Exchange and correlation contributions to superconducting electron pairing

J. J. Shirron and J. Ruvalds

Department of Physics, University of Virginia, Charlottesville, Virginia 22901

(Received 2 June 1986)

The screening of the electron-phonon and Coulomb interactions in an electron gas is considered with use of various forms of the exchange correction term G(q). A solution of the Eliashberg equations including G(q) is achieved with conventional approximations, and the resulting superconducting transition temperatures T_c are found to be very sensitive to the form of exchange. Smooth functional forms of G(g), such as the Hubbard model, yield only small deviations from the randomphase approximation, which greatly overestimates T_c for simple metals such as Na and Li. However, an exchange function with a peak near $q \approx 2k_F$ (e.g., the forms proposed by Devreese and independently by Overhauser) greatly reduces T_c and may explain the mysterious absence of superconductivity in simple metals such as Na, Li, and Rb. These many-body effects may also be significant in superconductors with more complex energy-band structures.

I. INTRODUCTION

A remarkable feature of our understanding of the origin of superconductivity in metals is the uncertainty in theoretical predictions of the superconducting transition temperature T_c . As an example of this dilemma, the alkali metals Na, K, and Li are notable for their lack of superconductivity and have very simple nearly-free-electron band structures. Nevertheless, some calculations indicate that Li should have a finite T_c and a resolution of this mystery may shed some light on corrections which may be influential in other metals as well.

The present paper is concerned with the screening of the Coulomb interaction in metals with a view toward the influence of exchange and correlation contributions on the electron-electron pairing interaction which is responsible for superconductivity. Since we wish to isolate these many-body effects, we neglect the complicating features of band-structure details by assuming a free-electron gas of electrons. Furthermore, we represent the lattice dynamics by a simple ion response function.

Even forty years after the discovery of superconducting materials, the understanding of the basic interactions responsible for the observations was very much in doubt. Hence the suggestion by Fröhlich¹ that electron-phonon coupling could provide a mechanism for superconductivity provided an essential breakthrough in that it predicted an isotope effect for T_c which was then verified experimentally.

The classic work of Bardeen, Cooper, and Schrieffer (BCS) (Ref. 2) established the key role of electron pairing induced by the exchange of phonons, and provided the microscopic theoretical basis for experimental analysis as well as theoretical work. Nevertheless, predictions of T_c were restricted to qualitative reliability in part because of the weak-coupling approximations invoked in the theory.

Currently, the standard computational approaches to T_c rely on the Eliashberg equations³ which yield a convenient integral equation for the order parameter in terms of the electron-electron scattering potential. We use this

procedure as well.

On the basis of the BCS and Eliashberg results, a convenient weak-coupling approximate result for the transition temperature is

$$T_{c} \simeq 1.1 \hbar \omega_{D} \exp\left[\frac{-1}{\lambda - \mu^{*}}\right], \qquad (1)$$

where ω_D is the cutoff frequency for the phonons involved in the pairing interaction, λ represents the electron-phonon coupling, and μ^* is the effectively screened Coulomb repulsion between electrons. The reduction of the screened Coulomb interaction by the detailed structure of the Eliashberg equations was demonstrated in the Thomas-Fermi approximation by Morel and Anderson⁴ and a very useful empirical relation for T_c [similar to Eq. (1) in the weak-coupling limit] was obtained by McMillan⁵ from extensive numerical analysis of the Eliashberg equations.

Exchange and correlation contributions to superconductivity have received scant attention in comparison to the extensive investigations of band-structure and phonon effects. The random-phase approximation (RPA) works extremely well in many studies of the electron response in metals.⁶ Nevertheless, a very thorough investigation of the Eliashberg equations by Rietschel and Sham⁷ has recently demonstrated that the RPA greatly overestimates T_c for a free-electron gas. Hence the inclusion of selfenergy and vertex corrections was necessary to achieve reasonable superconducting temperatures in their study.⁷ An alternate approach by Vignale and Singwi⁸ has demonstrated the importance of vertex corrections and electron-hole correlations in determining the electronelectron pairing, and furthermore their study suggests the intriguing possibility of achieving superconductivity in certain doped semiconductors on the basis of screened Coulomb interactions without recourse to the phononmediated coupling.

Our work is motivated by the recent progress achieved in calculations of the exchange and correlation contributions to the dielectric function of an electron gas. Preliminary estimates⁹ of the electron-phonon coupling including exchange as a function of electron density revealed dramatic departures from the RPA predictions. Hence we were motivated to carry out solutions of the Eliashberg equations including the Coulomb repulsion on an even footing with the electron-phonon interaction.

Our analysis invoked four different forms of the exchange function G(q), which are compared by Mahan,¹⁰ and were derived independently by the following authors: Hubbard,¹¹ Devreese *et al.*,¹² Singwi *et al.* (STLS),¹³ and Overhauser *et al.*¹⁴ The major variations among these authors show up in the momentum dependence of G(q), which we find to have a significant influence on T_c .

Our selection of the exchange functions G(q) is meant to explore the relevance of the distinguishing features to superconductivity. There is spirited debate in regard to the validity of various approximations and methods used in the determination of these many-body corrections,¹⁵ and we trust that our investigation will add a constructive element to the understanding of these many-body effects and their role in superconductors.

٢

ſ

We summarize some key features of the RPA and the various exchange correction results in Sec. II. The superconducting electron-gap equations are examined in Sec. III, and the solutions are developed including exchange and correlations. The conclusions of our study are given in Sec. IV.

II. RPA AND EXCHANGE CORRELATION

Coulomb interactions in a metal are screened very effectively. The screen reduces the direct electron-electron repulsion to a short range and renders it comparable to the effective electron-ion coupling. The effective Coulomb potential may be expressed as

$$V(q,\omega) = \frac{4\pi e^2}{q^2 \epsilon(q,\omega)} , \qquad (2)$$

where the dielectric function $\epsilon(q,\omega)$ represents the response of the electron gas as a function of momentum q and frequency ω . In the RPA, ϵ is found to be a complex function $\epsilon = \epsilon_1 + i\epsilon_2$, where the real and imaginary parts are given by⁶

$$\epsilon_{1}(q,\omega) = 1 + \frac{q_{FT}^{2}}{q^{2}} \left\{ \frac{1}{2} + \frac{p_{F}}{4q} \left[\left(\frac{(\omega + q^{2}/2m)^{2}}{(qv_{F})^{2}} - 1 \right) \ln \left| \frac{\omega - qv_{F} + q^{2}/2m}{\omega + qv_{F} + q^{2}/2m} \right| - \left(\frac{(\omega - q^{2}/2m)^{2}}{(qv_{F})^{2}} - 1 \right) \ln \left| \frac{\omega - qv_{F} - q^{2}/2m}{\omega + qv_{F} - q^{2}/2m} \right| \right\},$$
(3)

$$\epsilon_{2}(q,\omega) = \begin{cases} \frac{\pi}{2} \frac{q_{FT}^{2}}{q^{2}} \frac{\omega}{qv_{F}}, & 0 \le \omega \le qv_{F} - q^{2}/2m \\ \frac{\pi}{2} \frac{q_{FT}^{2}}{q^{2}} \frac{q_{F}}{q} \left[1 - \frac{(\omega - q^{2}/2m)^{2}}{(qv_{F})^{2}} \right], & -\frac{q^{2}}{2m} \le \omega - qv_{F} \le \frac{q^{2}}{2m} \\ 0, & \omega \ge qv_{F} + \frac{q^{2}}{2m} \end{cases}$$
(4)

where q_{FT} is the Fermi-Thomas screening wave vector, given by

$$q_{\rm FT}^2 = 3\omega_p^2 / (v_F)^2 , \qquad (5)$$

and v_F is the Fermi velocity. The notation uses the conventional $\hbar = 1$ and presumes a free-electron mass m. The plasma frequency is defined as $\omega_p^2 = 4\pi ne^2/m$, where n is the electron density.

In the long-wavelength limit ϵ_1 takes on the expected values

$$\epsilon_1(0,\omega) = 1 - \omega_p^2 / \omega^2 , \qquad (6)$$

$$\lim_{q \to 0} \epsilon_1(q,0) = 1 + q_{\rm FT}^2 / q^2 = 1 + 3\omega_p^2 / (qv_F)^2 .$$
 (7)

Within the RPA, Morel and Anderson⁴ found the Coulomb repulsion parameter in the static limit

$$\mu_{\rm RPA} = N(E_F) V(\omega = 0) = \frac{k_{\rm FT}^2}{8k_F^2} \ln \left[\frac{4k_F^2 + k_{\rm FT}^2}{k_{\rm FT}^2} \right].$$
(8)

Furthermore, the solution of the Eliashberg equations yields a reduced effective coupling

$$\mu_{\rm RPA}^* = \frac{\mu_{\rm RPA}}{1 + \mu_{\rm RPA} \ln(\omega_D / \omega_F)} , \qquad (9)$$

where the cutoff phonon frequency ω_D is generally much smaller than the Fermi frequency ω_F . In most studies, it has been customary to choose $\mu^*_{\text{RPA}} \approx 0.1$ and thus associate the dominant superconducting features with the electron-phonon coupling λ .

Considerable progress has been achieved in studies of the dielectric function which improve on the RPA by including exchange and correlation effects. A major improvement of these studies beyond the RPA is a more accurate description of certain exact limits, such as requirements on the form of the pair correlation function.¹⁰⁻¹⁴ However, a consensus has not been reached on the exchange function G(q) calculated by various authors and therefore we examine the influence of exchange on T_c by using four representative functions found by independent approaches to the problem.¹¹⁻¹⁴

An interesting comparison of the exchange calculation is made by Mahan,¹⁰ and the details of these computations are described in the references which we shall abbreviate as Hubbard,¹¹ Devreese,¹² STLS,¹³ and Overhauser.¹⁴ A comparison of the exchange functions G(q) derived by the above authors is shown in Fig. 1. It is noteworthy that the early Hubbard work yields a weak variation of Gwith respect to q. The self-consistent approach of Singwi et al. (STLS) gives also a smooth behavior of G. By contrast the Devreese result shows a strong peak in G near $q \approx 2k_F$ and it is interesting to note that the maximum of the Devreese G extends above unity. Overhauser has emphasized the importance of a possible peak structure near $2k_F$ and examined the consequences of a Lorentzian peak with an adjustable width and height, and in particular, suggested probes of the metal lattice dynamics to distinguish the structure in G(q).¹⁴

More recent investigations of the possible peak structure in G(q) are discussed in Ref. 15. It would be interesting to examine other forms of G(q) as well, and hopefully the present results will encourage future work in this direction.

We find that the predominant influence of exchange forces is on the electron-electron screening. Thus the secondary influence of exchange on the electron-ion coupling is not emphasized here, especially since other factors such as band structure influence the lattice dynamics in a very significant way. Thus we write the electron-electron dielectric function in the form¹²

$$\epsilon_{e-e}(q,\omega) = \frac{1}{1-G(q)} + \epsilon_{\text{RPA}}(q,\omega) - 1 . \qquad (10)$$

This form is equivalent to the Overhauser-Kukkonen¹⁶ expression when their summation over electron spins is performed. The exchange correction G(q) thus radically changes the electron-electron potential over a wide momentum range as shown in Fig. 2. In the long-wavelength limit the RPA result for the static function $\epsilon_{e-e}(q,0)$ is valid, but otherwise the exchange corrections cause $\epsilon_{e-e}(q,0)$ to change dramatically in magnitude and possibly even in sign as seen in the case of the Devreese G function in Fig. 2. The origin of the attractive region in the electron-electron coupling is traced to the sharp peak in G(q) near $q \approx 2k_F$, and thus this distinction is crucial to the superconductivity analysis.

From Eq. (10) we see that the crucial point is that the region $G(q) \approx 1$ yields a large value of the screening dielectric function ϵ_{ee} , and thus the Overhauser Lorentzian peak near $q \approx 2k_F$ will also yield a negative region in the electron-electron potential, *providing* that the strength of the peak in G(q) is comparable to the Devreese function.

Clearly, the exchange function G(q) will also significantly modify the dielectric function $\epsilon_{e\cdot e}$ at finite frequencies. Thus a reliable investigation of T_c in our study requires a solution of the Eliashberg equations which require a summation over momenta at various frequencies.

It is tempting to speculate whether the attractive region in the electron-electron potential induced by the Devreese G(q) function may lead to superconductivity without the requirement of electron-phonon interactions. Unfor-





FIG. 1. Exchange functions G(q) as a function of momentum as derived by various authors. The early Hubbard calculation yields a smooth function lowest in magnitude of the group, and the Singwi (STLS) result is considerably larger over the entire q range. The Devreese G is notable for a sharp peak near $q \approx 2k_F$ which has a strong influence on the superconducting transition temperature T_c .

FIG. 2. Effective static electron-electron interaction as a function of momentum is shown for four screening approximations for an electron density represented by $r_s = 3$. The RPA yields the strongest screened Coulomb force, whereas the Hubbard model and the STLS choices of the exchange function G(q) decrease the potential further. In contrast to the smooth behavior of the other curves, the Devreese exchange function gives a sharp drop in the potential near $q \approx 2k_F$, which reflects their corresponding peak in G(q).

tunately, when the interaction shown in Fig. 2 is appropriately averaged over momentum, our analysis does not yield a finite T_c for a single-component electron gas. The latter conclusion is in accord with investigations performed previously by Devreese and co-workers.

To complete our formulation of the superconducting transition temperature we introduce the phonon dielectric function in a rudimentary form, namely, the bare ion response in the long-wavelength limit, i.e.,

$$\epsilon_{\rm ph} = -\frac{\Omega_p^2}{\omega^2} , \qquad (11)$$

where the ion plasma frequency is $\Omega_p^2 = 4\pi nze^2/M$, where z is the valency and M is the ion mass. This simple expression is in the spirit of our electron-gas model which neglects band-structure effects and other contributions to the phonons. The exchange corrections to $\epsilon_{\rm ph}$ appropriate to the electron screening of test charges were found by direct computations to yield only negligible deviations in the phonon spectrum in the RPA. A more accurate description of the phonon spectrum has been achieved by Price *et al.*,¹⁷ and it is interesting to note that their calculations also yield small changes in the phonon spectrum due to exchange.

III. SUPERCONDUCTIVITY

The electron-scattering problem is conveniently analyzed in terms of the Eliashberg gap equation

$$\Delta_{\mathbf{k}} = \int d\xi_{\mathbf{k}'} \frac{\Delta_{\mathbf{k}}}{E(\mathbf{k}')} K_c(\mathbf{k}, \mathbf{k}') \tanh \left[\frac{E(\mathbf{k}')}{2k_B T} \right], \qquad (12)$$

where the electron quasiparticle energy is

$$E(\mathbf{k}) = (\Delta_{\mathbf{k}}^2 + \xi_{\mathbf{k}}^2)^{1/2} , \qquad (13)$$

where ξ_k is the energy transfer in the two-particle scattering process. Generally the gap is presumed isotropic in cases such as the alkali metals which are well represented by the free-electron approximation, i.e., $\Delta_k \cong \Delta$. Furthermore the kernel is just the total effective interaction

$$K_c(k,k') = \frac{4\pi e^2}{q^2 \epsilon_{\text{total}}(k,k',\omega)} , \qquad (14)$$

where

$$\epsilon_{\text{total}} = \epsilon_{e-e}(q,\omega) + \epsilon_{\text{ph}} , \qquad (15)$$

in terms of the dielectric functions defined in Eqs. (10) and (11). Our solution of the Eliashberg integral equation involves a numerical integration over momentum. The procedure is to consider one electron on the Fermi surface, and thus transform the kernel K_c into a function of the frequency measured relative to the Fermi energy E_F ,

$$\omega \equiv E_F - \frac{k'^2}{2m} , \qquad (16)$$

where k' is the momentum of the other electron involved in the scattering. Thus $K_c(\omega)$ represents the average potential experienced by an electron on the Fermi surface due to other electrons displaced from the Fermi surface by an energy ω . The kernel $K_c(\omega)$ displays the familiar weak attractive region at low frequencies coming from the electronphonon interaction and a reduced Coulomb repulsion over a much wider energy range. This behavior is evident in Fig. 3 where the RPA result for K_c presents a standard for comparison. It is interesting to note that the two exchange corrections yield a similar *net* attractive depth in K_c , but the impact on superconductivity of the exchange functions is actually quite different. The structure of the frequency dependence of K_c is vital to an accurate determination of T_c , and Fig. 3 provides the insightful observation that the Devreese G(q) function causes the strongest reduction in the effective electron-electron coupling.

A solution of the Eliashberg equations can be found by the two-square-well model for the interaction kernel K_c which represents the traditional approach.^{4,5} A state of the art study of the Eliashberg equations is available in the work of Rietschel and Sham,⁷ and their recent results provide further support for the reliability of the twosquare-well approximation. A schematic representation of the approximation to the repulsive part V_R and the attractive component $-V_0$ of the kernel is shown in Fig. 4. In the computation of T_c the cutoff energies are determined by the zero in K_c at $\omega = \omega_0$ and at $\omega_{max} = E_F$. The amplitude V_0 was determined by finding the equivalent area in the attractive regions in $K_c(\omega)$ by direct numerical integration and then choosing V_0 to match the computed area. The solution of the Eliashberg equations within this model gives⁷ a transition temperature

$$k_B T_c = 1.1 \omega_0 \exp\left[\frac{-1}{\lambda - \mu^*}\right], \qquad (17)$$

where

$$\lambda \equiv V_0 , \qquad (18a)$$

and



FIG. 3. Superconducting electron kernel K_c which enters in the Eliashberg equations is plotted as a function of frequency. The solid curve gives the RPA result, and the exchange and correlation corrections are shown using the Hubbard G(q) by the dashed curve, and the Devreese G(q) by the dotted curve. The electron gas is chosen to a density corresponding to $r_s=3$, valency z=1, and ionic mass M=86.



FIG. 4. Schematic representation of the two-square-well model used to approximate the kernel $K_c(\omega)$ which enters the Eliashberg equations. The model yields an analytic solution for $T_c(V_0, V_R, \omega_0, E_F)$, and the various parameters V_0, V_r, ω are determined by direct numerical evaluation of kernel $K_c(\omega)$.

$$\mu^* = \frac{V_R}{1 + V_R \ln(E_F/\omega_0)} \ . \tag{18b}$$

The condition for the occurrence of superconductivity is $\lambda > \mu^*$. Our computation of V_R and subsequently μ^* follows the Morel and Anderson⁴ approach of tracing the static limit of the electron-electron dielectric function (neglecting ions for the moment), and then performing an average over the momentum. In the RPA, our results agree with Ref. 4 as expected, but the exchange and correlation contributions tend to reduce V_R and thus lower μ^* as well. Although this situation should favor superconductivity, the screening of the electron-phonon part of the kernel K_c must be considered on an equal footing, and here the variation of the exchange function G(q) as a function of momentum is found to play a key role in determining T_c .

A typical result of our calculations of the superconducting transition temperatures is shown in Fig. 5 as a



FIG. 5. Computed superconducting transition temperatures are shown as a function of r_s using z = 1 and M = 86. The RPA greatly overestimates T_c for the nonsuperconducting alkali metals Na, K, Rb, and Cs. The Hubbard and STLS forms of the exchange function G(q) modify T_c considerably as shown, but the G(q) function with a peak near $q \approx 2k_F$ (Devreese case) dramatically lowers T_c to values below 0.1 K.

function of the electron-gas parameter r_s . First of all we notice that the RPA greatly overestimates T_c for Na, K, Li, and other alkali metals whose r_s values are in the range depicted in Fig. 5. This conclusion is in accord with calculations of Rietschel and Sham,⁷ who concluded that self-energy and vertex corrections are very important. Our calculations of T_c including the exchange function show that the Hubbard and STLS choices for G(q) yield substantial deviations from the RPA but nevertheless also overestimate T_c . However, the appearance of a peak in G(q) near $q \cong 2k_F$ greatly reduces T_c as shown in the example of Fig. 5 using the Devreese G(q) function. This case lowers T_c to values below 0.1 K and in effect suggests that very minor changes in the parameters would eliminate superconductivity altogether for a simple freeelectron gas.

As an additional check, we computed T_c using the Overhauser model of a Lorentzian function peaked near $q \approx 2k_F$. When the width and height of the Lorentzian was adjusted to resemble the Devreese G(q) function, very low values of $T_c < 0.1$ K were also found for the same range of r_s values.

A direct comparison with experiment is shown in Fig. 6, where appropriate values of the valency z and the ion mass M were used in the examples Al, Li, Na, and K. With these specified parameters the RPA overestimate of T_c is quite striking, especially in the case of Li. The data for these materials as well as a comprehensive review of previous studies for the alkali metals is given by Grimwall,¹⁸ and his exposition reveals Li as perhaps the most anomalous case. However, the exchange and corre-



FIG. 6. Comparison of the superconducting transition temperatures computed for Al, Li, Na, and K using appropriate free-electron and ion mass parameters. The lines connecting the computed points are only a guide to the eye, and the experimental values are shown by triangles. The RPA greatly overestimates T_c for all the simple metals considered, and the Hubbard exchange correction yields only a small decrease from the RPA. However, the strong peak in the exchange function G(q) found by Devreese dramatically lowers T_c (dotted curve) and may account for the mysterious absence of superconductivity in Li, Na, and K.

lation function G(q) may explain the lack of superconductivity in Li providing that a peak near $q \cong 2k_F$ occurs with strength comparable to the Devreese function which gives $T_c(\text{Li}) \le 0.06$ K in our calculations. Similarly the Devreese G(q) choice yields good agreement for other alkali metals including Na and K as shown in Fig. 6. We find similar results for the T_c of Rb and Cs, in that the Devreese function gives $T_c < 0.004$ K, whereas the RPA greatly overestimates T_c in the range 3-4 K for these materials.

Although aluminum would appear exceptional in that it has $T_c = 1.2$ K in contrast to the lower value of $T_c \cong 0.08$ found by using the Devreese G function in our calculation, it is interesting that band-structure effects in that instance should be more influential than in the case of the simplest alkali metals. The enhanced T_c values observed in amorphous Al provide further evidence for the importance of structural effects. Nevertheless the exchange and correlation contributions provide a significant influence on T_c of Al as shown in Fig. 6 by comparison to the RPA. In the event that the peak structure in G(q) is reduced by higher-order contributions as suggested by the Singwi group,¹⁵ it may be that the free-electron model in fact would yield T_c in closer agreement with experiment for aluminum.

The significant reductions in T_c achieved by the peak structure in G(q) may be traced to a strong reduction in the electron-phonon coupling parameter λ which is not compensated by the corresponding reduction in the Coulomb repulsion parameter μ^* . These reduced values of the parameters are compared to the RPA case in Fig. 7, where the approximate Eliashberg kernel $K_c(\omega)$ is shown for $r_s = 3.0$, z = 1, and M = 86. Since T_c depends on the net coupling $\lambda - \mu^*$ in an exponential form, a decrease in λ of the order shown in Fig. 7 is sufficient to lower T_c very substantially.



FIG. 7. Two-square-well approximation to the Eliashberg kernel $K_c(\omega)$ is shown in the RPA by solid lines. By comparison the exchange function Devreese G(q) reduces the Coulomb interactions and simultaneously lowers the electron repulsion μ^* as well as the magnitude of the electron-phonon coupling λ . The net reduction results in exceedingly small values of $T_c < 0.1$ K. Here the valency was chosen as z = 1, $r_s = 3$, and the ion mass is M = 86.

Since the exchange and correlation effects modify the Coulomb repulsion parameter μ^* as well as the electronphonon coupling λ , it is natural to wonder if these corrections could be discerned in a modification of the isotope effect. From our direct computations of T_c as a function of the ion mass M, we find the normal isotope relation $T_c \approx AM^{-1/2}$ to be reasonably well satisfied; although the value of the coefficient A is naturally very sensitive to the exchange function G(q) used in the analysis.

IV. CONCLUSIONS

Our solutions of the Eliashberg equations for a simple free-electron gas reveal that the exchange and correlation contributions to the screening of the Coulomb interaction may have a profound influence on the superconducting transition temperature. Using various forms of the exchange function G(q) proposed by others in a different context, we find that smooth functional forms of G(q), which are similar in magnitude and structure to the early Hubbard and Singwi forms, yield relatively small corrections to the RPA method (of order 10%). However, the RPA calculations overestimate T_c by more than an order of magnitude for the alkali metals.

In the event that a sharp peak structure near $q \cong 2k_F$ occurs in G(q) and the strength of the peak is comparable to the function obtained by the Devreese group, the exchange and correlation corrections enhance the screening of the Coulomb force sufficiently to eliminate the superconducting electron pairing. Using the Devreese function G(q) reduces T_c to very low values below 0.1 K in comparison to $T_c^{\text{RPA}} \cong 10$ K for electron-gas parameters suitable for typical metals. Thus the forms of the G(q) function derived by Devreese *et al.* and suggested independently by Overhauser may provide the basis for explaining the mysterious absence of superconductivity in Na, K, Li, and other alkali metals whose simple Fermi surfaces are amenable to the free-electron model used here.

More recent advances in the study of these electron correlations suggest other forms of the exchange function and hopefully our results will stimulate further research in this area. Our present analysis demonstrates the range of influence of the exchange functions on T_c and intermediate cases should be examined as well. Unfortunately a single parameter such as T_c cannot by itself distinguish uniquely the form of the G(q) function, but it is remarkable that the superconducting pairing is so sensitive to the structure of these exchange contributions.

By necessity, we have been limited to the use of a static exchange function G(q) although the formalism is readily applicable to a full dynamic expression for $G(q,\omega)$. In view of the sensitivity of the computed T_c values to structure in G(q), the need for a dynamic solution for the exchange function becomes even more relevant.

Phonons have been treated in a very simple manner in our work, and it is certain that the application of more refined solutions of the lattice dynamics will strongly influence the values of T_c in the RPA as they are known to be important in pseudopotential calculations performed previously by several authors.¹⁸ By the same token, it would be interesting to combine the salient features of the lattice dynamics with the exchange corrections which are predominant in our study.

A natural extension of the present analysis to systems with charge-density (CDW) and spin-density waves (SDW) is also warranted by the results in the superconductors. In fact, as Overhauser has emphasized, there may well be a competition between the formation of a CDW, SDW, or a superconducting state, and it is reasonable to expect that the structure of the exchange function G(q) may influence the corresponding phases.

Finally, we mention the possible extension of the present analysis to other mechanisms of superconductivity such as the acoustic plasmon modes which may occur in alloys whose band structures exhibit two electronic carriers with somewhat different effective masses.¹⁹ Such electronic mechanisms require a thorough investigation beyond the RPA, as exemplified by the recent work of Grabowski and Sham²⁰ which demonstrates the vital importance of self-energy and vertex corrections: They also find that the RPA grossly overestimates T_c , but their final results (including self-energy and vertex terms) yields a maximum superconducting temperature of $T_c \cong 60$ K from the nonphonon mechanism. Their intriguing conclusion could be checked independently by including the

- ¹H. Fröhlich, Phys. Rev. 79, 845 (1950).
- ²J. L. Bardeen, L. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
- ³G. M. Eliashberg, Zh. Eksp. Teor. Fiz. 38, 966 (1960) [Sov. Phys.—JETP 11, 696 (1960)].
- ⁴P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).
- ⁵W. L. McMillan, Phys. Rev. 167, 331 (1968).
- ⁶For an excellent introduction and review, see D. Pines and P. Nozieres, *Quantum Liquids* (Benjamin, New York, 1966), Chap. 5.
- ⁷H. Rietschel and L. J. Sham, Phys. Rev. B 28, 5100 (1983).
- ⁸G. Vignale and K. S. Singwi, Phys. Rev. B 31, 2729 (1985); 32, 2156 (1985).
- ⁹J. T. Devreese, F. Brosens, and J. Ruvalds (unpublished).
- ¹⁰G. Mahan, Many-Particle Physics (Plenum, New York, 1981), and references cited therein.
- ¹¹J. Hubbard, Proc. R. Soc. London, Ser. A 243, 336 (1957).
- ¹²F. Brosens, L. F. Lemmens, and J. T. Devreese, Phys. Status Solidi **74**, 45 (1976); **81**, 551 (1977).
- ¹³K. S. Singwi, A. Sjolander, M. P. Tosi, and R. H. Land, Phys. Rev. B 1, 1044 (1970).

exchange and correlation screening of the Coulomb interaction in a manner similar to the present work.

Our results provide one example of the importance of many-body effects in the calculation of superconducting transition temperatures of simple metals. Other correlation effects such as spin fluctuations should be influential as well, and have been invoked²¹ to resolve discrepancies between experiments and calculated T_c values in transition metals. Thus the influence of many-body contributions to the superconducting electron pairing may also be significant in compounds with more complex band structures.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge stimulating discussions with Han Ru-Qi, David Mitchell, Sheng Qing-Guang, P. F. Tua, and I. Tüttő. Our interest in the exchange functions was stimulated by J. T. Devreese and F. Brosens, and we are indebted to them for many helpful ideas and suggestions. Conversations with A. Overhauser, R. V. Coleman, and S. E. Schnatterly are appreciated. This research was supported by the U.S. Department of Energy Grant No. DEF 605-84-ER45113.

- ¹⁴Y. R. Wang, M. Ashraf, and A. W. Overhauser, Phys. Rev. B 30, 5580 (1984).
- ¹⁵For an interesting review of the exchange and correlation formalism see, for example K. S. Singwi, *Recent Progress in Many-Body Theories*, Vol. 198 of *Lecture Notes in Physics* (Springer-Verlag, Berlin, 1983). A recent diagrammatic study of the G(q) function is developed by A. Holas, P. K. Aravind, and K. S. Singwi, Phys. Rev. B 20, 4912 (1979).
- ¹⁶A. W. Overhauser and C. A. Kukkonen, Phys. Rev. B 20, 550 (1979).
- ¹⁷D. L. Price, K. S. Singwi, and M. P. Tosi, Phys. Rev. B 2, 2983 (1970).
- ¹⁸A comprehensive review of calculations involving bandstructure effects and empirical data is in G. Grimwall, *The Electron-Phonon Interaction in Metals*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1981); the case of Li is given on p. 255.
- ¹⁹J. Ruvalds, Adv. Phys. 30, 677 (1981).
- ²⁰M. Grabowski and L. J. Sham, Phys. Rev. B 29, 6132 (1984).
- ²¹H. Rietschel and H. Winter, Phys. Rev. Lett. 43, 1256 (1979).