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The Physical Interpretation of Mean Free Path and the Integral Method

Abstract: In previous papers, general expressions for the linear electronic transport constants of solids were obtained in terms of a conjugate function $\psi^\dagger$ related, by a linear inhomogeneous integral equation, to the function (of electron state) ψ measured by the "flux." It is now shown that

$$\tau\psi^\dagger = \int_0^\infty \psi|t)\, dt\ ,$$

where the integrand is the expectation of ψ for an electron which at time t earlier was in the specified state (of which $\psi^\dagger$ is a function) and $1/\tau$ is the collision frequency. In particular, the vector mean free path $\tau\mathbf{v}^\dagger$ is: "the limit, after a virtually infinite time, of the mean displacement, in Brownian motion, of the position of an electron initially in the specified state." If there is a force (e.g. that due to a magnetic field) accelerating the electrons between collisions, then a linear transport constant is the same functional of an "extended conjugate" $\psi^{\dagger e}$ as it is of $\psi^\dagger$ in the absence of the force. It is shown that $\tau\psi^{\dagger e}$ is obtained (instead of $\tau\psi^\dagger$) when the integrand in the integral above is replaced by the "expectation after time t" as modified by the accelerations between collisions. The relation of the present formalism to the Shockley-Chambers theory is discussed.

In previous papers[1, 2] a mathematical procedure (the "integral method") for handling the Boltzmann equation for electrons in solids was introduced and applied to the theory of electronic thermal conduction[1] and to the theory of the galvanomagnetic effects.[2] It sometimes happens in statistical physics that an idea which was introduced as formal mathematics turns out to be interpretable by a simple physical concept. The purpose of the present note is to explain such a physical interpretation of the integral method and, specifically, of the "vector mean free path"[2] construct to which it led.

The Boltzmann equation for electrons in a crystal solid may be written for present purposes as

$$\mathfrak{D}_{\rm rel}h = g\ , \tag{1}$$

where h is a component of the distribution function, $f(\Gamma)$, with which we are dealing, g is a "generator" function treated as known, and $\mathfrak{D}_{\rm rel}$ is the integral operator giving the rate of change of h due to the relaxation processes:[3]

$$\{\mathfrak{D}_{\rm rel}h\}(\Gamma) = I(\Gamma')\Big(h(\Gamma')T(\Gamma';\Gamma) - h(\Gamma)T(\Gamma;\Gamma')\Big). \tag{2}$$

As in references 1 and 2, Γ stands for the variables specifying the electron state, crystal momentum $\mathbf{p}$ together with the discrete variables (spin and band index), $I(\Gamma)$ stands for integration $\int d^3\,\mathbf{p}\ldots\ldots$ over the Brillouin zone and summation over the discrete variables, and we define the relaxation time $\tau(\Gamma)$ by the equation

$$\frac{1}{\tau} \equiv I(\Gamma')T(\Gamma;\Gamma')\ . \tag{3}$$

Let $\psi(\Gamma)$ be any electron variable satisfying the condition

$$I\psi f^0 = 0\ , \tag{4}$$

where $f^0(\Gamma)$ is the "equilibrium" function satisfying

$$\mathfrak{D}_{\rm rel}f^0 = 0\ . \tag{5}$$

[Where Boltzmann statistics applies, f^0 is just the Maxwell-Boltzmann distribution function for thermal equilibrium. In general, however, when Fermi statistics applies, $f^0 = f_0\,(1-f_0)$ where $f_0(\Gamma)$ is the Fermi distribution function.]

The conjugate, $\psi^\dagger$, of ψ is given by[2a]

$$\psi^\dagger(\Gamma) - I(\Gamma')T(\Gamma;\Gamma')\tau(\Gamma')\psi^\dagger(\Gamma') = \psi(\Gamma)\ . \tag{6}$$

It has the property

$$I\psi h = -I\psi^\dagger\tau\mathfrak{D}_{\rm rel}h\ . \tag{7}$$

By (1) and (7),

$$I\psi h = -I\tau\psi^\dagger g\ . \tag{8}$$

Thus the expectation of some magnitude of interest, $\psi(\Gamma)$, for the distribution represented by h is known in terms of a sum-integral over g if the conjugate of ψ is known. The vector mean free path is

$$\mathbf{l} \equiv \tau \mathbf{v}^\dagger \tag{9}$$

where $\mathbf{v} = \partial\epsilon/\partial\mathbf{p}$ is the electron velocity, $\epsilon(\Gamma)$ the electron energy according to the single-electron model. Then (8) gives for the electron current density associated with h

$$\mathbf{J} = -\frac{e}{(2\pi\hbar)^3} I\mathbf{v}h = \frac{e}{(2\pi\hbar)^3} I\mathbf{l}g \ . \tag{10}$$

The conductivity in the absence of a magnetic field is hence[2]

$$\sigma(0) = \frac{e^2}{(2\pi\hbar)^3 kT} I\mathbf{l}\mathbf{v}f^0 \ . \tag{11}$$

It is convenient to introduce the integral operator $\mathcal{L}$, defined as follows:

$$\mathcal{L}\psi \equiv \tau(\Gamma) I(\Gamma') T(\Gamma;\Gamma') \psi(\Gamma') \ . \tag{12}$$

Since $T(\Gamma;\Gamma')$ expresses the differential rate, corresponding to (2), of scattering[3] from state Γ to the neighborhood of state Γ', $\mathcal{L}\psi$ is the expectation of ψ for an electron which has been scattered *once* from the specified initial state. (The factor τ provides for normalization.) Eq. (6) may be written

$$(1-\mathcal{L})\tau\psi^\dagger = \tau\psi \ . \tag{13}$$

The interpretation put forward here of the relation between ψ and its conjugate $\psi^\dagger$ is as follows: For an electron in a given state Γ at time t, there will be a normalized probability function $P(\Gamma,t|\Gamma',t')$ for the possible states Γ' reached by the electron, as a result of scattering, at a time t'. (That is to say, P as a function of Γ',t' is the solution of the equation $\partial P/\partial t' = \mathfrak{D}_{\rm rel}P$ for a "delta function" at time t as boundary condition. It represents the ensemble of possible "histories," $\Gamma'(t')$, of the electron.) Then it is asserted that

$$\tau\psi^\dagger = \mathcal{R}\psi \ , \tag{14}$$

where

$$\mathcal{R}\psi \equiv \mathrm{Lim}(t'' \to \infty) \int_t^{t''} I(\Gamma') P(\Gamma,t|\Gamma',t') \psi(\Gamma') dt' \ . \tag{15}$$

This relation (14) is easily proved.[4] The probability that the electron will not have been scattered out of the state Γ by time t' is $\exp\{(t-t')/\tau(\Gamma)\}$. Therefore the contribution to $\mathcal{R}\psi$ from the interval *before* the electron is first scattered (after time t) is

$$\int_t^\infty \psi(\Gamma) \exp\{(t-t')/\tau(\Gamma)\} dt' = \tau\psi \ .$$

The contribution from all times *after* the first scattering is obviously $\mathcal{L}(\mathcal{R}\psi)$. Therefore

$$\mathcal{R}\psi = \tau\psi + \mathcal{L}\mathcal{R}\psi \ , \tag{16}$$

or

$$(1-\mathcal{L})\mathcal{R}\psi = \tau\psi \ . \tag{17}$$

Eqs. (13) and (17) are consistent with the proposed relation (14).

As was shown in reference 2, the solution of (13) is unique except that addition of any invariant of scattering (a function, $a(\Gamma)$, which has the same value for any two states between which scattering occurs) to $\tau\psi^\dagger$ yields another solution. (But any two solutions differing by a/τ give the same value for a transport constant—e.g. for (11).) On the other hand the function $\mathcal{R}\psi$ given by (15) is unique. If we wish a unique specification, therefore, we may prefer to choose as our standard solution of (13) the one equal to $(1/\tau)\mathcal{R}\psi$.[5]

It is proposed to call $\mathcal{R}\psi$ the "relaxation integral" of ψ. The vector mean free path (9) has a simple physical interpretation as the relaxation integral $\mathcal{R}\mathbf{v}$: *The vector mean free path is the limit, after a virtually infinite time, of the mean displacement, in Brownian motion, of the position of an electron initially in the specified state.*

The extended theory

Frequently in practice one wishes to deal with the Boltzmann equation given by adding to the left-hand side of (1) the rate of change of h due to various fields (not expressed by their influence on g), such as a magnetic field $\mathbf{H}$, "biasing" electric field $\mathbf{E}$,[6] or the field expressing the electron acceleration due to a strain gradient.[7] In these cases there is an acceleration,

$$\partial\mathbf{p}/\partial t = \mathbf{F}(\Gamma) \ , \tag{18}$$

of the electron between collisions. A function $\psi(\Gamma)$ changes between collisions at the rate

$$(\partial/\partial t)_{\rm fields}\psi = G\psi \tag{19}$$

where

$$G \equiv \mathbf{F}(\Gamma)\cdot\partial/\partial\mathbf{p} \ . \tag{20}$$

Eq. (1) should be replaced by

$$\mathfrak{D}h = g \ , \tag{1e}$$

where

$$\mathfrak{D} = \mathfrak{D}_{\rm rel} - G \ . \tag{21}$$

The integral method generalizes as follows:* In place of $\psi^\dagger$ we have an "extended conjugate" $\psi^{\dagger e}$ satisfying the equation[8]

$$(1-\mathcal{L}-\tau G)\tau\psi^{\dagger e} = \tau\psi \ , \tag{13e}$$

and instead of (8) the relation

$$I\psi h = -I\tau\psi^{\dagger e} g \ . \tag{8e}$$

In formulas such as (11), for example, we have to replace $\mathbf{l}$ by an "extended mean free path"

$$\mathbf{l}^e \equiv \tau\mathbf{v}^{\dagger e} \tag{9e}$$

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*It should be understood that the function $\psi^{\dagger e}$ defined by eqs. (13e) and (14e) as given in the text exists only if the extension of (4) holds for ψ (i.e. if $I\psi f^0 = 0$ where f^0 is the steady-state distribution function, satisfying $\mathfrak{D}f^0 = 0$). The appropriate extension of the theory is obtained by replacing ψ on the right hand sides of (13e) and (14e) by $\psi - (I\psi f^0/If^0)$. (The definition (15e) of $\mathcal{R}^e$, and the proof which follows, are still valid, and apply to any magnitude—denoted there by ψ —satisfying the extension of (4). We are extending the definition of $\psi^{\dagger e}$ here, and leaving the definition of $\mathcal{R}^e$ unchanged.) It can be shown that (8e) as given in the text then continues to hold. Thus the more general form of (9e) (needed when an electric field contributes to G, for example) may be written

$$\mathbf{l}^e = \mathcal{R}^e(\mathbf{v}-\mathbf{u})$$

where $\mathbf{u}$ is the average of $\mathbf{v}$ over the steady state, $I\mathbf{v}f^0/If^0$.

The first three terms of the series development

$$\tau\psi^{\dagger e}=\tau\psi^{\dagger}+\tau\{G(\tau\psi^{\dagger})\}^{\dagger}$$
$$+\tau\{G(\tau\{G(\tau\psi^{\dagger})\}^{\dagger})\}^{\dagger}+\ldots\ldots, \tag{22}$$

with[9]

$$G=-\frac{e}{c}\left(\mathbf{v}\times\mathbf{H}\right)\cdot\frac{\partial}{\partial\mathbf{p}}, \tag{23}$$

give the general results obtained in Section 2 of reference 2 for the galvanomagnetic effects.

It is an obvious question for investigation whether the generalization of (14) holds for $\psi^{\dagger e}$. The relaxation processes and the acceleration (18) will together generate, from an initial electron state Γ at time t, an ensemble of possible states represented by $P^e(\Gamma,t|\Gamma',t')$, the generalization of $P(\Gamma,t|\Gamma',t')$. The "extended relaxation integral"

$$\mathcal{R}^e\psi\equiv\mathrm{Lim}(t''\to\infty)\int_t^{t''}I(\Gamma')P^e(\Gamma,t|\Gamma',t')\psi(\Gamma')dt' \tag{15e}$$

is the corresponding generalization of the function defined by (15). The relation we are conjecturing is then

$$\tau\psi^{\dagger e}=\mathcal{R}^e\psi\ . \tag{14e}$$

This conjecture turns out to be correct. The proof is as follows:

The probabilities of scattering to the neighborhoods of given final states now vary with time as the electron is accelerated. The probability that an electron will not have been scattered by time t'' if it was certainly in state Γ' at time t' is now

$$S(t'|t'')=\exp\left\{-\int_{t'}^{t''}dt_1/\tau(t_1)\right\}, \tag{25}$$

where $\tau(t_1)$ means the value of τ for the state, Γ_1, which the unscattered electron has reached by time t_1. Suppose $\phi(t_1)$ is some magnitude varying along the unscattered path. We define an operation $Q(t')$ as follows:

$$Q(t')\phi\equiv\int_{t'}^{\infty}\phi(t_1)\{-\partial S(t'|t_1)/\partial t_1\}dt_1\ . \tag{26}$$

Thus, for initial state Γ at time t, $Q(t)\phi$ is the expectation of the value of ϕ at the instant before the first subsequent scattering. Then the generalization of (16) is

$$\mathcal{R}^e\psi=Q(t)\left(\int_t^{t_1}\psi(t_2)dt_2+\{\mathcal{L}\mathcal{R}^e\psi\}(t_1)\right). \tag{27}$$

We now have to obtain two auxiliary formulas involving Q. For the first, we rewrite (26) as

$$Q(t')\phi=\int_{t'}^{\infty}\phi(t_1)\big(S(t'|t_1)/\tau(t_1)\big)dt_1 \tag{28}$$

by making use of (25) to express the derivative of S. Hence,

$$d\{Q(t')\phi\}/dt'=\int_{t'}^{\infty}\Big(\phi(t_1)/\tau(t_1)\Big)(\partial S/\partial t')dt_1$$
$$-\phi(t')S(t'|t')/\tau(t')$$
$$=\Big(Q(t')\phi-\phi(t')\Big)\Big/\tau(t')\ .$$

Now, $Q(t')\phi$ is a path variable, and therefore differentiation with respect to t' is, by (19), equivalent to operating on $Q\phi$ with G. Hence, finally,

$$\phi=(1-\tau G)\,Q\phi \tag{29}$$

where $\phi(t_1)$ and $Q(t_1)\phi$ are regarded as functions of Γ_1 generated by varying the initial state Γ while holding t and t_1 fixed. The second required formula is obtained by substituting $\int_t^{t_1}\psi(t_2)dt_2$ for ϕ in (26), integrating by parts on the right-hand side, and making use of (28). Then

$$Q(t)\int_t^{t_1}\psi(t_2)dt_2=Q(t)\{\tau\psi\}\ . \tag{30}$$

By substituting (30) into (27) we obtain

$$\mathcal{R}^e\psi=Q(t)\{\tau\psi+\mathcal{L}\mathcal{R}^e\psi\}\ . \tag{31}$$

From (29) and (31) we have

$$(1-\mathcal{L}-\tau G)\mathcal{R}^e\psi=\tau\psi\ . \tag{17e}$$

Again, (13e) and (17e) are consistent with the proposed relation (14e). Provided (1e) has a unique solution,[10] all the solutions of (13e) for $\tau\psi^{\dagger e}$ should give the same value for the right-hand side of (8e) and hence for the derived transport constants. The function $\mathcal{R}^e\psi$ will be one of these solutions,[11] the one satisfying (14e), and might as well be taken as *the* solution.

The results (8e), (14e) lead directly to auto-correlation theorems such as appear in the general theory of transport processes.[12] For example the (ohmic) conductivity in the presence of a magnetic field (with G given by (23)) is

$$\sigma(\mathbf{H})=\frac{e^2}{(2\pi\hbar)^3kT}\int_0^{\infty}dt\{If^0\,\mathbf{v}|t)^e\,\mathbf{v}\} \tag{32}$$

where

$$\psi|t)^e\equiv I(\Gamma')P^e(\Gamma,0|\Gamma',t)\psi(\Gamma')\ . \tag{33}$$

In more conventional notation, this formula may be written[13]

$$\sigma=(1/nkT)\int_0^{\infty}dt<\mathbf{J}(t)\mathbf{J}(0)>\ , \tag{34}$$

where $\mathbf{J}$ is the electric current density and n is the electron density $(1/2\pi\hbar)^3If_0$.

The theory of the Boltzmann equation developed here is a mirror image—so to speak—of the Shockley-Chambers theory.[14] In the latter the solution of (1) or (1e) is obtained, essentially, by applying the adjoint[8] of the $\mathcal{R}$, or $\mathcal{R}^e$, operator to the right-hand side. The two theories join together in the results of the type of (32) to which they both lead. The scopes of the two theories, as presented here and as presented in Heine's paper,[14] are somewhat different. The assumption of isotropic scattering in Shockley-Chambers (which is concerned with the case $\psi=\mathbf{v}$) is equivalent to omitting the term in $\mathcal{L}$ from (16) and (27). On the other hand the present paper does not treat the situation where g in (1) and (1e) is a function of time.[15] A more fundamental limitation in the present paper is the restriction to Markoffian relaxation processes. This restriction excludes transport phenomena in thin bodies, and the anomalous skin effects, where scattering of the electrons from the surfaces is significant. This surface scattering appears as a correlation between the times of successive scatterings, if the position of the electron is suppressed as a variable in the Boltzmann equation. The Chambers theory applies to (and was developed in connection with) this situation.[14, 16, 17] The definitions (15), (15e) of the relaxation integral obviously may be directly extended to include non-Markoffian relaxation; but the analysis in the present paper does not have this elasticity, because it depends on the properties of the function $S(t'|t'')$ given by eq. (25). The generalization of the results given here (i.e. of (8) and (8e) with ${}_\tau\psi^\dagger$ and ${}_\tau\psi^{\dagger e}$ given by (14) and (14e) and hence by (15) and (15e)) to include non-Markoffian processes in the relaxation integral is in fact valid. This statement will be justified in a subsequent paper dealing with the general theory of the Boltzmann equation, in which the present results and those of Shockley, Chambers and Heine will appear as particular cases in a more general analysis.

Acknowledgment

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References and footnotes

1. P. J. Price, *IBM Journal* **1**, 147 (1957).
2. P. J. Price, *IBM Journal* **1**, 239 (1957).
2a. The question of the uniqueness of the solution of this equation is discussed in reference 2 (the beginning of Section 5).
3. Where Fermi rather than Boltzmann statistics applies, the primary Boltzmann equation is not linear, and eqs. (1), (2) give the *linearized* equation for small disturbances of equilibrium—with T, the effective probability for transitions, not identical (for inelastic scattering) with the literal probability for transitions to unoccupied states. (See the discussion from eq. (24) to eq. (31) of reference 1.) In the interpretation below (leading to eq. (16), for example, and to the interpretation of the mean free path stated in the second paragraph following (16)) of P and the operators $\mathcal{L}$ and $\mathcal{R}$, T is accordingly to be regarded as a "model" probability function when Boltzmann statistics does not apply and there is appreciable inelastic scattering.
4. The argument which follows has not been made quite rigorous; for we are dividing the ensemble of electron "histories" into classes, and applying the Lim operation to them separately, without examining the mathematical implications of doing this. It would not be right to separate off all the histories for which $\int\psi(t')dt'$ remained positive (or for which it remained negative), for example, since their separate contribution to (15) is obviously infinite; and therefore we would prefer to prohibit *any* reversal of the operations I and Lim in (15).
5. We have assumed the *existence* of the function defined by (15). The condition (4) on ψ is evidently necessary for the existence of $\mathcal{R}\psi$, since $P(\Gamma,t|\Gamma',t')\rightarrow(\text{const})f^0(\Gamma')$ as $t'\rightarrow\infty$, and may be shown to be also a necessary condition for (13) to have a solution.
6. For the "hot electron" problem one may also (when Boltzmann statistics applies) obtain a useful result from the homogeneous equation obtained by setting $h=f$, $g=-e\mathbf{E}\cdot\partial f/\partial\mathbf{p}$. On applying (8) and an integration by parts one gets the general formula
$I f\psi=-e\mathbf{E}\cdot I f\partial({}_\tau\psi^\dagger)/\partial\mathbf{p}$.
7. H. Kroemer, *RCA Review* **18**, 332 (1957).
8. More generally, the left-hand side of (13e) is $-{}_\tau\mathcal{D}^*{}_\tau\psi^{\dagger e}$, where the adjoint $\mathcal{A}^*$ of an operator $\mathcal{A}$ is such that $I\phi\mathcal{A}\psi=I\psi\mathcal{A}^*\phi$. This extension belongs, however, to a more general theory which will be published separately. In (21) and (13e) it has been assumed that $(\partial/\partial\mathbf{p})\cdot\mathbf{F}=0$ and hence that $G^*=-G$.
9. With G representing a magnetic field, it is still $f_0(1-f_0)$ which satisfies (5) and for which (4) has to be satisfied if (13e) is to have a solution (and if (15e) is to exist). The relation $G^*=-G$ of footnote 8 is obviously satisfied (but see footnote 11 of reference 2).
10. If the solution be written as the sum of a series of which the $(n+1)$'th term is proportional to G^n (in the sense of eq. (22)), then provided this sum converges the solution is unique.
11. Again, provided the function $\mathcal{R}^e\psi$ defined by (15e) *exists*. See footnotes 5 and 9.
12. See, for example, R. Kubo, *Proc. Phys. Soc. Japan* **12**, 570 (1957). This paper is essentially more general than the present one, in that it is fully quantum-mechanical: the results are expressed in a form independent of representation, whereas the present paper treats the electron reduced density matrix in a representation in which hypothetically [but see W. Kohn and J. M. Luttinger, *Phys. Rev.*, **108**, 590 (1957)] the rate of change of the diagonal elements depends only on the diagonal elements themselves. The factors in $<>$, in eq. (34) of the present paper, are understood to each contribute only diagonal elements in this Γ representation, but (34) is then an exact consequence of (1) or (1e). The corresponding result in Kubo is not thus restricted, but it is only an approximate consequence of the fundamental quantal equation of motion.
13. The factor $(1-f_0)$ in (32) (i.e. in f^0) takes care of the limitation on the fluctuations imposed by the Pauli exclusion principle. (See the discussion around eq. (74) of reference 1. The difficulty stated in the last sentence of the paragraph containing eq. (74) is resolved by the results of the present paper.)
14. V. Heine, *Phys. Rev.* **107**, 431 (1957). See especially the Appendix.
15. The generalization of (13) and (13e) so that (8) and (8e) remain true, for g a harmonic function of time, is technically trivial. It will be given in the forthcoming general treatment.
16. R. G. Chambers, *Proc. Roy. Soc.* A, **202**, 378 (1950).
17. P. J. Price, *Bull. Am. Phys. Soc.*, Series II, **2**, 340 (1957).

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