Nonetheless, the over-all qualitative picture suggests that there is no particular mystery in understanding the properties we calculate in terms of the theory we use. We are, therefore, generally encouraged by the results of these calculations. We hope that our form factors will prove useful in future studies on the noble metals. With the computed form factors it may now be possible to do systematic quantitative calculations of the electronic properties of these metals just as has been done for the simple metals.

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Electronic Properties of Liquid Metals*

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It is shown that an approximation for the n-body ionic correlation permits the generalization of nearly free-electron formulas for some of the electronic properties of liquid metals. The electrical resistivity is considered in detail and it is shown that a result identical in form to that due to Ziman can be obtained, but in terms of an effective potential involving both the electron-ion potential and the static structure factor. Some further assumptions are necessary for this effective potential to be approximately evaluated. The numerical work strongly indicates that the effective potential differs little from the commonly used pseudopotentials. Finally, generalized expressions are obtained for the electrical resistivity and Knight shift for liquid metal alloys.

I. INTRODUCTION

THIS work is concerned with an extension of the nearly free-electron model for the electronic properties of liquid metals. The specific property we discuss is the electrical resistivity, ρ. The well-known Ziman formula for ρ is the lowest-order result and yields[1]

$$\rho=\frac{m^2}{12Ze^2n_e\hbar^3\pi^3}\Omega^2\int_0^{2k_F}q^3dq\,S(q)\,|\langle\mathbf{k}|v|\mathbf{k}+\mathbf{q}\rangle|^2, \quad (1)$$

where n_e is the number density of electrons, Z is the nominal valence, k_F is the Fermi wavevector, and Ω is the total volume of the system. In (1) it is understood that

$$|\mathbf{k}|=|\mathbf{k}+\mathbf{q}|=k_F \quad (2)$$

and

$$n_e/Z=n_i=\text{density of ions}=N/\Omega. \quad (3)$$

The potential matrix element is defined by

$$\Omega\langle\mathbf{k}|v|\mathbf{k}'\rangle=v(\mathbf{k}-\mathbf{k}')=\int d\mathbf{r}\,e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}v(r), \quad (4)$$

where v is a pseudopotential describing the interaction between an electron and a single self-consistently screened ion. $S(q)$ represents the liquid structure factor and is defined by

$$S(q)=1/N\ll\rho_{\mathbf{q}}\rho_{-\mathbf{q}}\gg-N\delta_{\mathbf{q},0}, \quad (5)$$

with

$$\rho_{\mathbf{q}}=\sum_{i=1}^{N}e^{-i\mathbf{q}\cdot\mathbf{R}_i}, \quad (6)$$

where $\mathbf{R}_i$ gives the instantaneous position of the ith ion. In (5) the brackets denote an ensemble average over ionic configurations. The liquid structure factor $S(q)$ is readily obtained from either x-ray or neutron-diffraction experiments or may be sufficiently well represented by the hard-core structure factor for a suitable choice of parameters.[2]

The derivation of (1) may be made clear if we rewrite the result as

$$\rho=m/n_ee^2\tau, \quad (7)$$

with

$$\frac{1}{\tau}=\left\langle\left\langle\frac{2\pi}{\hbar}\frac{1}{\Omega}\int\frac{d\mathbf{k}'}{(2\pi)^3}|v(\mathbf{k}-\mathbf{k}')\rho_{\mathbf{k}-\mathbf{k}'}|^2\times(1-\cos\theta_{\mathbf{k},\mathbf{k}'})\delta(E_F-E_{k'})\right\rangle\right\rangle, \quad (8)$$

where

$$E_{k'}=\hbar^2k'^2/2m, \quad (9)$$

and

$$E_F=\hbar^2k_F^2/2m.$$

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[1] J. M. Ziman, Phil. Mag. 6, 1013 (1961).
[2] N. W. Ashcroft and J. Lekner, Phys. Rev. 145, 83 (1966).

Equation (1) therefore represents (within the context of the adiabatic approximation) the ensemble average of the resistivity calculated in Born approximation for elastic scattering from each configuration of the ions.

Since its introduction in 1961, the Ziman formula has been found to be in reasonable agreement with both the magnitude and temperature dependence of the resistivity of pure liquid metals. Its extension to liquid metal alloys has also been successful.[3] The formula has, in fact, become the working model of the field in that most experimental data is interpreted in terms of the parameters of (1); viz., v, S, and k_F.

Recently, however, some attempts have been made to obtain higher-order corrections to (1).[4,5] These efforts have encountered severe difficulties, principal among which is the lack of knowledge of the n-body ionic correlation functions. Only the two-body ionic correlation, which is essentially the liquid structure factor, is reasonably well known. Furthermore, even if an approximation for the three-body and higher ionic correlation functions is made one usually encounters intractable multidimensional integrals in the expression for ρ. Finally, even with approximate evaluation of the integrals, one finds that the "Born series" is not converging rapidly, and hence any conclusions drawn concerning the validity of the lowest-order result, Eq. (1), are dubious.

Our effort has been directed towards making a consistent approximation for the n-body ionic correlation, summing the relevant perturbation series to infinite order, and casting the result in an expression identical in form to the Ziman formula. It is clear from what follows that our approximation still neglects a large number of terms whose contribution to the transport coefficients is difficult to assess. The analysis does, however, include a substantial set of terms previously unaccounted for in low-order calculations, and thus may be simply regarded as a step in the direction of obtaining a complete theory of transport in liquid metals. Alternatively, the formalism presented below may be viewed as a theory of transport of a "model" liquid metal whose physical structure is given to all orders of the correlation functions by the approximation introduced in Sec. II.

In Sec. II we outline the ionic correlation approximation and its consequences on the form of the resistivity ρ. In Sec. III we present the details of the calculation of the effective-scattering function appearing in the generalized Ziman formula for ρ. The numerical considerations are presented in Sec. IV, and the extensions of our method to alloys are given in Sec. V. We conclude with a brief application of our method to the Knight shift (Sec. VI) which leads to a formula reminiscent of the expression due to Faber.

II. DERIVATION OF RESISTIVITY

In a recent paper Rubio[6] has obtained a nonperturbative evaluation of the resistivity from a derivation based on the Greenwood formula.[7] We consider his expression evaluated at zero temperature and to lowest order in the small parameter of the nearly free-electron theory, $(k_F l)^{-1}$, where l is the mean free path of an electron at the Fermi surface. The meaning of the $(k_F l)^{-1}$ expansion is this: We view the electrons as independent particles weakly perturbed by the *linear superposition of potentials* of the self-consistently screened ions. Note that this does not regard the individual single-site potentials themselves as being weak in the usual sense that an expansion in "v" is appropriate. Rather, it is only necessary to assume that the total scattering effect (i.e., including correlation) is slight. To lowest order in $(k_F l)^{-1}$, Rubio's formula then reduces to

$$\rho=\frac{m}{n_e e^2}\frac{2\pi}{\hbar}\int\frac{d\mathbf{k}'}{(2\pi)^3}W(E_F,\mathbf{k},\mathbf{k}')\times(1-\cos\theta_{\mathbf{k},\mathbf{k}'})\delta(E_F-E_{k'}), \quad (10)$$

where

$$\mathbf{k}=\hat{z}k_F. \quad (11)$$

[*Note added in proof.* Dr. L. Ballentine has informed us that Rubio's result for ρ is, in fact, only correct to this order.] Thus we are led to seek an evaluation of the quantity $W(E_F,\mathbf{k},\mathbf{k}')$, which in simple Born approximation reduces to $\Omega^2 n_i S(\mathbf{k}-\mathbf{k}')\,|\langle\mathbf{k}|v|\mathbf{k}'\rangle|^2$. By applying the theorems developed by Taylor,[8] it follows that the analysis of Van Hove[9] may be used directly. This analysis yields the result that[9]

$$W(E_F,\mathbf{k},\mathbf{k}')=\Omega\sum_{n=0,m=0}^{\infty}\langle\langle[\langle\mathbf{k}|V(G^+V)^n|\mathbf{k}'\rangle\times\langle\mathbf{k}'|(VG^-)^mV|\mathbf{k}\rangle]_{\text{i.d.}}\rangle\rangle, \quad (12)$$

where

$$\langle\mathbf{k}|G^\pm|\mathbf{k}'\rangle=\left\langle\left\langle\left[\langle\mathbf{k}|\frac{1}{\mu-H\pm i\epsilon}|\mathbf{k}'\rangle\right]\right\rangle\right\rangle, \quad \epsilon=0^+ \quad (13)$$

$$=\delta_{\mathbf{k},\mathbf{k}'}G^\pm(k),$$

$$G^\pm(k)=[\mu-E_k-\Delta(k)\pm i\Gamma(k)]^{-1}. \quad (14)$$

The chemical potential μ is defined by

$$\mu=E_F+\Delta(k_F), \quad (15)$$

and the self-energy evaluated at the Fermi surface,

[3] N. W. Ashcroft and D. C. Langreth, Phys. Rev. **159**, 500 (1967).
[4] B. Springer, Phys. Rev. **154**, 621 (1967).
[5] T. Neal, thesis, Carnegie Institute of Technology, 1967 (unpublished).
[6] J. Rubio, J. Phys. C **2**, 288 (1969).
[7] D. Greenwood, Proc. Phys. Soc. (London) **73**, 745 (1959).
[8] A. W. B. Taylor, Physica **32**, 2030 (1966).
[9] L. Van Hove, Physica **21**, 905 (1955); **23**, 441 (1957).

$\Sigma^{\pm}(k)$, is given by the relation

$$\Sigma^{\pm}(k)=\Delta(k)\mp i\Gamma(k) \quad (\Delta,\Gamma \text{ real}). \tag{16}$$

In Eq. (13)

$$H(\mathbf{r})=-(\hbar^2/2m)\nabla^2+V(\mathbf{r}) \tag{17}$$

and

$$V(\mathbf{r})=\sum_{i=1}^{N} v(\mathbf{r}-\mathbf{R}_i). \tag{18}$$

The potential v describes the same interaction as before but in order that the eigenfunctions of H carry the true current it is not assumed to be a pseudopotential. It is, however, assumed to be local, Hermitian, spherically symmetric, and normalized so that

$$n_i\int d\mathbf{r}\, v(r)=-\tfrac{2}{3}E_F. \tag{19}$$

To explain the meaning of "i.d." in Eq. (12) which stands for "irreducible diagonal," we introduce the identity

$$\Omega\langle\mathbf{k}|V|\mathbf{k}'\rangle=v(\mathbf{k}-\mathbf{k}')\rho_{\mathbf{k}-\mathbf{k}'}. \tag{20}$$

Then a typical term in the expression for $W(E_F,\mathbf{k},\mathbf{k}')$ is

$$\frac{1}{\Omega^4}\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}\{[v(\mathbf{k}-\mathbf{k}_1)G^+(k_1)v(\mathbf{k}_1-\mathbf{k}_2) \times G^+(k_2)v(\mathbf{k}_2-\mathbf{k}')v(\mathbf{k}'-\mathbf{k}_3)(G^-(k_3)v(\mathbf{k}_3-\mathbf{k})] \times\langle\langle\rho_{\mathbf{k}-\mathbf{k}_1}\rho_{\mathbf{k}_1-\mathbf{k}_2}\rho_{\mathbf{k}_2-\mathbf{k}'}\rho_{\mathbf{k}'-\mathbf{k}_3}\rho_{\mathbf{k}_3-\mathbf{k}}\rangle\rangle\}_{\text{i.d.}}, \tag{21}$$

and the "i.d." demands that we are to retain only those contributions that arise when *all* the momenta, $\mathbf{k}$, $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}'$, $\mathbf{k}_3$, are distinct.

In the notation we have now defined we may give an alternative statement of the specific approximation made to obtain Eq. (10). It is the replacement

$$\frac{\hbar^2}{2m}\frac{2}{\pi}\frac{\Gamma(k)k}{[\mu-E_k-\Delta(k)]^2+\Gamma^2(k)}\to\delta(k-k_F)+O\left(\frac{\Gamma}{E_F}\right),$$

where

$$\Gamma/E_F=1/k_Fl,$$

and l is the mean free path which (as mentioned above) incorporates the effect of scattering from the linear superposition of potentials.

At this point we introduce our approximation for the ionic correlation. For the particular term appearing in (21) we write, for example,

$$\begin{aligned}&\frac{1}{N}\{\langle\langle\rho_{\mathbf{k}-\mathbf{k}_1}\rho_{\mathbf{k}_1-\mathbf{k}_2}\rho_{\mathbf{k}_2-\mathbf{k}'}\rho_{\mathbf{k}'-\mathbf{k}_3}\rho_{\mathbf{k}_3-\mathbf{k}}\rangle\rangle\}_{\text{i.d.}}\\ &=\left\{\frac{1}{N}\langle\langle\rho_{\mathbf{k}-\mathbf{k}_1}\rho_{\mathbf{k}_1-\mathbf{k}}\rangle\rangle\frac{1}{N}\langle\langle\rho_{\mathbf{k}-\mathbf{k}_2}\rho_{\mathbf{k}_2-\mathbf{k}}\rangle\rangle \times\frac{1}{N}\langle\langle\rho_{\mathbf{k}-\mathbf{k}'}\rho_{\mathbf{k}'-\mathbf{k}}\rangle\rangle\frac{1}{N}\langle\langle\rho_{\mathbf{k}-\mathbf{k}_3}\rho_{\mathbf{k}_3-\mathbf{k}}\rangle\rangle\right\}_{\text{i.d.}}\\ &=S(\mathbf{k}-\mathbf{k}_1)S(\mathbf{k}-\mathbf{k}_2)S(\mathbf{k}-\mathbf{k}')S(\mathbf{k}-\mathbf{k}_3).\end{aligned} \tag{22}$$

As discussed by Ballentine and Heine[10] such a "geometric approximation"[11] is based on the neglect of fluctuations from the mean. It permits us to correctly describe scattering by pairs of ions while approximating the effects of larger clusters by treating them in an averaged sense, as outlined in detail in Ref. 10. The approximation has destroyed the symmetry of the expression on the left-hand side of Eq. (22): It is clearly unchanged under the transformation

$$\mathbf{k}\to\mathbf{k}_1\to\mathbf{k}_2\to\mathbf{k}'\to\mathbf{k}_3\to\mathbf{k},$$

while the right-hand side does not possess this property. The approximation, however, has been made in such a manner as to direct the asymmetry onto the particular vector $\mathbf{k}$, which is the dominant vector in the expression. Finally, we note that a straightforward application of this correlation approximation when applied to the calculation of the self-energy yields a result consistent with the generalized optical theorem discussed by Rubio.[6] This analysis is presented in Appendix A.

Substitution of the ionic correlation approximation in the term considered above gives

$$\Omega^2 n_i\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}\frac{1}{\Omega^5}[v(\mathbf{k}-\mathbf{k}_1)S(\mathbf{k}-\mathbf{k}_1)G^+(k_1)v(\mathbf{k}_1-\mathbf{k}_2) \times S(\mathbf{k}-\mathbf{k}_2)G^+(k_2)v(\mathbf{k}_2-\mathbf{k}')]S(\mathbf{k}-\mathbf{k}') \times[v(\mathbf{k}'-\mathbf{k}_3)S(\mathbf{k}-\mathbf{k}_3)G^-(k_3)v(\mathbf{k}_3-\mathbf{k})], \tag{23}$$

where we note that since $S(0)$ is finite the restriction imposed by i.d. may now be discarded.

If an entirely similar approximation is made in *each* of the other terms contributing to $W(E_F,\mathbf{k},\mathbf{k}')$, we find that the result may be readily summed to give

$$W(E_F,\mathbf{k},\mathbf{k}')=n_i\Omega^2\langle\mathbf{k}|\nu|\mathbf{k}'\rangle S(\mathbf{k}-\mathbf{k}')\langle\mathbf{k}'|\nu^\dagger|\mathbf{k}\rangle, \tag{24}$$

with

$$\begin{aligned}&\langle\mathbf{k}|\nu|\mathbf{k}'\rangle\\ &=\langle\mathbf{k}|\left\{v+v\left[\sum_{\mathbf{k}_1}|\mathbf{k}_1\rangle\frac{S(\mathbf{k}-\mathbf{k}_1)}{\mu-E_{k_1}-\Sigma^+(k_1)}\langle\mathbf{k}_1|\right]v+\cdots\right\}|\mathbf{k}'\rangle\\ &=\langle\mathbf{k}|\left\{v+\nu\left[\sum_{1\mathbf{k}}|\mathbf{k}_1\rangle\frac{S(\mathbf{k}-\mathbf{k}_1)}{\mu-E_{k_1}-\Sigma^+(k_1)}\langle\mathbf{k}_1|\right]v\right\}|\mathbf{k}'\rangle.\end{aligned} \tag{25}$$

As a consequence the resistivity is now given by

$$\rho=\frac{m^2}{12Ze^2n_e\hbar^3\pi^3\Omega^2}\int_0^{2k_F}q^3dq\,S(q)\,|\langle\mathbf{k}|\nu|\mathbf{k}+\mathbf{q}\rangle|^2. \tag{26}$$

[10] L. E. Ballentine and V. Heine, Phil. Mag. 9, 617 (1964).

[11] The terminology is based on the work of J. L. Beeby and S. F. Edwards, Proc. Roy. Soc. (London) **A274**, 395 (1963); J. L. Beeby, Proc. Roy. Soc. (London) **A279**, 82 (1964). Their approximation was made without the "i.d." restriction. The approximation is also related to the "chain approximation" of F. Cyrot-Lackmann, Advan. Phys. **16**, 393 (1967); see also J. L. Beeby and J. Hubbard, J. Phys. C **2**, 556 (1969), for some discussion of the physical significance and further applications of this approximation.

This equation is identical in *form* to that obtained by Ziman in Born approximation, with the replacement $v \rightarrow \nu$. As indicated above, within the proviso that Eq. (26) is based on an approximation for the ionic structure, one can begin to understand the considerable qualitative success of the Ziman formula.

III. EVALUATION OF ν

We now seek to evaluate ν. As is shown below, the assumption that the electron-ion potentials do *not* overlap for any configuration of the ions renders separable the integral Eq. (25) for ν. This "muffin-tin" approximation, though reasonably well satisfied in a solid metal, is conceptually rather ambiguous for liquid metals. Although the approximation has been used widely in connection with liquids, it is clear that by choosing a fixed "muffin-tin zero" one tends to end up with the spherically symmetric parts of the potentials being confined to spherical regions whose radii fluctuate from site to site. Arguments in support of the approximation for disordered systems have been given by Beeby.[12] We view its use here as a necessary evil in order to effect an estimate of ν, and as we see in Sec. IV, it is important in checking the optical theorem to verify that the single-site potentials are strictly of the muffin-tin type at all stages.

To simplify the calculation we assume that $\Gamma(k)$ is arbitrarily small and independent of k:

$$\Gamma(k)=\epsilon, \quad E_F \gg \epsilon > 0. \tag{27}$$

We also assume that $\Delta(k)$ is independent of k:

$$\Delta(k)=\Delta. \tag{28}$$

(With these approximations we are limiting ourselves to a self-consistent check of the nearly free-electron model.)

The equation defining ν now becomes

$$\langle \mathbf{k}|\nu|\mathbf{k}'\rangle = \langle \mathbf{k}| \left\{ v + v\left[\sum_{\mathbf{k}_1} |\mathbf{k}_1\rangle \frac{S(\mathbf{k}-\mathbf{k}_1)}{\mu - E_{k_1} - \Delta + i\epsilon} \langle \mathbf{k}_1| \right] v + \cdots \right\} |\mathbf{k}'\rangle, \tag{29}$$

which may be rearranged to give

$$\langle \mathbf{k}|\nu|\mathbf{k}'\rangle = \langle \mathbf{k}| \left\{ t + t\left[\sum_{\mathbf{k}_1} |\mathbf{k}_1\rangle \frac{S(\mathbf{k}-\mathbf{k}_1)-1}{\mu - E_{k_1} - \Delta + i\epsilon} \langle \mathbf{k}_1| \right] t + \cdots \right\} |\mathbf{k}'\rangle, \tag{30}$$

where we have introduced the t matrix at the energy $E_F=\mu-\Delta$:

$$t = v + v\left[\sum_{\mathbf{k}_1} |\mathbf{k}_1\rangle \frac{1}{\mu - E_{k_1} - \Delta + i\epsilon} \langle \mathbf{k}_1| \right] t. \tag{31}$$

[12] J. L. Beeby, Proc. Roy. Soc. (London) **A279**, 82 (1964).

In real space

$$\langle \mathbf{x}|t|\mathbf{y}\rangle = \sum_L t_l(x,y) Y_L(\hat{\mathbf{x}}) Y_L^*(\hat{\mathbf{y}}), \tag{32}$$

where the Y's are spherical harmonics and L is a combined index for both the orbital quantum number l and the magnetic quantum number m. Using the Rayleigh expansion

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_L (i)^l j_l(kr) Y_L(\hat{\mathbf{k}}) Y_L^*(\hat{\mathbf{r}}),$$

where the j_l's are spherical Bessel functions,[13] we may determine the matrix elements of t in momentum space:

$$\Omega \langle \mathbf{k}|t|\mathbf{k}'\rangle = (4\pi)^2 \sum_l t_l(k,k') Y_L(\hat{\mathbf{k}}) Y_L^*(\hat{\mathbf{k}}'), \tag{33}$$

with

$$t_l(k,k') = \int_0^\infty x^2 dx \int_0^\infty y^2 dy\, j_l(kx) j_l(k'y) t_l(x,y). \tag{34}$$

If $|\mathbf{k}| = |\mathbf{k}'| = k_F$, comparison with the standard expression yields[14]

$$t_l(k_F,k_F) = -(\hbar^2/2mk_F) e^{i\delta_l} \sin\delta_l, \tag{35}$$

where the phase shifts, δ_l, are evaluated at the Fermi energy E_F.

Applying an analysis similar to that of Beeby[12] we find (see Appendix B)

$$\langle \mathbf{k}|\nu|\mathbf{k}'\rangle = \frac{2\pi\hbar^2}{mk_F} \frac{1}{\Omega} \sum_{l_1,l_2} 4\pi Y_{l_1,0}(\hat{\mathbf{k}}) Y_{l_2,0}^*(\hat{\mathbf{k}}') \times \mathcal{T}(l_1,l_2), \quad \hat{\mathbf{k}}=\hat{\mathbf{z}}, \tag{36}$$

where

$$\mathcal{T}(l_1,l_2) = T^{11}(l_1,l_2) + \sum_{i,j=1} \sum_{l,l'} T^{1i}(l_1,l) G^{ij}(l,l') T^{j1}(l'l_2) + \cdots, \tag{37}$$

$$T^{11}(l_1,l_2) = -\delta_{l_1,l_2} \exp(i\delta_{l_1}) \sin\delta_{l_1}, \tag{38}$$

$$T^{12}(l_1,l_2) = T^{21}(l_1,l_2) = -\delta_{l_1,l_2} (2mk_F^2/\hbar^2) (\partial/\partial k) t_{l_1}(k_F,k)\,|_{k=k_F}, \tag{39}$$

$$T^{22}(l_1,l_2) = -\delta_{l_1,l_2} (2mk_F^3/\hbar^2) \times (\partial/\partial k)(\partial/\partial k') t_{l_1}(k,k')\,|_{k=k_F,\, k'=k_F}, \tag{40}$$

$$G^{22}(l_1,l_2) = 0, \tag{41}$$

$$G^{21}(l_1,l_2) = G^{12}(l_1,l_2) = -(2i/3\pi Z)(2l_1+1)^{1/2}(2l_2+1)^{1/2}, \tag{42}$$

[13] We use the notation of A. Messiah, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1966), p. 489.

[14] A. Messiah, Ref. 13, p. 817.

$$G^{11}(l_1,l_2)=-\sum_{l_3}(2l_3+1)c^{l_3}(l_1 0 l_2 0)\times(I^S(l_3)+I^R(l_3)), \quad (43)$$

$$I^R(l)=(2l+1)/3\pi Z, \quad (44)$$

and

$$I^S(l)=\frac{2}{\pi}\int_0^\infty kdk[S(k)-1]\times\left[\int_0^\infty RdR\sin(kR)h_l^+(k_FR)j_l(k_FR)\right]. \quad (45)$$

Again h_l^+ is another spherical Bessel function[13] and[15]

$$c^l(l_1m_1l_2m_2)=\left(\frac{4\pi}{2l+1}\right)^{1/2}\int\sin\theta d\theta d\varphi\times Y_{L_1}(\theta,\varphi)Y_{L_2}^*(\theta,\varphi)Y_L(\theta,\varphi). \quad (46)$$

Note that, though the above was derived using the muffin-tin assumption, no explicit dependence on this assumption remains in the final result.

We have used these equations to evaluate ν and to compute ρ for several metals. The density of the liquid metal determines k_F, and the liquid-structure factor was described by the theoretical hard-core structure factor as determined by Ashcroft and Lekner.[2] Phase shifts were obtained in the following manner: For $l\geq 2$ the Born approximation[16] was used in connection with a pseudopotential

$$\delta_l=-\frac{2mk_F}{\hbar^2}\int_0^\infty j_l^2(k_Fr)v(r)r^2dr, \quad (47)$$

where

$$v(r)=\frac{1}{(2\pi)^3}\int d\mathbf{q}e^{i\mathbf{q}\cdot\mathbf{r}}v(q), \quad (48)$$

$$v(q)=-\tfrac{2}{3}E_F\frac{1}{n_i}\frac{k_s^2\cos qR_c}{q^2+k_s^2}, \quad (49)$$

and

$$k_s^2=4k_F/\pi a_0, \quad a_0=\hbar^2/me^2,$$

with R_c chosen to yield the correct ρ from the Ziman formula and consistent with other Fermi-surface data.[3] We chose Thomas-Fermi screening instead of Lindhard screening because the latter leads to infinities in T[22]. These arise essentially from the long-range Friedel oscillations in real space and in the spirit of a muffin-tin approximation should be neglected. This is the only point for which we explicitly consider the restrictions of the muffin-tin approximation. The phase shifts for $l=0$ and $l=1$ were determined by use of the Friedel sum rule and the requirement that the Ziman expression evaluated with phase shifts yield the experimental result:

$$\rho=\frac{\hbar}{3\pi Ze^2n_ek_F^2}\int_0^{2k_F}q^3dq\times S(q)\left|\sum_l(2l+1)e^{i\delta_l}\sin\delta_lP_l(1-q^2/2k_F^2)\right|^2, \quad (50)$$

where the P_l's are Legendre polynomials. Finally, to obtain the derivatives of $t_l(k,k')$ we used the formulas of Beeby[12]:

$$(\partial/\partial k)\,\mathrm{Im}t_l(k,k_F)|_{k=k_F}=(\partial/\partial k)\,\mathrm{Im}t_l(k_F,k)|_{k=k_F}=[\partial s_l(k)/\partial k]|_{k=k_F}\cos\delta_l\sin\delta_l, \quad (51)$$

$$(\partial/\partial k)(\partial/\partial k')\,\mathrm{Im}t_l(k,k')|_{k=k_F,\,k'=k_F}=\{[\partial s_l(k)/\partial k]|_{k=k_F}\}^2\cos^2\delta_l, \quad (52)$$

$$(\partial/\partial k)\,\mathrm{Re}t_l(k,k_F)|_{k=k_F}=(\partial/\partial k)\,\mathrm{Re}t_l(k_F,k)|_{k=k_F}=[\partial s_l(k)/\partial k]|_{k=k_F}\cos^2\delta_l, \quad (53)$$

and

$$(\partial/\partial k)(\partial/\partial k')\,\mathrm{Re}t_l(k,k')|_{k=k_F,\,k'=k_F}=(\partial/\partial k)(\partial/\partial k')\int_0^\infty x^2dx\int_0^\infty y^2dy\,j_l(kx)j_l(k'y)\times\mathrm{Re}t_l(x,y)|_{k=k_F,\,k'=k_F}. \quad (54)$$

Here

$$s_l(k)=\int_0^\infty x^2dx\,j_l(kx)s_l(x), \quad s_l(k_F)=\tan\delta_l(E_F), \quad (55)$$

where

$$s_l(x)=\frac{-2mk_F}{\hbar^2}j_l(k_Fx)v(x)+\frac{2}{\pi}P\int_0^\infty k^2dk\int_0^\infty z^2dz\frac{j_l(kx)j_l(kz)}{E_F-E_k}s_l(z). \quad (56)$$

We evaluated both $s_l(k)$ and $\mathrm{Re}t_l(k,k')$ only to first order in the potential. This procedure allows us to include the first nonvanishing contribution from each term. The whole calculational scheme outlined above although somewhat arbitrary is reasonable in view of the muffin-tin assumption which in the first place permitted us to get to this point. Note that the approximations that we make to evaluate t and its derivatives are concerned *only* with estimating the scattering properties of a single ion.

IV. NUMERICAL RESULTS

The results of calculation for Na, Zn, and Al are shown in Figs. 1–3. (Results of a similar nature were also obtained for Li, K, Rb, and In.) We have plotted

[15] The notation is chosen so that the tabulations of E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1964), p. 178, may be used.

[16] A. Messiah, Ref. 13, p. 406.

as a function of the momentum transfer at the Fermi surface, q, the absolute value of the scattering factor:

$$f(q)=\frac{2}{Z\pi}\left|\sum_l (2l+1)e^{i\delta_l}\sin\delta_l P_l(1-q^2/2k_F^2)\right|, \quad (57)$$

$$F(q)=\frac{2}{Z\pi}\left|\sum_{l_1,l_2}(2l_1+1)^{1/2}(2l_2+1)^{1/2}\times\mathcal{T}(l_1,l_2)P_{l_2}(1-q^2/2k_F^2)\right|. \quad (58)$$

The angular-momentum expansion was cut off at $l=6$. For the alkalis convergence was obtained with five iterations of the expression (37) for $\mathcal{T}$, while seven to ten iterations were required for the polyvalent elements. We show in Fig. 4 how the resistivity varies through the calculation. The large change in the low-order corrections is familiar.[4] We estimate that after 10 iterations the numerical results are accurate to 20%.

As presented these results are encouraging. We have, however, unearthed an interesting inconsistency in an attempt to numerically check the generalized optical theorem.[6] As shown in Appendix A it *should* be true that [using Eqs. (27) and (28)]

$$-\mathrm{Im}\langle\mathbf{k}|v|\mathbf{k}\rangle=\pi\sum_{k'}\langle\mathbf{k}|v|\mathbf{k}'\rangle S(\mathbf{k}-\mathbf{k}')\times\delta(E_F-E_{k'})\langle\mathbf{k}'|v|\mathbf{k}\rangle. \quad (59)$$

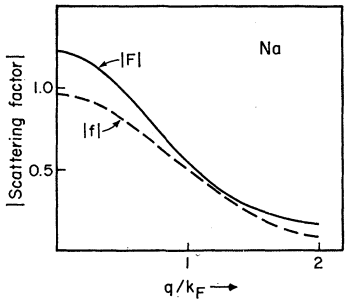

FIG. 1. Numerical results for Na. The single-site scattering factor $f(q)$ is denoted by - - - and the converged effective scattering factor $F(q)$ is denoted by ——.

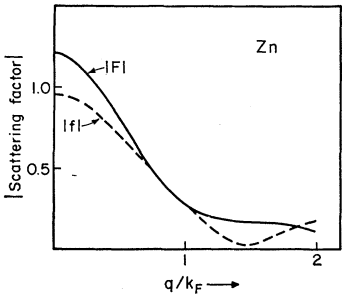

FIG. 2. Numerical results for Zn. The single-site scattering factor $f(q)$ is denoted by - - - and the converged effective scattering factor $F(q)$ is denoted by ——.

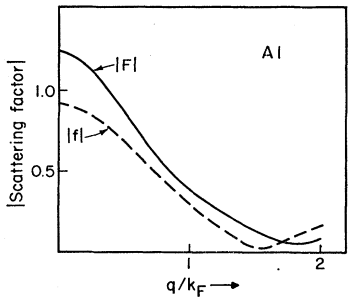

FIG. 3. Numerical results for Al. The single-site scattering factor $f(q)$ is denoted by - - - and the converged effective scattering factor $F(q)$ is denoted by ——.

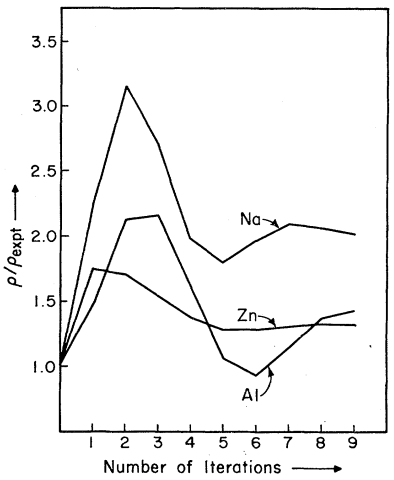

FIG. 4. Computed resistivity as function of number of iterations for Na, Zn, and Al.

Table I gives the relevant computed numbers and it is apparent that the disagreement is significant. It is quite crucial to keep in mind, however, that the *real part of* $\langle\mathbf{k}|v|\mathbf{k}\rangle$ (which is approximately equal to $0.8E_F$) is *larger* than the imaginary part. An immediate consequence of this is that a correction of only 5% in the absolute magnitude of $\langle\mathbf{k}|v|\mathbf{k}\rangle$ would restore agreement with the optical theorem. The disagreement in Table I is therefore not so poor as it appears although its *source* is a very interesting question. It can be traced to neglect of the muffin-tin assumption in the construction of the single-site potential [Eqs. (48) and (49)]. To

TABLE I. Numerical check of generalized optical theorem. The first column gives the element, the second and third columns and the fourth and fifth columns refer to the potentials introduced in Eqs. (49) and (60), respectively. In both cases a comparison of the right-hand side (RHS) and left-hand side (LHS) of Eq. (59) is made in units of E_F for each element.

Element	LHS_{49}	RHS_{49}	LHS_{60}	RHS_{60}
Na	0.142	0.016	0.0063	0.0059
Zn	0.172	0.049	0.0152	0.0146
Al	0.094	0.058	0.0507	0.0571

substantiate this hypothesis we performed the calculation using a potential that was explicitly consistent with the muffin-tin approximation; that is, a potential that rigorously vanished outside the muffin-tin radius, and therefore suffered no further deletions by making the muffin-tin approximation. In the notation of Eq. (48), we took

$$\begin{aligned} v(r)&=0 \qquad\qquad \text{for } r<R_c, \quad r>\tfrac{1}{2}\sigma \\ &=(e^2/r)e^{-ksr} \quad \text{for } R_c<r<\tfrac{1}{2}\sigma. \end{aligned} \tag{60}$$

Here $\frac{1}{2}\sigma$ is the hard-sphere radius used to describe the effective physical size of the ions.[2] Making no attempt to fit this potential in lowest order, we determined all the phase shifts in Born approximation ($l_{\max}=6$). Iteration of the expression for ν again led to convergence, but this time the generalized optical theorem was satisfied as shown in Table I. This agreement is the basis of our explanation of the earlier inconsistency. The difficulty is clearly an artifact of the muffin-tin approximation and we have no way of relating how this inconsistency affects the validity of the data presented in Figs. 1–4.

V. EXTENSION TO ALLOYS

We may extend the analysis for ρ to the case of alloys with an arbitrary number of components. The theorems of Taylor[8] still apply and hence so does the formalism of Van Hove.[9]

The typical term considered in Sec. II for the expansion of $W(E_F,\mathbf{k},\mathbf{k}')$ is now

$$\begin{aligned} &\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3}\frac{1}{\Omega^4}\sum_{\substack{\alpha_1,\alpha_2,\alpha_3\\ \beta_1,\beta_2}}\{[v^{\alpha_1}(\mathbf{k}-\mathbf{k}_1)G^+(k_1)v^{\alpha_2}(\mathbf{k}_1-\mathbf{k}_2)G^+(k_2) \\ &\times v^{\alpha_3}(\mathbf{k}_2-\mathbf{k}')v^{\beta_1}(\mathbf{k}'-\mathbf{k}_3)G^-(k_3)v^{\beta_2}(\mathbf{k}_3-\mathbf{k})] \\ &\times\langle\langle\rho_{\mathbf{k}-\mathbf{k}_1}{}^{\alpha_1}\rho_{\mathbf{k}_1-\mathbf{k}_2}{}^{\alpha_2}\rho_{\mathbf{k}_2-\mathbf{k}'}{}^{\alpha_3}\rho_{\mathbf{k}'-\mathbf{k}_3}{}^{\beta_1}\rho_{\mathbf{k}_3-\mathbf{k}}{}^{\beta_2}\rangle\rangle\}_{\text{i.d.}}. \end{aligned} \tag{61}$$

Here the Greek indices designate the type of component, and

$$\rho_{\mathbf{q}}{}^{\alpha}=\sum_{i=1}^{N_\alpha}e^{-i\mathbf{q}\cdot\mathbf{R}_i{}^{\alpha}}, \tag{62}$$

with $x_\alpha=N_\alpha/N$ the concentration of component α, and $\mathbf{R}_i{}^{\alpha}$ the instantaneous position of the ith ion of the component α. For each term in the sum over Greek indices, the fluctuation argument used in Eq. (22) may be applied to approximate the ionic correlation

$$\begin{aligned} &[\langle\langle\rho_{\mathbf{k}-\mathbf{k}_1}{}^{\alpha_1}\rho_{\mathbf{k}_1-\mathbf{k}_2}{}^{\alpha_2}\rho_{\mathbf{k}_2-\mathbf{k}'}{}^{\alpha_3}\rho_{\mathbf{k}'-\mathbf{k}_3}{}^{\beta_1}\rho_{\mathbf{k}_3-\mathbf{k}}{}^{\beta_2}\rangle\rangle]_{\text{i.d.}} \\ &=(N_{\alpha_1}N_{\beta_2})^{1/2}S_{\alpha_1\alpha_2}(\mathbf{k}-\mathbf{k}_1)S_{\alpha_2\alpha_3}(\mathbf{k}-\mathbf{k}_2) \\ &\qquad\times S_{\alpha_3\beta_1}(\mathbf{k}-\mathbf{k}')S_{\beta_1\beta_2}(\mathbf{k}-\mathbf{k}_3), \end{aligned} \tag{63}$$

where

$$S_{\alpha\beta}(q)=S_{\beta\alpha}(q)=\frac{1}{(N_\alpha N_\beta)^{1/2}}\langle\langle\rho_{\mathbf{q}}{}^{\alpha}\rho_{-\mathbf{q}}{}^{\beta}\rangle\rangle-(N_\alpha N_\beta)^{1/2}\delta_{\mathbf{q},0}$$

is the generalization of $S(q)$. This "geometric approximation" again allows the expansion for $W(E_F,\mathbf{k},\mathbf{k}')$ to be resummed. Let

$$\tilde{v}^{\alpha}=x_\alpha v^{\alpha} \tag{64}$$

and

$$(x_\alpha x_\beta)^{1/2}s_{\alpha\beta}(q)=S_{\alpha\beta}(q). \tag{65}$$

Then the result for the resistivity may be rewritten

$$\begin{aligned} \rho=\frac{m^2}{12Z^*e^2n_e\hbar^3\pi^3}\Omega^2\sum_{\alpha,\beta}\int_0^{2k_F}q^3dq\langle\mathbf{k}|\nu^{\alpha}|\mathbf{k}+\mathbf{q}\rangle(x_\alpha x_\beta)^{1/2} \\ \times S_{\alpha\beta}(q)\langle\mathbf{k}+\mathbf{q}|\nu^{\beta\dagger}|\mathbf{k}\rangle, \end{aligned} \tag{66}$$

where Z^* is the average valence and

$$\begin{aligned} \langle\mathbf{k}|x_\alpha\nu^{\alpha}|\mathbf{k}'\rangle=\langle\mathbf{k}|\Big\{\tilde{v}^{\alpha}+\sum_{\beta}x_\beta\nu^{\beta} \\ \times\Big[\sum_{\mathbf{k}_1}|\mathbf{k}_1\rangle\frac{s_{\beta\alpha}(\mathbf{k}-\mathbf{k}_1)}{\mu-E_{k_1}-\Sigma^+(k_1)}\langle\mathbf{k}_1|\Big]\tilde{v}^{\alpha}\Big\}|\mathbf{k}'\rangle. \end{aligned} \tag{67}$$

This is the generalization of the result of Ashcroft and Langreth.[3] We note that an analysis similar to that in Appendix A may be carried out to demonstrate the self-consistency (in the sense of the generalized optical theorem[6]) of this approximation for alloys.

VI. KNIGHT SHIFT

As noted by Edwards, the Knight shift is proportional to[17]

$$K^{\alpha}=C\Big\langle\Big\langle-\frac{\mathrm{Im}}{\pi}\frac{1}{N_\alpha}\sum_{i=1}^{N_\alpha}\langle\mathbf{R}_1{}^{\alpha}|\frac{1}{\mu-H+i\epsilon}|\mathbf{R}_i{}^{\alpha}\rangle\Big\rangle\Big\rangle, \tag{68}$$

where we consider an alloy with an arbitrary number of components and seek the Knight shift of the type-α nuclei. This expression is to be evaluated in the absence of a magnetic field. As in the previous section,

$$H=-\frac{\hbar^2}{2m}\nabla^2+\sum_{\alpha}\sum_{i=1}^{N_\alpha}v^{\alpha}(\mathbf{r}-\mathbf{R}_1{}^{\alpha}). \tag{69}$$

Equation (68) is equivalent to

$$\begin{aligned} K^{\alpha}=C\Big\langle\Big\langle-\frac{\mathrm{Im}}{\pi}\frac{1}{N_\alpha}\frac{1}{\Omega} \\ \times\sum_{\mathbf{k},\mathbf{k}'}\langle\mathbf{k}|\frac{1}{\mu-H+i\epsilon}|\mathbf{k}'\rangle\rho_{\mathbf{k}'-\mathbf{k}}{}^{\alpha}\Big\rangle\Big\rangle. \end{aligned} \tag{70}$$

Using arguments similar to those of Van Hove,[9] we may

[17] S. F. Edwards, Proc. Roy. Soc. (London) **A267**, 518 (1962). The constant of proportionality equals $\frac{4}{3}\pi(eh/4\pi mc)^2$ if we ignore the electron-exchange enhancement of the Pauli susceptibility.

define an expression $\mathcal{K}^\alpha(\mathbf{k},\mathbf{k}')$ such that

$$K^\alpha = -C\frac{\mathrm{Im}}{\pi}\frac{1}{\Omega}\Big\{\sum_{\mathbf{k}} G^+(k) + \frac{1}{N_\alpha}\sum_{\mathbf{k},\mathbf{k}';\mathbf{k}\neq\mathbf{k}'} G^+(k)\mathcal{K}^\alpha(\mathbf{k},\mathbf{k}')G^+(k')\Big\} \quad (71)$$

and

$$\mathcal{K}^\alpha(\mathbf{k},\mathbf{k}') = \sum_{n=0}^{\infty}\langle\langle\{\langle\mathbf{k}|V(G^+V)^n|\mathbf{k}'\rangle\rho_{\mathbf{k}'-\mathbf{k}}{}^\alpha\}_{\text{i.d.}}\rangle\rangle. \quad (72)$$

A typical term in the expansion of $\mathcal{K}^\alpha(\mathbf{k},\mathbf{k}')$ is

$$\sum_{\mathbf{k}_1,\mathbf{k}_2}\frac{1}{\Omega^3}\sum_{\beta_1,\beta_2,\beta_3}\{[v^{\beta_1}(\mathbf{k}-\mathbf{k}_1)G^+(k_1) \times v^{\beta_2}(\mathbf{k}_1-\mathbf{k}_2)G^+(k_2)v^{\beta_3}(\mathbf{k}_2-\mathbf{k}')] \times\langle\langle\rho_{\mathbf{k}-\mathbf{k}_1}{}^{\beta_1}\rho_{\mathbf{k}_1-\mathbf{k}_2}{}^{\beta_2}\rho_{\mathbf{k}_2-\mathbf{k}'}{}^{\beta_3}\rho_{\mathbf{k}'-\mathbf{k}}{}^\alpha\rangle\rangle\}_{\text{i.d.}}. \quad (73)$$

If we consider the vector $\mathbf{k}$ dominant (as in Sec. II), then the geometric approximation discussed above for alloys yields

$$\{\langle\langle\rho_{\mathbf{k}-\mathbf{k}_1}{}^{\beta_1}\rho_{\mathbf{k}_1-\mathbf{k}_2}{}^{\beta_2}\rho_{\mathbf{k}_2-\mathbf{k}'}{}^{\beta_3}\rho_{\mathbf{k}'-\mathbf{k}}{}^\alpha\rangle\rangle\}_{\text{i.d.}} = (N_{\beta_1}N_\alpha)^{1/2}S_{\beta_1\beta_2}(\mathbf{k}-\mathbf{k}_1)S_{\beta_2\beta_3}(\mathbf{k}-\mathbf{k}_2) \times S_{\beta_3\alpha}(\mathbf{k}-\mathbf{k}'). \quad (74)$$

Alternatively the vector $\mathbf{k}'$ could be considered dominant, in which case the geometric approximation would be

$$\{\langle\langle\rho_{\mathbf{k}'-\mathbf{k}}{}^\alpha\rho_{\mathbf{k}-\mathbf{k}_1}{}^{\beta_1}\rho_{\mathbf{k}_1-\mathbf{k}_2}{}^{\beta_2}\rho_{\mathbf{k}_2-\mathbf{k}'}{}^{\beta_3}\rangle\rangle\}_{\text{i.d.}} = (N_\alpha N_{\beta_3})^{1/2}S_{\alpha\beta_1}(\mathbf{k}'-\mathbf{k})S_{\beta_1\beta_2}(\mathbf{k}'-\mathbf{k}_1) \times S_{\beta_2\beta_3}(\mathbf{k}'-\mathbf{k}_2). \quad (75)$$

Proceeding with Eq. (74) we substitute back and resum to obtain (see Sec. V for notation)

$$\mathcal{K}^\alpha(\mathbf{k},\mathbf{k}') = N_\alpha\sum_\beta\langle\mathbf{k}|x_\beta v^\beta|\mathbf{k}'\rangle s_{\beta\alpha}(\mathbf{k}-\mathbf{k}'). \quad (76)$$

Then

$$K^\alpha = -C\frac{\mathrm{Im}}{\pi}\frac{1}{\Omega}\{\sum_{\mathbf{k}} G^+(k) + \sum_{\mathbf{k},\mathbf{k}';\mathbf{k}\neq\mathbf{k}'} G^+(k) \times\sum_\beta\langle\mathbf{k}|x_\beta v^\beta|\mathbf{k}'\rangle s_{\beta\alpha}(\mathbf{k}-\mathbf{k}')G^+(k')\}. \quad (77)$$

By working with Eq. (75) instead of Eq. (74) we would obtain a different expression for $\mathcal{K}^\alpha(\mathbf{k},\mathbf{k}')$ but the same result for K^α. Equation (77) is a generalization of the result of Faber.[18] His result may be written (within the context of the nearly free-electron approximation)

$$K^\alpha = -C'\frac{\mathrm{Im}}{\pi}\frac{1}{\Omega}\{\sum_{\mathbf{k}} G^+(k) + \sum_{\mathbf{k},\mathbf{k}';\mathbf{k}\neq\mathbf{k}'} G^+(k) \times\sum_\beta\langle\mathbf{k}|x_\beta u^\beta|\mathbf{k}'\rangle s_{\beta\alpha}(\mathbf{k}-\mathbf{k}')G^+(k')\}. \quad (78)$$

[18] T. E. Faber, Advan. Phys. 15, 547 (1966); 16, 637 (1967).

The coefficient of proportionality has changed because Faber used a pseudopotential, u^β, and therefore needed to correct for core-orthogonalization terms.

VII. CONCLUSIONS

We have shown that a geometric approximation for the ionic correlation leads to a generalization of certain nearly free-electron formulas for properties of liquid metals. These generalized formulas are identical in form to the low-order results but include, in an approximate manner, corrections to all orders. Numerical work for the electrical resistivity indicates that the higher-order corrections are *not* small in magnitude. However, these terms tend to cancel among themselves yielding a small net correction to the low-order result.

The success of the geometric approximation used here suggests that its application to other liquid metal properties might prove fruitful. Further work with model liquid calculations may help to determine the validity of the approximation.

ACKNOWLEDGMENT

We wish to thank Professor J. W. Wilkins for a helpful remark leading to the proof of the generalized optical theorem.

APPENDIX A: GENERALIZED OPTICAL THEOREM

The generalized optical theorem is a self-consistency relation between Σ and W.[6] The specific form of this relation that we shall consider is, in our notation

$$\Gamma(k) = \frac{1}{\Omega}\sum_{k'} W(E_F,\mathbf{k},\mathbf{k}') \times\frac{\Gamma(k')}{(\mu-E_{k'}-\Delta(k'))^2+\Gamma^2(k')}. \quad (A1)$$

To obtain expressions for Γ and Δ, note that Σ arises from a calculation of the configuration averaged resolvent [Eqs. (13) and (14)]. As in the calculation of $W(E_F,\mathbf{k},\mathbf{k}')$, the theorems of Taylor[8] allow us to use Van Hove's[9] formalism from which we find:

$$\Sigma^+(k) = \sum_{n=0}^{\infty}\langle\langle\{\langle\mathbf{k}|V(G^+V)^n|\mathbf{k}\rangle\}_{\text{i.d.}}\rangle\rangle. \quad (A2)$$

A typical term in this expansion is

$$\sum_{\mathbf{k}_1,\mathbf{k}_2}\frac{1}{\Omega^3}\{[v(\mathbf{k}-\mathbf{k}_1)G^+(k_1)v(\mathbf{k}_1-\mathbf{k}_2)G^+(k_2)v(\mathbf{k}_2-\mathbf{k})] \times\langle\langle\rho_{\mathbf{k}-\mathbf{k}_1}\rho_{\mathbf{k}_1-\mathbf{k}_2}\rho_{\mathbf{k}_2-\mathbf{k}}\rangle\rangle\}_{\text{i.d.}}.$$

The vector $\mathbf{k}$ is dominant (Sec. II); so, in the same manner as in the text, we approximate the ionic

correlation by, for example,

$$\frac{1}{N}\{\langle\langle\rho_{\mathbf{k}-\mathbf{k}_1}\rho_{\mathbf{k}_1-\mathbf{k}_2}\rho_{\mathbf{k}_2-\mathbf{k}}\rangle\rangle\}_{\text{i.d.}}=S(\mathbf{k}-\mathbf{k}_1)S(\mathbf{k}-\mathbf{k}_2), \quad \text{(A3)}$$

and substituting back we find

$$N\sum_{\mathbf{k}_1,\mathbf{k}_2}\frac{1}{\Omega^3}v(\mathbf{k}-\mathbf{k}_1)S(\mathbf{k}-\mathbf{k}_1)G^+(k_1)v(\mathbf{k}_1-\mathbf{k}_2)\times S(\mathbf{k}-\mathbf{k}_2)G^+(k_2)v(\mathbf{k}_2-\mathbf{k}).$$

Applying this approach to the other contributions to the sum and then summing, we obtain

$$\Sigma^+(k)=N\langle\mathbf{k}|\nu|\mathbf{k}\rangle. \quad \text{(A4)}$$

It also follows that

$$\Sigma^-(k)=N\langle\mathbf{k}|\nu^\dagger|\mathbf{k}\rangle. \quad \text{(A5)}$$

Now to establish Eq. (A1),[19] define an operator $G^\pm$ which has the property

$$\tilde{G}^\pm=\sum_{\mathbf{k}'}|\mathbf{k}'\rangle S(\mathbf{k}-\mathbf{k}')G^\pm(\mathbf{k}')\langle\mathbf{k}'|. \quad \text{(A6)}$$

Then working independently of a specific representation

$$\nu=v+\nu\tilde{G}^+v \quad \text{or} \quad v=\nu-\nu\tilde{G}^+v \quad \text{(A7)}$$

and

$$\nu^\dagger=v+v\tilde{G}^-\nu^\dagger \quad \text{or} \quad v=\nu^\dagger-v\tilde{G}^-\nu^\dagger. \quad \text{(A8)}$$

Substituting (A7) in (A8) and vice versa

$$\nu^\dagger=v+\nu\tilde{G}^-\nu^\dagger-\nu\tilde{G}^+v\tilde{G}^-\nu^\dagger, \quad \text{(A9)}$$

$$\nu=v+\nu\tilde{G}^+\nu^\dagger-\nu\tilde{G}^+v\tilde{G}^-\nu^\dagger, \quad \text{(A10)}$$

and subtracting

$$\nu^\dagger-\nu=\nu(\tilde{G}^--\tilde{G}^+)\nu^\dagger. \quad \text{(A11)}$$

Taking plane-wave matrix elements, we arrive at Eq. (A1).

APPENDIX B

This analysis follows closely the work of Beeby.[12] By the definitions introduced in the text, the first term in the expansion of ν [Eq. (30)] is given by

$$\Omega\langle\mathbf{k}|t|\mathbf{k}'\rangle=-\frac{2\pi\hbar^2}{mk_F}\sum_L 4\pi Y_L(\mathbf{k})Y_L^*(\hat{\mathbf{k}}')e^{i\delta_l}\sin\delta_l. \quad \text{(B1)}$$

The next term may be reduced to (note $|\mathbf{k}|=|\mathbf{k}'|=k_F$)

$$\Omega\langle\mathbf{k}|t\Big[\sum_{\mathbf{k}_1}|\mathbf{k}_1\rangle\frac{S(\mathbf{k}-\mathbf{k}_1)-1}{\mu-E_{k_1}-\Delta+i\epsilon}\langle\mathbf{k}_1|\Big]t|\mathbf{k}'\rangle$$
$$=(4\pi)^2\sum_{L_1,L_2}Y_{L_1}(\hat{\mathbf{k}})Y_{L_2}^*(\mathbf{k}')\times\Big\{(4\pi)^2n_i\sum_{\mathbf{k}_1}\frac{1}{\Omega}\int_0^\infty x_1^2dx_1\int_0^\infty x_2^2dx_2t_{l_1}(k_F,x_1)\times j_{l_1}(k_1x_1)Y_{L_1}^*(\hat{\mathbf{k}}_1)\Big[\frac{1}{\mu-E_{k_1}-\Delta+i\epsilon}\times\Big(\int_0^\infty d\mathbf{R}\,g(R)e^{i(\mathbf{k}-\mathbf{k}_1)\cdot\mathbf{R}}-(2\pi)^3\delta(\mathbf{k}-\mathbf{k}_1)\Big)\Big]\times Y_{L_2}(\hat{\mathbf{k}}_1)j_{l_2}(k_1x_2)t_{l_2}(x_2,k_F), \quad \text{(B2)}$$

where we have introduced the identity

$$S(q)-1=n_i\int d\mathbf{R}\,g(R)e^{i\mathbf{q}\cdot\mathbf{R}}-n_i(2\pi)^3\delta(\mathbf{q}) \quad \text{(B3)}$$

involving the pair-correlation function $g(R)$, normalized so that

$$g(R)\to 1 \quad \text{as} \quad R\to\infty. \quad \text{(B4)}$$

Further reduction leads eventually to a consideration of the integral

$$I=\int_0^\infty k_1^2dk_1j_{l_1}(k_1x_1)j_{l_2}(k_1x_2)\times j_{l_3}(k_1R)\frac{1}{\mu-E_{k_1}-\Delta+i\epsilon}. \quad \text{(B5)}$$

Use of the muffin-tin approximation reduces the integral to a convenient result. Accordingly, we assume (changing the zero of energy) that the electron-ion potentials are nonzero *only* within a sphere of radius R_m surrounding each ion and that in no configuration of the ions do these spheres overlap. This implies $t_l(x,y)=0$ if either $x>R_m$ and/or $y>R_m$, and $g(R)=0$ if $R<R_m$. The integral (B5) then yields[12]

$$I=\tfrac{1}{2}\pi(2mk_F/\hbar)h_{l_3}^+(\tilde{k}_FR)j_{l_1}(\tilde{k}_Fx_1)j_{l_2}(\tilde{k}_Fx_2), \quad \text{(B6)}$$

where

$$\tilde{k}_F=k_F+i\epsilon', \quad \epsilon'=\tfrac{1}{2}k_F(\epsilon/E_F). \quad \text{(B7)}$$

Using this result, Eq. (B2) becomes (note $\mathbf{k}=\hat{\mathbf{z}}k_F$)

$$-(4\pi)^2\sum_{L_1,L_2}Y_{L_1}(\hat{\mathbf{k}})Y_{L_2}^*(\hat{\mathbf{k}}')\times\Big\{\Big[4\pi n_i\sum_{l_3}\frac{2m\tilde{k}_F}{\hbar^2}(2l_3+1)c^{l_3}(l_1m_1l_2m_2)\delta_{m_1,m_2}\int_0^\infty R^2dR[g(R)-1]t_{l_1}(k_F,\tilde{k}_F)h_{l_3}^+(\tilde{k}_FR)j_{l_3}(k_FR)t_{l_2}(\tilde{k}_F,k_F)\Big]$$
$$+\Big[4\pi n_i\sum_{l_3}\frac{2m\tilde{k}_F}{\hbar^2}(2l_3+1)c^{l_3}(l_1m_1l_2m_2)\delta_{m_1,m_2}\int_0^\infty R^2dR\,t_{l_1}(k_F,\tilde{k}_F)h_{l_3}^+(\tilde{k}_FR)j_{l_3}(k_FR)t_{l_2}(\tilde{k}_F,k_F)$$
$$-4\pi n_it_{l_1}(k_F,k_F)(2l_1+1)^{1/2}\delta_{m_1,0}(1/\epsilon)\delta_{m_2,0}(2l_2+1)^{1/2}t_{l_2}(k_F,k_F)\Big]\Big\}. \quad \text{(B8)}$$

[19] This proof was suggested to us by J. W. Wilkins (private communication).

Introducing the identities[20]

$$\int_0^\infty R^2dR\, h_l^+(\tilde{k}_F R) j_l(k_F R) = \frac{1}{k_F(k_F{}^2+(\epsilon'-ik_F)^2)}\left(1+i\frac{\epsilon'}{k_F}\right)^{-l-1}, \tag{B9}$$

$$n_i\int_0^\infty R^2dR[g(R)-1]h_l^+(k_F R) j_l(k_F R) = \frac{1}{(2\pi^2)}\int_0^\infty kdk[S(k)-1]\int_0^\infty RdR\sin(kR)h_l^+(k_F R) j_l(k_F R), \tag{B10}$$

and expanding in ϵ' where necessary to remove divergences, we find

$$\begin{aligned}\frac{2\pi\hbar^2}{mk_F}\sum_{L_1,L_2} 4\pi Y_{L_1}(\hat{\mathbf{k}})Y_{L_2}{}^*(\hat{\mathbf{k}}')\Big\{&(-\exp(i\delta_{l_1})\sin\delta_{l_1})\Big(-\sum_{l_3}(2l_3+1)c^{l_3}(l_1m_1l_2m_2)\delta_{m_1,m_2}\\
&\times\Big[\frac{2l_3+1}{3\pi Z}+\frac{2}{\pi}\int_0^\infty kdk[S(k)-1]\Big(\int_0^\infty RdR\sin(kR)h_{l_3}{}^+(k_F R)j_{l_3}(k_F R)\Big)\Big]\Big)(-\exp(i\delta_{l_2})\sin\delta_{l_2})\\
&+\Big(-\frac{2mk_F{}^2}{\hbar^2}\frac{\partial}{\partial k}t_{l_1}(k_F,k)\Big|_{k=k_F}\Big)\Big((2l_1+1)^{1/2}\delta_{m_1,0}\Big(-\frac{2i}{3\pi Z}\Big)\delta_{m_2,0}(2l_2+1)^{1/2}\Big)(-\exp(i\delta_{l_2})\sin\delta_{l_2})\\
&+(-\exp(i\delta_{l_1})\sin\delta_{l_1})\Big((2l_1+1)^{1/2}\delta_{m_1,0}\Big(-\frac{2i}{3\pi Z}\Big)\delta_{m_2,0}(2l_2+1)^{1/2}\Big)\Big[-\frac{2mk_F{}^2}{\hbar^2}\frac{\partial}{\partial k}t_{l_2}(k,k_F)\Big|_{k=k_F}\Big]\Big\}.\end{aligned} \tag{B11}$$

Here use has been made of the sum rule[21]

$$\sum_{l_3}(2l_3+1)c^{l_3}(l_1m_1l_2m_2)\delta_{m_1,m_2} = (2l_1+1)^{1/2}(2l_2+1)^{1/2}\delta_{m_1,0}\delta_{m_2,0}. \tag{B12}$$

Similar structure appears in higher order. In this form it is clear that we can make a cutoff in the angular momentum expansion since the phase shifts decrease rapidly with increasing l. Furthermore, the matrix series may be simplified by noting that each matrix contains a $\delta_{m,m'}$ on the two magnetic quantum numbers m and m', which means that any product or sum of such matrices also has this property. Coupling this with the fact that

$$Y_{L_1}(\hat{\mathbf{k}}) = Y_{L_1}(\hat{\mathbf{z}}) = [(2l_1+1)/4\pi]^{1/2}\delta_{m_1,0}, \tag{B13}$$

we see that we need only work in the subspace where all magnetic quantum numbers are zero. Using this observation and introducing the cutoff in angular-momentum indices, we obtain the answer given in the text.

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[20] A. Erdelyi *et al.*, *Table of Integral Transforms II* (McGraw- Hill Book Co., New York, 1954), Vol. II, p. 63.
[21] A. Messiah, Ref. 13, p. 1057.