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Nonlocal pseudopotential theory of electron transport in liquid metals

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The problem of electrical resistivity ρ_R of liquid metals has been formulated in terms of nonlocal pseudopotentials, and application is made to liquid Cd. It is shown that in this scheme the first-order effective mass of the electron enters into Ziman's nearly-free-electron formula of electrical resistivity. Significant differences in ρ_R values using local and nonlocal pseudopotentials are found. Possible corrections to the nearly-free-electron theory of ρ_R are discussed.

I. INTRODUCTION

The study of electron transport in liquid metals provides a sensitive index of the electron-ion potential and hence of the electronic structure of the system. Ziman's formulation[1] of the electrical-conductivity problem using the Boltzmann equation has been widely used with the electron-ion scattering represented by local pseudopotentials. Although this nearly-free-electron theory has successfully accounted for the observed resistivities, ρ_R, in a large number of liquid metals, there exist some quantitative discrepancies. Various reasons have been put forward in an attempt to bridge the gap between theory and experiment. These include possible corrections[2-4] to the Boltzmann equation arising from higher orders of perturbation theory and also corrections to the simple Ziman formula which come from the orthogonalized-plane-wave nature of the electronic wave functions.[5] Also, there has been some uncertainty[6] as to whether a free or effective mass should appear in the Ziman formula.

In this paper we examine the role of the nonlocal pseudopotential in resistivity calculations. It will be shown that, in the nonlocal pseudopotential scheme, an effective mass does enter the Ziman formula. Use of this effective mass, which is obtained from the nonlocal pseudopotential, is analogous to the inclusion of "core corrections" to the Ziman formula, of the kind discussed, for example, by Faber,[5] but the correction factor is obtainable quantitatively in our treatment.

We have applied the present theory to calculate the electrical resistivity, ρ_R, of liquid Cd. The case of Cd is of special interest because of the following two main reasons: (i) Recently Shyu *et al.*[7] have computed the resistivity for eight elements using their local pseudopotentials which include many-body corrections. They obtain satisfactory agreement with experiment, except in the case of Cd. However, the electron-ion potential of Cd is known to have a strongly nonlocal character. Stark and Falicov[8] have obtained an accurate nonlocal pseudopotential for Cd by fitting the band structure to the experimental Fermi surface in the solid. This potential has been used to calculate the superconducting transition temperature[9] and also the Knight shift in both the solid[10] and liquid[11] phase, in good agreement with experiment. The effective mass calculated[12] from this potential as a function of temperature explains the sudden change of the Knight shift upon melting. (ii) Greenfield and Wiser[13] (GW) have used the Stark-Falicov pseudopotential[8] to calculate ρ_R of liquid Cd and find large discrepancies between theory and experiment[14] (a factor of 3.6). They argue that these discrepancies are due to a severe breakdown of the Born approximation on which the Ziman formula is based. The work of GW has received some attention[15-17] in the literature in recent years. Evans[16] has suggested as an alternate explanation of the discrepancy that the Stark-Falicov potential might not be appropriate to calculations in the liquid phase.

Our result using the Stark-Falicov pseudopotential for liquid Cd is in disagreement with the work of GW.[13] In fact, including the effective-mass correction which GW[13] have failed to take into account, we find our result for ρ_R (52 $\mu\Omega$ cm) to be in better agreement with experiment (34 $\mu\Omega$ cm) than has hitherto been obtained. Thus, we find no convincing evidence for a breakdown of the Born approximation for liquid Cd.

In Sec. II we outline briefly the Ziman formula as applied to nonlocal pseudopotentials. Our results for liquid Cd are presented and compared with both experiment and earlier calculations in Sec. III. In Sec. IV we comment on some of the possible corrections to the Ziman formula.

II. FORMAL THEORY

A. Boltzmann equation

Although there are a number of careful discussions of the Boltzmann equation for various systems in the literature, for the purpose of the discussion to follow it is useful to outline some of the salient features. We shall adopt the approach of Berger *et al.*[18] taking it to leading order in the scattering, and applying it to the case of a nonlocal pseudopotential in a liquid metal.

The starting point is the Kubo formula for the diagonal part of the conductivity tensor

$$\sigma^{zz} = -\frac{1}{\tilde{V}}\mathrm{Tr}\left(\frac{\partial f}{\partial H}\lim_{s\to 0^+}\frac{1}{2}\left[J^z(s)j^z + j^z J^z(s)\right]\right). \qquad (1)$$

H is the Hamiltonian in the absence of the external electric field, f is the Fermi operator, j^z is a component of the current operator,

$$J^z(s) = \int_0^\infty dt\, e^{-st} e^{iHt/\hbar} j^z e^{-iHt/\hbar}, \qquad (2)$$

$\tilde{V}$ is the volume of the system, and the trace in Eq. (1) is taken over one-electron states.

We shall assume, following Greenwood,[3] that in evaluating the conductivity to leading order in the scattering the Hamiltonian H in Eqs. (1) and (2) may be replaced by $H_o + W$ where H_o is the one electron kinetic energy and W is the liquid-metal pseudopotential. We shall refer to this as assumption A. Now, working in the representation of plane (pseudo) waves $|\vec{k}\rangle$ it follows[18] for j diagonal in the $|\vec{k}\rangle$ representation that, to leading order in the scattering,

$$J^z_{\vec{k}} = \langle\vec{k}|J^z(0^+)|\vec{k}\rangle$$

is the solution of

$$0 = j^z_{\vec{k}} - \frac{2\pi}{\hbar}\sum_{\vec{k}'}(1-\delta_{\vec{k}\vec{k}'})|\langle\vec{k}|W|\vec{k}'\rangle|^2 \times (J^z_{\vec{k}} - J^z_{\vec{k}'})\delta(E_{\vec{k}} - E_{\vec{k}'}), \qquad (3)$$

where

$$E_{\vec{k}} = \langle\vec{k}|H_o|\vec{k}\rangle + \langle\vec{k}|W|\vec{k}\rangle. \qquad (4)$$

If Eq. (3) is decoupled by replacing $|\langle\vec{k}|W|\vec{k}'\rangle|^2$ by its thermal average (denoted $\langle\ \rangle_{\mathrm{av}}$) over the positions of the scatterers, it becomes the Boltzmann equation of interest. Assuming that $\langle|\langle\vec{k}|W|\vec{k}'\rangle|^2\rangle_{\mathrm{av}}$ depends only on the magnitudes of $\vec{k}$, and $\vec{k}'$ and on the angle $\theta_{\vec{k}\vec{k}'}$ between $\vec{k}$ and $\vec{k}'$, and that $E_{\vec{k}}$ is spherically symmetric (these conditions hold for both local and nonlocal pseudopotentials in the liquid metal), the Boltzmann equation has the solution

$$J^z_{\vec{k}} = \frac{j^z_{\vec{k}}\hbar(2\pi)^2}{\vec{k}^2\tilde{V}}\frac{dE_k}{dk} \times\left(\int d\Omega'\langle|\langle\vec{k}|W|\vec{k}'\rangle|^2\rangle_{\mathrm{av}}(1-\cos\theta_{\vec{k}\vec{k}'})\right)^{-1}. \qquad (5)$$

The integration is over the solid angle Ω' with $|\vec{k}'|$ kept equal to $|\vec{k}|$.

B. Role of the effective mass

To obtain σ^{zz} to leading order in the scattering it is sufficient to replace $J^z(0^+)$ in the Kubo formula in Eq. (1) by the expression (5) and to retain only the leading contribution $[\partial f(E_{\vec{k}})/\partial E_{\vec{k}}]\delta_{\vec{k}\vec{k}'}$ to the factor $\partial f/\partial H$. Then Eq. (1) reduces to

$$\rho_R = \frac{1}{\sigma^{zz}} = \frac{3\tilde{V}}{4\hbar|j_{\vec{k}_F}|^2}\int d\Omega'\langle|\langle\vec{k}_F|W|\vec{k}'\rangle|^2\rangle_{\mathrm{av}} \times(1-\cos\theta_{\vec{k}_F\vec{k}'}) \qquad (6)$$

where $\vec{k}_F$ is a vector on the Fermi surface. Note that the density of states factor [dE_k/dk in Eq. (5)] cancels with a similar factor from the trace in Eq. (1) so that there is no effective mass contribution to the resistivity from this source.

In order to assign a value to the matrix elements $j_{\vec{k}} = \langle\vec{k}|j|\vec{k}\rangle$ we need to know what current is carried by the pseudowave $|\vec{k}\rangle$. This current is carried by the true wave function $\psi_{\vec{k}}$ which corresponds to the pseudowave $|\vec{k}\rangle$. The pseudowaves $|\vec{k}\rangle$ which have been used as a basis in deriving Eq. (6) from the Kubo formula are by definition eigenfunctions of the *diagonal part* H_d of the pseudo-Hamiltonian $H_o + W$, i.e.,

$$\langle\vec{k}|H_d|\vec{k}'\rangle \equiv \delta_{\vec{k}\vec{k}'}(\langle\vec{k}|H_o + W|\vec{k}'\rangle) = E_{\vec{k}}\delta_{\vec{k}\vec{k}'}, \qquad (7)$$

where $E_{\vec{k}}$ is the same as in Eq. (4).

Now note that the true wave functions $\psi_{\vec{k}}$ which correspond to pseudowaves $|\vec{k}\rangle$ are eigenfunctions (with *same* eigenvalues $E_{\vec{k}}$) of the true Hamiltonian $H_o + V'$ which corresponds to the pseudo-Hamiltonian H_d.

It has been shown by Faber[19] that with the above definitions

$$\int \psi^*_{\vec{k}}\nabla\psi_{\vec{k}}\,d\vec{r} = \frac{im}{\hbar^2}\nabla_{\vec{k}}E_{\vec{k}} \qquad (8)$$

from which it follows that the general expression

$$-\frac{\hbar e}{2mi}\int d\vec{r}\,(\psi^*_{\vec{k}}\nabla\psi_{\vec{k}} - \psi_{\vec{k}}\nabla\psi^*_{\vec{k}})$$

for the current carried by $\psi_{\vec{k}}$ reduces to $-(e/\hbar)\nabla_{\vec{k}}E_{\vec{k}}$. Thus our identification of $j_{\vec{k}}$ with this current gives

$$j_{\vec{k}} = -(e/\hbar)\nabla_{\vec{k}}E_{\vec{k}} \equiv -ev_{\vec{k}}. \qquad (9)$$

The proof of Eq. (8) given by Faber relies on disregarding the difficulties which arise when one considers the effects of exchange and correlation of the conduction electrons. However, approximations of this kind are already inherent in the form chosen for W by Stark and Falicov[8] and we shall not go more deeply into this matter in the present paper.

Given these limitations, the result of Eq. (9) does not contain explicitly the true wave function $\psi_{\vec{k}}$ or the potential V' appearing in the above discussion, but only H_d, i.e., Eqs. (6) and (9) give the natural separation of H_0+W into two parts H_d and H_0+W-H_d, the former part determining the properties $E_{\vec{k}}$ and $j_{\vec{k}}$ of the basic states $|\vec{k}\rangle$ and the latter giving the scattering between them.

At this point one should note a serious shortcoming of the local pseudopotentials which have been used in the past in resistivity calculations. A local pseudopotential cannot give the correct dependence of $E_{\vec{k}} = \langle\vec{k}|H_0|\vec{k}\rangle + \langle\vec{k}|W|\vec{k}\rangle$ on $\vec{k}$, since in the local pseudopotential scheme $\langle\vec{k}|W|\vec{k}\rangle$ is independent of $\vec{k}$ (and equal to $-\frac{2}{3}E_F$). Thus if the less sophisticated local pseudopotential is used instead of the correct nonlocal one in calculating $j_{\vec{k}}$ from Eq. (9), there is no contribution to $j_{\vec{k}}$ or $v_{\vec{k}}$ from the pseudopotential W, and $v_{\vec{k}_F}$ and $j_{\vec{k}_F}$ reduce to their free-electron values. This difficulty does not arise if the nonlocal pseudopotential is used since in that case the correct dependence of $\langle\vec{k}|W|\vec{k}\rangle$ on $\vec{k}$ is not suppressed. Thus

$$j_{\vec{k}_F} = \frac{-e\hbar k_F}{m_1^*} \equiv \frac{-e\hbar k_F}{m} - \frac{e}{\hbar}\left(\frac{\partial}{\partial k}\langle\vec{k}|V|\vec{k}\rangle\right)_{\vec{k}=\vec{k}_F} \qquad (10)$$

and an effective mass which is different from the free-electron mass should be used in the Ziman formula.

It is easy to see from the above derivation of Eq. (9) for $j_{\vec{k}}$ that inserting the current in Eq. (10) into the resistivity in Eq. (6) has the same effect as applying the "core correction" factor

$$k^2\left|\int \psi_{\vec{k}}^* \nabla \psi_{\vec{k}}\, d\vec{r}\right|^2$$

found by Faber,[5] to the conventional Ziman formula (where the free-electron Fermi velocity is used). In fact, Faber has pointed out[19] that the above core correction factor is equal to $(m_1^*/m)^2$ where m_1^* is the first-order effective mass defined by Eq. (10). Faber's rough estimate[5] of the size of the core correction factor, which was made by approximating $\psi_{\vec{k}}$ by an orthogonalized plane wave is consistent with the value of $j_{\vec{k}_F}$ which we obtain from Eq. (10). It should be emphasized, however, that such core corrections are not consistent with the use of a local pseudopotential and should not be considered as a valid remedy for the shortcomings of the latter. Neither is it correct, as has been pointed out by Edwards[20] and others (who worked with local pseudopotentials) to use the *exact* eigenvalues of H_0+W in place of $E_{\vec{k}}$ in Eq. (9).

III. CALCULATIONS AND RESULTS

In order to compute the electrical resistivity we approximate the total pseudopotential of the metal by a sum of pseudopotentials centered at individual ion sites $\vec{R}_\nu$. The pseudopotential matrix elements can then be written

$$\langle\vec{k}|W|\vec{k}'\rangle = \frac{1}{N}\sum_\nu e^{i(\vec{k}-\vec{k}')\cdot\vec{R}_\nu} \times \omega_{\mathrm{L}}(|\vec{k}-\vec{k}'|) + \langle\vec{k}|\omega_{\mathrm{NL}}|\vec{k}'\rangle], \qquad (11)$$

where w_{L} and w_{NL} are, respectively, the local and nonlocal parts of the single-ion pseudopotential. For Cd the nonlocal pseudopotential of Stark and Falicov[8] has the following form

$$\langle\vec{k}|\omega_{\mathrm{NL}}|\vec{k}'\rangle = \frac{4\pi}{\Omega_0}\sum_l (2l+1)\lambda_l T_l(k)\, T_l(k')\, P_l(\cos\theta_{kk'}), \qquad (12)$$

where Ω_0 is the volume per atom. The summation over the orbital angular momentum l is carried out over the outermost occupied core orbitals of Cd. The parameters λ_l and the local form factors $w_L(q)$ were determined empirically from the Fermi-surface data. T_l is the Bessel transform of the radial part of the lth core orbital, R_l

$$T_l(k) = \int_0^\infty dr\, j_l(kr) R_l(r) r^2. \qquad (13)$$

It is important to note that while the nonlocal part of the pseudopotential in Eq. (12) can be generated for continuous values of momentum transfer, $q=|\vec{k}-\vec{k}'|$ from the information available in the literature,[8] the local part, $w_L(q)$ is available only for four reciprocal-lattice vectors that cover the range $0.8 < q/2k_F < 1$. However, Allen *et al.*[9] have used an interpolation procedure to compute $w_L(q)$ for $0 < q/2k_F < 1$ for their calculation of electron-phonon mass enhancement in solid Cd. In our present calculation we have used the form factors of Allen *et al.*[9] after suitable volume renormalizing[21,22] for the appropriate density of the liquid.

Inserting Eq. (11) into Eq. (6) one finds

$$\rho_R = \frac{3\pi\Omega_0}{2v_F^2 e^2\hbar}\int_{-1}^{1} dx(1-x)\left(\omega_L[\sqrt{2}\,k_F(1-x)^{1/2}] + \frac{4\pi}{\Omega_0}\sum_l \lambda_l(2_l+1)P_l(x)\,T_l^2(k_F)\right)^2 I[\sqrt{2}\,k_F(1-x)^{1/2}], \qquad (14)$$

where the liquid structure factor $I(q)$ is defined by the thermal average

$$I(q)=\left\langle \frac{1}{N}\sum_{\mu\nu} e^{i\vec{q}\cdot(\vec{R}_\nu-\vec{R}_\mu)}\right\rangle_{\text{av}}.$$

In our computations we have used the experimental interference functions.[23]

Using the free-electron value for $v_{\vec{k}_F}$ we compute ρ_R from Eq. (14) to be 72 $\mu\Omega$ cm. As pointed out above the effective mass correction does enter in the leading order in the nonlocal pseudopotential treatment. We find the effective mass in Eq. (10) to be $0.85m$. Including this effective mass correction in Eq. (14), our theoretical value for ρ_R is 52 $\mu\Omega$ cm whereas the experimental value is 34 $\mu\Omega$ cm.

At this point it is interesting to compare our nonlocal results with those obtained from local pseudopotentials and with the nonlocal result of Greenfield and Wiser.[13] Using the model potential of Animalu and Heine as listed by Harrison[22] we obtain $\rho_R = 6$ $\mu\Omega$ cm in marked contrast with both experiment and our nonlocal result. Using the pseudopotential values of Shyu *et al.*[7] we reproduce their value of $\rho_R = 20$ $\mu\Omega$ cm. The sensitivity of ρ_R to the choice of pseudopotential has already been pointed out in the literature. Our findings further confirm this point.

Recently Greenfield and Wiser[13] using a Stark-Falicov pseudopotential[8] have calculated ρ_R of liquid Cd to be 3.6 times that of the experiment. They interprete this discrepancy as "evidence" for the breakdown of the Born approximation for liquid Cd. However, our result using the Stark-Falicov pseudopotential[8] differs from that of GW[13] and is in much better agreement with experiment. The source of the discrepancy, we believe, is probably due in part to numerical error in GW's calculation. We find no substantial evidence for the breakdown of the Born approximation.

To further illustrate the delicate role of the pseudopotential in liquid resistivity calculations, we present in Fig. 1 (a) comparison of the local and nonlocal pseudopotentials and in Fig. 2 the integrands of Eq. (14) for local and nonlocal pseudopotentials. It is obvious from these figures that the node of the potential plays a crucial role in determining the magnitude of the resistivity. However, the position of this node is arbitrary to a certain extent, depending on the model selected. In comparing theory with experiment, care must be taken in choosing a potential that has been shown to describe several other electronic properties well. The Stark-Falicov potential[8] seems to meet this criterion. Although our present nonlocal result for ρ_R is nearer to experiment than previous calculations there still remain appreciable quantitative differences between theory and experiment and further work is necessary to bridge this gap.

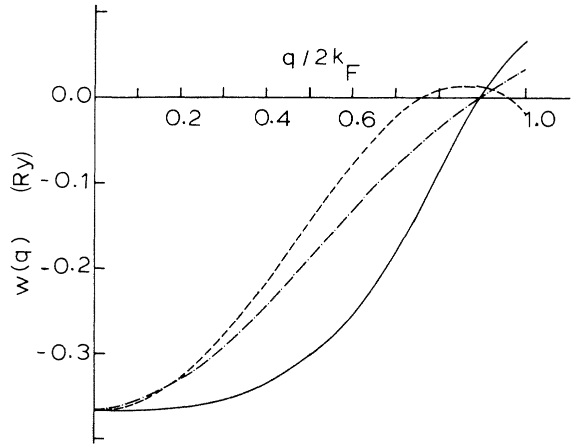

FIG. 1. Pseudopotential form factors (in Ry) for scattering on the Fermi surface ($|\vec{k}| = |\vec{k}'| = k_F$); dashed line, and dash-dotted line are, respectively, local potentials of Animalu and Heine, and Shyu *et al*. Solid line is the nonlocal pseudopotential of Stark and Falicov. Note that these curves do not contain volume-renormalization factors.

IV. DISCUSSION

At the present time there is no satisfactory theory of the leading corrections to the Ziman formula in Eq. (14). Attempts have been made by Springer[2] and Ashcroft *et al.*[4] to go beyond the leading order

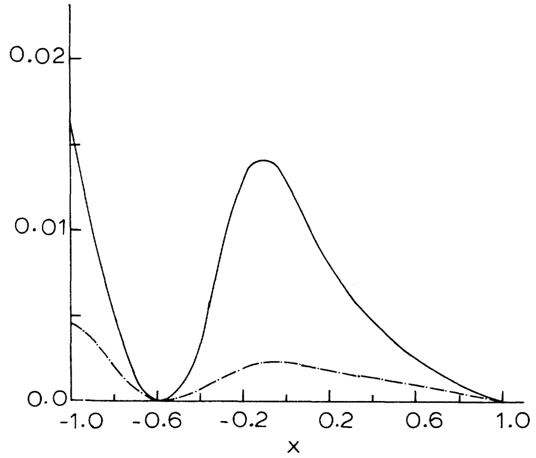

FIG. 2. Integrand of Eq. (14) as a function of x, the cosine of the angle between $\vec{k}$ and $\vec{k}'$. Dash-dotted line is obtained by using the local pseudopotential of Shyu *et al*., while the solid line corresponds to that using the nonlocal pseudopotential of Stark and Falicov. Note that these curves do not contain correction due to volume-renormalization of pseudopotential form factors.

in perturbation theory in conductivity calculations. Their work is based on the assumption that the pseudopotential W may be treated as if it were a true potential even in such higher-order calculations. Their results should not be considered accurate because of the objections to the use of this assumption as discussed by Greenwood,[3] and also because of their use of the local potential approximation which as we have seen is not capable even of giving the correct electronic effective mass for the calculation.

There have also been suggestions that even the assumption A as stated in Sec. II, might need to be modified. For example, Austin *et al.*[24] have suggested that an additional normalization factor may be needed in the expression for the transition probability obtained in the conventional way from the matrix $\langle\vec{k}|W|\vec{k}'\rangle$. Still other corrections have been proposed by Faber. Work is in progress on these aspects of the problem.

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