

Exchange and Correlation Effects in Electron-Phonon Scattering in Normal Metals*

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The theory of Bardeen for the electron shielding of the perturbation potential arising from lattice vibrations is extended to cover exchange and correlation effects. The method is to set up a self-consistent set of one-electron equations, and calculate the effect of the perturbation in the charge densities. The exchange term is corrected to conform to the results of the Bohm-Pines theory, but the plasma wave function is assumed not to be disturbed by the lattice. With this approximate model, a solution to the problem can be obtained. For small-angle scattering, the results do not return to the original Bardeen values. The interaction potential matrix element depends on the initial electron wave vector \mathbf{k} as well as on the difference between initial and final state wave vectors. Hence, to use the results an average over \mathbf{k} must be made, and we make an average over the Fermi surface. The general effect of the exchange hole is to increase the scattering.

I. INTRODUCTION

THE problem of the scattering of electrons by lattice vibrations in a solid is complicated by the fact that both the ions and the particle electrons are shielded by electron clouds. If the electron cloud around an ion vibrated rigidly with the ion, we would have complete shielding of the perturbation outside the cell. If the hole around an electron moved rigidly with the electron, and did not tend to pick up some of the lattice motion itself, we would have no exchange and correlation effects other than the effect on the equilibrium properties such as the unperturbed energy functions. The shielding around an ion was treated by Bardeen,¹ and a discussion of the exchange and correlation problem was given by Bardeen and Pines.²

The purpose of this paper is to extend the Bardeen¹ method to take account of exchange and correlation effects. Bardeen and Pines treated the same problem by taking the complete system of phonons and electrons, the latter interacting with the phonons as well as among themselves, and making canonical transformations which were designed to produce a Hamiltonian in which appear "new electrons" which do not interact with each other, "new phonons," and a plasma which is roughly independent of the "new electrons" and "new phonons." They demand also a certain kind of self-consistency requirement, which then yields a new effective electron-phonon interaction matrix element. This method is rigorous. But at the end of their transformations [see Eqs. (4.5) and (4.7) of reference 2] the electrons are still interacting by means of the short-range term in the Hamiltonian (their $H_{s.r.}$). It is only by assuming that this remaining interaction is negligible that these authors conclude that their present result confirms the 1937 Bardeen result for the long-wave modes.³ The

short-range term will affect, however, not just the matrix elements for large $\mathbf{k}-\mathbf{k}'$ (where \mathbf{k} is the initial state wave vector and \mathbf{k}' the final state wave vector for the electron in the interaction) but rather the matrix elements for all $\mathbf{k}-\mathbf{k}'$. In the present paper we separate out the effect of $H_{s.r.}$ and calculate its consequence on the matrix element. We do not find the 1937 Bardeen result even in the limit $\mathbf{k}-\mathbf{k}' \rightarrow 0$.

In Sec. III, we treat exchange in the Hartree-Fock equation, and show that the matrix element is not independent of the initial electron wave vector \mathbf{k} , even when free-electron wave functions are used, and even when the ion part is treated as independent of \mathbf{k} . In Sec. IV, we modify the exchange term of the potential in the Hartree-Fock equation to conform to the general results of the Bohm-Pines⁴ theory and thereby construct an approximate one-electron equation incorporating exchange and correlation effects. The basic approximation involved is that the lattice does not affect the plasma part of the electron system wave function. The solution then follows exactly the plan of Sec. III, and the effect of the short-range electron interaction is thereby calculated.

It should be mentioned that the exchange and correlation effects are quite different from the Coulomb effect. (We term the Coulomb effect that which gives the Bardeen result.) The Coulomb effect is a shielding of the positive ion, the exchange and correlation effect is shielding of the negative electron, the two screening clouds having different charge sign. When the electron cloud around an ion picks up the lattice motion from the ion, it tends to shield the ion vibrations, whereas the hole around an electron, when it picks up the lattice motion from the ion, will tend to scatter the electron more. We find in addition that the effect of including exchange in the unperturbed energy functions is also to increase the scattering.

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¹ J. Bardeen, Phys. Rev. **52**, 688 (1937).

² J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

³ The author is profoundly grateful to Professor Bardeen for a conversation in which this was pointed out. See however footnote 7.

⁴ D. Pines, Phys. Rev. **92**, 626 (1953). Reference is also made to D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953). These articles are abbreviated as PIV and BP111, respectively.

II. THE METHOD OF BARDEEN

Starting from a one-electron equation

$$(\hat{p}^2/2m + V_{\text{ion}} + V_{\text{elec}})\psi(\mathbf{k}, 1) = E(\mathbf{k})\psi(\mathbf{k}, 1),$$

where V_{ion} is the potential from the quiet lattice, and V_{elec} is the electron-electron interaction potential (in general an integral operator), if we add to the Hamiltonian a perturbation δV_{ion} of the bare lattice potential (δV_{ion} representing the lattice vibrations), then there will be an associated perturbation δV_{elec} of V_{elec} . Bardeen¹ thus considered the matrix element of the total perturbation

$$v(\mathbf{k}, \mathbf{s}) = \int \psi(\mathbf{k} + \mathbf{s}, 1)^* \delta V \psi(\mathbf{k}, 1) d\mathbf{r}_1 \quad (1)$$

as the sum of two terms $v_{\text{ion}}(\mathbf{k}, \mathbf{s})$ and $v_{\text{elec}}(\mathbf{k}, \mathbf{s})$:

$$\begin{aligned} v_{\text{ion}}(\mathbf{k}, \mathbf{s}) &= \int \psi(\mathbf{k} + \mathbf{s}, 1)^* \delta V_{\text{ion}} \psi(\mathbf{k}, 1) d\mathbf{r}_1, \\ v_{\text{elec}}(\mathbf{k}, \mathbf{s}) &= \int \psi(\mathbf{k} + \mathbf{s}, 1)^* \delta V_{\text{elec}} \psi(\mathbf{k}, 1) d\mathbf{r}_1, \end{aligned} \quad (2)$$

where $v_{\text{ion}}(\mathbf{k}, \mathbf{s})$ is the matrix element of the bare lattice vibrations and is assumed known and independent of the initial electron wave vector \mathbf{k} , and where $v_{\text{elec}}(\mathbf{k}, \mathbf{s})$ is the associated effect of the electron-electron interaction and is considered unknown. The point of the calculation is to obtain $v_{\text{elec}}(\mathbf{k}, \mathbf{s})$. The notation is as follows: \mathbf{s} is the change in electron wave vector in a scattering process. In a normal process $\mathbf{s} = \boldsymbol{\sigma}$, where $\boldsymbol{\sigma}$ is the phonon wave vector, and in an umklapp process, $\mathbf{s} = \boldsymbol{\sigma} + \mathbf{K}$, where \mathbf{K} is a reciprocal lattice vector. $\psi(\mathbf{k}, 1)$ is the wave function for an electron in the k th state when the position coordinate is \mathbf{r}_1 . We shall frequently use just "1" to indicate " \mathbf{r}_1 " in the argument of a function.

Bardeen used the Hartree potential for V_{elec} so that

$$\delta V \psi(\mathbf{k}, 1) = \delta V_{\text{ion}} \psi(\mathbf{k}, 1) - e \int \frac{\delta \rho_{\text{Coul}}(2) \psi(\mathbf{k}, 1)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2, \quad (3)$$

where the effect in V_{elec} has been conceived as a perturbation in the charge density ρ_{Coul} :

$$\delta \rho_{\text{Coul}}(2) = -\delta [e \sum_{\mathbf{k} \text{ occ}'} |\psi(\mathbf{k}, 2)|^2], \quad (4)$$

and where δV_{ion} is the perturbation in the potential caused by the rigid ion motion neglecting any shielding effects. By first order perturbation theory we get

$$\delta \psi(\mathbf{k}, 1) = \sum_n [\hat{b}(\mathbf{k}, \mathbf{s}_n) \psi(\mathbf{k} + \mathbf{s}_n, 1) + \hat{b}(\mathbf{k}, -\mathbf{s}_n) \psi(\mathbf{k} - \mathbf{s}_n, 1)], \quad (5)$$

$$\hat{b}(\mathbf{k}, \mathbf{s}_n) = v(\mathbf{k}, \mathbf{s}_n) [E(\mathbf{k}) - E(\mathbf{k} + \mathbf{s}_n)]^{-1}. \quad (6)$$

Here $\mathbf{s}_n = \boldsymbol{\sigma} + \mathbf{K}_n$, and the sum over n is a sum over reciprocal lattice vectors, given $\boldsymbol{\sigma}$. Bardeen's result is

then obtained by substituting (4), (5), and (6) into (3), multiplying by $\psi(\mathbf{k} + \mathbf{s}, 1)^*$ and integrating.

$$\begin{aligned} v(\mathbf{k}, \mathbf{s}) &= v_{\text{ion}}(\mathbf{k}, \mathbf{s}) + \sum_{\mathbf{k} \text{ occ}'} \sum_n [\hat{b}(\mathbf{k}', \mathbf{s}_n) A_1 + \hat{b}(\mathbf{k}', -\mathbf{s}_n) A_2 \\ &\quad + \hat{b}(\mathbf{k}', \mathbf{s}_n)^* A_3 + \hat{b}(\mathbf{k}', -\mathbf{s}_n)^* A_4], \end{aligned} \quad (7)$$

where

$$\begin{aligned} A_i &= 2e^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \psi(\mathbf{k} + \mathbf{s}, 1)^* \psi(\mathbf{k}, 1) \Phi_i, \\ \Phi_1 &= \psi(\mathbf{k}' + \mathbf{s}_n, 2) \psi(\mathbf{k}', 2)^*, \\ \Phi_2 &= \psi(\mathbf{k}' - \mathbf{s}_n, 2) \psi(\mathbf{k}', 2)^*, \\ \Phi_3 &= \psi(\mathbf{k}' + \mathbf{s}_n, 2)^* \psi(\mathbf{k}', 2), \\ \Phi_4 &= \psi(\mathbf{k}' - \mathbf{s}_n, 2)^* \psi(\mathbf{k}', 2), \end{aligned} \quad (8)$$

and where the 2 in A_i is from spin. If plane wave electron functions are used to compute the integrals, we get

$$\begin{aligned} A_1 &= A_4 = \delta_{n,0} 4\pi e^2 / \Delta s^2 = \lambda E_0(s) \delta_{n,0}, \\ A_2 &= A_3 = 0, \end{aligned} \quad (9a)$$

where the delta function $\delta_{n,0}$ means zero unless $K_n = K$, and where

$$\begin{aligned} E_0(s) &= \hbar^2 s^2 / 2m, \\ \lambda &= 4\pi e^2 / \Delta s^2 E_0(s). \end{aligned} \quad (9b)$$

Here Δ is the crystal volume. Equation (8) can be rewritten

$$\begin{aligned} v(\mathbf{k}, \mathbf{s}) &= v_{\text{ion}}(\mathbf{s}) - \lambda \sum_{\substack{\mathbf{k} \text{ occ}' \\ \text{one spin}}} [a_s'(\mathbf{k}, \mathbf{k}') v(\mathbf{k}', \mathbf{s}) \\ &\quad + b_s'(\mathbf{k}, \mathbf{k}') v(\mathbf{k}', -\mathbf{s})^*], \end{aligned} \quad (10)$$

$$a_s'(\mathbf{k}, \mathbf{k}') = -2E_0(s) [E(\mathbf{k}') - E(\mathbf{k}' + \mathbf{s})]^{-1}, \quad (10a)$$

$$b_s'(\mathbf{k}, \mathbf{k}') = -2E_0(s) [E(\mathbf{k}') - E(\mathbf{k}' - \mathbf{s})]^{-1}. \quad (10b)$$

Further, v_{ion} is imaginary, and $v_{\text{ion}}(-\mathbf{s}) = -v_{\text{ion}}(\mathbf{s})$, whence it can be concluded that $v(-\mathbf{k}, -\mathbf{s}) = -v(\mathbf{k}, \mathbf{s})$. (We shall prove this later under more general circumstances.) Thus treating the imaginary parts only, of the equation, we get

$$v(\mathbf{k}, \mathbf{s}) = v_{\text{ion}}(\mathbf{s}) - \lambda \sum_{\mathbf{k} \text{ occ}'} a_s(\mathbf{k}, \mathbf{k}') v(\mathbf{k}', \mathbf{s}), \quad (11a)$$

$$a_s(\mathbf{k}, \mathbf{k}') = -4E_0(s) [E(\mathbf{k}') - E(\mathbf{k}' + \mathbf{s})]^{-1}, \quad (11b)$$

where the imaginary part of $v(\mathbf{k}, \mathbf{s})$ is meant. Now since the $a(\mathbf{k}, \mathbf{k}')$ are independent of \mathbf{k} , it follows that the v 's also are independent of \mathbf{k} , and we get Bardeen's solution

$$v(\mathbf{s}) = v_{\text{ion}}(\mathbf{s}) \frac{1}{1 + \lambda \sum_{\mathbf{k} \text{ occ}'} a_s(\mathbf{k}, \mathbf{k}')} \quad (12)$$

III. THE EFFECT OF EXCHANGE

In treating the effect of exchange, we revise equations (3)–(6) and combine them to form an equation analogous to (7). We may leave (5) and (6) as above if we understand $v(\mathbf{k}, \mathbf{s})$ and $E(\mathbf{k})$ to contain the exchange effects. (3) and (4) become on the Hartree-Fock model:

$$\delta V\psi(\mathbf{k}, 1) = \delta V_{\text{ion}}\psi(\mathbf{k}, 1) - e \int d\mathbf{r}_2 \frac{\delta \rho_{\text{Coul}}(2)\psi(\mathbf{k}, 1)}{|\mathbf{r}_1 - \mathbf{r}_2|} + e \int d\mathbf{r}_2 \frac{\delta \rho_{\text{ex}}(2, 1)\psi(\mathbf{k}, 2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (13)$$

$$\delta \rho_{\text{ex}}(2, 1) = -\delta \left[e \sum_{k_{\text{occ}}' \parallel \text{spins}} \psi(\mathbf{k}', 1)\psi(\mathbf{k}', 2)^* \right]. \quad (14)$$

Substituting (5) and (6) into (13) and (14), we get

$$v(\mathbf{k}, \mathbf{s}) = v_{\text{ion}}(\mathbf{k}, \mathbf{s}) + \sum_{k_{\text{occ}}'} \sum_n [b(\mathbf{k}', \mathbf{s}_n)(A_1 + B_1) + b(\mathbf{k}', -\mathbf{s}_n)(A_2 + B_2) + b(\mathbf{k}', \mathbf{s}_n)^*(A_3 + B_3) + b(\mathbf{k}', -\mathbf{s}_n)^*(A_4 + B_4)], \quad (15)$$

where the A 's were defined in (7) and evaluated in (9), and where

$$B_i = e^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \psi(\mathbf{k} + \mathbf{s}, 1)^* \psi(\mathbf{k}, 2) \Phi_i', \quad (16)$$

$$\begin{aligned} \Phi_1' &= \psi(\mathbf{k}' + \mathbf{s}_n, 1)\psi(\mathbf{k}', 2)^*, \\ \Phi_2' &= \psi(\mathbf{k}' - \mathbf{s}_n, 1)\psi(\mathbf{k}', 2)^*, \\ \Phi_3' &= \psi(\mathbf{k}' + \mathbf{s}_n, 2)^*\psi(\mathbf{k}', 1), \\ \Phi_4' &= \psi(\mathbf{k}' - \mathbf{s}_n, 2)^*\psi(\mathbf{k}', 1). \end{aligned}$$

Using free electron wave functions, we get

$$\begin{aligned} B_1 &= \lambda \delta_{n,0} s^2 E_0(s) |\mathbf{k} - \mathbf{k}'|^{-2} \Delta^{-1}, \\ B_2 &= B_3 = 0, \\ B_4 &= \lambda \delta_{n,0} s^2 E_0(s) |\mathbf{k} + \mathbf{k}' + \mathbf{s}|^{-2} \Delta^{-1}. \end{aligned} \quad (17)$$

The integrals which are zero are so because they are proportional to the delta function $\delta(2\sigma + \mathbf{K} - \mathbf{K}_n)$, which is zero except for the insignificant states of zero σ or some few σ 's on the surface of the Brillouin zone. The delta function $\delta_{n,0}$ means zero unless $K = K_n$.

Equation (15) may be written in a more compact form as

$$v(\mathbf{k}, \mathbf{s}) = v_{\text{ion}}(\mathbf{k}, \mathbf{s}) - \lambda \sum_{k_{\text{occ}}' \text{ one spin}} [a_s'(\mathbf{k}, \mathbf{k}')v(\mathbf{k}', \mathbf{s}) + b_s'(\mathbf{k}, \mathbf{k}')v(\mathbf{k}', -\mathbf{s})^*], \quad (18)$$

$$a_s'(\mathbf{k}, \mathbf{k}') = -\frac{E_0(s)}{E(\mathbf{k}') - E(\mathbf{k}' + \mathbf{s})} \left(2 - \frac{s^2}{|\mathbf{k} + \mathbf{k}' + \mathbf{s}|^2} \right), \quad (19)$$

$$b_s'(\mathbf{k}, \mathbf{k}') = -\frac{E_0(s)}{E(\mathbf{k}') - E(\mathbf{k}' - \mathbf{s})} \left(2 - \frac{s^2}{|\mathbf{k} - \mathbf{k}'|^2} \right). \quad (20)$$

To solve (18), we shall separate into real and imaginary parts. Further, we need write down only the imaginary equation, for v_{ion} is pure imaginary. The imaginary part of v then satisfies the following equation [obtained from (18)]

$$v(\mathbf{k}, \mathbf{s}) = v_{\text{ion}}(\mathbf{s}) - \lambda \sum_{k_{\text{occ}}' \text{ one spin}} [a_s'(\mathbf{k}, \mathbf{k}')v(\mathbf{k}', \mathbf{s}) - b_s'(\mathbf{k}, \mathbf{k}')v(\mathbf{k}', -\mathbf{s})], \quad (21)$$

where strictly speaking we should have a superscript "im" on v to indicate "imaginary part of." We shall omit this cumbersome notation and mean from here on "the imaginary part of v " by " v " itself. It can be seen that $v(-\mathbf{k}, -\mathbf{s}) = -v(\mathbf{k}, \mathbf{s})$. This follows from the fact (not proved here) that $v_{\text{ion}}(-\mathbf{s}) = -v_{\text{ion}}(\mathbf{s})$. For then the equation for $v(-\mathbf{k}, -\mathbf{s})$ is

$$\begin{aligned} v(-\mathbf{k}, -\mathbf{s}) &= -v_{\text{ion}}(\mathbf{s}) - \lambda \sum_{k_{\text{occ}}'} [a_{-s}'(-\mathbf{k}, \mathbf{k}')v(\mathbf{k}', -\mathbf{s}) - b_{-s}'(-\mathbf{k}, \mathbf{k}')v(\mathbf{k}', \mathbf{s})] \\ &= -v_{\text{ion}}(\mathbf{s}) - \lambda \sum_{k'} a_s'(\mathbf{k}, \mathbf{k}')v(-\mathbf{k}', -\mathbf{s}) - b_s'(\mathbf{k}, \mathbf{k}')v(-\mathbf{k}', \mathbf{s}), \end{aligned} \quad (22)$$

making use of the fact that $a_{-s}(-\mathbf{k}, -\mathbf{k}') = a_s(\mathbf{k}, \mathbf{k}')$, $b_{-s}(-\mathbf{k}, -\mathbf{k}') = b_s(\mathbf{k}, \mathbf{k}')$ and that for every \mathbf{k} in the sum there is a $-\mathbf{k}$. Now (22) is the same equation for the $v(-\mathbf{k}, -\mathbf{s})$ that (21) is for the $v(\mathbf{k}, \mathbf{s})$ except that there is a minus sign before the v_{ion} . Since the solutions are linear in v_{ion} , they must then be the negative of each other:

$$v(-\mathbf{k}, -\mathbf{s}) = -v(\mathbf{k}, \mathbf{s}), \quad (23)$$

which is what we wished to show. Use of this in (21) simplifies that equation to

$$v(\mathbf{k}, \mathbf{s}) = v_{\text{ion}}(\mathbf{s}) - \lambda \sum_{k_{\text{occ}}' \text{ one spin}} a_s(\mathbf{k}, \mathbf{k}')v(\mathbf{k}', \mathbf{s}), \quad (24)$$

where

$$\begin{aligned} a_s(\mathbf{k}, \mathbf{k}') &= a_s'(\mathbf{k}, \mathbf{k}') + b_s'(\mathbf{k}, -\mathbf{k}') \\ &= -\frac{E_0(s)}{E(\mathbf{k}') - E(\mathbf{k}' + \mathbf{s})} \\ &\quad \times \left[4 - \frac{s^2}{|\mathbf{k} + \mathbf{k}' + \mathbf{s}|^2} - \frac{s^2}{|\mathbf{k} - \mathbf{k}'|^2} \right]. \end{aligned} \quad (25)$$

The solutions to (24) can be obtained from the theory of linear integral equations (see Courant and Hilbert).⁵ However, it must be remarked that the one point $\mathbf{k} = \mathbf{k}'$ strictly speaking does not enter the Hartree-Fock sums, and it should be ruled out in (23). A glance at (25) shows that $a(\mathbf{k}, \mathbf{k})$ actually explodes. If we rule out, as

⁵ R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1953), Vol. 1, Secs. III 7 and 9.

we should, the points $\mathbf{k}'=\mathbf{k}$, then it is equivalent to defining the diagonal elements of $a(\mathbf{k},\mathbf{k}')$ as zero. Now if the term did not actually explode, the contribution to the sum of one term would be relatively very small since λ is proportional to Δ^{-1} , where Δ is the crystal volume. (Such is the case for the Coulomb contribution.) The difficulty may be overcome if we do not seek to find the rigorous solution to the set of Eqs. (24). There is a question anyway about whether in our case the numerator and denominator determinants in the solutions in the reference cited will converge rapidly, for although λ is small, the density of k states is compensatingly large.

The transport coefficients into which our matrix element ultimately goes are quite complicated things, and it is almost beyond question to attempt to use detailed information on the dependence of $v(\mathbf{k},\mathbf{s})$ on \mathbf{k} [see, however (31)]. Thus in (24), we use an iteration procedure for solving, trying for the zero order trial solution a constant $v_0(\mathbf{s})$. If we integrate Eq. (24) over all \mathbf{k} , then we can solve for v_0 in terms of

$$\langle a_s \rangle = [(4\pi/3)k_0^3]^{-2} \int d\mathbf{k} d\mathbf{k}' a_s(\mathbf{k},\mathbf{k}'), \quad (26)$$

and the result is

$$v_0(\mathbf{s}) = v_{\text{ion}}(\mathbf{s}) \frac{1}{1 + \lambda_0 \langle a_s \rangle}, \quad (27)$$

$$\lambda_0 = N\lambda = \frac{4\pi e^2}{\Delta_0 s^2 E_0(\mathbf{s})} = \left[12\pi \left(\frac{9\pi}{4} \right)^{\frac{1}{2}} \right]^{-1} \frac{r_s/a_n}{u^4}, \quad (28)$$

where r_s is the Wigner-Seitz cell radius, and $u = |\mathbf{k} - \mathbf{k}'|/2k_0$ is Bardeen's u . a_n is the Bohr radius. $\Delta_0 = \Delta/N$ is the atomic volume.

We arrive then for a zeroth approximation at a form identical to (12) but containing an exchange term as well as the Coulomb term, the divergence no longer appearing because the integrals involved smooth it over. As a first iteration, we may substitute (27) into the right hand side of (24), and get

$$v_1(\mathbf{k},\mathbf{s}) = v_{\text{ion}}(\mathbf{s}) \frac{1 + \lambda_0 (\langle a_s \rangle - \langle a_s(\mathbf{k}) \rangle)}{1 + \lambda_0 \langle a_s \rangle}, \quad (29)$$

$$\langle a_s(\mathbf{k}) \rangle = \frac{3}{4\pi k_0^3} \int d\mathbf{k}' a_s(\mathbf{k},\mathbf{k}'). \quad (30)$$

We may then hope that the correction term in the numerator of (29) is small. We may further refine the result by averaging (29) over the k 's on the Fermi surface. Denoting such an average by

$$[\langle a_s(\mathbf{k}) \rangle]_{\text{F.S.}} \equiv \frac{1}{4\pi k_0^2} \int_{\text{F.S.}} dS \langle a_s(\mathbf{k}) \rangle, \quad (31)$$

we find

$$[v_1(\mathbf{k},\mathbf{s})]_{\text{F.S.}} = v_{\text{ion}}(\mathbf{s}) \frac{1 + \lambda_0 (\langle a_s \rangle - [\langle a_s(\mathbf{k}) \rangle]_{\text{F.S.}})}{1 + \lambda_0 \langle a_s \rangle} \quad (32)$$

for our first iteration. It should be noted that there are no Coulomb contributions to any of the corrections introduced by the iterations, since for the Coulomb part, the $a(\mathbf{k},\mathbf{k}')$ do not depend on \mathbf{k} , so that averaging one way or another over \mathbf{k} will have no effect.

IV. EFFECT OF EXCHANGE, CORRECTED

According to the work of Bohm and Pines,⁴ if the Coulomb interaction between electrons in a solid is Fourier analyzed into two parts

$$e^2 |\mathbf{r}_1 - \mathbf{r}_2|^{-1} = 4\pi e^2 \Delta^{-1} \left(\sum_{k'' < k_c} (k'')^{-2} e^{i\mathbf{k}'' \cdot (\mathbf{r}_1 - \mathbf{r}_2)} + \sum_{k'' > k_c} (k'')^{-2} e^{i\mathbf{k}'' \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \right), \quad (33)$$

where the parameter k_c is

$$k_c = \beta k_0 = 0.353 (r_s/a_n)^{\frac{1}{2}} k_0, \quad (34)$$

then the exchange energy should be modified to include only the second term in (34). This is their conclusion, and one obtains the one-electron energies taking exchange and correlation into account by calculating⁶

$$\begin{aligned} E(k) &= \frac{\hbar^2 k^2}{2m^*} + \frac{1}{2} \frac{4\pi e^2}{\Delta} \sum_{k_{\text{occ}}} \int \int \psi(\mathbf{k},1)^* \psi(\mathbf{k}',2)^* \\ &\quad \times \sum_{k'' > k_c} (k'')^{-2} e^{i\mathbf{k}'' \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \psi(\mathbf{k}',1) \psi(\mathbf{k},2) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{\hbar^2 k^2}{2m^*} + \frac{2\pi e^2}{\Delta} \sum_{\substack{\mathbf{k}' \\ |\mathbf{k}' - \mathbf{k}| > k_c}} |\mathbf{k}' - \mathbf{k}|^{-2}, \end{aligned} \quad (35)$$

the $\frac{1}{2}$ entering so as not to count interactions twice. This corresponds to a simple modification of the exchange hole around the electron, the modification not altering the role of the wave functions, i.e., of the exchange charge density

$$\rho_{\text{ex}}(2,1) = -e \sum_{k_{\text{occ}} \parallel \text{spins}} \psi(\mathbf{k}',1)^* \psi(\mathbf{k}',2), \quad (36)$$

but altering only the Coulombic nature of the interaction law. We conclude that the corrected exchange potential is then given by

$$\begin{aligned} V_{\text{ex}} \psi(\mathbf{k},1) &= e \Delta^{-1} \int d\mathbf{r}_2 \rho_{\text{ex}}(2,1) \\ &\quad \times \sum_{k'' > k_c} 4\pi (k'')^{-2} e^{i\mathbf{k}'' \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \psi(\mathbf{k},2), \end{aligned} \quad (37)$$

and that this is superposed on the potential of a uniform smear of electrons, i.e., on the Hartree potential so that

⁶ The periodic part of the lattice potential could be handled by transforming a la Hubbard (reference 12), but we shall suppose that this part of the potential may be taken care of by use of an effective mass (see footnote 15 of reference 2). Hubbard derives an alteration in the exchange term also, but we neglect this. See the paragraph at the end of Sec. V below.

we may construct a new one-electron equation by writing

$$-\frac{\hbar^2}{2m^*}\nabla^2\psi(\mathbf{k},1)-e\int\frac{\rho_{\text{Coul}}(2)}{|\mathbf{r}_1-\mathbf{r}_2|}\psi(\mathbf{k},1)d\mathbf{r}_2 \\ +e\Delta^{-1}\int d\mathbf{r}_2\rho_{\text{ex}}(2,1)\sum_{k''>k_c}4\pi(k'')^{-2}e^{i\mathbf{k}''\cdot(\mathbf{r}_1-\mathbf{r}_2)} \\ \times\psi(\mathbf{k},2)=E_k\psi(\mathbf{k},1). \quad (38)$$

We are here not deriving but constructing by a plausibility argument an equation which will have the correct physical interpretation (in the sense that an exchange hole superposed on a uniform smear is a good model), which will reproduce the correct one-electron energies (in the sense that the article of Pines⁴ provides the correct expression), and the set of which, for all the electrons, is self-consistent (in the sense that the set of Hartree-Fock equations is self-consistent). To (38) we must add the electron-lattice interaction. The correct way is to add the total electron-lattice interaction to the system Hamiltonian, and work from there. What we do here amounts to neglecting the influence of the electron-lattice interaction on the plasma part of the total electron system wave function and vice versa. We thus are isolating and then calculating the influence of the short-range exchange-correlation term. We can describe our model in more physical terms, as follows. The long-range correlations, described by the plasma (in its lowest state) provide a "correlation hole" around each particle electron in addition to the "exchange hole" which is the interpretation of the short-range or exchange term in the Hamiltonian. Our approximation is that the "correlation hole" does not tend to pick up the lattice vibrations in contrast to the exchange hole, which does. We call this the "rigid correlation hole approximation."

We may now perturb the Coulomb and exchange charge densities. We get an equation like (15) except that

$$B_i=4\pi e^2\Delta^{-1}\int\int\sum_{k''>k_c}e^{i\mathbf{k}''\cdot(\mathbf{r}_1-\mathbf{r}_2)} \\ \times(k'')^{-2}\psi(\mathbf{k}+\mathbf{s},1)^*\psi(\mathbf{k},2)\Phi_i'd\mathbf{r}_1d\mathbf{r}_2. \quad (39)$$

The remainder of the derivation is the same as in Sec. III and yields the same Eq. (24) except that

$$a_s(\mathbf{k},\mathbf{k}')=-\frac{E_0(s)}{E(\mathbf{k}')-E(\mathbf{k}'+\mathbf{s})} \\ \times\left[4-\left\{\frac{s^2/|\mathbf{k}+\mathbf{s}+\mathbf{k}'|^2\cdots|\mathbf{k}+\mathbf{s}+\mathbf{k}'|>k_c}{0\cdots|\mathbf{k}+\mathbf{s}+\mathbf{k}'|<k_c}\right\} \right. \\ \left. -\left\{\frac{s^2/|\mathbf{k}-\mathbf{k}'|^2\cdots|\mathbf{k}-\mathbf{k}'|>k_c}{0\cdots|\mathbf{k}-\mathbf{k}'|<k_c}\right\}\right]. \quad (40)$$

Now we return to the solution given by (27) and (29) and calculate the average a 's. Let

$$\kappa=\mathbf{k}'+\mathbf{s}. \quad (41)$$

Then

$$\langle a_s \rangle = \left(\frac{4\pi}{3}k_0^3\right)^{-1} \int d\mathbf{k}' \left\{ -\frac{E_0(s)}{E(\mathbf{k}')-E(\mathbf{k}'+\mathbf{s})} \right. \\ \times \left[4 - \left(\frac{4\pi}{3}k_0^3\right)^{-1} \int_{|\kappa+\mathbf{k}'|>k_c} d\mathbf{k} \frac{s^2}{|\kappa+\mathbf{k}'|^2} \right. \\ \left. - \left(\frac{4\pi}{3}k_0^3\right)^{-1} \int_{|\kappa-\mathbf{k}'|>k_c} d\mathbf{k} \frac{s^2}{|\kappa-\mathbf{k}'|^2} \right] \left. \right\}. \quad (42)$$

Using the notation of Pines⁴ (Appendix I)

$$W(\kappa) = -\frac{4\pi e^2}{8\pi^3} \int_{|\kappa+\mathbf{k}'|>k_c} d\mathbf{k}' \frac{1}{|\kappa+\mathbf{k}'|^2}, \quad (43)$$

we have

$$\langle a_s \rangle = -\left(\frac{4\pi}{3}k_0^3\right)^{-1} \int d\mathbf{k}' \frac{E_0(s)}{E(\mathbf{k}')-E(\mathbf{k}'+\mathbf{s})} \\ \times \left[4 + \frac{3\pi}{2} \frac{s^2}{k_0^3 e^2} (W(\kappa) + W(\mathbf{k}')) \right]. \quad (44)$$

where we have used $W(-\mathbf{k})=W(\mathbf{k})$. Our W 's differ from Pines⁴ only in that k may be as large as $3k_0$. The two regions that Pines distinguishes, $0 \leq \kappa \leq k_0 - k_c$ and $k_0 - k_c < \kappa < k_0$ may have the second extended to $k_0 - k_c < \kappa < k_0 + k_c$. The third region $k_0 + k_c < \kappa < 3k_0$ we introduce causes no difficulty at all, for in that region there is no restriction on the sum, and we get a Bardeen type expression. We summarize the results. Let $x = k/k_0$. Then

$$h(x) \equiv -\frac{1}{12u^2} \frac{3\pi}{2} \frac{s^2}{k_0^3 e^2} W(k) \\ = f(x) - \beta \cdots 0 < x < 1 - \beta \\ = \frac{1}{4} - \frac{\beta}{2} + \frac{1-x^2}{4x} \ln \frac{1+x}{\beta} \\ + \frac{3x^2-1+\beta^2}{8x} \cdots 1 - \beta < x < 1 + \beta \\ = f(x) \cdots 1 + \beta < x < 3, \\ f(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|. \quad (45)$$

Thus

$$\langle a_s \rangle = -\frac{3}{4\pi k_0^3} \int dk' \frac{E_0(s)}{E(k') - E(k' + s)} \times \left[4 - 12u^2 \left\{ h\left(\frac{k'}{k_0}\right) + h\left(\frac{|k' + s|}{k_0}\right) \right\} \right]. \quad (46)$$

Similarly we find

$$[\langle a_s(k) \rangle]_{\text{F.S.}}^{\text{Exch}} = \frac{3}{4\pi k_0^3} \int dk' \frac{E_0(s)}{E(k') - E(k' + s)} \times 12u^2 \left\{ h'\left(\frac{k'}{k_0}\right) + h'\left(\frac{|k' + s|}{k_0}\right) \right\}, \quad (47)$$

where

$$\frac{1}{6x} \ln \left| \frac{1+x}{1-x} \right| \dots 0 < x < 1-\beta, \quad 1+\beta < x < 3, \quad (48)$$

$$h'(x) = \frac{1}{6x} \ln \frac{1+x}{\beta} \dots 1-\beta < x < 1+\beta.$$

The rest of the calculation is in Appendix A. Figure 2 shows $xh(x)$ and $xh'(x)$ for $r_s = 4a_h$. (46) and (47) are to be substituted into (32), which is the basic form of our solution.

V. DISCUSSION AND SUMMARY⁷

We have presented a calculation of the exchange and correlation effects on the scattering of electrons in a normal metal. Our model supposes that the electron-

⁷ Note added in proof. Dr. D. Pines (private communication) has shown how the Bardeen-Pines paper (reference 2) can be reconciled with the preceding paper. In effect our approximations correspond to the adiabatic approximation which in Bardeen and Pines' terminology (which we use in this Note) is characterized by setting their $g(\mathbf{k}, \mathbf{K}) = 0$, and letting $\omega_{\mathbf{K}} = 0$. Then to define $v_{\mathbf{K}}, \mathbf{K}$, let

$$f(\mathbf{k}, \mathbf{K}) = v_{\mathbf{K}}, \mathbf{K} [E_{\mathbf{K}} - E_{\mathbf{K}-\mathbf{k}} + W_{\mathbf{K}} - W_{\mathbf{K}-\mathbf{k}}]^{-1},$$

where $E_{\mathbf{k}}$ is the free electron kinetic energy and $W_{\mathbf{K}}$ is the exchange energy [(B5) of footnote 2]. Then Eq. (B4) is identical with our results, for the exchange effects.

Furthermore, Pines and Bardeen have shown that our results for the "modified exchange" problem can be obtained by using a different canonical transformation from the one used in reference 2. Starting with their Hamiltonian (4.5) neglecting electron-plasmon, phonon-plasmon, and phonon recoil terms, one employs the transformation generated by

$$S = i \sum_{\mathbf{K}, \mathbf{k}} f(\mathbf{k}, \mathbf{K}) q_{\mathbf{k}} C_{\mathbf{K}}^* C_{\mathbf{K}-\mathbf{k}},$$

such that

$$i[S, H] = - \sum_{\mathbf{k} > k_0} \{v_{\mathbf{k}}^i - iM_{\mathbf{k}} U_{\mathbf{k}}\} q_{\mathbf{k}} \rho_{\mathbf{k}} - \sum_{\mathbf{k} > k_0} v_{\mathbf{k}}^i q_{\mathbf{k}} \rho_{\mathbf{k}},$$

where

$$H = \sum_{\mathbf{K}} E_{\mathbf{K}} C_{\mathbf{K}}^* C_{\mathbf{K}} + \frac{1}{2} \sum_{\mathbf{k} > k_0} M_{\mathbf{k}}^2 \rho_{\mathbf{k}}^* \rho_{\mathbf{k}}.$$

In the $[S, H]$ commutator, one keeps the exchange terms as in Appendix B of reference 2. It then follows from the above equations and from the definition of $u_{\mathbf{k}}$ from the self-consistency requirement that one obtains our screened Hartree-Fock expression for $v_{\mathbf{k}}, \mathbf{K}$.

The author is grateful for Dr. Pines' permission to include this note.

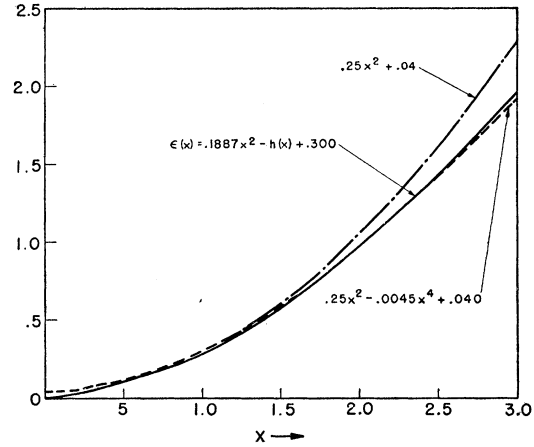


FIG. 1. Approximate energy functions. ϵ is defined from $E = (\hbar^2 k^2 / 2m)(r_s/a_h) \rho \epsilon$. The full curve is the accurate expression, the dashed curve is the approximation used for calculations, and given by (B1). The dot-dashed curve shows the nearest that a parabolic form would achieve. All this is for $r_s/a_h = 4$.

plasma oscillations are not altered by the lattice vibrations, but form a "rigid correlation hole" about each particle electron, which hole does not pick up the lattice motion. However, there is a modified exchange hole about the electrons (the modification being a deviation from the Hartree-Fock term, and in Pines' terminology⁸ constituting a "correlation effect"), and this hole does pick up the lattice motion, and will help scatter the electrons.

With this as starting point, we have extended the 1937 Bardeen method, which is applicable since we still have a set of self-consistent one-electron equations for the electrons. The results are expressed in terms of integrals involving the usual energy denominators $E(\mathbf{k}) - E(\mathbf{k} + \mathbf{s})$ but we must use the one-electron energies including exchange and correlation effects. This makes the integrals quite formidable, although still straightforward in principle. To gain numbers, we have approximated the proper $E(\mathbf{k})$ by a curve of the form given in Eq. (A1) of Appendix A. Figure 1 shows how such a curve fits the true function for $r_s = 4a_h$, corresponding to sodium. From there on, the details are carried out in Appendix A, where for future reference, some of the recurring integrals are tabulated. Computations for a one-electron energy function with different coefficients p and q can easily be made from the tables.

The results are conveniently described in terms of the shielding factor S , where $v(\mathbf{k}, \mathbf{s}) = S v_{\text{ion}}(\mathbf{s})$. S is written out in (32) and at the end of Appendix A and is of the form $S_{\text{num}}/S_{\text{den}}$, where the numerator differs from 1 only through the fact that the matrix element depends on \mathbf{k} , and where the denominator corresponds to the old Bardeen term, but which now includes the exchange correction.

⁸ D. Pines, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. I, bottom of p. 373.

Our first general result, as emphasized before, is that the matrix element is not independent of the initial electron state wave-vector \mathbf{k} . The effect is to *decrease* the matrix element (i.e., S_{num} is less than 1). The effect fortunately is already quite small in the first iteration. This can be seen from Fig. 2, where if $h(x)$ and $h'(x)$ were the same, we would have $S_{\text{num}}=1$. It is evident from the figure that the curves do not differ tremendously. The numerical values can be seen in Table III. In the limit $u \rightarrow 0$, this effect does not vanish (see Appendix A). Our second result is that in the limit of vanishing u , we do *not* get the 1937 Bardeen result, both because S_{num} does not approach 1 and because the energy denominator in S_{den} reflects the exchange term. Otherwise we would indeed get the old result, for in the limit as u approaches zero, the exchange terms in (44) go to zero faster than the Coulomb term. (See Appendix A for the limit $u \rightarrow 0$.)

The effect of the exchange correction is to make S_{den} much smaller than previously, and thus to *increase* the matrix element. And this arises not only from the fact that the exchange hole perturbation unites with the ion vibration to help scatter the electron, but also because the one-electron energies including exchange decrease the magnitude of the Coulomb term itself. This can be seen from Table III, for the quantity $F(u)$ there corresponds to the free-electron $f(u)$, and is always smaller than $f(u)$. It is to be noted that by itself the effect of the exchange hole is to give "antishielding," as has been mentioned several times before. There seems to be nothing preventing this effect being larger than the shielding of the ions. What it would mean is that the electron is scattered more by the hole around it than it

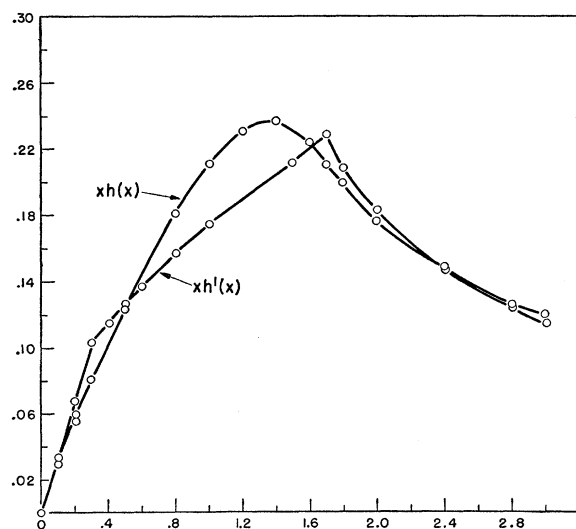


FIG. 2. $xh(x)$ and $xh'(x)$, defined by (50) and (53). In the calculations for $xh'(x)$, the regions $x > 1+\beta$ and $x < 1-\beta$ give some errors. At $x=1+\beta$, the error was to continue the $x > 1+\beta$ type of region down always to $x=1.6$. At $x=1-\beta$, the error was to extrapolate the curve from the $x > 1-\beta$ region down to $x=0$. Both these errors were estimated and found to give corrections in the third significant figure of $G(u, h')$ and were therefore neglected.

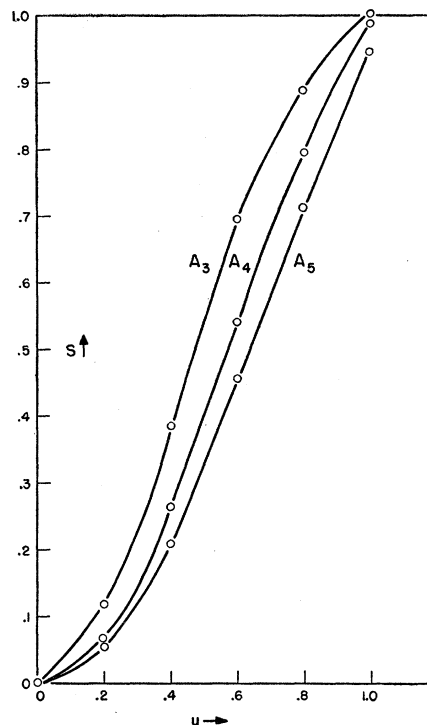


FIG. 3. The shielding factor S . The labels $A_3 A_4 A_5$ mean S for $r_s/a_h=3, 4, 5$, respectively. [See Eq. (B26).]

is shielded from the ion by the cloud around the latter. We find in fact that for $r_s=3a_h$, and $u=1$, there is "antishielding," but of such a small amount that it is within the calculational error.

The results are shown graphically in Fig. 3, where the subscripts 3, 4, 5, refer to $r_s/a_h=3, 4, 5$. The comparison with the Bardeen¹ theory is shown in Fig. 4. We see that as anticipated in the Introduction, the new curves augment the matrix element significantly. The matrix element always appears squared in the transport coefficients, and we find, for example, that $v(s)^2$ for $r_s/a_h=4$, and $u=1$ is 1.7 times the Bardeen value. The balance of the umklapp region with the nonumklapp region has far-reaching consequences in the thermoelectric power.^{9,10}

We have used plane-wave wave functions to obtain the selection rules in the A 's and B 's in (15) and (39). Brooks¹¹ has shown how to extend the calculation to the case of modulated plane waves, and his approach, slightly modified, can be applied to the present formulation of the problem, including exchange effects. We have not sought to see what alteration this makes, but we take the opportunity here to mention that the theory is not restricted to plane wave functions. The mathematical complications that ensue may be summed up by

⁹ M. Bailyn, Phys. Rev. **112**, 1587 (1958).

¹⁰ M. Bailyn (to be published). This is a detailed calculation of the thermoelectric power based on the expression derived in (7).

¹¹ H. Brooks (private communication). Professor Brooks informs me that these corrections seem to be rather large.

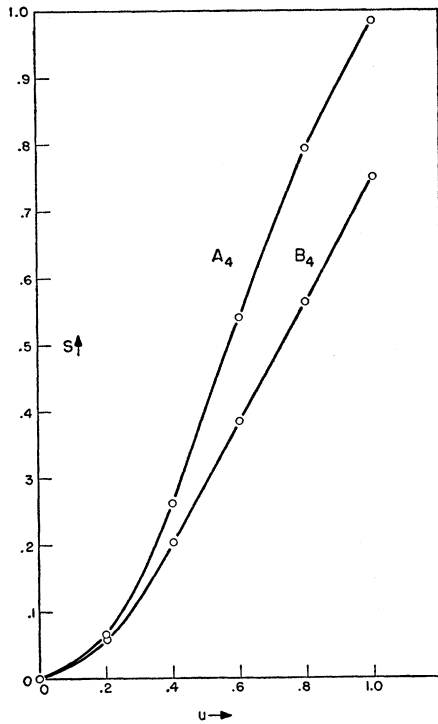


FIG. 4. Comparison with the Bardeen result (B_4) and the result of this paper (A_4) for $r_s/a_h=4$. The figure, owing to the scale, gives the impression that as u approaches zero, the curves join. This is not so. See the discussion at the end of Sec. V.

saying that instead of (24), which represents n equations in n unknowns, $v(\mathbf{k}, \mathbf{s})$, $\mathbf{k}=\mathbf{k}_1 \cdots \mathbf{k}_n$, we would get nm equations in nm unknowns, $v(\mathbf{k}+\mathbf{K}, \mathbf{s})$, $\mathbf{k}=\mathbf{k}_1 \cdots \mathbf{k}_n$, $\mathbf{K}=\mathbf{K}_1 \cdots \mathbf{K}_m$, where the \mathbf{K} 's represent reciprocal lattice vectors. By restricting the \mathbf{K} 's to nearest or next-nearest neighbors, one can get a manageable result. However, if one were to make corrections of this sort, one would do better to treat the unperturbed lattice more rigorously than we have done, and to start from perhaps the Hubbard¹² formulation of the problem.

Finally a word about a consistent taking account of exchange and correlation effects in the calculation of the transport coefficients. The simplest consistent calculation is to neglect exchange effects and to use an effective mass approximation for the energies. The "first order" exchange and correlation correction would then consist of two parts: (1) the correction as originally conceived by Blatt¹³ and most recently calculated by Fletcher and Larson¹³ which reflects the first order change in the energy function and (2) the corrected matrix element as described in the present paper. A "second order" correction would use the second order energy correction of Fletcher and Larson, and would require the use of this same corrected energy function in the matrix element

calculation presented above. Thus if Fletcher and Larson's second order energy could be approximated by the form in (A1), we would merely have to change the numbers of some of our coefficients in calculating the new matrix element.¹⁴

ACKNOWLEDGMENTS

The author is indebted to Professor Harvey Brooks for many discussions and communications on the shielding problem, and for letting him see some notes before publication, to Professor J. Bardeen for a discussion in which many points were clarified, and to Professor D. Pines for his comments which have been quoted in reference 7. He would also like to thank Dr. J. Kaplan for patiently listening and suggesting.

APPENDIX A. CALCULATION OF THE AVERAGE a 's

We seek here to finish evaluating the integrals in (46) and (47). We shall use an energy function of the general form

$$E(\mathbf{k}') = \text{const} + (\hbar^2 k_0^2 / 2m) (p x^2 - q x^4), \quad x = k'/k, \quad (\text{A1})$$

where p and q are numbers chosen to make a good fit to the true energy function. An example of the fit we obtain is given in Fig. 1 for $r_s = r a_h$. The values of p and q are given in Table I for various r_s .

The energy denominators become with (A1)

$$\frac{E_0(s)}{E(\mathbf{k}') - E(\mathbf{k}' + \mathbf{s})} = \frac{(s/k_0)^2}{8pq} \frac{1}{A\mu^2 + B\mu + C}, \quad (\text{A2})$$

where

$$\begin{aligned} \mu &= \hat{k}' \cdot \hat{s}, \\ A &= 2x^2 u^2, \\ B &= [-(1/2q) + x^2 + 4u^2]ux, \\ C &= [-(1/2q) + x^2 + 2u^2]u^2, \\ (B^2 - 4AC)^{1/2} &= xu[(1/2q) - x^2]. \end{aligned} \quad (\text{A3})$$

There are two types of integrals in (46) and (47), one where (A2) is multiplied by a function of k' , and for

TABLE I. Quantities from (B1), (B21), and (B22).

r_s/a_h	p	q	U_1	U_2	U_3	U_5	W_0
3	1.800	0.0377	0.380	-0.136	0	-0.003	0
4	1.325	0.0180	0.300	-0.060	-0.025	0	0
5	1.200	0.0069	0.192	0	0	-0.0105	0.013
r_s/a_h	W_{-1}	U_0'	U_1'	U_2'	W_0'	W_{-1}'	
3	0.360	0.097	0.107	-0.0100	-0.027	0.423	
4	0.360	0.070	0.115	-0.0133	-0.027	0.420	
5	0.322	0.050	0.120	-0.0170	-0.027	0.420	

¹² J. Hubbard, Proc. Phys. Soc. (London) **A67**, 1058 (1954). See in particular Eq. (50).

¹³ J. G. Fletcher and D. C. Larson, Phys. Rev. **111**, 455 (1958). See references cited there.

¹⁴ Note added in proof. A detailed calculation of the transport properties of the alkali metals including these corrections will be published soon.

which the k' integral is written

$$\int d\mathbf{k}' = 2\pi k_0^3 \int_0^1 x^2 dx \int_{-1}^1 d\mu, \quad (\text{A4})$$

the other where (A2) is multiplied by a function of $|\mathbf{k}' + \mathbf{s}|$. The latter is performed by changing to the variable $x = |\mathbf{k}' + \mathbf{s}|/k_0$. In terms of x , the energy denominator becomes

$$\frac{E_0(s)}{E(\mathbf{k}') - E(\mathbf{k}' + \mathbf{s})} = -\frac{(s/k_0)^2}{8pq} \frac{1}{A\mu^2 - B\mu + C}, \quad (\text{A5})$$

and the x integral becomes

$$\begin{aligned} \int d\mathbf{k}' &= 2\pi k_0^3 \left[\int_0^{1-2u} x^2 dx \int_{-1}^1 d\mu \right. \\ &\quad \left. + \int_{1-2u}^{1+2u} x^2 dx \int_{\mu_c}^1 d\mu \right] \cdots u < 0.5 \\ &= 2\pi k_0^3 \int_{2u-1}^{2u+1} x^2 dx \int^1 d\mu, \cdots u > 0.5, \end{aligned} \quad (\text{A6})$$

where μ_c is the cosine of the angle at which, for a given x magnitude, the radial vector x cuts the surface of the sphere of radius 1 about $x = s/k_0$ as center. It is given by

$$\mu_c = \frac{x^2 + 4u^2 - 1}{4u}. \quad (\text{A7})$$

The results are

$$\langle a_s \rangle_{\text{Coul}} = 12u^2 F(u), \quad (\text{A8})$$

$$\langle a_s \rangle_{\text{Exch}} = -12u^2 G(u; h), \quad (\text{A9})$$

where

$$F(u) = \frac{1}{2up} \int_0^1 dx x \frac{\ln g_0}{1 - 2qx^2}, \quad (\text{A10})$$

$$\begin{aligned} G(u; h) &= \frac{3u}{2p} \int_{1-2u}^{1+2u} dx x h(x) \frac{\ln g}{1 - 2qx^2}, \cdots u < 0.5 \\ &= \frac{3u}{2p} \left[\int_0^{1-2u} dx x h(x) \frac{\ln g_0}{1 - 2gx^2} \right. \\ &\quad \left. + \int_{1-2u}^{1+2u} dx x h(x) \frac{\ln g}{1 - 2gx^2}, \cdots u > 0.5 \right] \end{aligned} \quad (\text{A11})$$

where

$$g_0 = \left| \frac{x+u}{x-u} \frac{1-q\epsilon(-)}{1-q\epsilon(+)} \right|, \quad (\text{A12})$$

$$g = \left| \frac{4u(x \pm u)}{1-x^2} \frac{1-q(1 \pm x^2)}{1-q\epsilon(\pm)} \right| \cdots \begin{cases} + \cdots x < 1 \\ - \cdots x > 1 \end{cases}, \quad (\text{A13})$$

$$\epsilon(\pm) = 2x^2 + 4u^2 \pm 4ux. \quad (\text{A14})$$

The quantity q is rather small, and we have expanded to first order in q to make the calculations:

$$\begin{aligned} F(u) &\cong \frac{1}{2up} \int_0^1 dx x \left[(1 + 2qx^2) \ln \left| \frac{x+u}{x-u} \right| + 8qux \right] \\ &= \frac{1}{p} f(u) + \frac{q}{p} \left[\frac{1-u^4}{4u} \ln \left| \frac{1+u}{1-u} \right| + \frac{1}{2} u^2 + \frac{3}{2} \right], \end{aligned} \quad (\text{A15})$$

$$G(u; h) \cong \frac{3u}{2p} \int_{x_0}^{1+2u} dx x h(x) [(1 + 2qx^2) Q(x, u) + qR(x, u)], \quad (\text{A16})$$

where

$$x_0 = \begin{cases} 1-2u \cdots u < 0.5 \\ 0 \cdots u > 0.5, \end{cases} \quad (\text{A17})$$

$$Q(x, u) = \begin{cases} \ln \left| \frac{x+u}{x-u} \right| \cdots x < |2u-1| \\ \ln \left| \frac{4u(x \pm u)}{1-x^2} \right| \cdots \begin{cases} + \cdots x < 1 \\ - \cdots x > 1 \end{cases}, \cdots x > |2u-1|, \end{cases} \quad (\text{A18})$$

$$R(x, u) = \begin{cases} 8ux \cdots x < |2u-1| \\ -1 + 4u^2 \pm 4ux + x^2 \cdots \begin{cases} + \cdots x < 1 \\ - \cdots x > 1 \end{cases}, \cdots x > |2u-1|. \end{cases} \quad (\text{A19})$$

The integrals can be performed once and for all for the various r_s values if we can expand $h(x)$ and $h(x)'$. We could of course trace h back to the energy expansion in (A1), but this is a misleading simplification, since as x gets large, the energy becomes insensitive to $h(x)$, so that great variations in $h(x)$ may be altogether neglected in the energy expression for large x . In fact, $h(x)$ is rather difficult to expand, and we have been forced to use two regions. The expansions are of the form

$$\begin{aligned} xh(x) &= U_1x + U_2x^2 + U_3x^3 + U_5x^5 \cdots x < 1.6 \\ &= W_{-1}x^{-1} + W_0, \cdots x > 1.6, \end{aligned} \quad (\text{A20})$$

$$\begin{aligned} xh'(x) &= U_0' + U_1'x + U_2'x^2 \cdots x < 1.6 \\ &= W_0' + W_{-1}'x^{-1}, \cdots x > 1.6, \end{aligned} \quad (\text{A21})$$

where the U 's are constants appropriate to region 1, and the W 's to region 2. See Table I for the values. From Fig. 2, we see that for $x < 1 - \beta$, and for $x \cong 1 + \beta$, there are errors, in $h'(x)$. We have calculated the effect of these errors and found them to be negligible. With these expansions, the G 's become

$$\begin{aligned} G(u, h) &= (3u/(2p)) [U_1S_1^{(1)} + U_2S_2^{(1)} + U_3S_3^{(1)} \\ &\quad + U_5S_5^{(1)} + W_0S_0^{(2)} + W_{-1}S_{-1}^{(2)} \\ &\quad + 2q(U_1S_3^{(1)} + U_2S_4^{(1)} + U_3S_5^{(1)} + W_0S_2^{(2)} \\ &\quad + W_{-1}S_1^{(2)}) + q(U_1T_1^{(1)} + U_2T_2^{(1)} + U_3T_3^{(1)} \\ &\quad + U_5T_5^{(1)} + W_0T_0^{(2)} + W_{-1}T_{-1}^{(2)})], \end{aligned} \quad (\text{A22})$$

$$\begin{aligned} G(u, h') &= (3u/(2p)) [U_0'S_0^{(1)} + U_1'S_1^{(1)} + U_2'S_2^{(1)} \\ &\quad + W_0'S_0^{(2)} + W_{-1}'S_{-1}^{(2)} + 2q(U_0'S_2^{(1)} \\ &\quad + U_1'S_3^{(1)} + U_2'S_4^{(1)} + W_0'S_2^{(2)} \\ &\quad + W_{-1}'S_1^{(2)}) + q(U_0'T_0^{(1)} + U_1'T_1^{(1)} \\ &\quad + U_2'T_2^{(1)} + W_0'T_0^{(2)} + W_{-1}'T_{-1}^{(2)})], \end{aligned} \quad (\text{A23})$$

TABLE II. Quantities from (B23) and (B24). $S_4^{(1)}$ was obtained by graphical interpolation.

u	$S_0^{(1)}$	$S_1^{(1)}$	$S_2^{(1)}$	$S_3^{(1)}$	$S_4^{(1)}$	$S_5^{(1)}$	$S_{-1}^{(2)}$
0.2	0.818	0.797	0.802	0.826	(0.865)	0.913	0
0.4	1.609	1.452	1.543	1.611	(1.735)	2.037	0.026
0.6	2.214	1.950	1.863	1.918	(2.130)	2.575	0.063
0.8	2.139	1.814	1.767	1.832	(2.075)	2.482	0.113
1.0	1.743	1.423	1.390	1.442	(1.618)	1.974	0.140
u	$S_0^{(2)}$	$S_1^{(2)}$	$S_2^{(2)}$	$T_0^{(1)}$	$T_1^{(1)}$	$T_2^{(1)}$	$T_3^{(1)}$
0.2	0	0	0	-0.136	-0.064	-0.110	-0.160
0.4	0.023	0.044	0.067	0.253	0.119	-0.126	-0.637
0.6	0.122	0.226	0.369	1.228	0.681	0.076	-0.649
0.8	0.228	0.426	0.789	2.407	1.563	0.644	-0.193
1.0	0.300	0.585	1.238	3.590	2.623	1.464	+0.640
u	$T_5^{(1)}$	$T_{-1}^{(2)}$	$T_0^{(2)}$				
0.2	-0.285	0	0				
0.4	-1.108	-0.022	+0.087				
0.6	-1.817	-0.160	-0.168				
0.8	-2.192	-0.342	-0.540				
1.0	-1.476	-0.495	-0.920				

TABLE III. Quantities from (B8), (B9), and (B27). The subscripts 3, 4, 5 refer to $r_s/a_h = 3, 4, 5$. The $S^{(B)}$'s are the corresponding quantities on the Bardeen^a theory. The accuracy is at most to two significant figures.

u	F_3	$G_3(u, h)$	$G_3(u, h')$	S_3	$S_3^{(B)}$
0.2	0.591	0.035	0.029	0.117	0.076
0.4	0.569	0.159	0.119	0.384	0.254
0.6	0.528	0.351	0.253	0.695	0.454
0.8	0.462	0.456	0.316	0.887	0.633
1.0	0.320	0.485	0.342	1.012	0.800
u	F_4	$G_4(u, h)$	$G_4(u, h')$	S_4	$S_4^{(B)}$
0.2	0.773	0.040	0.032	0.066	0.058
0.4	0.741	0.148	0.127	0.264	0.204
0.6	0.686	0.319	0.268	0.540	0.385
0.8	0.593	0.415	0.360	0.795	0.564
1.0	0.404	0.432	0.386	0.987	0.752
u	F_5	$G_5(u, h)$	$G_5(u, h')$	S_5	$S_5^{(B)}$
0.2	0.834	0.036	0.031	0.051	0.047
0.4	0.800	0.136	0.121	0.208	0.170
0.6	0.737	0.288	0.256	0.455	0.333
0.8	0.636	0.388	0.343	0.713	0.508
1.0	0.428	0.426	0.366	0.948	0.707

^a See reference 1.

where

$$\begin{aligned} S_n^{(1)} &= \int_{x_0}^{1.6} dx x^n Q(x, u), \\ S_n^{(2)} &= \int_{1.6}^{2u+1} dx x^n Q(x, u), \\ T_n^{(1)} &= \int_{x_0}^{1.6} dx x^n R(x, u), \\ T_n^{(2)} &= \int_{1.6}^{2u+1} dx x^n R(x, u). \end{aligned} \quad (\text{A24})$$

The S 's and T 's are given in Table II.

The combined results in first iteration from (32) give

$$v_1(k, s) = v_{\text{ion}}(s) S = v_{\text{ion}}(S_{\text{num}}/S_{\text{den}}), \quad (\text{A25})$$

where

$$\begin{aligned} S_{\text{num}} &= 1 - [(9\pi/4)^{1/2}\pi]^{-1}(r_s/a_h) \\ &\quad \times [G(u, h) - G(u, h')]/u^2, \\ S_{\text{den}} &= 1 + [(9\pi/4)^{1/2}\pi]^{-1}(r_s/a_h) \\ &\quad \times [F(u) - G(u, h)]/u^2. \end{aligned} \quad (\text{A26})$$

The numerical results for the G 's and the S are given in Table III.

The limiting case $u=0$ is always of interest. Starting from (A10), we find

$$\begin{aligned} L F(u) &= (1/p)(1+2q), \\ L G(u; h) &= (1/p)(1+2q)[6h(1)]u^2, \\ L G(u; h') &= (1/p)(1+2q)[6h'(1)]u^2. \end{aligned} \quad (\text{A27})$$

Thus

$$L S = \frac{1 - [(9\pi/4)^{1/2}\pi]^{-1}(r_s/a_n)p^{-1}(1+2q)6[h(1)-h'(1)]}{1 + [(9\pi/4)^{1/2}\pi]^{-1}(r_s/a_n)p^{-1}(1+2q)u^{-2}}$$

$$= u^2 \left[(9\pi/4)^{1/2}\pi \frac{a_n}{r_s} \frac{p}{1+2q} - \left\{ 3(1-\frac{1}{2}\beta)^2 - \ln \frac{2}{\beta} \right\} \right]. \quad (A28)$$

We see that the exchange effect does not drop out for two reasons: (1), the numerator retains a value not equal to 1 reflecting the dependence of the matrix element on k , and (2), the denominator, although allowing G to be negligible compared to F , has an effect arising from the use of one-electron energy functions differing from the free electron one through the use of $p \neq 1$ and $q \neq 0$.

Thermoelectricity and Resistivity in Metal Alloys at Low Temperatures

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A simple model is proposed for the "resonant scattering" of electrons from foreign atoms in a crystal lattice. The model assumes the existence of highly selective scattering mechanisms characterized by widths of the order of 10^{-4} electron volts and larger; in this sense it is similar to the model of Korringa and Gerritsen (1953), although the present model makes use of only the general analytical characteristics of the relaxation time and does not specify the details of the scattering mechanism. Mott's well-known approximation formula $S = (\pi^2 k^2 T / 3e) [d \ln \sigma(E) / dE]_{E=E_F}$ for the absolute thermoelectric power of a metal alloy is strictly valid and physically meaningful only at temperatures $kT \ll a$, where $2a$ is the width of the resonance. At temperatures $kT \gg a$ the formula leads to useful and valuable information on the thermoelectric properties of alloys, but the formula in this temperature region has only a rather artificial physical meaning. In the intermediate temperature region where kT is comparable to a , the Mott formula is entirely invalid. But it is in precisely this intermediate temperature range that the resistance and thermoelectric anomalies occur, so that Mott's approximation cannot be used for the treatment of these anomalies. The model satisfactorily explains many of the details of this anomalous behavior. It is suggested that the solvent metals used in the experimental studies of these effects will have to be much purer than those presently available before we shall be able to specify unambiguously the effects of a given kind of impurity.

I. INTRODUCTION

THERE is an increasing interest nowadays in the electric and magnetic properties of noble metals and their alloys.¹ Among the many interesting and unsolved problems in this field is that of understanding the nature of the electron scattering which causes certain well-known anomalies² or departures from the "simple" behavior exemplified, for example, by Matthiessen's rule. That these problems are by no means simple is demonstrated by the fact that it has been found extremely difficult to explain even the sign of the absolute thermoelectric power of the pure metals at room temperature.³ Schmitt⁴ and Yosida⁵ have attempted to explain the low-temperature "resistivity maximum" in CuMn alloys on the basis of a spin-dependent interaction between the scattered electron and the d electrons of the impurity ion; their work not only supplies a specific mechanism for the electron scattering but also

attempts to connect the electrical with the magnetic properties of CuMn alloys. However, the work of Schmitt and Yosida has led only to a very qualitative understanding of a few rather general aspects of the problem and furnishes little in the way of details of the known electrical behavior of noble metal alloys.

Earlier, Korringa and Gerritsen⁶ proposed a "resonance scattering" model which led to a fairly detailed description of the low-temperature resistivity and magnetoresistance of dilute alloys of copper, silver, or gold containing manganese. While their treatment has some quantum mechanical basis, their arguments for the existence of "resonance states" very near the Fermi level are not very convincing. However, since the transport properties of these alloys are determined primarily by the scattering of the electrons having kinetic energies within a few kT of the Fermi level energy E_F , it would seem that the actual scattering mechanism (or mechanisms) must be highly "selective" or "discriminating." This selectivity will probably turn out to be due at least in part to some kind of spin-sensitive interaction,⁷ as proposed by Korringa, Schmitt, and

¹ See, e.g., the *Report on the International Conference on the Electronic Properties of Metals at Low Temperatures, Geneva, New York, August 25-29, 1958* [Revs. Modern Phys. (to be published)].

² D. K. C. MacDonald, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, Part 1.

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⁶ J. Korringa and A. N. Gerritsen, Physica 19, 457 (1953).

⁷ A recent contribution has been made by A. D. Brailsford and A. W. Overhauser, Phys. Rev. Letters 3, 331 (1959). A very similar calculation has also been made recently by A. J. Dekker (private communication).