Resistivity and Hall Effect in Liquid Metals*

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We assume a liquid metal in which the unscreened electron-ion interaction is the sum of spherically symmetric potentials. Using an exact expression for the conductivity tensor in a magnetic field $\mathbf{H}$, we obtain expressions for the Hall constant R and for the zero-magnetic-field frequency-dependent conductivity tensor $\sigma_{\mu\mu}{}^0(\omega)$ in the form of power-series expansions in the potential. Effects due to the electron spin are ignored. Calculations are done for Zn, Li, and Na using the pseudopotentials calculated by Harrison. For Zn it is shown that the series for $\sigma_{\mu\mu}{}^0(\omega)$ converges slowly if it converges at all. It is concluded that the small-pseudopotential approximation is not convenient for, and possibly not valid for, dealing with electrical transport in liquid metals.

I. INTRODUCTION

THE study of liquid metals has been retarded for many years by severe experimental and theoretical difficulties. The experimental difficulties are not particularly germane to this paper; they are reviewed in a recent article by Cusack.[1] The theoretical difficulties of such a study are certainly no less harsh. They may be emphasized by first considering the case of a crystalline metal. From x-ray diffraction experiments, we can obtain definitive information about the crystal structure.[2,3] Knowing only the crystal structure and, apart from its symmetry, being completely ignorant of the crystal potential, we can use group theory[4,5] to simplify greatly the eigenfunction and eigenvalue problems. The Bloch-Floquet theorem allows us to label each electron energy eigenfunction by a wave vector $\mathbf{k}$. If interband transitions are neglected, the time rate of change of $\mathbf{k}$ is proportional to the Lorentz force experienced by a single electron. This fact makes it possible to calculate the transport properties of crystalline metals since incoherent scattering can only be due to imperfections in the crystal structure.

On the other hand, an x-ray diffraction experiment performed on a liquid metal tells us only that we are dealing with a system having some short-range order of an undetermined nature but no long-range order.[2,3] There are no symmetry properties which can be used to simplify the problem, and there is no Bloch theorem to give us information about the electronic eigenfunctions of the system. It is no longer necessarily true that the wave vector is a good quantum number. For these and other reasons, work on liquid metals has not been noted for its abundance or its success. Indeed, until recently, work was concentrated on trying to explain

the static resistivity[6–8] of liquid metals in the absence of a magnetic field. This work achieved some qualitative success for the alkali metals, but, in general, rested on unsatisfactory bases and gave poor agreement with those experimental numbers which had been obtained.[9] The early work is also reviewed in the article by Cusack.[1]

Within the last five years, however, the theoretical outlook has taken a decided turn for the better due mainly to the introduction of the pseudopotential.[10–13] Moreover, many experimental difficulties have been overcome. Greenfield[14] and Enderby[15] have recently obtained new and more accurate experimental values for the Hall constants of several liquid metals. Optical[16,17] and other properties of a few liquid metals have also been measured. As the experimental situation cleared, it became evident that the electrical transport properties of liquid metals could be explained on the basis of a nearly free-electron model. Briefly, this model assumes that the electronic energy eigenfunctions may be labeled by a $\mathbf{k}$ vector just as for free electrons. Further, the Fermi surface is assumed spherical, and it is supposed that all deviations from completely free-electron behavior may be obtained by some form of perturbation procedure. For instance, measurements of the Hall constant R have shown only small percentage deviations from the free-electron value R_0. In Table I, we show the recent experimental results for R/R_0. Those

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1 N. Cusack, Rept. Progr. Phys. 26, 361 (1963).
2 N. S. Gingrich, Rev. Mod. Phys. 15, 90 (1943).
3 K. Furukawa, Rept. Progr. Phys. 25, 395 (1962).
4 H. Jones, *The Theory of Brillouin Zones and Electronic States in Crystals* (North-Holland Publishing Company, Amsterdam, 1960).
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9 N. Cusack and J. Enderby, Proc. Phys. Soc. (London) 75, 395 (1960).
10 J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959); 118, 1153 (1960).
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12 B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. 127, 276 (1962).
13 M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).
14 A. Greenfield (to be published). I am informed by Dr. Greenfield that his measured value for the Hall constant of Zn agrees exactly with that obtained by Enderby. Their values of R/R_0 differ because they used different values for the density of liquid Zn.
15 J. Enderby, Proc. Phys. Soc. (London) 81, 772 (1963); see also G. Busch and Y. Tieche, Phys. Kondens. Materie 1, 78 (1963).
16 L. G. Schulz, Advan. Phys. 6, 102 (1957).
17 G. Wilson and S. Rice (private communication).

TABLE I. Recent experimental values of R/R_0, τ_d/τ_c, and $2/k_F l$ for several liquid metals. $2/k_F l$ and τ_d/τ_c were calculated using the data of Wilson[a] for Cd and In and of Bradley et al.[b] for other metals.

	R/R_0	Probable error	Reference	$\hbar/\varepsilon_F \tau_c = 2/k_F l$	τ_d/τ_c (Exptl.)
Zn	1.06	4%	15	0.10	0.2
	1.01	4%	14		
Cd	1.04	4%	15	0.08	0.1
	0.99	4%	14		
In	1.05	5%	15	0.07	0.2
	0.93	4%	14		
Pb	0.88	7%	15	0.24	0.6
	0.72	15%	14	0.14	
Sn	1.00	4%	14	0.13	0.3
Bi	0.69	4.5%	14	0.35	1.0
Ga	0.97	2.5%	14	0.07	0.2
Tl	0.76	4%	14		0.4
Hg	0.99	4%	14	0.19	0.4

[a] E. G. Wilson, Ph.D. thesis, University of Cambridge, 1962 (unpublished).
[b] Reference 20.

optical experiments which have been performed, and which measure the complex index of refraction, generally give a good fit to the Drude equations.[18] The fourth column of Table I gives the ratio of the uncertainty in energy due to collisions to the Fermi energy ε_F. This dimensionless quantity $\hbar/\tau\varepsilon_F$ is the natural expansion parameter to describe deviations from free-electron-like behavior. The relaxation time τ is obtained from conductivity measurements if we assume the density of electrons and their charge and mass are given by the free-electron values.

These results are somewhat disconcerting. The electron-ion interaction in the liquid should be something akin to an atomic potential inside the core and a screened coulomb interaction outside the core and should presumably scatter the electrons strongly. Until recently, it was very hard to understand how such an interaction could lead to scattering so weak that the free-electron wave function is a good first approximation. The introduction of the pseudopotential, however, led to a better understanding of these nearly-free-electron results since the pseudopotential was "small" and thus consistent with a perturbation expansion. Using this property of the pseudopotential, Ziman[19] and Bradley, Faber, Ziman, and Wilson[20] have obtained qualitatively accurate results for the static resistivity and thermoelectric powers of various liquid metals. Harrison[21] has calculated a pseudopotential for Zn and used it to obtain, among other things, a calculated value of the static resistivity of liquid Zn in good agreement with experiment. However, these authors treated

only the lowest-order terms of an expansion in powers of the pseudopotential.

An entirely different approach was used by Edwards.[22] Starting from an exact expression for the static conductivity tensor, he used a Green's function method to evaluate it for a random system in the limit of weak interactions and zero magnetic field.

Another approach to the problem of liquid metals was made by Chester and Thellung[23] and by Verboven.[24] They evaluated an exact expression for the static conductivity tensor due to Kubo[25] by a perturbation method due to Van Hove.[26] Their work is applicable to a system with any degree of order. While they obtain expressions for the lowest three orders of an expansion of the conductivity in powers of the potential, no calculations are done.

None of this work, however, is applicable to the case of a nonzero magnetic field or to nonzero frequency. Further, apart from the formal papers of Edwards, of Chester and Thellung, and of Verboven, the theoretical work has been done in the relaxation-time approximation which, when generalized to finite magnetic field, leads only to the free-electron Hall constant. Thus, though it is precisely the Hall-constant measurements and optical measurements which give the most striking and compelling evidence for the nearly free-electron model, the calculations done to date give no test of the model.

A calculation of the optical properties would present serious difficulties since accurate experiments on liquid metals have been performed only for a few liquids and only for frequencies large compared to $1/\tau$. But in the absence of detailed information concerning the electronic eigenvalue distribution, it is convenient to calculate the optical constants only for $\omega\tau\ll1$. It was thus decided to work with the Hall constant. The decision was helped by the knowledge that the measurements of Greenfield and of Enderby would soon be available.

While some of the previous work has proceeded formally beyond lowest-order perturbation theory, no one has yet calculated the magnitude of the higher-order terms. Thus the question of the convergence of the power series has not been investigated at all. One could say that this is irrelevant because of the good agreement of the lowest order terms with experiment. But while the nearly-free-electron model has much experimental evidence to back it up, this evidence is not conclusive and it is not at all certain that we may conveniently obtain good results by perturbing from a system of free electrons. It must be shown that use of a particular expansion parameter leads to quick convergence of the

[18] F. Seitz, Modern Theory of Solids (McGraw-Hill Book Company, Inc., New York, 1940), p. 629 ff.
[19] J. M. Ziman, Phil. Mag. 6, 1013 (1961).
[20] C. C. Bradley, T. E. Faber, J. M. Ziman, and E. G. Wilson, Phil. Mag. 7, 865 (1962).
[21] W. Harrison, Phys. Rev. 129, 2503, 2512 (1963); General Electric Research Laboratories Report No. 63-RL-(3322M), 1963 (unpublished).

[22] S. F. Edwards, Phil. Mag. 3, 1020 (1958).
[23] G. V. Chester and A. Thellung, Proc. Phys. Soc. (London) 73, 745 (1959).
[24] E. Verboven, Physica 26, 1091 (1960).
[25] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957). Equation (2) of this paper is obtained from Eq. (5-13) of Kubo's paper.
[26] L. Van Hove, Physica 21, 517 (1955); 23, 441 (1957).

series and good agreement with experiment. Heretofore, everyone has used the pseudopotential as the expansion parameter. It will be shown below that use of the pseudopotential leads to very poor convergence of the expansion for the frequency-dependent conductivity tensor.

The present work obtains information valid in the presence of a magnetic field and for nonzero frequency by a different method from those outlined above. Starting with an exact expression for the conductivity tensor for arbitrary frequency and magnetic field due to Kubo,[25] we obtain in Sec. II explicit theoretical expressions for the Hall constant[27] and for the zero-magnetic-field frequency-dependent conductivity tensor in the limit $T=0$. In Sec. III some numerical results are obtained and discussed. Our conclusions are presented in Sec. IV.

II. THE HALL CONSTANT

A. Reduction of the Kubo Formula

Throughout this paper it will be assumed that we are dealing with a rectangular parallelepiped 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, charge by e, and density by n. We assume the system has unit volume, and that the electronic distribution function is the one appropriate to $T=0$.

The total electronic Hamiltonian in the absence of the external electric field will be denoted by $\mathcal{3C}$ and is the sum of $\mathcal{3C}_0'$, the kinetic energy in the presence of the magnetic field, and $\mathcal{3C}_1$, which is the sum of electron-electron and electron-ion interactions.

It will be assumed that the ions are stationary classical particles. The justification for this is that metals melt at temperatures well in excess of their Debye temperature θ_D in the crystal. Since x-ray pictures of the liquid show short-range order still exists, it is reasonable to suppose that this short-range order restricts the ionic motion to frequencies similar to and smaller than those in the crystal. Thus all characteristic frequencies of ion motion ω have $\omega \ll kT$ so that recoil effects are negligible compared to the thermal spread in electron energy. However, even though the ions may be regarded as stationary during collisions, the ion distribution still changes in time over times short compared to the duration of the experiment. Thus we really measure some time-averaged quantity to which essentially all ionic distributions contribute. We should therefore calculate first for fixed ionic positions and then average the calculated quantity.

Under these conditions, if we neglect all terms higher than first order in $\mathbf{H}$, it is well known that an electric field E_y will be induced in the y direction which will be

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[27] R. Kubo (to be published) has used the Wigner distribution function to obtain the Hall constant.

proportional to both the magnetic field $\mathbf{H}$ and to J_x, the current density in the x direction. The constant of proportionality is the Hall constant R. Denoting by $\sigma(\omega)$ the conductivity tensor for frequency ω and for arbitrary magnetic field, R is given in terms of the static conductivity tensor $\sigma(0)$ by

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

where $\sigma_{xy}{}^{\mathrm{H}}(0)$ 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 $\sigma(0)$ for zero magnetic field.

We start by obtaining $\sigma_{xy}{}^{\mathrm{H}}(0)$ from an exact expression for the conductivity tensor for arbitrary magnetic field given by Kubo.[25] His expression is

$$\sigma_{xy}(0) = -i \int_0^\infty t\,dt\{\mathrm{Tr}\rho[J_y, J_x(t)]\}, \qquad (2)$$

$$J_x(t) = \exp(i\mathcal{3C}t) J_x \exp(-i\mathcal{3C}t), \qquad (3)$$

$$\rho = \exp(-\beta\mathcal{3C})/\mathrm{Tr}\exp(-\beta\mathcal{3C}), \qquad (4)$$

where β has the usual definition of $1/kT$ and the curly brackets in Eq. (2) denote the normalized average over ionic positions. Equation (2) assumes the Hamiltonian to be Hermitian and that the externally applied forcing field is adiabatically turned on at $t=-\infty$. It is shown in Appendix A that Eq. (2) may be written

$$\sigma_{xy}(0) = -i \int_0^\infty t\,dt\{\mathrm{Tr}\rho[J_y, U_-(t) \\ \times (J_y \sin\omega_c t + J_x \cos\omega_c t)]\}, \qquad (5)$$

where ω_c is the free-electron cyclotron frequency and $U_-(t)$ is defined by

$$U_-(t) J_x = \exp[i\mathcal{3C}t] \exp[-i\mathcal{3C}_0' t] J_x \\ \times \exp[i\mathcal{3C}_0' t] \exp[-i\mathcal{3C}t]. \qquad (6)$$

Following Kubo, it is convenient at this point to introduce a different notation. We define for arbitrary operators A and B

$$A^\times B = [A, B]. \qquad (7)$$

It then follows that

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

In this notation Eq. (6) may be written

$$U_-(t) J_x = \exp[i\mathcal{3C}^\times t] \exp[-i\mathcal{3C}_0'{}^\times t] J_x. \qquad (8)$$

From now on, in this section, we shall deal only with the terms of Eq. (2) which are linear in the magnetic field. All relations will be valid only to this order in $\mathbf{H}$. Consider Eq. (5). If $\omega_c \tau_c \ll 1$, where τ_c is the time over which current correlations disappear, the $\sin\omega_c t$ factor is first order in the magnetic field. If we assume the electron density, mass, and charge to be equal to their free-electron values, we can obtain an estimate of τ_c from measurements of the conductivity. It turns out

to be of the order of 10^{-15}–10^{-16} sec. We shall later define a quantity τ which will be equivalent to τ_c. Calculations of τ will show it to be of the same magnitude. Thus, an assumption of this order of magnitude for τ_c is self-consistent. We then have $\omega_c\tau_c \approx 10^{-4}$–$10^{-5}$ for $H = 10^4$ G and certainly $\omega_c\tau_c \ll 1$ for reasonable values of H. Thus we can get the linear magnetic-field dependence of the term in $\sin\omega_c t$ merely by setting $H = 0$ in the remainder of the integrand. By using Eq. (5–11) of the paper by Kubo,[25] this part of Eq. (5) may easily be shown to equal $-2 \operatorname{Im}\sigma_{\mu\mu}{}^0(\omega_c)$, where $\sigma_{\mu\mu}{}^0(\omega)$ is any diagonal component of the frequency-dependent conductivity tensor for zero magnetic field. We get

$$\sigma_{xy}{}^H(0) = -2 \operatorname{Im}\sigma_{\mu\mu}{}^0(\omega_c) - i$$

$$\times \int_0^\infty t\,dt\{\operatorname{Tr}\rho[J_y, U_-(t)J_x]\}. \quad (9)$$

Each factor in the integral term of Eq. (9) depends on the magnetic field, but, as we are only interested in the linear magnetic-field dependence of $\sigma_{xy}(0)$, we can treat each factor in each term separately.

The magnetic-field dependence of the current operators may be treated by going to a specific gauge since any physical result must be gauge independent; we choose

$$A = A_y = Hx. \quad (10)$$

If this is the only magnetic-field dependence present, the integral term in Eq. (9) becomes

$$i\int_0^\infty \omega_c t\,dt \sum_i \{\operatorname{Tr}\rho[ex_i, J_x(t)]\} = \operatorname{Im}\sigma_{\mu\mu}{}^0(\omega_c), \quad (11)$$

and this term just cancels half the first term of Eq. (9). If, then, the linear magnetic field dependence of $U_-(t)$ and of ρ were to vanish, we would have for the Hall constant the simple expression

$$R_1 = -\frac{e}{mc}\frac{\operatorname{Im}\sigma_{\mu\mu}{}^0(\omega_c)}{\omega_c[\sigma_{\mu\mu}{}^0(0)]^2} = -\frac{ie}{mc}\frac{d}{d\omega}\frac{1}{\sigma_{\mu\mu}{}^0(\omega)}\bigg|_{\omega=0}. \quad (12)$$

The magnetic-field dependence of $U_-(t)$ comes from interference between the electronic motion in the magnetic field and in the scattering field of the nuclei and other electrons. Thus, if the duration of the collision τ_d with a scattering center were small enough, Eq. (12) would be valid. The relevant parameter is τ_d/τ_c. If τ_d is assumed to be the time required to traverse one interionic distance in the liquid, we get the values in Table I.

The large values for τ_d/τ_c make it unlikely that Eq. (12) is valid for these metals. For Na and Li, the corresponding ratios are 0.02 and 0.07, respectively, so it seems as if Eq. (12) should be at least approximately valid for the alkali metals. We shall return to Na and Li in a later section. For most metals, however,

we must deal with the contribution from $U_-(t)$; it is most convenient to leave this till after we have examined $\sigma_{\mu\mu}{}^0(\omega_c)$.

B. Derivation of $\sigma_{\mu\mu}{}^0(\omega)$

The starting point in our derivation of $\sigma_{\mu\mu}{}^0(\omega)$ is Eq. (5–10) of Kubo's paper.[25]

$$\sigma_{\mu\mu}{}^0(\omega) = -i\int_0^\infty e^{-i\omega t}dt\{\operatorname{Tr}[\rho, e\sum_i x_{i\mu}]J_\mu(t)\}, \quad (13)$$

where $x_{i\mu}$ is the μth component of the position vector of the ith electron. The calculation will be done for the case of independent electrons and a scattering potential which is the sum of spherically symmetric terms centered on each ion. It is convenient to reduce Eq. (13) immediately for this case. When the magnetic field vanishes we may write

$$\mathcal{H} = \sum_i H_i = \sum_i (H_{0i} + V_i), \quad (14)$$

where H_{0i} is that part of H_i diagonal in a plane-wave representation and the sum is over electronic coordinates. We then have

$$\sum_i \operatorname{Tr}[\rho, x_{i\mu}]J_\mu(t) = e\sum_i \operatorname{Tr}\rho[x_{i\mu}, \dot{x}_{i\mu}(t)]. \quad (15)$$

In terms of one-particle operators this reduces to

$$\sigma_{\mu\mu}{}^0(\omega) = -ie^2\int_0^\infty e^{-i\omega t}dt\{\operatorname{Tr}[f, x_\mu]U_-(t)\dot{x}_\mu\}, \quad (16)$$

where f is the one-electron Fermi function and the trace is to be taken with respect to eigenfunctions of the one-electron Hamiltonian. We shall use the cumulant theorem[28] to treat Eq. (16). All the proofs necessary for the application of the cumulant theorem to the present case are given in an excellent paper by R. Kubo[28] and will not be repeated here. The theorem allows us to express the normalized average of an exponential as the exponential of a function called the cumulant function.

Forgetting about the time integration, we can consider Eq. (16) as the average of $U_-(t)$. To express $U_-(t)$ as an exponential we note from Eq. (8) that

$$dU_-(t)/dt = iU_-(t)V^\times(t), \quad (17)$$

where

$$V^\times(t) = [\exp(itH_0{}^\times)V]^\times. \quad (18)$$

The solution of Eq. (17) is

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

$$= \exp_-\left\{i\int_0^t V^\times(t')dt'\right\}. \quad (19)$$

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

Defining the average of an operator A by

$$\langle A\rangle = \text{Tr}[f,x_\mu]A\dot{x}_\mu/\text{Tr}[f,x_\mu]\dot{x}_\mu, \qquad (20)$$

and noting that

$$\text{Tr}[f,x_\mu]\dot{x}_\mu = ni/m, \qquad (21)$$

the conductivity tensor is

$$\sigma_{\mu\mu}{}^0(\omega) = (ne^2/m)\left\{\int_0^\infty e^{-i\omega t}dt\langle U_-(t)\rangle\right\}, \qquad (22)$$

$$\langle U_-(t)\rangle = \exp[\psi(t)]$$

$$\psi(t) = i\int_0^t dt_1\langle V^\times(t_1)\rangle_c$$

$$-\int_0^t dt_1\int_0^{t_1}dt_2\langle V^\times(t_2)V^\times(t_1)\rangle_c$$

$$-i\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3$$

$$\times\langle V^\times(t_3)V^\times(t_2)V^\times(t_1)\rangle_c+\cdots. \qquad (23)$$

The subscript c on the curly brackets indicates that the cumulant average is to be taken. The cumulant average is identical to the average of Eq. (20) except that certain moments of lower order are subtracted. To illustrate we give the definitions of the first three cumulant averages

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

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

$$\langle A_iA_jA_k\rangle_c = \langle A_iA_jA_k\rangle - \langle A_i\rangle\langle A_jA_k\rangle - \langle A_j\rangle\langle A_iA_k\rangle$$
$$-\langle A_iA_j\rangle\langle A_k\rangle + 2\langle A_i\rangle\langle A_j\rangle\langle A_k\rangle.$$

We shall proceed by first expanding $\psi(t)$ in powers of V, after which the time integration of Eq. (22) will be done. It has been shown by Kubo[25] that the quantity $-ie^2\,\text{Tr}[f,x_\mu]\dot{x}_\mu(t)$ is real. Therefore, $\psi(t)$ must be real to all orders in the expansion.

Expanding $[f,x_\mu]$ in powers of V and denoting the constant term by $[f,x_\mu]_0$ and the linear term by $[f,x_\mu]_1$, we see that $\psi(t)$ has no terms independent of or linear in V.

It has been shown by Kohn and Luttinger[29] that, in a plane-wave representation,

$$\langle \mathbf{k}|[f,x_\mu]_0|\mathbf{k}\rangle = (-ik_\mu/m)(\partial f_k{}^0/\partial\varepsilon_k), \qquad (24)$$

and

$$\langle\mathbf{k}|[f,x_\mu]_1|\mathbf{k}'\rangle = -iV_{\mathbf{kk}'}$$

$$\times\left(\frac{\partial}{\partial k_\mu}+\frac{\partial}{\partial k_\mu'}\right)\left(\frac{f_k{}^0-f_{k'}{}^0}{\varepsilon_{kk'}}\right), \quad \mathbf{k}\neq\mathbf{k}', \qquad (25)$$

where $f_k{}^0$ is the free-electron Fermi function. The

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[29] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

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second-order contribution to $\psi(t)$ is

$$\psi_2(t) = \sum_{\mathbf{kk}'}|V_{\mathbf{kk}'}|^2(k_\mu-k_\mu')\left[\frac{2}{mn}\left(k_\mu\frac{\partial f_k{}^0}{\partial\varepsilon_k}-k_\mu'\frac{\partial f_{k'}{}^0}{\partial\varepsilon_{k'}}\right)\right.$$

$$\times\int_0^t(t-\tau)d\tau\exp[i\varepsilon_{k'k}\tau]-\frac{2i}{n}\int_0^t dt_1$$

$$\left.\times\exp[i\varepsilon_{k'k}t_1]\left(\frac{\partial}{\partial k_\mu}+\frac{\partial}{\partial k_\mu'}\right)\left(\frac{f_k{}^0-f_{k'}{}^0}{\varepsilon_{kk'}}\right)\right]. \qquad (26)$$

In order to perform the time integrations we must investigate the behavior of the integrands for large time. Taking the Fourier transform of $\exp[\psi(t)]$ for frequencies such that $\omega\tau_c\ll1$ implies we are not concerned with structure occurring over times of order τ_c. The time integrals are done by using the asymptotic formula for large t

$$\int_0^t dt_1\exp[i\varepsilon t_1]\sim iP(1/\varepsilon)+\pi\delta(\varepsilon). \qquad (27)$$

We obtain

$$\psi_2(t) = -(t/\tau)-\delta, \qquad (28)$$

$$\frac{1}{\tau} = -\frac{2\pi}{mn}\sum_{\mathbf{kk}'}|V_{\mathbf{kk}'}|^2(k_\mu-k_\mu')^2\delta(\varepsilon_{k'k})\frac{\partial f_k{}^0}{\partial\varepsilon_k}, \qquad (29)$$

and

$$\delta = \frac{4}{n}\sum_{\mathbf{kk}'}P\frac{1}{\varepsilon_{k'k}}\left[\frac{1}{k^2}\frac{\partial}{\partial k}\left(\frac{\partial f_k{}^0}{\partial\varepsilon_k}|V_{\mathbf{kk}'}|^2kk_\mu(k_\mu-k_\mu')\right)\right.$$

$$\left.-|V_{\mathbf{kk}'}|^2(k_\mu-k_\mu')\frac{\partial}{\partial k_\mu}\left(\frac{f_k{}^0-f_{k'}{}^0}{\varepsilon_{kk'}}\right)\right]. \qquad (30)$$

From Eq. (23) we have for the time-dependent term in third order

$$\psi_3(t) = \frac{2i}{mn}\sum_{\mathbf{kk}'\mathbf{l}}\int_0^t dt_1\int_0^{t_1}dt_2\int_0^{t_2}dt_3\exp[i(t_1-t_2)\varepsilon_{k'k}]$$

$$\times[g(\mathbf{kk'l})\exp[i(t_2-t_3)\varepsilon_{lk}]$$

$$-g(\mathbf{k'kl})\exp[i(t_2-t_3)\varepsilon_{k'l}]],$$

where

$$g(\mathbf{kk'l}) = (k_\mu-k_\mu')V_{\mathbf{k'k}}V_{\mathbf{kl}}V_{\mathbf{lk'}}\left(k_\mu\frac{\partial f_k{}^0}{\partial\varepsilon_k}-l_\mu\frac{\partial f_l{}^0}{\partial\varepsilon_l}\right).$$

Under the assumption that $V_{\mathbf{k'k}}V_{\mathbf{kl}}V_{\mathbf{lk'}}$ is real, a lengthy but straightforward calculation gives

$$\psi_3(t) = -\alpha_3 t, \qquad (31)$$

where

$$\alpha_3 = \frac{4\pi}{mn}\sum_{\mathbf{kk'l}}V_{\mathbf{k'k}}V_{\mathbf{kl}}V_{\mathbf{lk'}}$$

$$\times\delta(\varepsilon_{k'k})\frac{\partial f_k{}^0}{\partial\varepsilon_k}(k_\mu-k_\mu')^2P\frac{1}{\varepsilon_{lk}}. \qquad (32)$$

In higher order, terms appear which increase faster than linearly with time. These terms, however, are of lower order in the volume than those which are linear in time and vanish as we allow the volume of the system to become large provided we take this limit before the limit $t \to \infty$. We shall neglect these terms. From Eq. (22) the conductivity tensor is

$$\sigma_{\mu\mu}{}^0(\omega) = \frac{ne^2}{m} \left\{ \frac{\tau'}{1+i\omega\tau'} \exp(-\delta') \right\} \qquad (33)$$

for small $\omega\tau'$. Here τ' comes from those terms to all orders which are linear in time, and δ' comes from those terms to all orders which are independent of time. It is important to note that the form of Eq. (33) is exact for $\omega\tau' \ll 1$ even though we have only exhibited some of the lowest order terms:

There exists one other treatment of the zero-magnetic-field case to which our results may be compared. Verboven[24] has calculated the static conductivity tensor using Kubo's formula and, instead of the cumulant theorem, a perturbation method due to Van Hove.[26] The two lowest orders of Eq. (33) for $\omega=0$ agree with Verboven's results. The present work also agrees with Verboven's result that the relaxation-time approximation is valid only for the two lowest orders of an expansion of $\sigma_{\mu\mu}{}^0(0)$ in powers of V.

The form of Eq. (33) is not suitable for calculations because of the complicated form of the scatterer average represented by the curly brackets. This is not a serious difficulty because we are dealing with a disordered macroscopic system in which fluctuations can be ignored. Thus in Eq. (23) we may replace all sums over scatterer position by the average of those sums over the scatterer ensemble. From now on we shall assume that this has been done and we shall drop the curly brackets.

C. Derivation of R

We now treat the contribution to R from the magnetic-field dependence of $U_-(t)$. The term to be calculated is, from Eq. (9),

$$\sigma' = -ie^2 \int_0^\infty t\,dt\, \text{Tr}[f,\dot{y}]U_-(t)\dot{x}, \qquad (34)$$

where we have made the same approximations as were made in treating $\sigma_{\mu\mu}{}^0(\omega)$. Since

$$\text{Tr}[f,\dot{y}]\dot{x} = -in\omega_c/m, \qquad (35)$$

we have

$$\sigma' = -(ne^2\omega_c/m)\int_0^\infty t\,dt\langle U_-(t)\rangle, \qquad (36)$$

and

$$\langle U_-(t)\rangle = \text{Tr}[f,\dot{y}]U_-(t)\dot{x}/\text{Tr}[f,\dot{y}]\dot{x} \qquad (37)$$

$$\sigma' = -(ne^2/m)\int_0^\infty \omega_c t\,dt\, \exp[\psi'(t)]. \qquad (38)$$

Here $\psi'(t)$ is the cumulant function for $U_-(t)$ at time t. It differs from Eq. (23) in that $V(t)$ is replaced by

$$V_1(t) = e^{itH_0'}Ve^{-itH_0'}. \qquad (39)$$

H_0' is the one-electron kinetic energy in the presence of the magnetic field. From Eqs. (23), (37), and (39) the general term of $\psi'(t)$ is of the form

$$\text{Tr}[f,\dot{y}]V_1{}^\times(t_n)\cdots V_1{}^\times(t_1)\dot{x}/\text{Tr}[f,\dot{y}]\dot{x}. \qquad (40)$$

The denominator may be treated by Eq. (35) so we need only treat the numerator. Restriction to the H-independent terms of $\psi'(t)$ implies we need only consider the independent and linear H-dependent terms of the numerator. That part of the numerator containing no magnetic-field dependence vanishes because the factors $\dot{x}$ and $\dot{y}$ in the average interfere destructively with each other. The magnetic field appears in the numerator of Eq. (40) in the current operators in f and in $V_1(t)$ through its dependence of H_0'. We choose the gauge $A = A_y = \mathbf{H}x$. Consider the magnetic field dependence coming from the current operators. The result is precisely what we got when dealing with $\sigma_{\mu\mu}{}^0(\omega)$ and these terms may be replaced by $-\delta'-t/\tau'$. The terms containing a magnetic field dependence coming from the $V_1(t)$ are treated as follows. We expand f in powers of V. The zeroth-order term f^0 will appear commuted with p_y, the momentum operator, and the commutator vanishes. In analogy with the treatment of the terms comprising δ', the other contributions are time-independent. The magnetic-field dependence of f is treated similarly by expanding in powers of $V - \omega_c p_y x$ and keeping only terms linear in ω_c. These terms are also time-independent. We denote both of these contributions by η. The lowest order term in η is second order and is given by

$$\eta_2 = (m/n\omega_c)\int_0^t dt_1\, \text{Tr}[f,\dot{y}]_1 V_1{}^\times(t_1)\dot{x},$$

where $\dot{y}$ and $\dot{x}$ are to be considered independent of H. After much labor and arithmetic

$$\eta_2 = -\frac{1}{mn}\sum_{\mathbf{kk'}} P\frac{1}{\varepsilon_{k'k}}(k_x'-k_x)\left[m\frac{f_k{}^0-f_{k'}{}^0}{\varepsilon_{kk'}}\frac{\partial}{\partial k_x'}|V_{\mathbf{kk'}}|^2 \right.$$
$$\left. +2(k_y-k_y')k_y'\frac{\partial}{\partial k_x'}\left(|V_{\mathbf{k'k}}|^2\frac{\partial}{\partial\varepsilon_{k'}}\frac{f_k{}^0-f_{k'}{}^0}{\varepsilon_{kk'}}\right)\right]. \qquad (41)$$

Equation (38) can now be integrated to give

$$\sigma' = (-ne^2/m)(\tau')^2\omega_c\exp[\eta-\delta']. \qquad (42)$$

From Eqs. (1), (9), (33), and (42) we get

$$R/R_0 = \exp[\delta'](1-\exp[\eta]) \approx 1+\delta-\eta_2, \qquad (43)$$

to second order in V.

From Eq. (43) it is easy to see that $R=R_0$ if $\eta=\delta'=0$, and from Eq. (33) and the work just done, this is

precisely the condition that a single relaxation time exists. Since δ and η_2 are at least of order V^2, $R/R_0 = 1$ for the two lowest order terms of an expansion in powers of V. If the expansion converges rapidly we can thus explain the remarkable stability of R/R_0 about unity for many liquid metals. The lowest-order deviation of R/R_0 from unity is given by Eqs. (30), (41), and (43).

III. NUMERICAL CALCULATIONS

For a liquid, $\sigma_{\mu\mu}{}^0(\omega)$ is independent of μ so that $(k_\mu - k_\mu')^2$ may be replaced by $\frac{1}{3}(\mathbf{k} - \mathbf{k}')^2$. Using the assumption of identical spherically symmetric scattering potentials centered on each ion, we may write

$$V(\mathbf{r}) = \sum_j \phi(|\mathbf{r} - \mathbf{r}_j|), \tag{44}$$

$$V_{\mathbf{k}'\mathbf{k}} = \sum_j \int d^3r \, \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]\phi(|\mathbf{r} - \mathbf{r}_j|),$$

$$= \sum_j \phi_{\mathbf{k}'\mathbf{k}} \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}_j]. \tag{45}$$

The quantity τ has been calculated in the limit $T = 0$ for several metals and the results are given in Table II. The pseudopotential matrix elements were obtained from Harrison's work by fitting a three parameter curve $A(|\mathbf{k} - \mathbf{k}'|/k_F)^2 + B|\mathbf{k} - \mathbf{k}'|/k_F + C$ to his graphs. Values of A, B, and C are also given in Table II. The structure factors $a(|\mathbf{k}|)$ were obtained from the work of Gamertsfelder[30] for Zn and from Gingrich and Heaton[31] for the other metals. The data are shown in Figs. 1 and 2. The sensitivity of τ to the pseudopotential was also investigated. Case I corresponds to Harrison's potentials. For Case II we uniformly added 0.01 Ry to Harrison's matrix elements and for Case III we uniformly subtracted 0.01 Ry. The error in Harrison's calculations is probably at least 0.015 Ry. For Zn, Case IV corresponds to Harrison's potential but a completely random liquid, and for Na, Case IV corresponds to a modification of the Harrison potential in which it is everywhere brought closer to zero in the important region by an amount within the probable error of that potential. Values of $\sigma_{\mu\mu}{}^0(0)$ at the melting point and of all the other necessary parameters were
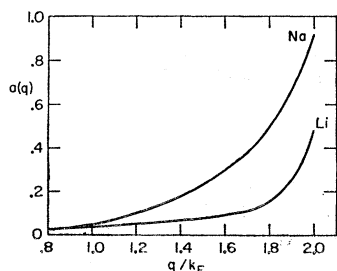

FIG. 1. Experimental curves of $a(q)$ for Li and Na. Data taken from Gingrich and Heaton (Ref. 32).
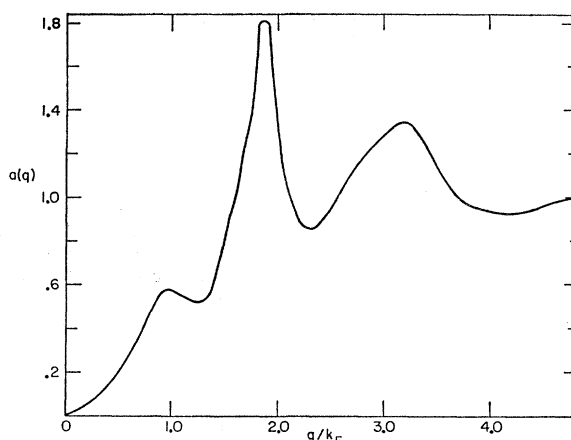

FIG. 2. Experimental curve of $a(q)$ for Zn taken from Gamertsfelder (Ref. 31).

taken from Cusack.[1] We note here that, as assumed in Sec. II, the calculated values of τ are all 10^{-15}–10^{-16} sec. Further discussion of these results is deferred till a later time.

It is possible to include the third-order contribution to the relaxation time given by Eq. (32). This requires a knowledge of the pseudopotential matrix elements $V_{\mathbf{k}\mathbf{k}'}$ for one of $\mathbf{k}$ and $\mathbf{k}'$ on the Fermi surface and one off, which is available only for Zn. From Eq. (33)

$$\tau' \approx \tau[1 - \alpha_3\tau], \tag{46}$$

for the two lowest order contributions.

A calculation of α_3 requires the three particle distribution function, and this is not known. However, use of the Kirkwood superposition approximation[32] allows us to express this in terms of two-particle functions. Defining

$$q = |\mathbf{k} - \mathbf{k}'|, \quad q' = |\mathbf{k} - \mathbf{l}|, \quad q'' = |\mathbf{k}' - \mathbf{l}|, \tag{47}$$

TABLE II. Lowest-order calculated values for τ, for Li, Na, and Zn. A, B, and C are coefficients of a three-parameter curve $Ax^2 + Bx + C$ fitted to Harrison's pseudopotential matrix elements. Li I corresponds to Li, Case I, and similarly for the other entries. The experimental values of τ are obtained from the dc conductivity measurements assuming the free-electron charge, mass, and density.

	A	B	C	$\tau \times 10^{15}$ (theory)	$\tau \times 10^{15}$ (exptl.)
Li I	0.038	0.087	−0.262	2.22	3.54
Li II	0.038	0.087	−0.252	1.48	
Li III	0.038	0.087	−0.272	1.91	
Na I	0.016	0.062	−0.188	4.86	15.2
Na II	0.016	0.062	−0.178	7.47	
Na III	0.016	0.062	−0.198	3.18	
Na IV	−0.040	0.220	−0.280	9.53	
Zn I	−0.035	0.343	−0.472	0.785	0.74
Zn II	−0.035	0.343	−0.462	0.715	
Zn III	−0.035	0.343	−0.482	0.816	
Zn IV	−0.035	0.343	−0.472	0.524	

[30] C. Gamertsfelder, J. Chem. Phys. 9, 450 (1941).
[31] N. S. Gingrich and L. Heaton, J. Chem. Phys. 34, 873 (1961).

[32] T. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956).
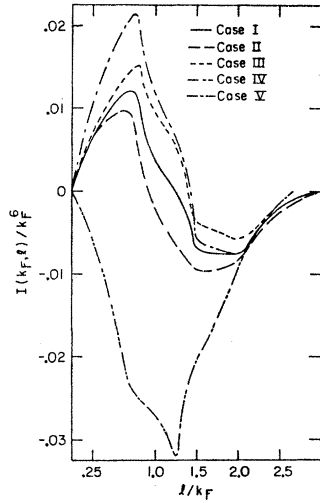
FIG. 3. Calculated values of $I(k_F,l)/k_F{}^6$ as a function of l/k_F for Zn used in evaluating Eq. (51). Curve I corresponds to Case I, etc.

TABLE IV. Theoretical values of τ' for Zn using the two lowest-order terms in the expansion. Zn I corresponds to use of Harrison's potential, Zn II to Harrison's potential matrix elements plus 0.01 Ry and Zn III to Harrison's potential matrix elements minus 0.01 Ry. Zn IV and Zn V refer to approximations made to the order in the liquid, and both use Harrison's potential.

	$\tau \times 10^{15}$ (theory)	$\alpha_3 \tau$	$\tau \times 10^{15}$ (theory)	τ' (exptl.)
Zn I	0.785	0.567	0.34	0.74×10^{-15}
Zn II	0.715	0.549	0.32	
Zn III	0.816	0.585	0.34	
Zn IV	0.524	0.130	0.46	
Zn V	0.785	0.838	0.13	

we get from Eqs. (32) and (45)

$$\alpha_3 = \frac{8m^2}{3k_F n N^2 (2\pi)^6} \int_0^\infty \frac{l}{k_F+l} P \frac{1}{k_F-l} I(k_F,l) \quad (48)$$

$$I(k_F,l) = N^3 \int_0^{2\pi} d\varphi \int_0^{2k_F} dq \int_{|k_F-l|}^{k_F+l} dq' q^3 q' \phi_{k''k} \phi_{kl} \phi_{lk''}$$

$$\times \left[1 + G(q) + G(q') + G(q'') + \frac{1}{(2\pi)^3 N} \right.$$

$$\left. \times \int d^3p \, G(p) G(|p+k-k''|) G(|p+k-l|) \right], \quad (49)$$

where $G(q) = a(q) - 1$ and $a(k) = (1/N) \sum_{ij} \{\exp[ik \cdot (r_i - r_j)]\}$ is the function obtained from x-ray scattering experiments and is related to the Fourier transform of the two-particle distribution function. N is the ion density. In Eq. (49), φ is the azimuthal angle of l measured relative to the plane of k and k', where k is the polar axis, and $k'' = k\hat{k}'$. In obtaining Eq. (49) it was assumed that ϕ_{kk} is independent of k. A numerical

TABLE III. Values of A, B, C needed to fit V_{kl} to Harrison's potential when k is on the Fermi surface and l is not. A, B, and C are coefficients of a three-parameter curve $Ax^2 + Bx + C$ fitted to Harrison's pseudopotential matrix elements. Values are for Zn.

l/k_F	A	B	C
0.25	−0.125	0.425	−0.465
0.50	−0.010	0.355	−0.510
0.75	−0.058	0.439	−0.546
1.00	−0.035	0.343	−0.472
1.25	−0.077	0.463	−0.571
1.50	−0.146	0.673	−0.690
1.75	−0.120	0.600	−0.682
2.0	−0.103	0.545	−0.659
2.5	−0.047	0.282	−0.407

calculation of Eq. (49) is quite lengthy, even by electronic computer. Further, it turns out that the expansion in powers of the pseudopotential converges quite slowly for Zn so it is not of much use to do the best possible calculation for α_3 unless we can also calculate higher terms, which is not yet possible. It should be noted that the use of Harrison's work for a calculation of the third-order term is somewhat dubious since his potential is not Hermitian when one of the wave vectors in $V_{kk'}$ is off the Fermi surface. This may lead to a considerable percentage error. Therefore, Eq. (49) was itself approximated. Five cases were calculated. Zn I, Zn II, and Zn III, already mentioned, were calculated with the additional approximation that in Eq. (49) we set

$$[1/(2\pi)^3 N] \int d^3p G(p) G(|p+k-k''|) G(|p+k-l|)$$

$$= \tfrac{1}{3}[G(q)G(q') + G(q)G(q'') + G(q')G(q'')]. \quad (50)$$

Zn IV corresponds to the use of the Harrison pseudopotential with a completely random liquid, $G(q) = N\delta(q)$. ZnV corresponds to the same pseudopotential with neglect of the product of three distribution functions in Eq. (49). This last is the simplest case containing order. The method of calculation used is as before. A three-parameter curve was fitted to Harrison's potential for values of $l/k_F = 0.25$, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, and 2.50. Values of A, B, and C obtained are given in Table III. $I(k_F,l)$ was then calculated on a computer for all five cases. The results of these calculations are given in Fig. 3 for the potential matrix elements in Ry. Equation (48) was then evaluated numerically and τ' obtained from Eq. (46). The results are given in Table IV.

A. Li and Na

The theoretical results for τ for these metals are quite poor when Harrison's potential is used. This is very disturbing as one would expect a perturbation procedure to give its best value for Na. The difficulty appears to reside with the pseudopotential and the measured values of $a(q)$. For Na IV, $V_{kk'}$ at $q = 2k_F$ was

assumed zero, and the values of $V_{kk'}$ for $q=k_F$ and $q=1.5k_F$ were reduced 0.01 Ry from Harrison's values, which are likely to be inaccurate by at least this amount. The result is a very much better, but still not good, value for τ. Another source of appreciable error for these metals is the measured values of $a(q)$. For the alkali metals $q=2k_F$ comes before the main peak in $a(q)$, and the values of this function for small q are proportionately more important. The error in measurement, however, is greatest at small q. For Na the main contribution to τ comes from values of q/k_F less than 1.6. In this region, $a(q)$ is less than 0.3 in Na, compared to unity for the random case, and a uniform decrease of only 0.05 in $a(q)$ from $q/k_F=1.0$ to $q/k_F=1.6$ would be sufficient to raise the value of τ for Na to the experimental value. Thus a slight change in both $V_{kk'}$ and $a(q)$ is more than sufficient to bring the results for Na into line with experiment. The same is true for Li.

B. Zn

The case of Zn is very different. Table II shows that a change of 0.01 Ry makes comparatively little difference in τ. Thus, while the pseudopotential may again be too large or too small, it does not matter so much when only second-order contributions to τ' are considered. These results for τ are quite good and are uniformly near the experimental value. The measured values of $a(q)$ are not likely to give much trouble since $q=2k_F$ is beyond the main peak as seen in Fig. 2. However, inclusion of third-order terms in τ' completely destroys the good agreement with experiment. If one assumes that the method used here is correct, this can only mean that the perturbation expansion for τ' is converging very slowly for Zn.

It is conceivable that use of the correct three-body distribution function would improve the results for τ'. We do not know this three-body function, and the best we can do is the Kirkwood superposition approximation. The difference between the Kirkwood approximation and Zn I should be less than the difference between Zn I and Zn V. If use of the Kirkwood approximation were to bring τ' to the experimental value, it would imply a very great dependence of the details of order in the liquid, a dependence so great that the difference between the exact order and the Kirkwood approximation might well be enough to destroy again any numerical agreement. If no change in the approximation to the order will suffice, we are left with the previous conclusion as to the rate of convergence of the power series. This justifies the approximation to the order made in calculating $I(k_F,l)$.

Perhaps the trouble lies in the use of Harrison's potential which is, after all, not Hermitian. This is conceivable but highly unlikely because Harrison's work was done in such a manner as to minimize $V_{kk'}$. Restriction to Hermitian pseudopotentials would then increase $V_{kk'}$ making the situation worse.

The reason for this poor convergence is not hard to find. In order that the expansion of τ' converge well, it is necessary that the scattering potential be small. It is precisely here that the pseudopotential is so valuable since it contains a term which cancels part of the real potential. Further, it is possible to adjust various parameters in the pseudopotential to obtain optimum cancellation of the real potential subject to certain conditions, such as hermiticity, which one may impose. However, Harrison's calculations[21] shows that the plane-wave pseudopotential matrix elements are not small compared to the Fermi energy for small momentum transfers. This gives no trouble in second order since the pseudopotential only appears in integrals which are heavily weighted to large momentum transfer. As we can see from Eq. (49), calculation of the higher-order contributions destroys this weighting. In these terms collisions of small momentum transfer may contribute an appreciable part of the entire term, leading, for the higher orders, to larger magnitudes than one would expect on the basis of the excellent agreement of second-order terms with experiment. This is quite unexpected. Previous calculations of the transport properties of liquid metals were confined to lowest order terms of an expansion in powers of the pseudopotential. The excellent agreement with experiment made it appear as if a suitable expansion parameter had been found to explain the nearly free-electron properties of liquid metals. Our calculation of the higher order term for Zn contradicts this conclusion. Convergence of the series for Zn is so slow that one must seriously question the usefulness of the small-pseudopotential approximation for the transport properties of liquid metals.

C. The Hall Constant

It is evident from Eq. (41) that R depends on the derivative of the pseudopotential matrix elements for arbitrary $\mathbf{k}$ and $\mathbf{k}'$. These matrix elements are known only for either or both of k and k' equal to k_F. Ordinarily one would make the momentum-independent pseudopotential approximation but in this case the momentum dependence of the pseudopotential may be quite important. In the absence of a more complete knowledge of V, any calculation of R would be very unreliable. If, by chance, a particular model were to give good second-order results for R/R_0 it would mean little. As we saw in the case of τ', a good second-order result is misleading when the matrix elements $V_{kk'}$ for small $|\mathbf{k}-\mathbf{k}'|$ are important in higher order terms. This is so for R/R_0. While no higher order terms have been obtained, it is plain that they would not contain the weighting to large $|\mathbf{k}-\mathbf{k}'|$ which is present in second order.

We may, then, expect that a second-order calculation of R/R_0, using the correct nonlocal potential, would give good results but that the inclusion of higher order terms would spoil the agreement with experiment. In

this case also, it does not appear possible to obtain a rapidly convergent expansion in powers of the potential and no numerical calculations were done.

The basic difficulty is as before. For small $|\mathbf{k}-\mathbf{k}'|$, $V_{\mathbf{k}\mathbf{k}'}$ is not small compared to ε_F. Unless this region of phase space is unimportant, the perturbation expansion must fail. The way out was suggested by Edwards.[22] He showed that one could sum a certain class of diagrams to all orders in V, thus introducing a complex energy. The imaginary part is related to the lifetime of the state. What we must do in the present case is to sum cumulants to all orders. However, choosing the correct cumulant to sum is a difficult problem and it might be necessary to sum just certain contributions to each moment in each cumulant rather than the cumulants themselves. Such a procedure would lead to an expansion in powers of the density in which the T matrix, rather than V, would appear. The expansion would be expected to converge well when the overlap of potentials from two neighboring scatterers is small. This is expected to hold for many simple metals.

IV. CONCLUSIONS

The results of our calculation are somewhat surprising. Lowest order terms in an expansion of $\sigma_{\mu\mu}{}^0(\omega)$ in the pseudopotential agree very well with experiment, and it would thus appear that a suitable expansion parameter has been found to explain the nearly free-electron properties of liquid metals. But calculation of the higher-order terms shows this to be illusory. Convergence of such an expansion is so slow in the case of Zn that one must seriously question the usefulness of the small-pseudopotential approximation for the transport properties of liquid metals.

Optical experiments show that the relaxation-time approximation should be very good for many liquid metals. Thus while the convergence of the power-series expansion for τ' is slow, the total contribution of higher-order terms is quite small. Our trouble arises because of the particular expansion used. The most urgent task, then, is to recast the theory of the transport properties of liquid metals into a form which eliminated the convergence problem. What is most probably necessary is to identify those parts of the cumulants to all orders which may be summed to give a result which is essentially independent of small angle scattering.

Further, if the pseudopotential is not a good expansion parameter for the transport properties of liquid metals, are there any other cases where its use gives an illusory agreement with experiment? It would be worthwhile to have a better pseudopotential calculation for several liquid metals so that this point could be checked.

APPENDIX A

The conductivity tensor is

$$\sigma_{xy}(0) = -i \int_0^\infty t dt \{\mathrm{Tr}\rho[J_y, J_x(t)]\}. \quad (A1)$$

We make the transformations

$$2J_1 = J_x + iJ_y, \quad 2J_2 = J_x - iJ_y, \quad J_3 = J_z. \quad (A2)$$

The new current operators obey the commutation relations

$$[J_1, J_2] = (e^2/2m)\omega_c,$$
$$[J_1, J_3] = [J_2, J_3] = 0, \quad (A3)$$

From Eq. (7) we can easily see

$$\begin{aligned}J_x(t) &= U_-(t)J_x{}^0(t)\\ &= U_-(t)[J_1 \exp(-i\omega_c t) + J_2 \exp(i\omega_c t)]\\ &= U_-(t)[J_x \cos\omega_c t + J_y \sin\omega_c t], \quad (A4)\end{aligned}$$

where

$$J_x{}^0(t) = \exp[i\mathcal{H}_0't]J_x \exp[-i\mathcal{H}_0't],$$

is the unperturbed motion of J_x.