, and need not be repeated here.

Finally, we should like to discuss one limiting case of the transport equation (68). If we go to the limit where there are very few impurities (i.e., where the average distance between impurities is much greater than the mean wavelength of the electrons) then we would expect that the only physical effect entering the transport equation would be just the scattering by a single impurity. This is easily seen to be the case from our explicit formulas. All terms except $C_k{}^0$ and the $W_{kk'}$ terms give higher order corrections in n, and vanish in the dilute limit.[8] Therefore in *the dilute case*

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[8] *Note added in proof.*—The order of magnitude of these terms can easily be estimated in the limit where the average wavelength of the electron is much greater than the range of the scattering potential r_0. Denoting a typical electron wave number by $\bar{k}$ and a mean magnitude of the scattering potential by $\bar{\varphi}$, the ratio of the terms of order n^2 to those of order n is $n(r_0{}^6/\bar{k})(m\bar{\varphi}/\hbar^2)^2$.

we just obtain the usual transport equation with the usual transition probabilities computed to the order in question. This result can be proved to arbitrary order, but we shall not give the general proof in this apper.

IV. ELECTRONS IN A PERIODIC POTENTIAL

In this section we shall generalize the results of the previous two sections to the case where the electrons are moving in a periodic potential as well as the external electric field and the field of the scattering centers. We shall take the same type of impurity potential as before but shall for simplicity assume that impurities may only be found at lattice sites. The perturbation H' is the same (4) the only difference now being that $\phi(r)$ represents the *difference* between the potential produced by an impurity atom and that of the original atom of the periodic lattice.

The interaction with the external field is of course given again by H_F as in (5). The main change comes in H_0. This is now given by

$$H_0 = \frac{p^2}{2m} + U, \tag{104}$$

where U is the periodic potential. We shall assume that the eigenfunctions and eigenvalues of (104) are known. Let us write

$$H_0\psi_l = \epsilon_l^{(0)}\psi_l. \tag{105}$$

Here l stands for the index pair (ν, k), ν telling us the band we are in, and k being a vector extending over the first Brillouin zone. As is well known, the functions ψ_l may be written as

$$\psi_l = \frac{e^{ik \cdot r}}{\sqrt{\Omega}} w_l(r), \tag{106}$$

where $w_l(r)$ is a function which has the periodicity of the lattice. The ψ_l are normalized to unity:

$$\int_\Omega \psi_{l'}^* \psi_l dr = \delta_{ll'}. \tag{107}$$

We shall use as our basic representation the representation in which H_0 is diagonal (which we shall often call for brevity the "l-representation"), just as we used the k-representation previously. To carry out the discussion of the previous two sections we must investigate the matrix elements of H' and C in this representation. We have

$$H'_{ll'} = \int \psi_l^* H' \psi_{l'} dr$$

$$= \frac{\phi_{ll'}}{\Omega} \left[\sum_i e^{-i(k-k') \cdot r_i} \right], \tag{108}$$

where

$$\phi_{ll'} = \int_\Omega e^{-i(k-k') \cdot r} w_l^* w_{l'} \phi(r) dr. \tag{109}$$

In deriving this we have used the fact that the impurities are located at lattice points. Equation (108) has exactly the same form as (22) except that $\phi_{kk'}$ is replaced by $\phi_{ll'}$. The diagonal elements of H' are

$$H'_{ll} = (N/\Omega)\phi_{ll}, \tag{110}$$

with

$$\phi_{ll} = \int |w_l|^2 \phi(r) dr. \tag{111}$$

In general the H'_{ll} will not vanish and will be some definite function of l. We adopt the following convention: if H'_{ll} does not vanish, we absorb this diagonal part of H' into H_0 and take as our unperturbed energy

$$\epsilon_l = \epsilon_l^0 + H'_{ll}. \tag{112}$$

Therefore we imagine from now on that H' has vanishing diagonal elements.

A detailed derivation of the general expression for C is given at the end of Appendix A. The result is quite simple, namely

$$C_{ll'} = ieE_\alpha^{(0)}$$

$$\times \left[\left(\frac{\partial}{\partial k_\alpha} + \frac{\partial}{\partial k_\alpha'} \right) \rho_{ll'} + \sum_{l''} (J_\alpha^{ll''} \rho_{l''l'} - \rho_{ll''} J_\alpha^{l''l'}) \right]. \tag{113}$$

In (113) the derivatives with respect to k and k' are purely formal and just mean that these operations are to be carried out as if k were a continuous variable. The quantity $J_\alpha^{ll'}$ is defined by

$$J_\alpha^{ll'} = \frac{1}{\omega} \left(\int_\omega w_{\nu k}^* \frac{\partial w_{\nu' k}}{\partial k_\alpha} dr \right) \delta_{kk'}, \tag{114}$$

where ω is the volume of a unit cell.

Once again we may write

$$C_{ll'} = C_{ll'}^{(0)} + C_{ll'}^{(1)} + C_{ll'}^{(2)} + \cdots, \tag{115}$$

$C_{ll'}^{(n)}$ being of order λ^n. However, $C_{ll'}^{(0)}$ has off-diagonal as well as diagonal elements in the present case.

Now everything leading to (25) and (26) may be repeated in the l-representation. This gives rise to equations which are formally identical with (25) and (26) except that k is replaced everywhere by l. The method of solution is identical, involving a split into diagonal and off-diagonal terms in l. Since all the algebra is identical we shall only state the results. Define

$$R_{ll'} = (\omega_{ll'} - is)f_{ll'}, \quad l \neq l'$$
$$= R_{ll'}^{(0)} + R_{ll'}^{(1)} + \cdots. \tag{116}$$

Then

$$R_{ll'}{}^{(0)} = (f_l - f_{l'})H_{ll'},\tag{117}$$

$$R_{ll'}{}^{(1)} = C_{ll'}{}^{(0)} + \sum_{l''}' H'_{ll''}H'_{l''l'}\left(\frac{f_l - f_{l''}}{\omega_{ll''} - is} - \frac{f_{l''} - f_{l'}}{\omega_{l''l'} - is}\right).\tag{118}$$

This gives the off-diagonal terms up till order λ^0. The "transport equation" up to the same order is

$$0 = C_l{}^{(0)} + C_l{}^{(1)} + C_l{}^{(2)} + \sum_{l'}'\left(\frac{\langle C_{ll'}{}^{(0)}H_{l'l}'\rangle}{d_{ll'}{}^-} - \text{c.c.}\right) + \sum_{l'}'\left(\frac{\langle C_{ll'}{}^{(1)}H_{l'l}'\rangle}{d_{ll'}{}^-} - \text{c.c.}\right)$$

$$+ \sum_{l',l''}\left[\left\langle\left(\frac{C_{ll''}{}^{(0)}H_{l''l'}}{d_{ll''}{}^-} - \frac{H_{ll''}'C_{l''l'}{}^{(0)}}{d_{l''l'}{}^-}\right)\frac{H_{l'l}'}{d_{ll'}{}^-}\right\rangle - \text{c.c.}\right] + i\sum_{l'}'(W_{l'l}f_l - W_{ll'}f_{l'}) + S + A.\tag{119}$$

Here

$$W_{l'l} = 2\pi\delta(\omega_{l'l})\left\{\langle|H_{l'l}'|^2\rangle + \sum_{l''}\left[\frac{\langle(ll'l''l)\rangle}{d_{ll''}{}^+} + \frac{\langle(ll''l'l)\rangle}{d_{ll''}{}^-}\right] + \sum_{l'',l'''}\left[\frac{\langle(ll'l'''l''l)\rangle}{d_{ll''}{}^+ d_{ll'''}{}^+} + \frac{\langle(ll'l'''l''l)\rangle}{d_{ll''}{}^- d_{ll'''}{}^-} + \frac{\langle(ll'''l'l''l)\rangle}{d_{ll'''}{}^- d_{ll''}{}^+}\right]\right\},\tag{120}$$

$$S = \sum_{l'}\langle|H'_{ll'}|^2\rangle\frac{(f_l - f_{l'})}{(d_{ll'}{}^-)^2}(\epsilon_{l'}{}^{(2)*} - \epsilon_l{}^{(2)}) - \text{c.c.},\tag{121}$$

$$\epsilon_l{}^{(2)} = \sum_{l''}\frac{\langle|H'_{ll''}|^2\rangle}{d_{ll''}{}^+},\tag{122}$$

$$A = \sum_{l',l''}\frac{\langle|H'_{ll''}|^2\rangle}{d_{ll'}{}^-}\frac{\langle|H'_{ll''}|^2\rangle}{d_{ll''}{}^-}\frac{(f_l - f_{l'})}{d_{l'l''}{}^+} - \text{c.c.}\tag{123}$$

The symbol $\langle\quad\rangle$ means the ensemble average again; that is, we must average the positions of the impurities over the lattice points. The quantity $W_{l'l}$ is again the total transition probability to order λ^4 of an electron going from state l to l' and includes the interference effects of the scattering from two impurities.

The detailed evaluation of these ensemble averages and commutator terms goes very much like the simpler plane-wave case. We shall not give these rather cumbersome formulas here, but hope to return to them in a later publication. One point of interest, however, should be mentioned.

In the plane-wave case we saw that only the diagonal elements of f contributed to average velocity or current. This is no longer true here, and off-diagonal elements of the density matrix make contributions to the current. The velocity operator is again

$$v_\beta = i[H_T, x_\beta] = i[H_0, x_\beta].\tag{124}$$

As is well known, the diagonal elements of v_β are given by

$$(v_\beta)_l = \partial\epsilon_l/\partial k_\beta.\tag{125}$$

On the other hand, v_β also has off-diagonal elements, which are easily[9] seen to be

$$(v_\beta)_{ll'} = -\omega_{ll'}J_\beta{}^{\nu'\nu}(k)\delta_{kk'}, \quad (l \neq l').\tag{126}$$

Therefore the average velocity consists of a diagonal

part $v_\beta{}^{(a)}$ and an off-diagonal part $v_\beta{}^{(b)}$:

$$\langle v_\beta\rangle = v_\beta{}^{(a)} + v_\beta{}^{(b)},\tag{127}$$

$$v_\beta{}^{(a)} = \sum_l f_l\frac{\partial\epsilon_l}{\partial k_\beta},\tag{128}$$

$$v_\beta{}^{(b)} = \sum_{l,l'}' f_{ll'}(v_\beta)_{l'l};\tag{129}$$

$v_\beta{}^{(a)}$ is the result one usually uses in transport theory, $v_\beta{}^{(b)}$ is new, and may be transformed somewhat.

$$v_\beta{}^{(b)} = \sum_{l,l'} f_{ll'}\omega_{ll'}J_\beta{}^{\nu'\nu}(k)\delta_{kk'}$$

$$= \sum_k \sum_{\nu\nu'(\nu\neq\nu')} f_{\nu k, \nu'k}\omega_{\nu k, \nu'k}J_\beta{}^{\nu'\nu}(k)$$

$$\times \sum_k \sum_{\nu,\nu'(\nu\neq\nu')}\frac{R_{\nu k, \nu'k}}{\omega_{\nu k, \nu'k} - is}\omega_{\nu k, \nu'k}J_\beta{}^{\nu'\nu}(k)$$

$$\times \sum_k \sum_{\nu,\nu'(\nu\neq\nu')} R_{\nu k, \nu'k}J_\beta{}^{\nu'\nu}(k).\tag{130}$$

To the lowest order (which is λ^{-1}), this gives

$$(v_\beta{}^{(b)})^{(0)}$$

$$= \sum_k \sum_{\nu,\nu'(\nu\neq\nu')}(f_{\nu k} - f_{\nu'k})H'_{\nu k, \nu'k}J_\beta{}^{\nu'\nu}(k)$$

$$= \sum_l f_l\sum_{\nu'}[H'_{\nu k', \nu'k}J_\beta{}^{\nu'\nu}(k) - J_\beta{}^{\nu\nu'}(k)H'_{\nu'k, \nu k}].\tag{131}$$

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[9] Luttinger and Karplus, reference 2.

This sum over ν' is easily evaluated, by using (113) with ρ replaced by H', and gives

$$(v_\beta^{(b)})^{(0)} = \sum_l f_l \frac{\partial(H'll)}{\partial k_\beta}. \tag{132}$$

Therefore $(v_\beta^{(b)})^{(0)}$ is zero, since we have chosen $H_{ll'}$ to be. If we had *not* chosen H'_{ll} zero, then (132) would give a contribution which is just of the form of (128), and would be the contribution to the velocity due to the first-order correction to the energy.

The next terms in $v_\beta^{(b)}$ (of order λ^0) are

$$(v_\beta^{(b)})^{(1)} = \sum_k \sum_{\nu,\nu'(\nu\neq\nu')} C_{\nu k,\nu'k}^{(0)} J_\beta^{\nu'\nu}(k)$$

$$+ \sum_k \sum_{\nu,\nu'(\nu'\neq\nu)} \sum_{l''}' \langle H'_{\nu k,l''} H'_{l'',\nu'k}\rangle$$

$$\times \left(\frac{f_l - f_{l''}}{\omega_{ll''} - is} - \frac{f_{l''} - f_{l'}}{\omega_{l''l'} - is}\right) J_\beta^{\nu'\nu}(k). \tag{133}$$

From (113), we have

$$C_{ll'}^{(0)} = ieE_\alpha(\rho_l - \rho_{l'}) J_\alpha^{\nu\nu'}(k)\delta_{kk'}, \tag{134}$$

where ρ_l is the Maxwell-Boltzmann distribution for H_0, evaluated in the state l. With this the first term of (133) is easily evaluated:

$$\sum_k \sum_{\nu,\nu'(\nu\neq\nu')} C_{\nu k,\nu'k}^{(0)} J_\beta^{\nu'\nu}(k)$$

$$= ieE_\alpha \sum_l \rho_l \sum_{\nu'} [J_\alpha^{\nu\nu'}(k) J_\beta^{\nu'\nu}(k) - J_\beta^{\nu\nu'}(k) J_\alpha^{\nu'\nu}(k)]$$

$$= +ieE_\alpha \sum_l \rho_l \left(\frac{\partial J_\alpha^l}{\partial k_\beta} - \frac{\partial J_\beta^l}{\partial k_\alpha}\right), \tag{135}$$

by using (2.17) of Karplus and Luttinger.[2] This term is independent of the collision mechanism, and was found previously by Karplus and Luttinger. The second term of (133) does depend on the collision mechanism, and is rather complex. There is no reason why (133) should vanish, and in general it does not. It is of considerable interest in connection with the Hall effect in ferromagnetics, and we leave its detailed discussion to a later publication on that subject.

APPENDIX A. DETAILED JUSTIFICATION OF THE ACCELERATION TERM

There are two points in our discussion which may appear somewhat mysterious: (1) How is it at all possible for an isolated rectangular block of material to carry a steady current and (2) why is $C_{kk'} \equiv -eE_\alpha^{(0)} \times [\rho(H_0+H'), x_\alpha]_{kk'}$ given by $ieE_\alpha^{(0)}(\partial/\partial k_\alpha + \partial/\partial k_\alpha') \times \rho_{kk'}$ where the operations $\partial/\partial k_\alpha$ and $\partial/\partial k_\alpha'$ are *formal* differentiations, as though k_α and k_α' were continuous variables. This latter result seems puzzling when one considers that for a finite block, with center of gravity at the origin, $x_{kk}=0$ which would also make $[\rho(H_0), x_\alpha]_{kk}$

$=0$, while according to our prescription $[\rho(H_0), x_\alpha]_{kk}$ $= -(\beta k_\alpha/m)K_0 e^{-\beta\epsilon k}$ [see Eq. (31)].

Since we have obtained physically reasonable results, many readers may not be disturbed by these doubts. However, for those who are, we shall now give a more careful derivation of our basic equations which we believe to be free of the objections just mentioned.

Instead of a block of material containing the electrons we consider a hollow circular cylinder. In such a cylindrical ring a steady current can be set up. For the following discussion we adopt cylindrical coordinates r, θ, and z. The inner and outer radii will be denoted by r_1 and r_2, the mean radius, $\frac{1}{2}(r_1+r_2)$, by $\bar{r}$, and the remaining two bounding surfaces by $z=0$ and $z=L_z$. This cylinder is situated in a spatially uniform but time-dependent magnetic field, parallel to the z-axis and given by

$$\mathcal{H}_z = -(2E^{(0)}c/s\bar{r})e^{st}. \tag{A1}$$

This field is chosen to give rise to an electric field of magnitude

$$E = E^{(0)}(r/\bar{r})e^{st}, \tag{A2}$$

and pointing in the direction of increasing θ. For a sufficiently thin ring $[(r_2-r_1)/r\ll1]$, this electric field is almost spatially uniform, so that if s is chosen small enough the ratio of the circular current to $E^{(0)}e^{st}$ will give the desired conductivity.

The unperturbed Hamiltonian (no impurities, no field) of this problem is

$$-\frac{1}{2m}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{\partial^2}{\partial z^2}\right).$$

However, since the electron wavelengths in question are much shorter than the macroscopic mean radius $\bar{r}$, we can without appreciable error neglect $(1/r)(\partial/\partial r)$ in comparison with $\partial^2/\partial r^2$. Further, since the ring is thin we may replace $(1/r^2)(\partial^2/\partial\theta^2)$ by $(1/\bar{r})(\partial^2/\partial\theta^2)$. This suggests the introduction of the following notation:

$$\xi = \bar{r}\theta, \quad \eta = r - r_1, \quad \zeta = z,$$

$$P_\xi = \frac{1}{i}\frac{1}{\bar{r}}\frac{\partial}{\partial\theta}, \quad P_\eta = \frac{1}{i}\frac{\partial}{\partial r}, \quad P_\zeta = \frac{1}{i}\frac{\partial}{\partial z}. \tag{A3}$$

Evidently the new variables satisfy the canonical commutation relations. In terms of these, the total Hamiltonian to the first order in $E^{(0)}$ is

$$H_T = H_0 + H' + H_F, \tag{A4}$$

where

$$H_0 = (1/2m)(P_\xi^2 + P_\eta^2 + P_\zeta^2),$$

$$H' = \lambda V(\xi,\eta,\zeta), \tag{A5}$$

$$H_F = (H_1/s)e^{st}, \quad H_1 = [eE^{(0)}/m]P_\xi,$$

which corresponds to Eqs. (2)–(15) in the text. If we call

$$L_1 \equiv 2\pi\bar{r}, \quad L_2 \equiv r_2 - r_1, \quad L_3 = L_z, \tag{A6}$$

the physical boundary conditions satisfied by the wave functions ψ are

$$\psi = 0 \text{ for } \eta = 0 \text{ or } L_2, \quad \xi = 0 \text{ or } L_3, \tag{A7}$$

and

$$\psi(\xi + L_1, \eta, \zeta) = \psi(\xi, \eta, \zeta); \tag{A8}$$

the last of these represents the singlevaluedness of the wave functions.

Now it can be easily shown that our results do not depend on the exact boundary conditions imposed at $\eta = 0$ and L_2, and at $\zeta = 0$ and L_3, as the current flow takes place in the ξ direction. For convenience we therefore replace (A7) by the periodic conditions

$$\psi(\xi, L_2, \zeta) = \psi(\xi, 0, \zeta); \quad \left(\frac{\partial \psi}{\partial \eta}\right)_{\xi, L_2, \zeta} = \left(\frac{\partial \psi}{\partial \eta}\right)_{\xi, 0, \zeta},$$

$$\psi(\xi, \eta, L_3) = \psi(\xi, \eta, 0); \quad \left(\frac{\partial \psi}{\partial \zeta}\right)_{\xi, \eta, L_3} = \left(\frac{\partial \psi}{\partial \zeta}\right)_{\xi, \eta, 0}. \tag{A7'}$$

The conditions (A7') and (A8) correspond exactly to the periodic boundary conditions used in Sec. II. As the basis for our representation we shall use the eigenfunctions of H_0 which satisfy (A7') and (A8). These are

$$\psi_k = \frac{1}{\Omega^{\frac{1}{2}}} e^{i(k_1\xi + k_2\eta + k_3\zeta)}$$

$$= \frac{1}{\Omega^{\frac{1}{2}}} e^{ik\cdot r} \tag{A9}$$

where k stands for (k_1, k_2, k_3), r stands (from here on) for (ξ, η, ζ), and $\Omega = L_1 L_2 L_3$.

In analogy with our development in the text, we now write the total density matrix as

$$\rho_T = \rho + \rho_F, \tag{A10}$$

where ρ_F represents the correction linear in the electric field. ρ_T satisfies the equation of motion:

$$i(\partial \rho_T / \partial t) = [H_T, \rho_T]. \tag{A11}$$

Substituting (A10) into (A11) and making the "Ansatz"

$$\rho_F = \left(-\frac{i}{s}C + \xi\right) e^{st}, \tag{A12}$$

gives

$$isf = -C + [H, f] + \frac{1}{s}[[H_1, \rho] - i[H, C]], \tag{A13}$$

where $H \equiv H_0 + H'$. Evidently (A13) will be satisfied if C obeys

$$i[H, C] = [H_1, \rho] \tag{A14}$$

and f satisfies

$$isf = -C + [H, f]. \tag{A15}$$

While C is defined by (A14) only to within an operator

which commutes with H, the total $\rho_F = -(i/s)C + f$ is, of course, unique.

We shall now show that

$$C = ieE^{(0)}(\partial \rho / \partial P_\xi) \tag{A16}$$

is a solution of (A14). Here $\partial / \partial P_\xi$ represents the formal derivative of the operator ρ, the latter being expressed as function of $\xi, \eta, \cdots P_\zeta$:

$$\rho = K \exp\left\{-\beta\left[\frac{1}{2m}(P_\xi^2 + P_\eta^2 + P_\zeta^2) + \lambda V(\xi, \eta, \zeta)\right]\right\}. \tag{A17}$$

This may be seen as follows. With (A16), we have

$$i[H, C] = i(HC - CH)$$

$$= -eE^{(0)}\left[(H_0 + \lambda V)\frac{\partial \rho}{\partial P_\xi} - \frac{\partial \rho}{\partial P_\xi}(H_0 + \lambda V)\right]$$

$$= eE^{(0)}\left(\frac{\partial H_0}{\partial P_\xi}\rho - \rho\frac{\partial H_0}{\partial P_\xi}\right)$$

$$= (e/m)E^{(0)}[P_\xi, \rho] = [H_1, \rho], \tag{A18}$$

since V is independent of P_ξ.

We shall next show that the matrix elements of C, as defined by (A16) are given in our representation by

$$C_{kk'} = ieE^{(0)}\left(\frac{\partial}{\partial k_1} + \frac{\partial}{\partial k_1'}\right)\rho_{kk'}, \tag{A19}$$

where $\partial / \partial k_1$ and $\partial / \partial k_1'$ are *formal* derivatives. This is the result used in Eq. (C7). These matrix elements are

$$C_{kk'} = \frac{1}{\Omega} ieE^{(0)} \int e^{-ik\cdot r} \frac{\partial \rho}{\partial P_\xi} e^{ik'\cdot r} dr$$

$$= \frac{1}{\Omega} ieE^{(0)} \lim_{|\epsilon| \to 0} \frac{1}{|\epsilon|} \int e^{-ik\cdot r}$$

$$\times [\rho(P + \epsilon, r) - \rho(P, r)] e^{ik'\cdot r} dr, \tag{A20}$$

where ϵ is a numerical vector in the ξ direction. [That is, $P + \epsilon \equiv (P_\xi + |\epsilon|, P_\eta, P_\zeta)$.] Equation (A20) follows directly from the definition of the formal derivative. Now

$$\rho(P + \epsilon, r) = e^{-i\epsilon\cdot r} \rho e^{i\epsilon\cdot r}, \tag{A21}$$

because the operator $e^{i\epsilon\cdot r}$ produces a displacement in momentum space. Equation (A21) may also be verified directly by expanding in a power series in the momentum. Inserting (A21) in (A20), we have

$$C_{kk'} = \frac{ieE^{(0)}}{\Omega} \lim_{|\epsilon| \to 0} \frac{1}{|\epsilon|}$$

$$\times \int [e^{-i(k+\epsilon)\cdot r} \rho e^{i(k'+\epsilon)\cdot r} - e^{-ik\cdot r} \rho e^{ik'\cdot r}] dr \tag{A22}$$

$$= ieE^{(0)} \lim_{|\epsilon| \to 0} \frac{1}{|\epsilon|} (\rho_{k+\epsilon, k'+\epsilon} - \rho_{k, k'}).$$

By definition of the formal derivative with respect to k_1 and k_1', (A22) is identical with the expression (A19).

Hence, in the present formulation, the correction to the density matrix is

$$\rho_F = \left(\frac{eE^{(0)}}{s} \frac{\partial \rho}{\partial P_\xi} + f \right) e^{st}, \qquad (A23)$$

where the f is the solution of the same transport equation as in the text.

We must still verify that, despite the extra term in (A23), we get the same physical current as before. Now in the present formulation the operator for velocity along the ξ direction is

$$v_\xi = \frac{1}{m} \left(P_\xi + \frac{eE^{(0)}}{s} e^{st} \right). \qquad (A24)$$

This expression is obtained formally from the relation

$$\dot{\xi} = i[H_T, \xi]$$

and may also be derived less formally by consideration of the motion of a wave packet. The expectation value of v_ξ is given by

$$\bar{v}_\xi = \mathrm{Tr}(\rho_T v_\xi)$$

$$= e^{st} \mathrm{Tr}\left[\frac{1}{m} f P_\xi + \frac{eE^{(0)}}{sm} \left(\frac{\partial \rho}{\partial P_\xi} \right) P_\xi + \rho \frac{eE^{(0)}}{sm} \right]$$

$$= e^{st} \left[\mathrm{Tr}\left(\frac{1}{m} f P_\xi \right) + \mathrm{Tr}\left(\frac{eE^{(0)}}{sm} \frac{\partial}{\partial P_\xi} (\rho P_\xi) \right) \right]. \quad (A25)$$

The same technique which led to (A19) now gives

$$\left[\frac{\partial}{\partial P_\xi} (\rho P_\xi) \right]_{kk} = \frac{\partial}{\partial k_1} (\rho P_\xi)_{kk}, \qquad (A26)$$

whose sum over k vanishes. Therefore

$$\bar{v}_\xi = e^{st} \mathrm{Tr}\left(f \frac{1}{m} P_\xi \right), \qquad (A27)$$

as required.

Bloch Case

The problem of electrons moving in a cylindrical ring with impurities as well as a periodic potential U can be treated in a very similar way. The unperturbed Hamiltonian becomes now

$$H_0 = (1/2m)(P_\xi^2 + P_\eta^2 + P_\zeta^2) + U(\xi, \eta, \zeta), \quad (A28)$$

while H' and H_F are unchanged. This leads again to the equation

$$isf = -C + (H, f), \qquad (A29)$$

where C must now satisfy (A14) with the present H, which includes the periodic potential. The solution is,

as before

$$C = ieE^{(0)}(\partial\rho/\partial P_\xi). \qquad (A30)$$

Next we want to obtain the matrix-elements of C in the representation of the Bloch waves

$$\psi_l(r) = (1/\Omega^{\frac{1}{2}}) w_l(r) e^{ik \cdot r}, \qquad (A31)$$

where l represents both quantum numbers ν and k and w_l has the same periodicity as U. Clearly, in analogy with Eqs. (A20) to (A22), we obtain

$$C_{ll'} = \frac{1}{\Omega} ieE^{(0)} \int w_l^* e^{-ik \cdot r} \frac{\partial\rho}{\partial P_\xi} w_{l'} e^{ik' \cdot r} dr$$

$$= \frac{1}{\Omega} ieE^{(0)} \lim_{|\epsilon| \to 0} \frac{1}{|\epsilon|} \int w_l^* e^{-ik \cdot r} (e^{-i\epsilon \cdot r} \rho e^{i\epsilon \cdot r} - \rho)$$
$$\times w_{l'} e^{ik' \cdot r} dr. \quad (A32)$$

Now we write

$$w_{\nu, k}^* e^{-i(k+\epsilon) \cdot r} = w_{\nu, k+\epsilon}^* e^{-i(k+\epsilon) \cdot r} - |\epsilon| \left(\frac{\partial}{\partial k_1} w_{\nu k}^* \right) e^{-ik \cdot r},$$
$$(A33)$$

$$w_{\nu', k'} e^{i(k'+\epsilon) \cdot r} = w_{\nu', k'+\epsilon} e^{i(k'+\epsilon) \cdot r} - |\epsilon| \left(\frac{\partial}{\partial k_1'} w_{\nu' k'} \right) e^{ik' \cdot r},$$

which gives

$$C_{ll'} = ieE^{(0)} \left[\left(\frac{\partial}{\partial k_1} + \frac{\partial}{\partial k_1'} \right) \rho_{ll'} \right.$$

$$\left. - \frac{1}{\Omega} \int e^{-ik \cdot r} \left(\frac{\partial w_l^*}{\partial k_1} \rho w_{l'} + w_l^* \rho \frac{\partial w_{l'}}{\partial k_1'} \right) e^{ik' \cdot r} dr \right]. \quad (A34)$$

To obtain Eq. (113) of the text, we note that

$$\rho w_l e^{ik' \cdot r} = \sum_{\nu''} w_{\nu''} e^{ik'' \cdot r} \rho_{\nu'' l},$$
$$w_l^* e^{-ik \cdot r} \rho = \sum_{\nu''} \rho_{l \nu''} w_{\nu''} e^{-ik'' \cdot r}, \qquad (A35)$$

so that the second term of (A34) becomes

$$- \frac{ieE^{(0)}}{\Omega} \int \left[\left(e^{-ik \cdot r} \frac{\partial w_l^*}{\partial k_1} w_{\nu''} e^{ik'' \cdot r} \right) \rho_{\nu'' l'} \right.$$

$$\left. + \rho_{l \nu''} \left(w_{\nu''}^* e^{-ik'' \cdot r} \frac{\partial w_{l'}}{\partial k_1'} e^{ik' \cdot r} \right) \right] dr. \quad (A36)$$

Now, denoting the volume per unit cell by ω, we have

$$\frac{1}{\Omega} \int w_{\nu''}^* e^{-ik'' \cdot r} \frac{\partial w_{l'}}{\partial k_1'} e^{ik' \cdot r} dr$$

$$= \frac{1}{\omega} \left(\int_\omega w_{\nu''}^* \frac{\partial w_{l'}}{\partial k_1'} dr \right) \delta_{k''k'} = J_1^{\nu''\nu'}, \quad (A37)$$

where $J_1^{\nu''\nu'}$ is the same expression previously defined in (114). Similarly, using the orthonormality of the ψ_l, we find

$$\frac{1}{\Omega}\int\frac{\partial w_l^*}{\partial k_1}e^{-ik\cdot r}w_{l''}e^{ik''\cdot r}dr$$

$$=\frac{1}{\omega}\left(\int_\omega\frac{\partial w_l^*}{\partial k_1}w_{l''}dr\right)\delta_{kk''}$$

$$=-\frac{1}{\omega}\left(\int_\omega w_l^*\frac{\partial w_{l''}}{\partial k_1''}dr\right)\delta_{kk''}=-J_1{}^{ll''}. \quad \text{(A38)}$$

Substituting these expressions in (A34) gives

$$C_{ll'}=ieE^{(0)}\left[\left(\frac{\partial}{\partial k_1}+\frac{\partial}{\partial k_1'}\right)\rho_{ll'}+\sum_{l''}(J_1{}^{ll''}\rho_{l''l'}-\rho_{ll''}J_1{}^{l''l'})\right], \quad \text{(A39)}$$

which is equivalent to Eq. (113) of the text.

APPENDIX B. ENSEMBLE AVERAGE THEOREM

Consider the quantity

$$M=\frac{1}{\Omega^n}\sum_{k_1,\cdots k_{n-1}}\sum_{\substack{i_1=1,\cdots N\\ \cdots\\ i_n=1,\cdots N}}\exp[-i(k-k_1)\cdot r_{i_1}]\exp[-i(k_1-k_2)\cdot r_{i_2}]\cdots\exp[-i(k_{n-1}-k)\cdot r_{i_n}]F(k_1,k_2,\cdots k_{n-1}), \quad \text{(B1)}$$

where r_i denotes the location of the impurity i, $N=$total number of impurities, $\Omega=$volume of container, and $F(k_1,\cdots k_{n-1})$ is a smooth function of its arguments. The function F approaches zero for $k_l b\gg 1$, where b is a length much smaller than the size of the container and independent of it.

We shall show that for the overwhelming majority of all arrangements, the difference between M and its "ensemble average" $\langle M\rangle$ becomes negligible as $\Omega\rightarrow\infty$, with (N/Ω) remaining fixed. $\langle M\rangle$ is defined by

$$\langle M\rangle=\int_\Omega\cdots\int_\Omega\frac{dr_1}{\Omega}\frac{dr_2}{\Omega}\cdots\frac{dr_N}{\Omega}M(r_1,r_2,\cdots r_N), \quad \text{(B2)}$$

and is just the average of M over all possible arrangements of the impurities.

In general several of the i_m will be equal. We now break up M into a number of terms

$$M=\sum_\alpha M_\alpha, \quad \text{(B3)}$$

where each M_α contains all the terms in M which differ only through an interchange of the impurities, e.g., M_1 might contain all the terms in M in which all i_m are equal to each other, M_2 those in which $i_1=i_2$ and $i_3=i_4=\cdots i_n$, but $i_1\neq i_3$, and so on. The general M_α will have the form

$$M_\alpha=\frac{1}{\Omega^n}\sum_{\substack{i_1=1,\cdots N\\ \cdots\\ i_m=1,\cdots N\\ i_j\neq i_l}}\exp(iK_1\cdot r_{i_1})\exp(iK_2\cdot r_{i_2})\cdots\exp(iK_{m-1}\cdot r_{i_{m-1}})\exp[-i(K_1+\cdots+K_{m-1})\cdot r_{i_m}]$$

$$\times G(K_1,\cdots K_{m-1}; K_m,\cdots K_{n-1}), \quad \text{(B4)}$$

where m and the K_l will depend on α; the K_l are certain linear combinations of the original variables k_l, spanning the same space; $G(K_1,\cdots K_{n-1})\equiv F(k_1,\cdots k_{n-1})$.

We shall now demonstrate that

$$|\langle M_\alpha\rangle|^2=\langle M_\alpha M_\alpha{}^*\rangle[1+O(1/N)]. \quad \text{(B5)}$$

It is elementary to verify that this is equivalent to the assertion that $M_\alpha-\langle M_\alpha\rangle$ is negligible compared to $\langle M_\alpha\rangle$, for the overwhelming number of arrangements. Since M is the sum of a finite number of M_α, the difference between M and $\langle M\rangle$ must then also be negligible compared to $\langle M\rangle$.

To prove (B5) we first note that

$$\langle M_\alpha\rangle=\frac{1}{\Omega^n}N(N-1)\cdots(N-m+1)\sum_{K_m,\cdots K_{n-1}}G(0,\cdots 0; K_m,\cdots K_{n-1})=\frac{1}{\Omega^n}N(N-1)\cdots(N-m+1)(\Omega^{n-m}I), \quad \text{(B6)}$$

where

$$I=\left[\frac{1}{(2\pi)^3}\right]^{n-m}\int\cdots\int dK_m\cdots dK_{n-1}G(0,\cdots 0; K_m\cdots K_{n-1}). \quad \text{(B7)}$$

Since m is a fixed number independent of N, we therefore have

$$\langle M_\alpha\rangle=(N/\Omega)^m I[1+O(1/N)]. \quad \text{(B8)}$$

To calculate $\langle M_\alpha M_\alpha^* \rangle$, we first write down

$$M_\alpha^* = \frac{1}{\Omega^n} \sum_{\substack{i_1' = 1, \cdots N \\ \vdots \\ i_m' = 1, \cdots N \\ i_j' \neq i_l'}} \exp(-iK_1' \cdot r_{i_1'}) \exp(-iK_2' \cdot r_{i_2'}) \cdots \exp(-iK_{m-1}' r_{i_{m-1}'})$$

$$\times \exp[-i(K_1' + \cdots K_{m-1}')r_{i_m}]G^*(K_1' \cdots K_{m-1}'; K_m', \cdots K_{n-1}'). \quad (B9)$$

When we multiply M_α by M_α^*, the resulting terms fall into two essentially different groups. In the first group, the contribution of which we will denote by $(M_\alpha M_\alpha^*)_I$ no members of the set $i_1, \cdots i_m, i_1', \cdots i_m'$ are equal; the second group $(M_\alpha M_\alpha^*)_{II}$ contains all the remaining terms.

Clearly

$$\langle (M_\alpha M_\alpha^*)_I \rangle = \frac{1}{\Omega^{2n}} N(N-1) \cdots (N-2m+1) \sum_{K_m, \cdots K_{n-1}} \sum_{K_m' \cdots K_{n-1}'} G(0, \cdots 0; K_m, \cdots K_{n-1})G^*(0, \cdots 0; K_m' \cdots K_{n-1}')$$

$$= \left(\frac{N}{\Omega}\right)^{2m} |I|^2 \left[1 + O\left(\frac{1}{N}\right)\right]. \quad (B10)$$

This is just equal to $|\langle M_\alpha \rangle|^2$ [see Eq. (B8)].

The ensemble average of $(M_\alpha M_\alpha^*)_{II}$ is of a smaller order of magnitude. As a typical set of terms contributing to $(M_\alpha M_\alpha^*)_{II}$, consider those in which $i_1 = i_1'$ but there are no other equalities in the set $i_1, \cdots i_m'$. Their ensemble average is

$$\frac{1}{\Omega^{2n}} N(N-1) \cdots (N-2m+2) \sum_{K_1, \cdots K_{n-1}} \sum_{K_1' \cdots K_{n-1}'} \delta(K_1, K_1')\delta(K_2, 0) \cdots \delta(K_{m-1}, 0)$$

$$\times \delta(K_1 + \cdots + K_{m-1}, 0)\delta(K_2', 0) \cdots \delta(K_{m-1}', 0)\delta(K_1' + \cdots + K_{m-1}', 0)G(K_1, \cdots K_{m-1}; K_m, \cdots K_{n-1})$$

$$\times G^*(K_1', \cdots K_{m-1}'; K_m', \cdots K_{n-1}') = \frac{1}{N}\left(\frac{N}{\Omega}\right)^{2m} |I|^2 \left[1 + O\left(\frac{1}{N}\right)\right], \quad (B11)$$

where the notation $\delta(A,B)$ is used for the Kronecker symbol. The essential role of the factors $\delta(K_1 + \cdots + K_{m-1}, 0)$ and $\delta(K_1' + \cdots + K_{m-1}', 0)$ will be noted.

Exactly the same reasoning applies to the other terms in $(M_\alpha M_\alpha^*)_{II}$. Therefore, we have shown that for a sufficiently large sample, M may be replaced by its ensemble average.

APPENDIX C. EXPANSION OF C

In order to obtain the expansion of the commutator C in powers of λ, we need first the expansion of ρ. We may write

$$\rho = Ke^{-\beta(H_0 + H')},$$

$$K^{-1} = \text{Tr}[e^{-\beta(H_0 + H')}].$$

Now it is easy to establish the following expansion[10]

$$(k|e^{-\beta(H_0+H')}|k') = e^{-\beta\epsilon_k}\delta_{kk'} - \frac{e^{-\beta\epsilon_{k'}} - e^{-\beta\epsilon_k}}{\omega_{kk'}}H_{kk'}' + \sum_{k''} \frac{H'_{kk''}H'_{k''k'}}{\omega_{k''k'}}\left[\frac{e^{-\beta\epsilon_{k'}} - e^{-\beta\epsilon_k}}{\omega_{kk'}} - \frac{e^{-\beta\epsilon_{k''}} - e^{-\beta\epsilon_k}}{\omega_{kk''}}\right] + \cdots. \quad (C1)$$

In this expression the terms with vanishing denominators have the limiting value obtained by letting them approach zero smoothly.

For K we obtain, to second order,

$$K^{-1} = \sum_k e^{-\beta\epsilon_k} - \sum_{k,k'} |H'_{kk'}|^2 \left[\frac{e^{-\beta\epsilon_k}(1 + \beta\omega_{kk'}) - e^{-\beta\epsilon_{k'}}}{\omega_{kk'}^2}\right], \quad (C2)$$

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[10] See, for example, R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948), Appendix I.

since we have assumed $H_{kk'} = 0$. If we write

$$K = K_0(1+\gamma), \tag{C3}$$

we obtain

$$K_0 = \left(\sum_k e^{-\beta\epsilon_k}\right)^{-1} = \frac{1}{\Omega}\left(\frac{2\pi\beta}{m}\right)^{\frac{3}{2}}, \tag{C4}$$

$$\gamma = K_0 \sum_{k,k'} |H'_{kk'}|^2 \left(\frac{e^{-\beta\epsilon_k}(1+\beta\omega_{kk'}) - e^{-\beta\epsilon_{k'}}}{\omega_{kk'}^2}\right). \tag{C5}$$

In (C5), just as in the discussion of the transport Eq. (34), we may replace $|H_{kk'}|^2$ by its ensemble average, and obtain

$$\gamma = K_0 \sum_{k,k'} \langle|H'_{kk'}|^2\rangle \frac{e^{-\beta\epsilon_k}(1+\beta\omega_{kk'}) - e^{-\beta\epsilon_{k'}}}{\omega_{kk'}^2}$$

$$= K_0 \sum_{k,k'} \langle|H'_{kk'}|^2\rangle\beta\frac{e^{-\beta\epsilon_k}}{\omega_{kk'}},$$

if we interchange the indices k and k' in the last term. In this term we must interpret the denominator as a principal value when it vanishes, since the original expression for γ is perfectly regular when $\omega_{kk'}$ approaches zero. Therefore, we write

$$\gamma = \sum_k K_0\beta e^{-\beta\epsilon_k} \sum_{k'} P\frac{|H'_{kk'}|^2}{\omega_{kk'}}$$

$$= K_0\beta\frac{n}{(2\pi)^3} \sum_k e^{-\beta\epsilon_k} \int dk' P\frac{|\phi_{kk'}|^2}{\omega_{kk'}}. \tag{C6}$$

We note for future reference that γ is proportional to n, the density of impurities.

From (27), we have

$$C_{kk'} = ieE_\alpha^0\left(\frac{\partial}{\partial k_\alpha} + \frac{\partial}{\partial k_\alpha'}\right)\rho_{kk'}$$

$$= ieE_\alpha^0(1+\gamma)\left(\frac{\partial}{\partial k_\alpha} + \frac{\partial}{\partial k_\alpha'}\right)\left[\rho_k\delta_{kk'} + \frac{\rho_k-\rho_{k'}}{\omega_{kk'}}H'_{kk'} + \sum_{k''}\frac{H'_{kk''}H'_{k''k'}}{\omega_{k''k'}}\left(\frac{\rho_{k'}-\rho_k}{\omega_{kk'}} - \frac{\rho_{k''}-\rho_k}{\omega_{kk''}}\right)\right]. \tag{C7}$$

Here

$$\rho_k \equiv K_0 e^{-\beta\epsilon_k}, \tag{C8}$$

the zeroth-order distribution function.

In the evaluation of $T_k^{(2)}(C)$, which is as far as we go in this paper, all we need is $C_{kk'}^{(1)}$ $(k \neq k')$ and $C_k^{(2)}$. From (C1), these are given by

$$C_{kk'}^{(1)} = ieE_\alpha^0 H_{kk'}'\left(\frac{\partial}{\partial k_\alpha} + \frac{\partial}{\partial k_\alpha'}\right)\frac{\rho_k-\rho_{k'}}{\omega_{kk'}}, \tag{C9}$$

and

$$C_k^{(2)} = ieE_\alpha^0\left[\gamma\frac{\partial\rho_k}{\partial k_\alpha} - \frac{\partial}{\partial k_\alpha}\sum_{k'}|H'_{kk'}|^2\frac{1}{\omega_{kk'}}\left(\frac{\rho_k-\rho_{k'}}{\omega_{kk'}} + \beta\rho_k\right)\right]$$

$$= ieE_\alpha^0\frac{\partial}{\partial k_\alpha}\left[\gamma\rho_k - \sum_{k'}|H'_{kk'}|^2\frac{1}{\omega_{kk'}}\left(\frac{\rho_k-\rho_{k'}}{\omega_{kk'}} + \beta\rho_k\right)\right]. \tag{C10}$$

Again, in (C10) as in (C5) we may replace $|H'_{kk'}|^2$ by its ensemble average, and obtain

$$C_k^{(2)} = ieE_\alpha^0\frac{\partial}{\partial k_\alpha}\left[\gamma\rho_k - \frac{n}{(2\pi)^3}\int dk'\frac{|\phi_{kk'}|^2}{\omega_{kk'}}\left(\frac{\rho_k-\rho_{k'}}{\omega_{kk'}} + \beta\rho_k\right)\right]. \tag{C11}$$

Since γ is proportional to n, so is $C_k^{(2)}$.

APPENDIX D. TIME-DEPENDENT PHENOMENA

We shall consider in this appendix another method of arriving at the transport equation. This method has the advantage of being able to treat the approach to the steady state (or to the equilibrium state) as well as the steady state itself. Instead of turning on the external field slowly, we imagine the following situation: Up to time $t=0$ we have a collection of electrons in equilibrium with a heat bath at same temperature T, and there is no external electric field present. Then at $t=0$ the contact with the heat bath is broken and the full electric field is turned on. This collection of electrons is now described by a single-particle density matrix ρ_T whose time development is given by (8), where $H_T=H+H_1$ and is independent of time. The problem is to find a solution of (8) which reduces to the equilibrium distribution ρ [given by (10)] at $t=0$.

To solve Eq. (8), we make what is essentially a Laplace transform of it. Define

$$F(s)=s\int^{\infty}e^{-st}\rho_T(t)dt. \tag{D1}$$

Since ρ_T is Hermitian and (D1) is a real operation, $F(s)$ is also a Hermitian operator. Without the factor s this would simply be the Laplace transform of ρ_T. This form has certain minor advantages for our problem. If we write $s=1/t_0$, then (D1) becomes

$$F(s)=\frac{1}{t_0}\int_0^{\infty}e^{-t/t_0}\rho_T(t)dt,$$

which is essentially an average of ρ_T, averaged over a time of order t_0 or $1/s$. [We might call (D1) the "Laplace average" of ρ_T.]

From this interpretation as a time average, we see that if ρ_T approaches a constant value, then

$$\lim_{t\to\infty}\rho_T(t)=\lim_{s\to 0_+}F(s). \tag{D2}$$

This theorem can be rigorously proved.[11] If ρ_T oscillates, then the right-hand side of (D2) gives the value of ρ_T at very long times averaged over these oscillations. This is, of course, just what we want physically, and therefore the object which will interest us is $F(s)$ for small positive s.

If one is interested in finite times, then it is necessary to use the usual inversion formula

$$\sigma_T(t)=\frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}e^{st}\frac{F(s)}{s}ds, \quad c>0. \tag{D3}$$

Taking the Laplace-average of (8), we obtain

$$is[F(s)-\rho]=[H_T,F(s)]. \tag{D4}$$

Defining

$$F(s)=\rho+f,$$

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[11] See B. van der Pol and H. Bremmer, *Operational Calculus* (Cambridge University Press, New York, 1950), p. 122.

and only going to the first order in E_α, we obtain

$$isf=[H_1,\rho]+[H,f]. \tag{D5}$$

This equation is identical with Eq. (17) which is also needed for very small positive s, and therefore from now on the treatment is identical with that of Sec. II and, of course, yields the same answers.

From our present point of view, however, it is also possible to study the actual *approach* to the steady state. We shall not give a detailed analysis of this problem, but only indicate how it goes to the lowest order in λ. To this order, f_k satisfies Eq. (46) of Sec. II. Using the inversion (D3), we obtain

$$\frac{\partial\rho_{1k}(t)}{\partial t}=-eE_\alpha^0\frac{\partial\rho_k}{\partial k_\alpha}-\frac{N}{\Omega^2}\sum_{k'k'\neq k}|\phi_{kk'}|^2$$

$$\times 2\int_0^t[\rho_{1k}(t-\tau)-\rho_{1k'}(t-\tau)]\cos(\omega_{kk'}\tau)d\tau, \tag{D6}$$

where $\rho_1(t)$ is the term in ρ_T linear in the electric field.

This equation is rather different than the usual equation which describes the drift towards the steady state. In the conventional Boltzmann equation the rate of change of the distribution function at a certain instant depends only on the value of the distribution function at that instant. In (D6) on the other hand, the rate of change of the distribution function depends on all its previous values up to the instant in question. The more usual result is an approximation which is valid only if the relaxation time t_r is much greater than a typical "atomic time" t_a (see discussion immediately following Eq. (48) for definition of t_a).

To see this, let us *formally* expand $\rho_{1k}(t-\tau)$ in powers of τ and consider the contribution of the first two terms to (D6). We have

$$\int_0^t\rho_{1k}(t-\tau)\cos(\omega_{kk'}\tau)d\tau=\rho_{1k}(t)\int_0^t\cos(\omega_{kk'}\tau)d\tau$$

$$-\frac{\partial\rho_{1k}(t)}{\partial t}\int_0^t\tau\cos(\omega_{kk'}\tau)d\tau+\cdots. \tag{D7}$$

The first term is easily integrated, giving

$$\int_0^t\cos(\omega_{kk'}\tau)d\tau=\frac{\sin(\omega_{kk'}t)}{\omega_{kk'}}. \tag{D8}$$

As long as t is much greater than an atomic time t_a, this expression may be replaced in (D6) by $\pi\delta(\omega_{kk'})$, as is well known. The second term is most easily evaluated as follows:

$$\int_0^t\tau\cos(\omega_{kk'}\tau)d\tau=\frac{\partial}{\partial(\omega_{kk'})}\int_0^t\sin(\omega_{kk'}\tau)d\tau$$

$$=\frac{\partial}{\partial(\omega_{kk'})}\left(\frac{1-\cos(\omega_{kk'}t)}{\omega_{kk'}}\right).$$

The quantity being differentiated becomes, in the limit of $t \gg t_a$, just the principal value of $1/\omega_{kk'}$, so that we may write

$$\int_0^t \rho_{1k}(t-\tau)\cos(\omega_{kk'}\tau)d\tau = \rho_{1k}(t)\pi\delta(\omega_{kk'})$$
$$-\frac{\partial\rho_{1k}(t)}{\partial t}\frac{\partial}{\partial(\omega_{kk'})}P\left(\frac{1}{\omega_{kk'}}\right)+\cdots. \quad (D9)$$

In estimating the relative magnitude of the first two terms in (D9), we note first that

$$\partial\rho_{1k}(t)/\partial t \sim \rho_{1k}(t)/t_r.$$

On the other hand, if (D9) is inserted in (D6), the factor

$$\frac{\partial}{\partial(\omega_{kk'})}P\left(\frac{1}{\omega_{kk'}}\right)$$

will give something of the order $(\bar{\omega})^{-1}$ times what the factor $\pi\delta(\omega_{kk'})$ gives ($\bar{\omega}$ being a typical energy arising in the problem, $\bar{\omega}\sim t_a^{-1}$). Therefore, the ratio of the second to the first term is of the order t_a/t_r. Taking the first term gives the usual Boltzmann equation, as is easily seen by substitution. [The particular method given here for obtaining the Boltzmann equation from (D6) is due to Mr. S. T. Choh.] Thus, the usual Boltzmann equation describing the drift towards equilibrium is valid only if the relaxation time is much greater than an atomic time, and after a length of time much greater than an atomic time. Under other circumstances the more general (D6) must be used.

We may also use the above formalism to study the "free" relaxation. That is, suppose at time $t=0$ the ensemble of electrons is described by a density matrix ρ_0 which is *not* the equilibrium density matrix $\rho(H)$. We want to investigate how the distribution approaches the equilibrium one, there being no electric field present.

Instead of (D4) we now obtain

$$is[g(s)-\rho_0]=[H,g(s)], \quad (D10)$$

where $g(s)$ is the Laplace average of the total density matrix for the ensemble. If we write this as

$$isg(s)=is\rho_0+[H,g(s)], \quad (D11)$$

we see that the equation is formally identical with (D5), $f(s)$ being replaced by $g(s)$ and the commutator $[H_1,\rho]$ by $is\rho_0$. Therefore, the entire analysis may be formally carried over. To the lowest order in λ and for the case $t_r \gg t_a$ we obtain

$$\frac{\partial\rho_k(t)}{\partial t}=\sum_{k'(k'\neq k)}W_{kk'}{}^0[\rho_{k'}(t)-\rho_k(t)], \quad (D12)$$

the usual kinetic equation. In higher orders, or if t_r is not much greater than t_a, the kinetic equation is replaced by something more complicated.

As a final application of these methods we consider the case where the external field is periodic in time with an angular frequency of, say, ω. Then once again we must solve (8) subject to $\rho=\rho(H)$ at $t=0$ and with $H_T=H+H_1\cos\omega t$. Writing again $\rho_T=\rho+\rho_F$, and going only to the first order in the field, we obtain

$$i(\partial\rho_F/\partial t)=[H_1,\rho]\cos(\omega t)+[H,\rho_F]. \quad (D13)$$

Let us write

$$\rho_F=\tfrac{1}{2}[\rho^+(t)e^{i\omega t}+\rho^-(t)e^{-i\omega t}]. \quad (D14)$$

Clearly ρ^- is the Hermitian conjugate of ρ^+. Inserting this in (D13), we obtain for $\rho^+(t)$ the equation

$$i(\partial\rho^+/\partial t)-\omega\rho^+=[H_1,\rho]+[H,\rho^+]. \quad (D15)$$

The Laplace-average of this gives (since $\rho^+=0$ at $t=0$)

$$isf^+(s)-\omega f^+(s)=[H_1,\rho]+[H,f^+(s)], \quad (D16)$$

where $f^+(s)$ is the Laplace-average of $\rho^+(t)$. We need $f^+(s)$ for small s again. (D16) is identical with (D5) except for the additional term $(-\omega f^+)$ on the left-hand side. This can be taken into account very simply: in the energy denominator in the nondiagonal equations $\omega_{kk'}$ is replaced by $\omega_{kk'}+\omega$, and in the diagonal equation we have an extra term ωf_k^+ on the left-hand side. The method of solution is, however, identical and we obtain to lowest order

$$\omega f_k^+=ieE_\alpha{}^0\frac{\partial\rho_k}{\partial k_\alpha}+2\pi i\frac{N}{\Omega^2}\sum_{k'(k'\neq k)}|\phi_{kk'}|^2$$
$$\times\delta(\omega_{kk'}+\omega)(f_k^+-f_{k'}^+). \quad (D17)$$

Unless the external field oscillates with a frequency comparable to an atomic frequency the ω is completely negligible compared to the $\omega_{kk'}$ in the δ function, and we obtain

$$i\omega f_k^+=-eE_\alpha{}^0\frac{\partial\rho_k}{\partial k_\alpha}+\sum_{k'(k'\neq k)}W_{kk'}{}^0(f_{k'}^+-f_k^+). \quad (D18)$$

This is just the equation one ordinarily would use, since after long times

$$\rho_F=\tfrac{1}{2}(f^+e^{i\omega t}+f^-e^{-i\omega t}). \quad (D19)$$

In higher approximations the situation is again more complicated.

APPENDIX E. JOULE HEAT

To obtain the Joule heat we must solve (8) correct to the second order in E_α. Let us write

$$\rho_T=\rho+\rho_F+\rho_2, \quad (E1)$$

where ρ_F is linear in the field and ρ_2 is quadratic. Substituting in (8) and equating equal powers of E_α, we obtain

$$i(\partial\rho_2/\partial t)=[H_F,\rho_F]+[H,\rho_2], \quad (E2)$$

ρ_F satisfying (13). Using (15) and (16) this becomes

$$i(\partial\rho_2/\partial t)=[H_1,f]e^{2st}+[H,\rho_2], \qquad (E3)$$

(E3) has the solution

$$\rho_2=ge^{2st}, \qquad (E4)$$

yielding

$$2isg=[H_1,f]+[H,g]. \qquad (E5)$$

Now we are interested, in the quadratic correction to the mean energy of the system (apart from the interaction energy with the external field). That is,

$$(\bar{H})_2=\text{Tr}(\rho_2 H)=e^{2st}\,\text{Tr}(gH). \qquad (E6)$$

To obtain this trace, we need only multiply (E5) by H and take the trace. Then

$$2is\,\text{Tr}(gH)=\text{Tr}([H_1,f]H)+\text{Tr}([H,g]H). \qquad (E7)$$

Making use of the *formal* operator identity,

$$\text{Tr}(A[B,C])=\text{Tr}([A,B]C), \qquad (E8)$$

Eq. (E7) becomes

$$2is\,\text{Tr}(gH)=\text{Tr}(f[H,H_1]). \qquad (E9)$$

However,

$$[H,H_1]=-eE_\alpha^{(0)}[H,x_\alpha]=ieE_\alpha^{(0)}v_\alpha, \qquad (E10)$$

so that

$$\text{Tr}(gH)=\frac{eE_\alpha^{(0)}}{2s}\,\text{Tr}(fv_\alpha)$$

$$=\frac{eE_\alpha^{(0)}\bar{v}_\alpha}{2s}. \qquad (E11)$$

$\bar{v}_\alpha$ is just the average velocity as computed from f. Therefore, the quadratic correction to the energy at any time t is

$$(\bar{H})_2=\frac{eE_\alpha^{(0)}\bar{v}_\alpha}{2s}e^{2st}. \qquad (E12)$$

On the other hand, the power absorbed per unit volume due to the Joule heat is just

$$P(t)=E_\alpha(t)j_\alpha(t)=E_\alpha^{(0)}j_\alpha(t)e^{st}, \qquad (E13)$$

where $j_\alpha(t)$ is the average current density of an electron at time t. This is

$$j_\alpha(t)=\frac{e}{\Omega}\bar{v}_\alpha e^{st}. \qquad (E14)$$

Therefore, the power absorbed for the entire volume, $P(t)$, is

$$P(t)=eE_\alpha^{(0)}\bar{v}_\alpha e^{2st}. \qquad (E15)$$

The total *energy* absorbed up till the time t is clearly

$$\int_{-\infty}^{t}P(t)dt=\frac{eE_\alpha^{(0)}\bar{v}_\alpha e^{2st}}{2s}, \qquad (E16)$$

which is identical with (B12).

Incidentally, the same method of proof shows that there is no linear correction to the energy. Multiplying (13) by H and taking the trace, we obtain

$$(\bar{H})_1=e^{st}\,\text{Tr}(Hf)$$

$$=\frac{e^{st}}{is}[\text{Tr}(H([H,f]+[H_1,\rho]))]=0, \qquad (E17)$$

by (E7).

The somewhat formal operations implied by using (E7) may easily be verified with the explicit expressions given in the paper.

APPENDIX F. QUANTUM STATISTICS

When the electron density is sufficiently high, the exclusion principle must, of course, be taken into account. Provided that the dynamical interaction of the electrons is still neglected, we shall see that the only change required in our formalism is a change in the form of the equilibrium density matrix: instead of the Maxwell-Boltzmann form (10) we have to use the Fermi-Dirac expression

$$\rho=1/[e^{\beta(H-\zeta)}+1], \qquad (F1)$$

where ζ is the chemical potential determined by the density of the electron gas.

It is convenient in this derivation to make use of the formalism of second quantization. All operators are then thought of as being operators in occupation-number space. The wave function ψ of the system becomes an operator

$$\psi=\sum_r a_r\psi_r, \qquad (F2)$$

where the ψ_r are some complete set of functions for a single electron. The a_r are the destruction operators which satisfy the commutation relations

$$a_r a_{r'}^\dagger+a_{r'}^\dagger a_r=\delta_{rr'}, \qquad (F3)$$

where $a_r^\dagger$ is the adjoint of a_r, and is the creation operator for the state r. The operator representing the number of particles in the state r is

$$n_r=a_r^\dagger a_r. \qquad (F4)$$

Consider now a "one-particle" operator. That is, an operator of the form

$$R_T=\sum_i R_i, \qquad (F5)$$

where R_i depends only on the dynamical variables of the ith electron. We introduce the notation $\tilde{R}_T$ to mean the form of this operator in the second-quantized formalism. Then, as is well known,

$$\tilde{R}_T=\sum_{r,r'}a_r^\dagger a_{r'}R_{rr'}, \qquad (F6)$$

where $R_{rr'}$ are the ordinary matrix elements of the one-particle operator R_i in the r representation. The

total Hamiltonian is of this form, so that we have

$$\tilde{H}_T = \sum_{r,r'} a_r{}^\dagger a_{r'} (H_T)_{rr'}. \tag{F7}$$

Calling the density matrix in this representation $\tilde{\rho}_T$, we have for its time development

$$i\frac{\partial \tilde{\rho}_T}{\partial t} = [\tilde{H}_T, \tilde{\rho}_T]. \tag{F8}$$

In order to calculate the expectation value of any one-particle operator such as the current, we need the trace of the product of this operator with $\tilde{\rho}_T$. Therefore, we need objects of the form

$$\langle R \rangle = \mathrm{Tr}(\tilde{\rho}_T \tilde{R}_T) = \sum_{r,r'} \mathrm{Tr}(\tilde{\rho}_T a_r{}^\dagger a_{r'}) R_{rr'}$$

$$= \sum_{r,r'} [R_{rr'} (\rho_T)_{r'r}], \tag{F9}$$

where

$$(\rho_T)_{rr'} = \mathrm{Tr}(\tilde{\rho}_T a_r{}^\dagger, a_r). \tag{F10}$$

Equation (F9) may be written

$$\langle R \rangle = \mathrm{Tr}(R\rho_T), \tag{F11}$$

where Tr means the trace in the r representation, and we are viewing $(\rho_T)_{rr'}$ as a matrix in that representation.

To find the equation satisfied by $(\rho_T)_{rr'}$, we multiply (F8) by $a_{r'}{}^\dagger a_r$ and take the trace. This gives

$$i\partial(\rho_T)_{rr'}/\partial t$$
$$= \mathrm{Tr}(a_{r'}{}^\dagger a_r [\tilde{H}_T, \tilde{\rho}_T])$$
$$= \mathrm{Tr}([a_{r'}{}^\dagger a_r, \tilde{H}_T]\tilde{\rho}_T) \tag{F12}$$
$$= \mathrm{Tr}[\sum_{r''} (a_{r'}{}^\dagger a_{r''} (H_T)_{rr''} = a_{r''}{}^\dagger a_r (H_T)_{r''r'})\tilde{\rho}_T],$$

where we have made use of the commutation relations (F3). Using (F10) we now have

$$i\partial(\rho_T)_{rr'}/\partial t$$
$$= \sum_{r''} [(H_T)_{rr''}(\rho_T)_{r''r'} - (\rho_T)_{rr''}(H_T)_{r''r'}] \tag{F13}$$
$$= (H_T, \rho_T)_{rr'}.$$

In matrix notation,

$$i\partial\rho_T/\partial t = [H_T, \rho_T]. \tag{F14}$$

Therefore, the object which we need, ρ_T, satisfies the same equation of motion that the ρ_T satisfied without statistics. The only difference is that the unperturbed value of ρ_T is now different. Without the electric field we have $\tilde{\rho}_T = \tilde{\rho}$, the density matrix which defines the equilibrium state of a collection of N dynamically independent Fermi-Dirac particles.

Let the equilibrium value of ρ_T be called ρ. Then

$$\rho_{rr'} = \mathrm{Tr}(\tilde{\rho} a_{r'}{}^\dagger a_r). \tag{F15}$$

To find what this is, choose for r the representation which makes H diagonal. In this representation $\tilde{\rho}$ is diagonal in the corresponding n_r's. Therefore, we get

$$\rho_{rr'} = \mathrm{Tr}(\tilde{\rho} a_r{}^\dagger a_r)\delta_{rr'}$$
$$= \mathrm{Tr}(\tilde{\rho} n_r)\delta_{rr'}. \tag{F16}$$

The quantity multiplying $\delta_{rr'}$ is just exactly the definition of the Fermi-Dirac distribution function for the state r. Therefore, we may write (F16) in the form (F1), which proves the original assertion.

The same method of proof goes though if one has Bose-Einstein statistics instead of Fermi-Dirac.

Finally, we notice that, as a consequence of this theorem, when we derive the transport equation we still obtain the same collision terms as previously. These are *linear* and f_k and not of the form $f_k(1-f_{k'})$, as has sometimes been suggested. This difference can lead to physical consequences when, say, there are spin-orbit forces present, and the transition probabilities are not symmetric in k and k'.