Electron Transport in Amorphous Materials. I

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It is shown that, when scattering from uncorrelated sets of scatterers is properly considered in a one-electron plane-wave representation, the expectation value of the electron velocity is expressed as an infinite hierarchy of time-dependent exponentials. The lowest-order correction to the free-electron Hall constant, which was incorrectly derived in a recent paper, is rederived and the error corrected.

I. INTRODUCTION

In a previous paper,[1] hereafter referred to as A, an expression for the Hall constant R of liquid metals was obtained as a perturbation expansion in powers of the potential. I have recently realized that the derivation of A contains an error. It is the purpose of the present paper to present the correct derivation. The numerical results presented in A are unchanged but extra terms appear in the expression for R. These terms come from the expansion of the distribution function in powers of the scattering potential.

Throughout this paper it will be assumed that we are dealing with a rectangular parallelopiped of liquid metal with its principal axes along x, y, and z, that a constant magnetic field $\mathbf{H}$ is applied in the z direction, and that a constant electric field $\mathbf{E}$ is applied in the x direction. We set $\hbar=1$, denote the electronic mass by m, the charge by e, and the density by n. We assume that the system has unit volume and that the ions are stationary classical particles. This last was justified in A.

The total electronic Hamiltonian in the absence of the external electric field will be denoted by $\mathcal{H}$ and is the sum of $\mathcal{H}_0'$, the kinetic energy in the presence of the magnetic field, and $\mathcal{H}_1$, which is the sum of electron-electron and electron-ion interactions.

Denoting the conductivity tensor for frequency ω for arbitrary $\mathbf{H}$ by $\sigma(\omega)$, R is given by

$$R=\sigma_{xy}{}^{H}(0)/\mathbf{H}[\sigma_{\mu\mu}{}^{0}(0)]^{2}, \tag{1}$$

where $\sigma_{xy}{}^{H}(0)$ is the x–y component of the static conductivity tensor linear in $\mathbf{H}$, and $\sigma_{\mu\mu}{}^{0}(0)$ is any diagonal component of $\boldsymbol{\sigma}(0)$ for $\mathbf{H}=0$.

Using the Kubo expression for the conductivity[2]

$$\sigma_{xy}(0)=-ie\int_0^\infty dt\,\mathrm{Tr}\{\rho y^{\times}J_x(t)\}$$

and repeatedly integrating by parts over time we may obtain

$$\sigma_{xy}{}^{H}(0)=\sigma_1+\sigma_2,$$
$$\sigma_1=-\tfrac{3}{2}\,\mathrm{Im}\sigma_{\mu\mu}{}^{0}(\omega_c),$$
$$\sigma_2=-i\int_0^\infty tdt\{\mathrm{Tr}\rho[J_y,U_-{}^{H}(t)J_x]\}, \tag{2}$$

where ω_c must be small enough so that $\omega_c\tau_c\ll 1$, (τ_c is the electronic relaxation time for $\mathbf{H}=0$), ρ is the many-electron distribution function, J_y is the current density in the y direction, and J_x and J_y are assumed independent of $\mathbf{H}$. $U_-{}^{H}(t)$ is defined by

$$U_-{}^{H}(t)\dot{x}=\exp[it\mathcal{H}^{\times}]\exp[-it\mathcal{H}_0'^{\times}]\dot{x},$$

where

$$\exp[A^{\times}]B=\exp[A]B\exp[-A],\ A^{\times}B=[A,B].$$

The gauge used in obtaining Eq. (2) is

$$A_y=\tfrac{1}{2}\mathbf{H}x,\ A_x=-\tfrac{1}{2}\mathbf{H}y.$$

The curly brackets in Eq. (2) represent an average over the scatterer ensemble, and ω_c is the free-electron cyclotron frequency.

Starting from an exact expression for the conductivity tensor for arbitrary frequency and magnetic field due to Kubo,[2] we obtain in Sec. II explicit expressions for the lowest order terms of the zero-magnetic-field frequency-dependent conductivity tensor. In Sec. II we also show that inclusion of the scattering from uncorrelated sets of scatterers causes the electron velocity to vary with time as a hierarchy of time-dependent exponentials. In Sec. III we obtain the lowest order correction to the free-electron Hall constant.

II. DERIVATION OF $\sigma_{\mu\mu}{}^{0}(\omega)$

The starting point in our derivation is Eqs. (5)–(10) of Kubo's paper.[2]

$$\sigma_{\mu\mu}{}^{0}(\omega)=-ie\int_0^\infty \exp[-i\omega t]\{\mathrm{Tr}[\rho,\textstyle\sum_i x_{i\mu}]J_\mu(t)\}dt, \tag{3}$$

where $x_{i\mu}$ is the μth component of the position vector of the ith electron.

The calculation is done for independent electrons interacting via a scattering potential which is the sum

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[1] B. Springer, Phys. Rev. **136**, A115 (1964).

[2] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

of spherically symmetric terms centered on each ion. When the magnetic field vanishes we may write

$$\mathcal{H}=\sum_i H_i=\sum_i(H_{0i}+V_i).$$

H_{0i} is that part of H_i diagonal in a plane-wave representation and the sum is over electronic coordinates. Eq. (3) becomes

$$\sigma_{\mu\mu}{}^0(\omega)=-ie^2\int_0^\infty e^{-i\omega t}dt\{\mathrm{Tr}[f,x_\mu]U_-(t)\dot{x}_\mu\}, \quad (4)$$

where $\dot{x}_\mu$ is the μth component of the electron velocity operator, f is the one-electron Fermi distribution function, and the trace is taken with respect to one-electron wave functions. $U_-(t)$ is the same as $U_-{}^H(t)$ but with $\mathbf{H}=0$.

Taking the trace in Eq. (4) with respect to plane waves gives

$$\sigma_{\mu\mu}{}^0(\omega)=e^2\int_0^\infty e^{-i\omega t}dt\{\phi_1(t)+\phi_2(t)\}, \quad (5)$$

$$\phi_1(t)=-i\sum_k[f^0,x_\mu]_{kk}\langle k|U_-(t)\dot{x}_\mu|k\rangle,$$

$$\phi_2(t)=-i\sum_{kl}[f-f^0,x_\mu]_{kl}\langle l|U_-(t)\dot{x}_\mu|k\rangle, \quad (6)$$

where f^0 is the free-electron Fermi function.

A. Evaluation of $\phi_1(t)$

From Eq. (A3) in Appendix A we have

$$\phi_1(t)=-\sum_k\frac{k_\mu{}^2}{m^2}\frac{\partial f_k{}^0}{\partial\epsilon_k}\langle U_-(t)\rangle_k,$$

$$\langle U_-(t)\rangle_k=N\sum_{k\ \mathrm{angle}}mk_\mu\langle k|U_-(t)\dot{x}_\mu|k\rangle, \quad (7)$$

$$N^{-1}=\sum_{k\ \mathrm{angle}}k_\mu{}^2.$$

$U_-(t)$ is now expressed as an ordered exponential. From the definition

$$dU_-(t)/dt=iU_-(t)V^\times(t), \quad (8)$$

$$V^\times(t)=[\exp(itH_0{}^\times)V]^\times.$$

For ease in writing we will abbreviate $V^\times(t)$ by $t^\times$. The solution of Eq. (8) is

$$U_-(t)=\sum_{n=0}^\infty(i)^n\int_0^t dt_1\cdots\int_0^{t_{n-1}}dt_nt_n{}^\times\cdots t_1{}^\times$$

$$=\exp_-\left[i\int_0^t V^\times(t')dt'\right]. \quad (9)$$

The cumulant theorem[3] may now be used to give

$$\langle U_-(t)\rangle_k=\exp[\psi_k(t)],$$

$$\psi_k(t)=\sum_{n=1}^\infty(i)^n\int_0^t dt_1\cdots\int_0^{t_{n-1}}\times dt_n\langle t_n{}^\times\cdots t_1{}^\times\rangle_{kc}. \quad (10)$$

[3] R. Kubo, J. Phys. Soc. Japan **17**, 1100 (1962).

The average of Eq. (10) is defined in Eq. (7). The subscript k denotes that the matrix element is taken with respect to the wave vector $\mathbf{k}$ and the subscript c denotes the cumulant average is to be taken. This is the same as the average of Eq. (7) except that certain lower order moments are to be subtracted. To illustrate we give the definitions of the first two cumulant averages.

$$\langle A\rangle_c=\langle A\rangle,$$

$$\langle A_iA_j\rangle_c=\langle A_iA_j\rangle-\langle A_i\rangle\langle A_j\rangle.$$

In the present case $\langle V\rangle_k=0$.

The Fourier transform of $\exp[\psi_k(t)]$ will always be taken for frequencies ω such that $\omega\tau_c\ll1$. This implies that we are not concerned with structure occurring over times of order τ_c. Therefore, the time integrals in $\psi_k(t)$ can be done using the asymptotic expression

$$\int_0^t dt'\exp(i\epsilon t')\approx iP\left(\frac{1}{\epsilon}\right)+\pi\delta(\epsilon).$$

B. Time Dependence of $\psi_k(t)$

In the nth order term of $\psi_k(t)$, the ionic positions appear as

$$\sum_{\alpha,\beta,\cdots\delta}\exp[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}_\alpha]\exp[i(\mathbf{k}'-\mathbf{l})\cdot\mathbf{x}_\beta]\cdots\times\exp[i(\mathbf{m}-\mathbf{k})\cdot\mathbf{x}_\delta],$$

where $\mathbf{x}_\alpha$, $\mathbf{x}_\beta$, $\cdots$ $\mathbf{x}_\delta$ are the scatterer coordinates. We are dealing with a disordered macroscopic system in which fluctuations can be ignored. Therefore, we may replace all independent sums over scatterer positions by the average of those sums over the scatterer ensemble. From now on we shall assume this has been done. The curly brackets in Eq. (2) are now superfluous and can be dropped. For a liquid only relative positions are important. Thus in the limit of infinite volume but constant density, if any wave vector appears more than twice, the scatterers factor into uncorrelated sets. For the same reason, every independent set of scatterer variables appearing gives a factor Ω, the system volume. Thus, as $\Omega\to\infty$, these terms appear multiplied by δ functions and, after the sum over wave vectors which must be taken eventually, they appear with finite weight. These are the terms which give factors of t^β, $\beta>1$, and so must be treated before the Fourier transform can be taken.

We expand $\psi_k(t)$ in powers of V and take the matrix elements with respect to plane waves. Each scatterer δ function will cause the appearance of a diagonal matrix element which does not contain all of the time variables in the term. Such a diagonal matrix element will be referred to as a subdiagonal matrix element. A product of such matrix elements, all with respect to the same wave vector and whenever the product does not include all the time variables in the term, will also be referred to as a subdiagonal matrix element. The time variables in a given subdiagonal matrix element may include all the subscripts from t_α to t_β and no others and

these will be called continguous time variables. Consider first the highest order moment in each term of $\psi_k(t)$ and, specifically, those contributions which contain no scatterer δ functions. We call these terms $\psi_{k1}(t)$. Each term of $\psi_{k1}(t)$ depends only on time differences and is invariant under translation of the time origin but there is only one free time variable. Therefore, $\psi_{k1}(t)$ is at most linear in time and may be written

$$\psi_{k1}(t)=\alpha_k t+\beta_k, \tag{11}$$

where α_k and β_k are independent of time. This is seen more explicitly in Appendix B. We may evaluate the lower order contributions to α_k and β_k from Eq. (10). From Eqs. (10) and (C2) the term $n=2$ is, for large time

$$=\sum_l |V_{kl}|^2\left[2\left(1-\left(\frac{l}{k}\right)\cos\theta_{kl}\right)\frac{\partial}{\partial\epsilon_k}P\left(\frac{1}{\epsilon_{kl}}\right)-2\pi t(1-\cos\theta_{kl})\delta(\epsilon_{kl})\right]. \tag{12}$$

Using techniques similar to those in A we can show that the time-dependent part of the $n=3$ term is

$$4\pi t\sum_{lm} V_{kl}V_{lm}V_{mk}(1-\cos\theta_{kl})\delta(\epsilon_{kl})P(1/\epsilon_{mk}). \tag{13}$$

The remaining contributions to the highest order moment in each term of $\psi_k(t)$ all contain at least one scatterer δ function, each of which will make two wave vectors match. Some of these δ functions will cause wave vectors to equal $\mathbf{k}$, some will cause wave vectors to equal $\mathbf{k}'\neq\mathbf{k}$, but there will be a δ function from the time integrations making $\epsilon_{kk'}=0$, and some will cause wave vectors to equal $\mathbf{k}'$ with $\epsilon_{kk'}\neq 0$. The first thing to notice is that the maximum time dependence of a given term depends on the number of free time variables in that term. For the time dependence to be greater than linear, the time variables must factor into at least two independent sets. Otherwise the term is at most linear in time and will be denoted by $\psi_{k2}(t)$. This is shown more explicitly in Appendix B.

Consider the highest order moment in each term of $\psi_k(t)$. From what has been said we can restrict consideration to those sets of scatter δ functions which cause a separation into independent sets of contiguous time variables and from now on we will assume this restriction. Suppose all scatterer δ functions of the first kind and only such δ functions are used explicitly. In this case, the variables break up into independent sets in terms of the average defined by Eq. (7) and, by the cumulant theorem, such terms must cancel against contributions to the lower order moments. Now consider what happens when all δ functions of the second kind are explicitly used. The highest order moment factors into two parts, one of which is a subdiagonal matrix element with respect to the wave vector $\mathbf{k}'$. From Appendix C, $\langle k'|U_-(t)\dot{x}|k'\rangle$ has angular dependence k_x' so the subdiagonal matrix element can be transformed into one with respect to the wave vector $\mathbf{k}$. The term is now seen to cancel against one contribution to that product of two lower order moments which has the same factorization of time variables. In fact the contributions from δ functions of the first two kinds to the highest order moment cancels all the contributions to this product of lower order moments in which the time dependence of the product can be changed by the factor containing the earliest time variables. The remainder of this product can then be treated just as the highest order moment. This same procedure can be used for all terms in the cumulant.

We have still not treated the contributions from δ functions of the third kind. Let us first consider that part of the fourth-order cumulant which couples t_4 with t_3. The result is

$$=\sum_l |V_{kl}|^2\left(\frac{l}{k}\right)\cos\theta_{kl}\left[\frac{\partial}{\partial\epsilon_k}P\left(\frac{1}{\epsilon_{kl}}\right)\right](i)^2\int_0^t dt_1\int_0^{t_1}dt_2\times[\langle t_2{}^\times t_1{}^\times\rangle_k-\langle t_2{}^\times t_1{}^\times\rangle_l] \tag{14}$$

plus some time-independent terms. The part of Eq. (14) containing $\langle t_2{}^\times t_1{}^\times\rangle_l$ is one term in the expansion of $\langle U_-(t)\rangle_l$. In the general-order cumulant, the largest subdiagonal matrix element containing all time variables from some t_α to t_1 and no others and which arises from a δ function of the third type is plainly a term of $\langle U_-(t)\rangle_l$ and as we go term by term through $\psi_k(t)$ we will eventually obtain all terms of $[\langle U_-(t)\rangle_l-1]$ multiplied by a complicated time-independent coefficient. These terms may be written

$$\sum_l F_{kl}[\langle U_-(t)\rangle_l-1]. \tag{15}$$

The lowest order contribution to F_{kl} is given by Eq. (14).

This exhausts the contributions to the highest order moment in each term of $\psi_k(t)$. Except for $\psi_{k1}(t)$ we denote by $\psi_{k2}(t)$ all terms at most linear in time.

The part of Eq. (14) containing $\langle t_2{}^\times t_1{}^\times\rangle_k$ comes from one of the subtracted lower order moments. We have seen that, in the general term of $\psi_k(t)$, the lower order moments which have not cancelled against contributions to the highest order moment may be treated in a manner identical to what is done above. These terms may be incorporated into the previous results in an obvious manner depending on the number and type of scatterer δ functions they contain. We get finally

$$\psi_k(t)=\psi_{k1}(t)+\psi_{k2}(t)+\sum_{kl} F_{kl}[\langle U_-(t)\rangle_l-1]. \tag{16}$$

The leading term of F_{kl} is given by Eq. (14) and is quadratic in V. The leading term of $\psi_{k2}(t)$ is quartic in V. The same procedure is now applied to $\langle U_-(t)\rangle_l$ to give the result that elimination of the scatterer δ functions from $\langle U_-(t)\rangle_k$ causes it to be expressed as an infinite hierarchy of exponentials. From Eq. (6) we will want

$$\int_0^\infty dt\,\exp[\psi_k(t)-i\omega t], \tag{17}$$

which may be evaluated as a power series in V if we treat $\sum_l F_{kl}\langle U_-(t)\rangle_l$ as a perturbation. The leading terms are

$$\exp[\psi_k(t)]\approx\exp[\psi_{k1}(t)+\psi_{k2}(t)-\textstyle\sum_l F_{kl}] +\sum_l F_{kl}\exp[\psi_{k1}(t)+\psi_{l1}(t)], \quad (18)$$

which is accurate enough to obtain the three leading terms in the expansion of Eq. (17) in powers of V and the lowest order correction to the free-electron Hall constant.

From a physical point of view these results are quite straightforward. Energy-conserving scattering from uncorrelated sets of scatterers is given by δ functions of the first two types and these terms are responsible for the initial exponential form of $\langle U_-(t)\rangle_k$. It is also possible, however, for the electron to be scattered into a virtual state by one scatterer, then to undergo energy-conserving scattering by scatterers uncorrelated with the first set and finally to scatter back into the initial state by a scatterer in the initial set. When scattering in the virtual state is confined in time by the initial and final states, the finite lifetime of the virtual state restricts the time dependence to a linear one. This is the case when noncontiguous time variables are coupled by a δ function of the third type. When contiguous time variables are coupled by a δ function of the third type, scattering in the virtual state is not restricted in time and higher order time dependences can appear. However, this is inconsistent with the finite lifetime of the virtual state unless all terms of this type sum to give a contribution which becomes less important as time increases. Thus the form of Eq. (14).

C. Evaluation of $\phi_2(t)$

We will only need the lowest order term of $\phi_2(t)$ because it is already of order V^0. From Appendices A, C, and D

$$\phi_2(t)=\frac{1}{m^2}\sum_{kl}|V_{kl}|^2\langle U_-(t)\rangle_k\Big[2P\Big(\frac{1}{\epsilon_{lk}}\Big)\Big(k_\mu^2\frac{\partial}{\partial\epsilon_k}+k_\mu l_\mu\frac{\partial}{\partial\epsilon_l}\Big) -\Big(k_\mu^2\frac{\partial^2}{\partial\epsilon_k^2}+k_\mu l_\mu\frac{\partial}{\partial\epsilon}\frac{\partial}{\partial\epsilon_l}\Big)\Big]A_{kl}, \quad (19)$$

$$A_{kl}=(f_k^0-f_l^0)/\epsilon_{kl}.$$

From Eqs. (6), (7), (10), and (19) we get

$$\sigma_{\mu\mu}{}^0(\omega)=-e^2\sum_k\Delta_k\int_0^\infty\exp[\psi_k(t)-i\omega t]dt$$

$$\Delta_k=\frac{k_\mu^2}{m^2}\frac{\partial f_k^0}{\partial\epsilon_k}+\sum_l\frac{|V_{kl}|^2}{m^2}\Big[k_\mu^2P\Big(\frac{1}{\epsilon_{kl}}\Big)\frac{\partial^2 f_k^0}{\partial\epsilon_k^2} +k_\mu l_\mu P\Big(\frac{1}{\epsilon_{kl}}\Big)\Big(\frac{\partial}{\partial\epsilon_k}+\frac{\partial}{\partial\epsilon_l}\Big)A_{kl}\Big]. \quad (20)$$

In the limit of zero temperature the two lowest order terms of $\sigma_{\mu\mu}{}^0(\omega)$ are the same as were obtained in A because $\psi_k(t)$ may be replaced by $\psi_{k1}(t)$. The numerical results of A are unchanged.

III. THE HALL CONSTANT

From Eq. (2) we must still calculate

$$\sigma_2=-i\int_0^\infty tdt\,\mathrm{Tr}\rho[J_y,U_-{}^{\mathrm{H}}(t)J_x]. \quad (21)$$

In terms of one-electron operators and in a plane-wave representation this is

$$\sigma_2=\Big(\frac{ie^2}{m}\Big)\int_0^\infty tdt\sum_{kl}f_{kl}{}^{\mathrm{H}}(k_y-l_y)\langle l|U_-{}^{\mathrm{H}}(t)\dot{x}|k\rangle, \quad (22)$$

where f^H is the Fermi function for nonzero $\mathbf{H}$. Only terms of Eq. (22) to $0(V^{-2})$ are required.

A. Expansion of $U_-{}^H(t)$ in Powers of ω_c

It is not hard to see that, to first order in ω_c,

$$\exp[iH't]\approx\exp[iHt]-i\omega_c I(t,H)\exp[iHt]$$

where

$$I(t,H)=\frac{1}{2}\int_0^t dt'\exp[it'H^\times](p_y x-p_x y).$$

Therefore

$$U_-{}^{\mathrm{H}}(t)\dot{x}\approx U_-(t)\dot{x} -\omega_c\Big[\int_0^t U_-(t')V^\times(t')I(t',H_0)dt'\Big]^\times U_-(t)\dot{x}. \quad (23)$$

In a plane-wave representation the $\mathbf{k}',\mathbf{k}$ matrix element of the commutator is

$$=-\omega_c\int_0^t dt'\sum_l[\langle k'|U_-(t')V^\times(t')I(t',H_0)|l\rangle \times\langle l|U_-(t)\dot{x}|k\rangle+\text{c.c.}]. \quad (24)$$

Here we have the old problem of time dependence. $I(t',H_0)$ depends explicitly on t' and thus so will many matrix elements. We will show that, apart from $U_-(t)\dot{x}$, there is no time dependence and any additional factors of time which appear can be transformed into energy derivatives. This transformation will be possible whenever there is some time exponential $\exp[i\epsilon t']$ present in the matrix element containing $I(t',H_0)$ and such an exponential is always present unless $I(t',H_0)$ is included in a subdiagonal matrix element containing time variables contiguous with t_1 [see Eq. (10) for the definition of t_1]. We must show that such terms vanish. The technique used is similar to that of Appendix C.

We have

$$I(t',H_0)=\tfrac{1}{2}(p_y x-p_x y)t'.$$

Since $\langle k|x|k'\rangle=i(\partial/\partial k_x)\delta(\mathbf{k}-\mathbf{k}')$, any subdiagonal matrix element with respect to the wave vector $\mathbf{l}$ and containing $I(t',H_0)$ will be of the form

$$\sum V_{lk}\cdots\left[n_x\frac{\partial}{\partial n_y}-n_y\frac{\partial}{\partial n_x}\right]V_{nm}\cdots V_{ql}F_{k,\cdots n,m,\cdots q,l}, \quad (25)$$

where $F_{k,\cdots n,m,\cdots q,l}$ is only a function of the magnitudes of the wave vectors and the time variables and we sum over all wave vectors but $\mathbf{l}$.

Now $V_{nm}=\sum_\alpha \exp[i(\mathbf{m}-\mathbf{n})\cdot\mathbf{x}_\alpha]\phi_{nm}$ where ϕ_{nm} depends only on $|\mathbf{n}-\mathbf{m}|$ because ϕ is spherically symmetric. Thus we have

$$\left(n_x\frac{\partial}{\partial n_y}-n_y\frac{\partial}{\partial n_x}\right)V_{\mathrm{nm}}$$

$$=\sum_\alpha\frac{(n_xm_y-n_ym_x)}{|\mathbf{n}-\mathbf{m}|}\exp[-i(\mathbf{n}-\mathbf{m})\cdot\mathbf{x}_\alpha]\frac{\partial}{\partial|\mathbf{n}-\mathbf{m}|}\phi_{nm}$$

$$+\sum_\alpha i(n_xy_\alpha-n_yx_\alpha)\exp[-i(\mathbf{n}-\mathbf{m})\cdot\mathbf{x}_\alpha]\phi_{nm}, \quad (26)$$

where y_α is the y component of the position vector of the αth scatterer. We use Eq. (C2) to express n_x and m_x in terms of l_x; m_y and n_y in terms of l_y. The summation over interior wave vectors shows that there is no contribution to Eq. (25) from the first term of Eq. (26).

To deal with the second term of Eq. (26) we note that the scatterer average may be divided into two sums, one of which corresponds to a simple rotation of all scatterers about the direction of $\mathbf{l}$. The other sum corresponds to a change in angle between the scatterers and $\mathbf{l}$ or a change in the length of the scatterer position vectors and is invariant to the rotation about $\mathbf{l}$. We can now treat the second term of Eq. (26) in the same way as the first term and it also gives no contribution to Eq. (25). Therefore, subdiagonal matrix elements in question vanish. This cancellation only works for subdiagonal matrix elements containing $I(t',H_0)$ and operators which do not correspond to the presence of other preferred directions. The inclusion of other operators corresponding to the presence of preferred directions destroys the phase relations necessary for the cancellation.

The lowest order in V we have

$$\langle k'|U_-^{\mathrm{H}}(t)\dot{x}|k\rangle=\langle k'|U_-(t)\dot{x}|k\rangle$$

$$-\omega_c\int_0^t dt'\langle k'|V^\times(t')I(t',H_0)|k\rangle$$

$$\times[\langle k|U_-(t)\dot{x}|k\rangle-\langle k'|U_-(t)\dot{x}|k'\rangle].$$

The magnetic-field-dependent part of this term vanishes because the contribution to Eq. (22) that is symmetric in $\mathbf{k}$ and $\mathbf{l}$ is antisymmetric under interchange of the scatterer positions. This is shown in Appendix E. Thus, to $O(V^{-2})$ there is no contribution from $U_-^H(t)$ which is linear in ω_c.

From Appendix F we can obtain the contribution from the distribution function. We get

$$\sigma_2=e^2\sum_k R_k\omega_c\int_0^\infty t\langle U_-(t)\rangle_k dt+\tfrac{1}{2}\,\mathrm{Im}\sigma_{\mu\mu}{}^0(\omega_c)$$

$$R_k=\frac{1}{2m^2}\sum_l P\left(\frac{1}{\epsilon_{kl}}\right)(l_y-k_y)k_x$$

$$\times\left[\left(l_y\frac{\partial}{\partial l_x}-l_x\frac{\partial}{\partial l_y}\right)\left(|V_{kl}|^2\frac{\partial}{\partial\epsilon_l}A_{kl}\right)\right.$$

$$\left.+\left(k_x\frac{\partial}{\partial k_y}-k_y\frac{\partial}{\partial k_x}\right)\left(|V_{kl}|^2\frac{\partial}{\partial\epsilon_k}A_{kl}\right)\right]. \quad (27)$$

Finally, from Eqs. (2), (20), and (27) we get the results, valid *only* for the term linear in ω_c,

$$\sigma_{xy}{}^{\mathrm{H}}(0)=ie^2\sum_k(R_k-\Delta_k)\int_0^\infty dt\exp[\psi_k(t)-i\omega_c t], \quad (28)$$

and from Eqs. (1) and (20)

$$R=i\sum_k(R_k-\Delta_k)\frac{\int_0^\infty\exp[\psi_k(t)-i\omega_c t]dt}{e^2\mathbf{H}\left[\sum_k\Delta_k\int_0^\infty\exp[\psi_k(t)]dt\right]^2}. \quad (29)$$

Using Eq. (18) to perform the time integrations, expanding in powers of V, and denoting the free-electron Hall constant by R_0 we get

$$R/R_0=1+R_2,$$

$$R_2=\left[\sum_l F_{kl2}\alpha_l{}^2/(\alpha_k+\alpha_l)^2-\beta_k+(m/n)\alpha_k{}^2\right.$$

$$\left.\times\sum_l(R_l-\Delta_{l2})/\alpha_l{}^2+2(m/n)\alpha_k\sum_l\Delta_{l2}/\alpha_2\right]_{k=k_f}, \quad (30)$$

where α_l, α_k, and β_k are given by Eq. (12), R_l is given by Eq. (27), Δ_{l2} is the second-order term of Δ_l as given in Eq. (20), and F_{kl2} is

$$F_{kl2}=|V_{kl}|^2\left(\frac{l}{k}\right)(\cos\theta_{kl})\frac{\partial}{\partial\epsilon_k}P\left(\frac{1}{\epsilon_{kl}}\right). \quad (31)$$

The first two terms of Eq. (30) represent the deviation from the relaxation time approximation and the last two terms represent changes in the distribution function.

IV. CONCLUSION

The present work, in conjunction with A, shows two things: 1. The relaxation time approximation is valid only if the expansion converges rapidly. 2. An expansion in powers of the potential does not converge sufficiently rapidly.

As has been noted the potential matrix elements are not small compared with the Fermi energy for small momentum transfer. In higher order these terms enter in an important way when the energies of the initial and final states become nearly equal. It is therefore plain that some infinite series of terms must be used to obtain agreement with experiment. Recent works by Edwards[4] and Ballentine[5] have shown that these terms correspond to lifetime effects. That is, in between any two collisions the electron should be assumed to propagate not as a free particle but with a finite lifetime in any plane-wave state. Ballentine[5] used this consideration to sum the relevant diagrams for the diagonal matrix element of the Green's function. In the present case we must sum an analogous class of diagrams for the off-diagonal matrix elements of the Green's function. The terms to be summed are a subset of those containing what I have called scatterer δ functions of the second and third kinds. This summation has been done and it is hoped to report on it shortly.

APPENDIX A: EVALUATION OF $[f,x_\mu]_{kk'}$

We start from the expression for f in terms of its Laplace transform

$$f(H)=\frac{1}{2\pi i}\oint f(z)dz\frac{1}{z-H}. \tag{A1}$$

Expansion of $1/(z-H)$ in powers of V gives the following series:

$$\begin{aligned} f(H)&=f^0+f^1+f^2+\cdots \\ f^0&=\frac{1}{2\pi i}\oint f(z)dz\frac{1}{z-H_0}, \\ f^1&=\frac{1}{2\pi i}\oint f(z)dz\frac{1}{z-H_0}V\frac{1}{z-H_0}. \end{aligned} \tag{A2}$$

Using $x_\mu=i(\partial/\partial p_\mu)$, we get

$$[f^0,x_\mu]_{kk}=-i\frac{\partial f_k{}^0}{\partial k_\mu}, \tag{A3}$$

$$[f^1,x_\mu]_{kk'}=-iV_{kk'}\left(\frac{\partial}{\partial k_\mu}+\frac{\partial}{\partial k_\mu{}'}\right)A_{kk'},$$

$$A_{kl}=\frac{f_k{}^0-f_l{}^0}{\epsilon_{kl}}, \tag{A4}$$

$$[f^2,x_\mu]_{kk}=-i\sum_{k'}|V_{kk'}|^2\left(\frac{\partial}{\partial k_\mu}+\frac{\partial}{\partial k_\mu{}'}\right)\frac{\partial}{\partial\epsilon_k}A_{kk'}. \tag{A5}$$

These are the only three terms we shall need. These expressions have been obtained before by other authors.[6] The derivation is included here for completeness.

APPENDIX B: TIME DEPENDENCE OF A GENERAL TERM OF $\psi_k(t)$

Without loss of generality, we can restrict consideration to the fourth-order term of the form

$$\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\int_0^{t_3}dt_4 \times\exp[i\alpha\tau]\exp[i\beta\tau']\exp[i\gamma\tau''], \tag{B1}$$

where

$$\tau=t_3-t_4,\ \tau'=t_2-t_3,\ \tau''=t_1-t_2.$$

Equation (B1) may be transformed to

$$\int_0^t d\tau\int_0^{t-\tau}d\tau'\int_0^{t-\tau-\tau'}d\tau''(t-\tau-\tau'-\tau'') \times\exp[i\alpha\tau]\exp[i\beta\tau']\exp[i\gamma\tau'']. \tag{B2}$$

When no scatter δ functions are present, α, β, γ are all not equal and nonzero. Since the exponentials vanish when τ, τ', or τ'' get too large, the integral is plainly linear in time. When scatterer δ functions are present, they may cause a breakup of the integrand of Eq. (B2) into sets of independent time variables. For each independent set present, one of α, β, and γ must vanish. It is plain that the time dependence of Eq. (B2) goes up by one power of time for every one of α, β, and γ which vanishes. It is not hard to see that it is only when contiguous time variables are coupled that the time dependence of Eq. (B2) can increase.

APPENDIX C: ANGULAR DEPENDENCE OF $\langle k|\,U_-(t)\dot{x}\,|k\rangle$

A representative term of $\langle k|\,U_-(t)\dot{x}\,|k\rangle$ is

$$\sum_{k'l\cdots,n,m}V_{kk'}V_{k'l}V_{ln}\cdots V_{mk}n_xF(\epsilon), \tag{C1}$$

where $F(\epsilon)$ contains the rest of the term which is only a function of energy. It is easy to see that

$$n_\mu=n[k_\mu\cos\theta_{kn}/k +(1-k_\mu{}^2/k^2)^{1/2}\sin|\theta_{kn}|\cos\varphi_{kn}], \tag{C2}$$

where φ_{kn} is the azimuth angle of $\mathbf{n}$ about $\mathbf{k}$. The product of the V's in Eq. (C1) is invariant under rotation of all the wave vectors about any axis. There is present in the sum a term corresponding to a rotation of all the wave vectors by 180° about the direction of

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[5] L. E. Ballentine, Ph.D. thesis, University of Cambridge 1965 (unpublished).
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$\mathbf{k}$ showing that the $\sin|\theta_{kn}|$ term of Eq. (C2) cancels leaving only the angular dependence of k_x.

APPENDIX D: EVALUATION OF $\langle k'|U_-(t)x|k\rangle$

By definition

$$\langle k'|U_-(t)\dot{x}|k\rangle=\sum_{n=1}^{\infty}(i)^n\int_0^t dt_1\cdots\int_0^{t_{n-1}}dt_n \times\langle k'|t_n{}^{\times}\cdots t_1{}^{\times}\dot{x}|k\rangle.$$

Expand this in plane waves and substitute $t_n=t_{n-1}-\tau$. Performing the τ integration gives

$$\begin{aligned}&=\lim_{\epsilon\to 0^+}\sum_{n=1}^{\infty}(i)^{n-1}\int_0^t dt_1\cdots\int_0^{t_{n-2}}dt_{n-1}\\ &\times\sum_l\left[V_{lk}\langle k'|t_{n-1}{}^{\times}\cdots t_1{}^{\times}\dot{x}|l\rangle\exp[i\epsilon_{lk}t_{n-1}]/(\epsilon_{kl}+i\epsilon)\right.\\ &\left.-\langle l|t_{n-1}{}^{\times}\cdots t_1{}^{\times}\dot{x}|k\rangle V_{k'l}\exp[i\epsilon_{k'l}t_{n-1}]/(\epsilon_{lk'}+i\epsilon)\right]\\ &+\lim_{\epsilon\to 0^+}\sum_l\left[V_{k'l}\langle l|U_-(t)\dot{x}|k\rangle/(\epsilon_{lk'}+i\epsilon)\right.\\ &\left.-V_{lk}\langle k'|U_-(t)\dot{x}|l\rangle/(\epsilon_{kl}+i\epsilon)\right]. \quad \text{(D1)}\end{aligned}$$

Suppose $\mathbf{l}=\mathbf{k}'$ in the first and fourth terms and $\mathbf{l}=\mathbf{k}$ in the second and third terms. There is a δ function coming from the sum over scatterers which gives this term finite weight.[7]

Then consider the first two terms. These are

$$\begin{aligned}&\lim_{\epsilon\to 0^+}\sum_{n=1}^{\infty}(i)^{n-1}\int_0^t dt_1\cdots\int_0^{t_{n-2}}dt_{n-1}V_{k'k}\\ &\times\left[\langle k'|t_{n-1}{}^{\times}\cdots t_1{}^{\times}\dot{x}|k'\rangle-\langle k|t_{n-1}{}^{\times}\cdots t_1{}^{\times}\dot{x}|k\rangle\right]\\ &\times\exp[i\epsilon_{k'k}t_{n-1}]/(\epsilon_{kk'}+i\epsilon). \quad \text{(D2)}\end{aligned}$$

We expand $\langle k'|t_{n-1}{}^{\times}\cdots t_1{}^{\times}\dot{x}|k'\rangle$ in powers of V and take matrix elements with respect to plane waves. This diagonal matrix element may contain δ functions from the scatterer sums which make two wave vectors match. If no such δ functions are present the term is independent of time.

Now suppose a scatterer δ function does exist in the term. We take the largest subdiagonal matrix element which includes only time variables contiguous with t_1. We may perform the time integrations for all other time variables which will leave us with two types of terms. One will have a time-independent coefficient multiplying a diagonal matrix element and the other will have a coefficient whose only time dependence is exponential. For this latter term we may proceed as in the above.

[7] Ordinarily, these terms would vanish to lowest order in $1/\Omega$ since the scatterer average of the remaining V would be of order $1/\Omega^{1/2}$. However, there are initial factors of V coming from the distribution function. The ensemble average is taken over this product and is finite.

When these wave vector relations do not hold we simply repeat the procedure till we again hit a δ function making the remaining matrix element diagonal. In doing this, factors of t^{α} will appear. These can always be transformed into derivatives with respect to energy of the next highest time exponential. Such an exponential always exists because all terms without at least one higher time exponential have been put into a diagonal term.

Therefore, the lowest order contribution to the off-diagonal matrix element is

$$\langle k'|U_-(t)\dot{x}|k\rangle\approx\lim_{\epsilon\to 0^+}V_{k'k}\left[\langle k|U_-(t)\dot{x}|k\rangle-\langle k'|U_-(t)\dot{x}|k'\rangle\right]/(\epsilon_{kk'}+i\epsilon). \quad \text{(D3)}$$

APPENDIX E: EVALUATION OF $\int_0^t\langle k'|V^{\times}(t')I(t',H_0)|k\rangle$

By definition

$$I(t',H_0)=\frac{1}{2}\int_0^t\exp[iH_0{}^{\times}t'](p_yx-p_xy)dt', \quad \text{(E1)}$$

$$=\tfrac{1}{2}(p_yx-p_xy)t,$$

and

$$V^{\times}(t)I(t,H_0)=\tfrac{1}{2}t\exp[iH_0{}^{\times}t]V^{\times}(p_yx-p_xy). \quad \text{(E2)}$$

The matrix element of Eq. (E2) is

$$\tfrac{1}{2}it\exp[i\epsilon_{k'k}t']\left[(k_y'-k_y)\frac{\partial}{\partial k_x}-(k_x'-k_x)\frac{\partial}{\partial k_y}\right]V_{k'k}. \quad \text{(E3)}$$

To get the contribution of this quantity to Eq. (22) we note that it is there multiplied by a coefficient of the form $V_{kk'}\,S'_{kk'}$ where $S'_{kk'}=S'_{k'k}$ and we sum over k and k'. If we replace $it'\exp[i\epsilon_{k'k}t']$ by $S_{kk'}+A_{kk'}$ where $S_{kk'}=S_{k'k}$ and $A_{kk'}=-A_{k'k}$, we can combine each contribution to Eq. (22) with the contribution obtained by interchanging $\mathbf{k}$ and $\mathbf{k}'$. The result of this combination is a term of the form

$$\begin{aligned}&S_{kk'}S_{kk'}\left[(k_y'-k_y)\frac{\partial}{\partial k_x}-(k_x'-k_x)\frac{\partial}{\partial k_y}\right]|V_{kk'}|^2+S_{kk'}A_{kk'}\\ &\times\left\{V_{k'k}\left[(k_y'-k_y)\frac{\partial}{\partial k_x}-(k_x'-k_x)\frac{\partial}{\partial k_y}\right]V_{kk'}\right.\\ &\left.-V_{kk'}\left[(k_y'-k_y)\frac{\partial}{\partial k_x}-(k_x'-k_x)\frac{\partial}{\partial k_y}\right]V_{k'k}\right\}. \quad \text{(E4)}\end{aligned}$$

The first contribution to Eq. (E4) vanishes because $|V_{kk'}|^2$ is only a function of $|\mathbf{k}-\mathbf{k}'|$. The rest of Eq.

(E4) vanishes because the scatterer coordinate dependence is $\sum_{\alpha\beta} x_\alpha \cos[(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}_{\alpha\beta}]$ which vanishes to highest order in Ω for a macroscopic liquid.

APPENDIX F: EXPANSION OF f^H IN POWERS OF ω_c

Using the Laplace transform technique of Appendix A

$$f^H=\frac{1}{2\pi i}\oint f(z)dz\frac{1}{z-H'}$$

$$\approx\frac{1}{2\pi i}\oint f(z)dz \times\left[\frac{1}{z-H}+\frac{\omega_c}{2}\frac{1}{z-H}(p_xy-p_yx)\frac{1}{z-H}\right]. \quad \text{(F1)}$$

We require only the terms up to first order in V.

The contributions of zeroth order in V are

$$f^H=f^0+\frac{1}{2\pi i}\oint f(z)dz\left(\frac{1}{z-\epsilon_k}\right)^2(p_xy-p_yx)\tfrac{1}{2}\omega_c. \quad \text{(F2)}$$

The second term of Eq. (F2), when commuted with p_y in Eq. (22), gives a contribution of

$$\tfrac{1}{2}\,\mathrm{Im}\sigma_{\mu\mu}{}^0(\omega_c)$$

to σ_2. Using $\langle k|x|k'\rangle=i(\partial/\partial k_x)\delta(\mathbf{k}-\mathbf{k}')$, we have for the off-diagonal terms

$$\langle k|f^H|k'\rangle\approx f_{kk'0}+\omega_c f_{kk'1},$$

$$f_{kk'0}=A_{kk'}V_{kk'},\ A_{kk'}=(f_k{}^0-f_{k'}{}^0)/\epsilon_{kk'}, \quad \text{(F3)}$$

$$f_{kk'1}=\frac{1}{2}\left[\left(k_y'\frac{\partial}{\partial k_x'}-k_x'\frac{\partial}{\partial k_y'}\right)\left(V_{kk'}\frac{\partial}{\partial\epsilon_{k'}}A_{kk'}\right)-\left(k_y\frac{\partial}{\partial k_x}-k_x\frac{\partial}{\partial k_y}\right)\left(V_{kk'}\frac{\partial}{\partial\epsilon_k}A_{kk'}\right)\right]. \quad \text{(F4)}$$

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Electron Transport in Amorphous Materials. II

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It is shown that an expansion of the electronic part of the conductivity of an amorphous material in integral powers of the potential is not valid unless an infinite number of terms of the expansion are kept. These terms are summed and a new expansion is made in integral powers of a restricted class of potentials for which it is possible to keep only a finite number of terms. It is suggested that this is the solution to several difficulties which have arisen in the field in the past few years. Specific attention is drawn to the case of liquid Na.

I. INTRODUCTION

In two recent papers,[1,2] it was shown that a simple perturbation expansion of the conductivity of liquid metals in powers of the potential does not converge sufficiently rapidly to give reasonable agreement with experiment. It was further shown in I therefore that the relaxation time approximation is not valid. Lowest order perturbation theory often gave excellent agreement with experiment while inclusion of higher order terms destroyed this agreement. Evidently, it was necessary to sum a set of terms in the perturbation expansion.

The way out of this dilemma was indicated by Edwards,[3] who showed that, in between two collisions with some initial set of correlated scatterers, the electron should not be treated as a free particle but rather as propagating in a plane-wave state with a finite lifetime. This lifetime is given by the possibility of interaction with other scatterers not correlated with the initial set and is a result common to materials in which the particles scattering the electrons have only short range order. I shall refer to such materials as amorphous materials. We will see that, because of this special property, it is incorrect to expand the electronic contribution to the conductivity in integral powers of the potential and to keep only a finite number of terms. We will also see how to reformulate the problem, summing an infinite class of diagrams, to obtain a new expansion of the magneto-conductivity tensor in which it is valid to keep a finite number of terms.

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[3] S. F. Edwards, Proc. Roy. Soc. (London) **A267**, 518 (1962).