

# Exchange and Correlation Corrections to the Electron-Phonon Interaction\*

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The method of Bardeen and Pines for treating electron-phonon interactions in normal metals is extended to include exchange and correlation effects. The interaction matrix element is found to depend not only on electron momentum transfer but also on the initial electron wave vector. An average over initial wave vector direction is therefore made; the average taken is discussed as being more reasonable than that of Bailyn in a previous treatment. Shielding is also introduced in a more physical manner than in Bailyn's paper—via the dielectric constant as it arises in the random phase approximation. An alternate method of treating the problem in the long wavelength limit—employing deformation potential techniques—verifies the results of the above method in this limit.

## I. INTRODUCTION

THE treatment of electron-phonon interactions in metals necessitates a careful consideration of the screening processes. The electrons tend to follow the motion of the ions, with the result that the ion field is screened within a distance which turns out to be comparable to the interparticle spacing. On the other hand, the exchange hole and correlation effects screen the electron. Furthermore, they amplify the effects of lattice vibration and so tend to increase the electron-phonon interaction matrix elements. Recently, Bailyn,<sup>1</sup> by extending the self-consistent field method of Bardeen,<sup>2</sup> has attempted to include the effects of exchange and correlation on electron-phonon scattering. The approach was somewhat intuitive; Bailyn found it necessary, for instance, to make the *ad hoc* assumption that the lattice does not affect the plasma or collective, part of the electron system wave function. A more rigorous approach is provided by an extension of the procedure of Bardeen and Pines.<sup>3</sup> Their method involves the use of a canonical transformation to eliminate from the Hamiltonian terms linear in the phonon coordinates so as to decouple—to the desired order—electrons and phonons. The results yield both the interaction matrix elements and a sound wave dispersion relation. The long-range part of the Coulomb interaction is conveniently accounted for by the introduction of collective coordinates in the scheme of Bohm and Pines.<sup>4</sup>

The inclusion of exchange is not difficult in the adiabatic approximation. The results show that even in the limit of small electron momentum transfer, exchange effects are important in the interaction matrix element. In this limit exchange appears predominantly in the effective mass parameter, so that, as might be expected, the change in the energy spectrum—or equivalently in the density of states—accounts most importantly for the exchange corrections. We find, as did Bailyn, that the

matrix elements depend on the initial electron wave vector  $\kappa$  as well as the momentum transfer, in contrast to the situation without exchange. This is so even though we continue to take the part of the interaction due to the motion of the ions alone, which is assumed to be known, as independent of  $\kappa$ .

In Sec. II we discuss the Hamiltonian and by means of a canonical transformation derive an integral equation for the interaction matrix element. Section III deals with the solution of this equation to give the matrix elements—after an average over direction of  $\kappa$ —in terms of a power series in  $k$ , the magnitude of the momentum transfer. The first two terms in the series are calculated explicitly, and an expression in closed form is also given. In Sec. IV we approach the whole problem from a different point of view—that of treating the interaction between electrons and lattice in terms of a generalized deformation potential. As this approach yields only the first term in the power series in  $k$  obtained in Sec. III, it gives in essence an expression for the appropriate effective mass parameter in terms of the observed lattice constants of the metal. It also affords a comparison with the Bardeen-Pines result obtained by neglecting exchange effects.

## II. HAMILTONIAN AND INTEGRAL EQUATIONS FOR $v_{\kappa k}$

We start from the Hamiltonian introduced by Nakajima and employed by Bardeen and Pines

$$H_1 = \sum E_{\kappa} c_{\kappa}^* c_{\kappa} + \frac{1}{2} \sum (p_{\kappa}^* p_{\kappa} + \omega_{\kappa}^2 q_{\kappa}^* q_{\kappa}) + \sum v_{\kappa} q_{\kappa} \rho_{-\kappa} + \frac{1}{2} \sum M_{\kappa}^2 \rho_{\kappa} \rho_{-\kappa} + \sum (v_{\kappa}^i - v_{\kappa}) q_{\kappa} \rho_{-\kappa} + \frac{1}{2} \sum (\Omega_{\kappa}^2 - \omega_{\kappa}^2) q_{\kappa}^* q_{\kappa}. \quad (2.1)$$

We have separated out the parts of the total Hamiltonian which will not be of concern in treating the electron-phonon interaction—namely, the ion-ion interaction energy for the equilibrium configuration and the transverse phonon Hamiltonian. The electrons are described in second quantization by occupation numbers of a set of Bloch functions, with  $c_{\kappa}^*$  and  $c_{\kappa}$  the creation and destruction operators, respectively (the spin index has been suppressed). The system is taken in unit

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<sup>1</sup> M. Bailyn, Phys. Rev. **117**, 974 (1960).

<sup>2</sup> J. Bardeen, Phys. Rev. **52**, 688 (1937).

<sup>3</sup> J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

<sup>4</sup> D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

volume with periodic boundary conditions so that the set of allowable wave vectors is discrete. The deviations of the ions from their equilibrium positions have been described in terms of the ionic normal coordinates,  $q_k$ , and the conjugate momenta,  $p_k$ . The total effective matrix element for the electron-lattice interaction,  $v_k$ , has been written as the sum of  $v_k^i$  due to the motion of the ions—and assumed to be known—and  $v_k^p$  due to the compensating motion of the electrons.  $\Omega_k$  is the sound wave frequency associated with  $k$  as determined only from ion-ion interactions;  $\omega_k$  is the corresponding correct frequency. We have written the Coulomb interaction between electrons in the form

$$\frac{1}{2} \sum M_k^2 \rho_{-k} \rho_k, \quad (2.2)$$

where  $M_k^2 = 4\pi e^2/k^2$  for free electrons and

$$\rho_k = \sum c_{k-k}^* c_k; \quad \rho_{-k} = \sum c_k^* c_{k-k}. \quad (2.3)$$

We denote the first two summations in  $H_1$  by  $H_0$  and the third by  $H_I$ . A canonical transformation generated by  $S$  is made such that

$$i/\hbar [S, H_0] = -H_I, \quad (2.4)$$

so that to first order,  $H_I$  is eliminated. The most general  $S$  for this is given by Bardeen and Pines<sup>3</sup>:

$$S = \sum_{k, \kappa} [f(\mathbf{k}, \kappa) q_k - i g(k, \kappa) p_{-k}] c_{\kappa}^* c_{\kappa-k}. \quad (2.5)$$

In the adiabatic approximation, where we neglect phonon recoil,  $\omega^2 \rightarrow 0$ , and terms in  $S$  which are proportional to  $p_{-k}$  are not needed, for there no longer exist terms linear in  $p_k$  in  $[q_k, H_0]$ . Then the condition (2.4) becomes:

$$(1/\hbar) \sum_{k, \kappa} (E_{\kappa} - E_{\kappa-k}) c_{\kappa}^* c_{\kappa-k} f(\mathbf{k}, \kappa) q_k + \sum_{k, \kappa} v_k q_k c_{\kappa}^* c_{\kappa-k} = 0, \quad (2.6)$$

which, due to the independence of the  $q_k$ , gives

$$f(\mathbf{k}, \kappa) = -\hbar v_k / (E_{\kappa-k} - E_{\kappa}). \quad (2.7)$$

Then the interaction matrix element  $v_k$  can be determined by the condition that after the canonical transformation, the term linear in  $q_k$  in the third line of (2.1) be eliminated to the same order as that in the second line. The result of Bardeen and Pines is obtained in the approximation that in the commutator  $[\rho_{-k} \rho_k, S]$  only the direct terms are kept. We now include the diagonal exchange terms. It is no longer convenient to introduce  $v_k$  into the Hamiltonian as was done in (2.1); the elimination of terms linear in  $q_k$  to first order now leads to the condition (see Bardeen and Pines,<sup>3</sup> Appendix B):

$$\begin{aligned} & \sum_{\kappa', s} f(\mathbf{k}, \kappa') (4\pi e^2/k^2) [n(\kappa' - \mathbf{k}) - n(\kappa')] \\ & + \sum_{k'} (4\pi e^2/k'^2) [n(\kappa - \mathbf{k} - \mathbf{k}') - n(\kappa - k')] f(\mathbf{k}, \kappa) \\ & + \sum_{\kappa'} [4\pi e^2/(\kappa' - \kappa)^2] [n(\kappa') - n(\kappa' - \mathbf{k})] f(\mathbf{k}, \kappa') \\ & - (E_{\kappa} - E_{\kappa-k}) f(\mathbf{k}, \kappa) = \hbar v_k^i. \end{aligned} \quad (2.8)$$

In analogy with the system without exchange effects, we define  $v_{k\kappa}$  by:

$$f(\mathbf{k}, \kappa) = \hbar v_{k\kappa} / (E_{\kappa-k}^{(1)} - E_{\kappa}^{(1)}), \quad (2.9)$$

where the energies have been "renormalized" so as to include the exchange energy:

$$W_{k'} = - \sum_{k''} (4\pi e^2/k'') n(\mathbf{k}' - \mathbf{k}''), \quad (2.10)$$

$$E_{k'}^{(1)} = E_{k'} + W_{k'}. \quad (2.11)$$

Then (2.8) can be rewritten in terms of the effective matrix elements,  $v_{k\kappa}$ , giving an integral equation for them:

$$\begin{aligned} v_{k, \kappa} = v_k^i + \sum_{\kappa'} & \left( \frac{8\pi e^2}{k^2} - \frac{4\pi e^2}{|\kappa' - \kappa|^2} \right) \\ & \times \frac{[n(\kappa' - \mathbf{k}) - n(\kappa')]}{(E_{\kappa-k}^{(1)} - E_{\kappa}^{(1)})} v_{k\kappa'}. \end{aligned} \quad (2.12)$$

The singular character of the summation results from the neglect of correlation effects. In the scheme of Bohm and Pines<sup>4</sup> these are included by the introduction of extra degrees of freedom, the plasma coordinates, and the associated subsidiary conditions necessary to keep the total number of degrees of freedom unchanged. In the adiabatic approximation

$$\begin{aligned} H = \sum E_{\kappa} c_{\kappa}^* c_{\kappa} + \sum v_k^i q_k \rho_{-k} \\ + \frac{1}{2} \sum M_k^2 \rho_k \rho_{-k} + \frac{1}{2} \sum_{k < k_0} P_k^* P_k, \end{aligned} \quad (2.13)$$

with the subsidiary condition

$$P_k \Psi = 0, \quad (k < k_c), \quad (2.14)$$

where  $k_c$  is a critical wave vector of the order of the Fermi wave vector, determined by system energy minimization as discussed by Bohm and Pines.<sup>4</sup>

A canonical transformation can be made to obtain a Hamiltonian which describes independent plasma oscillations. The residual weak electron-plasmon and phonon-plasmon interactions can be neglected. We can apply the original transformation generated by (2.5) to the part of the Hamiltonian for which  $k > k_c$ , which has not been affected by the introduction of plasma coordinates. The elimination of electron-phonon coupling to first order then leads to a condition of the form (2.12), with the exception that  $|\kappa' - \kappa|$  is to be restricted to values greater than  $k_c$ . Almost equivalently, and perhaps somewhat more naturally in that it involves no abrupt cutoff, we can introduce a screening wave vector, which will be assumed to be of the order of the Fermi-Thomas screening wave vector:

$$\begin{aligned} v_{k\kappa} = v_k^i + \sum_{\kappa'} & \left( \frac{8\pi e^2}{k^2} - \frac{4\pi e^2}{|\kappa' - \kappa|^2 + k_s^2} \right) \\ & \times [n(\kappa' - \mathbf{k}) - n(\kappa')] (E_{\kappa-k}^{(1)} - E_{\kappa}^{(1)})^{-1} v_{k\kappa'}. \end{aligned} \quad (2.15)$$

This is essentially the equation Bailyn<sup>1</sup> has obtained by other means. We feel that the above method has established this relation on firmer theoretical grounds. Also, as noted above, we have treated shielding somewhat differently. Both methods can be discussed in the random phase approximation where one employs the dielectric constant  $\epsilon$  to describe shielding. Whereas Bailyn has taken

$$\begin{aligned} \epsilon &= \infty & \text{for } |\mathbf{k}' - \mathbf{k}| < k_c, \\ \epsilon &= 1 & \text{for } |\mathbf{k}' - \mathbf{k}| > k_c, \end{aligned} \quad (2.16)$$

we have chosen the conventional values:

$$\epsilon(|\mathbf{k}' - \mathbf{k}|) = 1 + 4\pi\alpha \approx 1 + k_s^2/|\mathbf{k}' - \mathbf{k}|^2. \quad (2.17)$$

That this choice is advantageous as well as reasonable will be clear in Sec. III.

### III. SOLUTION OF THE INTEGRAL EQ. (2.15)

The integral equation is in the form

$$v_{k\mathbf{k}} = v_k^i - \sum_{\mathbf{k}'} A(\mathbf{k}, \mathbf{k}') v_{k\mathbf{k}'}. \quad (3.1)$$

We solve by iteration. Taking first  $v_{k\mathbf{k}'}$  as independent of  $\mathbf{k}'$ , we eliminate the dependence on  $\mathbf{k}$  of the right-hand side of (3.1) by averaging over  $\mathbf{k}$  in a way to be specified. Then

$$v_k = v_k^i / (1 + \langle \sum_{\mathbf{k}'} A(\mathbf{k}, \mathbf{k}') \rangle_{\text{av}}). \quad (3.2)$$

Substitution of this into (3.1) gives a second approximation

$$v_{k\mathbf{k}} = v_k^i \left[ \frac{1 + \langle \sum_{\mathbf{k}'} A(\mathbf{k}, \mathbf{k}') \rangle - \sum_{\mathbf{k}'} A(\mathbf{k}, \mathbf{k}')}{1 + \langle \sum_{\mathbf{k}'} A(\mathbf{k}, \mathbf{k}') \rangle} \right]. \quad (3.3)$$

We consider processes in which both initial and final electron wave vectors are very near the Fermi surface. The requirements of energy conservation and the Pauli principle imply that these are the dominant processes, especially at low temperatures. Then the appropriate average is one over the Fermi surface. Thus, it seems that Bailyn's procedure of averaging over all values of  $\mathbf{k}$  within the Fermi surface is somewhat artificial, although its direct effect on the final result would be small. However, he now claims to improve on the first approximation by averaging the second approximation over the *Fermi surface*, and the difference in the two averages which appears in the numerator of the expression for  $v_{k\mathbf{k}}$  [compare with Eq. (3.3)] is described as a significant term. This is certainly unjustified in the long wavelength limit, the case which he explicitly considers. Nevertheless, as Bailyn noted, the dependence of  $v_{k\mathbf{k}}$  on  $\mathbf{k}$  is too complicated to be of any use in calculations, so we also take an average over the Fermi surface of (3.3). This just returns us to the first approximation.

Now, as we perform the integration, we note that the choice of a smooth function as a dielectric constant is advantageous computationally as well as preferable

physically. We no longer are forced to investigate separately the several regions delineated by the conditions imposed by the existence of a cutoff wave vector. This simplifies both the integration and the results.

We eliminate the index (1) on the energies; all energies will be taken as containing exchange contributions. In order to obtain an idea of the order of magnitude of the exchange effects, we first consider the long wavelength limit, where an immediate simplification can be made, and the final result obtained quickly.

$$\frac{n(\mathbf{k}' - \mathbf{k}) - n(\mathbf{k}')}{E_{\mathbf{k}' - \mathbf{k}} - E_{\mathbf{k}'}} \approx \left( \frac{dn}{dE} \right)_{\mathbf{k}'} \approx -\delta(E - E_F), \quad (3.4)$$

where  $E_F$  is the Fermi energy. Then in the effective mass approximation

$$\begin{aligned} \sum_{\mathbf{k}'} A(\mathbf{k}, \mathbf{k}') &= \frac{4\pi e^2}{k^2} \sum_{\mathbf{k}'} \left[ 2 - \frac{k^2}{|\mathbf{k} - \mathbf{k}'|^2 + k_s^2} \right] \\ &\quad \times \frac{m^*}{\hbar^2 k_F} \delta(\mathbf{k}' - k_F). \end{aligned} \quad (3.5)$$

The transition from sum to integral is made:  $\sum \rightarrow 1/(2\pi)^3 \int d^3\mathbf{k}'$ . The integration over  $\mathbf{k}'$  and  $\phi$  is trivial if we choose  $\mathbf{k}$  as the polar axis. In the limit  $k \rightarrow 0$   $|\mathbf{k}|$  as well as  $|\mathbf{k}'|$  is approximately equal to the Fermi wave vector,  $k_F$ . Making this substitution we find

$$v_k \approx \frac{v_k^i}{1 + (e^2 m^* / \pi \hbar^2 k_F) [4(k_F/k)^2 - \frac{1}{2} \ln |1 + 4(k_F/k_s)^2|]}, \quad (k \rightarrow 0). \quad (3.6)$$

As is obvious from the integral equation itself, the Coulomb term dominates the exchange term in this limit by a factor of the order of  $(k_F/k)^2$ . The effect of exchange is exhibited almost entirely in the effective mass parameter, and all previous results can be extended to include exchange in the long wavelength limit by just this modification in the energy spectrum. As  $k$  becomes an appreciable fraction of the Fermi wave vector, however, we would expect the higher order terms to become important. As the ratio of Coulomb to exchange terms in the denominator of (3.6) is of the order of  $10(k_F/k)^2$  we might expect that these terms would cease to be negligible in the range of  $k \approx \frac{1}{3}k_F$ . Of course, the derivation of Eq. (3.6) is not valid for  $k$  this large.

For more general  $k$ , it is convenient to eliminate one of the occupation number factors in (2.15) by a transformation of variables:  $\mathbf{k}' - \mathbf{k} \rightarrow -\mathbf{k}'$  in the terms involving the factor  $n(\mathbf{k}' - \mathbf{k})$ .

$$A(\mathbf{k}, \mathbf{k}') = (4\pi e^2) \left( \frac{4}{k^2} - \frac{1}{|\mathbf{k} - \mathbf{k}'|^2 + k_s^2} - \frac{1}{|\mathbf{k} + \mathbf{k}' - \mathbf{k}|^2 + k_s^2} \right) \frac{n(\mathbf{k}')}{E_{\mathbf{k}' - \mathbf{k}} - E_{\mathbf{k}'}}. \quad (3.7)$$

We will take the low-temperature limit for  $n(\kappa')$ :  $n(\kappa') = 1$  for  $\kappa' < k_F$  and  $n(\kappa') = 0$  for  $\kappa' > k_F$ . We note that it is permissible here to reverse the order of integration; that is, we may first average over  $\kappa$  on the Fermi surface. This average affects only the second and third terms in the numerator of (3.7). The former of these gives

$$\frac{1}{4\pi} \int d\Omega_{\kappa} \frac{1}{|\kappa - \kappa'|^2 + k_s^2} = \frac{1}{4k_F \kappa'} \ln \left| \frac{a+2x}{a-2x} \right|, \quad (3.8)$$

where

$$a = 1 + x_0^2 + x^2; \quad x = \kappa'/k_F; \quad x_0 = k_s/k_F. \quad (3.9)$$

The possible divergence of this integral is prevented by nonzero screening; i.e., by the existence of the correlation hole. The screening wave vector is of the order of magnitude of twice the Fermi wave vector, and it is easily seen that variation of its exact value from substance to substance will have little effect on the results. This is fortunate, as our method of introduction of  $k_s$  implies knowledge only of its order of magnitude. The other average over  $\kappa$  leads to a similar expression.

The first, or Coulomb term is the only one of the three which may be integrated without approximation (except, of course, for the expression of energy as a function of wave vector; we take the effective mass approximation to be sufficiently valid):

$$\frac{16\pi e^2}{k^2} \frac{1}{(2\pi)^3} \frac{2m^*}{\hbar^2} \int d^3\kappa' \frac{1}{|\kappa' - \mathbf{k}|^2 - \kappa'^2} = -\frac{m^* e^2}{\pi k \hbar^2} \left\{ \left[ 2(k_F/k)^2 - \frac{1}{2} \right] \ln \left| \frac{2k_F + k}{2k_F - k} \right| + \frac{2k_F}{k} \right\}, \quad (3.10)$$

which, as it must, reduces to the result of Bardeen and Pines<sup>3</sup> in the long wavelength limit.

The angular integration for the first exchange term involves only the energy denominator and is easily performed to obtain:

$$\frac{m^* e^2}{4\pi \hbar^2 k} \int dx \ln \left| \frac{2k_F x + k}{2k_F x - k} \right| \ln \left| \frac{a+2x}{a-2x} \right|. \quad (3.11)$$

The integral is clearly intractable as it stands. The last logarithmic term, involving quadratic functions of  $x$  in its argument, is the hardest to deal with exactly and fortunately is also the more convenient term to expand. A convenient expansion parameter is

$$2x/a = 2x/(1+x^2+x_0^2) \lesssim \frac{1}{2}.$$

This power series is then easily transformed into another in  $1/(1+x_0^2)$  whose coefficients are polynomials in  $x$ . This series converges rapidly, especially for small  $k$ , and it is easy to use in performing the integration. We are interested most in the region of small  $k$  for at least two reasons. First, we would expect the iteration procedure

for the solution of the integral Eq. (2.15) to converge most rapidly here, for the Coulomb contribution dominates here, and the matrix elements are independent of  $\kappa$  if only this term is kept. That is, if exchange and correlation are accounted for only in the energy denominator, the first approximation for  $v_k$  in the iteration process gives the complete solution. Secondly, the dielectric constant approximation used is most valid in the region of small  $k$ .

The integral (3.11) is conveniently expressed in terms of  $u = k/2k_F$ . The result is given to 1% accuracy for  $u$  less than 1 (a rather weak restriction) by:

$$\begin{aligned} & \frac{m^* e^2}{8\pi \hbar^2 k_F u} \int dx \ln \left| \frac{x+u}{x-u} \right| \ln \left| \frac{a+2x}{a-2x} \right| \\ &= \frac{m^* e^2}{2\pi \hbar^2 k_F u} \left\{ \frac{1}{1+x_0^2} \left[ \frac{x^2-u^2}{2} \ln \left| \frac{x+u}{x-u} \right| + xu \right] \right. \\ & \quad - \frac{1}{4} [(1+x_0^2)^{-2} - \frac{4}{3}(1+x_0^2)^{-3}] \\ & \quad \times \left[ (x^4-u^4) \ln \left| \frac{x+u}{x-u} \right| + u^4 \left( -\frac{x}{u} + \frac{1}{3} \frac{x^3}{u^3} \right) \right] \\ & \quad + (1+x_0^2)^{-3} \left[ \frac{x^6-u^6}{6} \ln \left| \frac{x+u}{x-u} \right| \right. \\ & \quad \left. \left. + \frac{u^6}{3} \left( -\frac{x}{u} + \frac{1}{3} \frac{x^3}{u^3} + \frac{1}{5} \frac{x^5}{u^5} \right) \right] \right\}. \quad (3.12) \end{aligned}$$

The evaluation of the second exchange term is somewhat more difficult. We make the change of variable  $\kappa' - \mathbf{k} = \kappa''$ . The region of integration in the  $\kappa''$ -space is over a Fermi sphere whose center is connected to the origin by the vector  $\mathbf{k}$ . We define  $\mu_c$  as the cosine of the angle between  $\mathbf{k}$  and a vector from the origin to the line of intersection of the two Fermi spheres, one of which is the region of integration and the other is centered at the origin.

$$2kk_F \mu_c = \kappa''^2 - k^2 - k_F^2. \quad (3.13)$$

If we are considering  $k < k_F$

$$\begin{aligned} \int d^3\kappa' \rightarrow 2\pi \left[ \int_0^{k_F-k} \kappa''^2 d\kappa'' \int_{-1}^1 d\mu \right. \\ \left. + \int_{k_F-k}^{k_F+k} \kappa''^2 d\kappa'' \int_{-1}^{-\mu_c} d\mu \right], \quad (3.14) \end{aligned}$$

where we have written  $\cos\theta'' = \mu$ . There is a corresponding expression for  $k > k_F$ . There reappears here the cancellation which was obscured by the transformation from the integral equation in the form (2.15); this form involved a factor of the difference of occupation numbers, restricting  $\kappa'$  to a region near the Fermi surface. The first integral in (3.14) is identical to that of the first

exchange term except for a minus sign and evaluation at  $k_F - k$  instead of  $k_F$ . The result (3.12) is then to be evaluated at limits  $x=1-2u$  and  $x=1$ . Thus, the total effective region of integration is that within a distance  $k$  of the Fermi surface; virtual processes occur only for electrons with wave vectors in this region. This is to be expected physically. The final integral is

$$\frac{m^*e^2}{4\pi\hbar^2k} \int_{1-2u}^{1+2u} dx \ln \left| \frac{a+2x}{a-2x} \right| \ln \left| \frac{u-x\mu_c}{u-x} \right|. \quad (3.15)$$

The argument of the second logarithm is complicated by the presence of  $\mu_c$ , a quadratic function of  $x$ . We found it necessary to approximate the cubic function of  $x$ ,  $u-x\mu_c$ , by the linear function which gave the best fit:  $u+1/2u-(1/2u)x$ . The first logarithm can be expanded as before, and the final result to the same accuracy as the term (3.12) is:

$$\begin{aligned} m^*e^2/\pi\hbar^2k & \left\{ (1+x_0^2)^{-1} \left[ \frac{1}{2}x^2 \ln |(x-u)z^{-1}| \right. \right. \\ & - \frac{1}{2}u^2 \ln |x-u| + \frac{1}{2} \ln |z| - \frac{1}{2}(u-1)x \\ & - \frac{1}{4}[(1+x_0^2)^{-2} - \frac{4}{3}(1+x_0^2)^{-3}] \\ & \times [x^4 \ln |(x-u)z^{-1}| - u^4 \ln |x-u| + \ln |z|] \\ & - (u^3-1)x - \frac{1}{2}(u^2-1)x^2 - \frac{1}{3}(u-1)x^3 \\ & + \frac{1}{6}(1+x_0^2)^{-3} [x^6 \ln |(x-u)z^{-1}| - u^6 \ln |x-u| \\ & + \ln |z| - (u^5-1)x - \frac{1}{2}(u^4-1)x^2 - \frac{1}{3}(u^3-1)x^3 \\ & \left. \left. - \frac{1}{4}(u^2-1)x^4 - \frac{1}{5}(u-1)x^5] \right\} \right\}_{x=1-2u}^{x=1+2u}, \quad (3.16) \end{aligned}$$

where

$$2uz = x - (2u^2 + 1). \quad (3.17)$$

To lowest order in  $u$ , (3.16) is

$$m^*e^2/2\pi\hbar^2k_F [4(1+x_0^2)^{-1} - 7(1+x_0^2)^{-2}/4 + 23(1+x_0^2)^{-3}/6], \quad (3.18)$$

which is independent of  $u$ . When the result (3.12) is evaluated between the limits  $x=1-2u$  and  $x=1$ , it is found that the lowest order terms are proportional to  $u$ . Collecting the results and keeping only constant and lower order terms, we have

$$v_k = v_k^i [1 + A(k_F/k)^2 - B]^{-1}, \quad (3.19)$$

where

$$A = 4m^*e^2/\pi\hbar^2k_F, \quad (3.20)$$

and

$$B = \frac{1}{3}A \{ [4(1+x_0^2)^{-1} - 7(1+x_0^2)^{-2}/4 + 23(1+x_0^2)^{-3}/6] + \frac{2}{3} \}. \quad (3.21)$$

This agrees, as it should, to order  $1/k^2$  with the previous result (3.6). As  $A/B \approx 5$ , the constant term gives about

a 1% correction to the  $1/k^2$  term for  $k=\frac{1}{2}k_F$ . The coefficient of the linear terms in  $k/k_F$  turns out to be somewhat less than  $B$ , so that (3.19) is quite accurate up to  $k$  of the order of  $\frac{1}{2}k_F$  or so.

As indicated in Sec. II, the effect of exchange was to introduce terms into the integral equation which depend on the initial electron wave vector, while the effect of correlation was to reduce these terms by the dielectric constant. However, one must not then attribute to exchange alone the expression for  $B$  above with  $x_0=0$ , for we have seen that the integrals involving exchange terms diverge when  $x_0^2 \rightarrow 0$  and several of the series expansions would suffer likewise. Exchange and correlation effects should be considered together; their combined effect is to increase the scattering—at least for  $k$  less than the Fermi wave vector.

Our results are simpler than Bailyn's due to the two improvements we have made and mentioned above. That is, we have performed averages consistently and we have introduced a dielectric constant which is a continuous function of wave vector. As Bailyn suggested, we could improve the approximate expressions for  $E$  by including a term proportional to  $\kappa^4$  as well as the quadratic effective mass term. This, however, complicates the integrals considerably, and as the resultant corrections to the energy curve are quite small (i.e., one can fit the actual curve quite well with a quadratic function of  $\kappa$  in the relatively small region of integration), we feel that use of the effective mass approximation is justified.

#### IV. PARAMETRIC FORMULATION

In the long wavelength limit we can employ a simpler method to determine the strength of the electron-phonon interaction. We will use the result of this method to verify the result obtained in previous sections in the same limit. The present approach also provides an expression for the effective mass parameter which appears in the expressions for the matrix elements obtained above.

We consider a crystal in which we treat the Fourier components of the lattice vibrations independently. In the adiabatic approximation, at least for long wavelength components, the electrons are able to redistribute themselves in such a way that their Fermi level remains constant throughout the crystal. Thus the Fermi level as defined here may be thought of as being composed of two contributions—the first of which,  $E(k_F)$ , depends only on the local electron density,  $\rho$ ; it includes the effects of exchange and correlation. The second contribution is of electrostatic origin—the total local charge density will not in general be zero—and may be described by a deformation potential,  $-V(\mathbf{x})$ , where the reference energy level is taken to be that at the surface of the  $s$  sphere appropriate to the density at  $\mathbf{x}$ . Then the distribution of electrons is determined by the condition  $E(k_F) - V(\mathbf{x}) = \text{constant}$ . The requirement

that Poisson's equation also be satisfied will yield the desired expression for the interaction matrix elements.

In the Fermi-Thomas approximation

$$3\pi^2\rho(\mathbf{x}) = \{2[E_F + V(\mathbf{x})]\}^{3/2}. \quad (4.1)$$

We would like a more general relationship between  $\rho$  and  $E_F$ —including exchange and correlation effects. We employ the jellium model of a metal in order to be able to make a comparison with the Bardeen-Pines results.  $E(k_F)$  is given<sup>5</sup> by:

$$E(k_F) = 3.68r_s^{-2} - 0.61r_s^{-1} - (0.44)(r_s + 7.8)^{-1} - \frac{1}{3}(0.44)r_s(r_s + 7.8)^{-2} \text{ ry}, \quad (4.2)$$

where Wigner's expression for the correlation energy has been employed, and  $r_s$ , the radius of the  $s$  sphere in units of the Bohr radius,  $a_0$ , can be expressed in terms of the ion density:

$$a_0r_s = (3/4\pi\rho)^{1/3} = (9\pi/4)^{1/3}1/k_F. \quad (4.3)$$

As we anticipate that the variation of the electron density from the ion density will be small, we treat  $\rho$  in the energy expression as the electron density. Taking the variation of the condition  $E(k_F) - V = \text{constant}$  we obtain an expression of the form:

$$\delta V = (me^4/2\hbar^2)f(\rho_0)\delta\rho, \quad (4.4)$$

where  $\rho_0$  is the density when no lattice vibrations are present.

We consider the Fourier components of this. We also have Poisson's equation to be satisfied:

$$v_k\rho q_k = M_k^2\delta\rho_k. \quad (4.5)$$

Since  $[\delta V(\mathbf{x})]_k = (v_k^i + v_k^p)q_k$ , the requirement of self-consistency yields the relation:

$$v_k = v_k^i[1 + 2\hbar^2 M_k^2 / me^4 f(\rho_0)]^{-1} \approx v_k^i me^4 f(\rho_0) / 2\hbar^2 M_k^2. \quad (4.7)$$

The term in  $f(\rho_0)$  proportional to  $\rho_0^{-1/3}$  when taken alone corresponds to the Bardeen-Pines result in the approximation in which exchange and correlation effects are neglected. If, in fact, we include it alone throughout the above treatment, we find exactly the Bardeen-Pines result [Eq. (3.9) in their paper].

We have used here a very accurate expression for the energy, and in the limit where this treatment is valid, we are justified in having great confidence in the results. We would like, therefore, to compare expression (4.7) with the corresponding equation in the treatment of Sec. III. In the long wavelength limit we may use the approximation (3.4). In this way we are at once led to the realization that whatever differences exist (to order  $k^2$ ) in the two expressions may be determined by a comparison of  $(\partial E/\partial k)_{k_F}$  and  $\partial E_F/\partial k_F$ . In the former

case we are concerned with the excitation spectrum with a fixed number of electrons—or quasi-particles; in the latter we must deal with the rate of change of the Fermi energy with number of electrons. That these may be different is a consequence of the existence of many-body effects; the energy of a quasi-particle depends not only on its momentum but also on the distribution of the remaining quasi-particles. For an investigation of the excitation spectrum we may use the values for specific heat given by Fletcher and Larson.<sup>6</sup> As assumptions have been made concerning isotropy, we investigate the ratio  $(\partial E/\partial k)_{k_F}/(\partial E_F/\partial k_F)$  for metals which very nearly satisfy this condition—Na and K. We find that the ratio is about 1.1 to 1.2; as Fletcher and Larson's calculations are estimated to have an accuracy of about 10% the results of the two calculations of this paper are seen to be in good agreement. Another estimate of the above ratio can be made employing the Landau<sup>7</sup> model of a Fermi liquid. That this model can be used directly for electrons in a metal in the approximation of a uniform background charge has been shown by Silin.<sup>8</sup> The difference of the ratio from one is found to be small to the order of the difference between the reciprocals of the "effective mass" and the mass as calculated without inclusion of electron correlation effects. Thus both masses include corrections due to the lattice. As calculations involving only lattice effects have produced effective masses which agree very well with empirical values, we again expect the deviation of the above ratio from one to be small. Indeed, we might want to use an expression for  $v_k$  such as we have derived in this section to "evaluate"  $m^*$  in the formulas of Sec. III, especially for small  $k$ . The alternative involves calculating exchange energies.

If we consider that the correction to the Bardeen-Pines result is small, we may rewrite expression (4.7) in a convenient form—in terms of  $k$ ,  $e^2$ ,  $v_0$ , the velocity of an electron at the Fermi surface, and  $\omega_p^2 = 4\pi Ne^2/m^*$  = the square of the plasma frequency for particles of mass  $m^*$ . We take

$$M_k^2 = 4\pi e^2/k^2, \quad (4.8)$$

and

$$\frac{1}{2}m^*v_0^2 = E_F \approx \frac{1}{2}e^2 a_0 \rho_0 (3\pi^2)^{1/3} \rho^{-1}. \quad (4.9)$$

Then

$$v_k \approx a_0^{-2} v_k^i \left[ \frac{1}{3} (v_0/a_0\omega_p)^2 - 0.011 (v_0/a_0\omega_p)^4 - 0.02 \left[ 1 + \frac{1}{3} (7.8 + r_s)^{-1} \right] (v_0/a_0\omega_p)^6 \right] k^2. \quad (4.10)$$

The correction terms are of the order of 5%, since  $v_0/(a_0\omega_p) \approx 1$ , at least if  $m^* \approx m$ . The terms in brackets correspond to  $1/\langle \sum_{\mathbf{k}'} A(\mathbf{k}, \mathbf{k}') \rangle$  in the other formulation. As expected, the previous treatment yields higher order

<sup>6</sup> J. F. Fletcher and D. C. Larson, Phys. Rev. **111**, 455 (1958).

<sup>7</sup> L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **30**, 1058 (1956) [translation: Soviet Phys.-JETP **3**, 920 (1957)].

<sup>8</sup> V. P. Silin, J. Exptl. Theoret. Phys. (U.S.S.R.) **33**, 495 (1957) [translation: Soviet Phys.-JETP **6**, 387 (1958)].

<sup>5</sup> F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

terms than this one; it is valid over a wider range of momentum transfers.

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## Electron Paramagnetic Resonance of Manganese in $\text{TiO}_2$

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The paramagnetic resonance spectrum of a manganese-doped single crystal of  $\text{TiO}_2$  in its rutile structure was investigated at a frequency of 9.505 kMc/sec at room temperature. The following results were obtained: The manganese atoms replace the  $\text{Ti}^{4+}$  ions in the rutile and exist as tetravalent ions having a spin value of  $S=3/2$  and strong admixtures of covalent bonds to their six oxygen neighbors. The parameters of the spin Hamiltonian were determined to be  $g=1.990$ ,  $|D|=12.1$  kMc/sec, and  $|E|=0.388$  kMc/sec. Within the accuracy of this experiment the magnetic hyperfine structure was isotropic and could be described by  $|A|=215$  Mc/sec.

#### INTRODUCTION

WITH only one exception, all previously investigated paramagnetic resonance data for manganese in various host crystals could be interpreted with the assumption that the manganese atoms exist in the crystals as  $\text{Mn}^{++}$  ions having a spin value of  $S=5/2$ . For all crystals the splitting of the  $^6\text{S}_{5/2}$  ground level of the  $\text{Mn}^{++}$  ions due to the influence of the crystalline field was so small that the paramagnetic spectra consisted either of a single hyperfine structure pattern or of several strongly overlapped hyperfine structure patterns, each showing the characteristic six-line splitting resulting from the spin  $I=5/2$  of the  $\text{Mn}^{55}$  nucleus.

Van Wieringen<sup>1</sup> and Matumura<sup>2</sup> systematically investigated the behavior of the  $g$  factors and the hyperfine structure parameters  $A$  for  $\text{Mn}^{++}$  in various host crystals. They showed that the parameter  $A$  decreases at a rate which is nearly proportional to the covalent character of the manganese bond to its crystal neighbors and that the  $g$  factor simultaneously increases slightly. Typical values for manganese atoms with strong ionic bonds (e.g.,  $\text{Mn-MgF}_2$ ) are  $g=2.001$  and  $|A|=271$  Mc/sec, whereas the resonances of manganese in  $\text{ZnSe}$ , which is an example of a  $\text{Mn}^{++}$  bond with strong covalent admixtures, can be described by  $g=2.01$  and  $|A|=180$  Mc/sec.

Mueller<sup>3</sup> observed the paramagnetic resonance spectrum of a manganese-doped single crystal of  $\text{SrTiO}_3$  and interpreted the spectrum using  $g=1.994$  and  $|A|=209$  Mc/sec. The combination of a relatively small

$A$  factor and a  $g$  factor that is less than two does not fit into the scheme of the  $\text{Mn}^{++}$  resonances. Therefore, Mueller explained the spectrum by assuming that in  $\text{SrTiO}_3$  the manganese atoms exist in a tetravalent state having a spin value of  $S=3/2$ .

The paramagnetic resonances of a manganese-doped  $\text{TiO}_2$  single crystal in its rutile structure are, to a certain extent, similar to the resonances of manganese in  $\text{SrTiO}_3$ , since, for both spectra, the  $g$  and  $A$  factors are nearly equal; thus Mueller's conclusions may also be extended to the resonances of manganese in rutile. In addition, however, manganese in rutile has a large fine-structure splitting, so that for most of the crystal orientations the hyperfine structure patterns are separated from each other. Therefore, the spin value, as well as the lattice position of the manganese impurity, can be determined in a more direct manner from the angular dependence of the resonances.

#### CRYSTAL STRUCTURE

The rutile form of  $\text{TiO}_2$  is a tetragonal crystal belonging to the class  $D_{4h}$ .<sup>4,5</sup> The unit cell (Fig. 1) consists of two nonequivalent  $\text{Ti}^{4+}$  ions. Each of these  $\text{Ti}^{4+}$  ions is surrounded by a slightly deformed oxygen octahedron, so that the local symmetry of a  $\text{Ti}^{4+}$  site is only orthorhombic. Nevertheless, there is overall tetragonal symmetry of the rutile crystal, because the surroundings of the two nonequivalent ions differ from one another only by a rotation of  $90^\circ$  around the  $c$  axis of the crystal. Thus the paramagnetic spectrum of an

<sup>1</sup> J. S. van Wieringen, Discussion Faraday Soc. **19**, 118 (1955).

<sup>2</sup> O. Matumura, J. Phys. Soc. Japan **14**, 108 (1959).

<sup>3</sup> K. A. Mueller, Phys. Rev. Letters **2**, 153 (1959).

<sup>4</sup> F. A. Grant, Revs. Modern Phys. **31**, 646 (1959).

<sup>5</sup> R. W. C. Wyckoff, *Crystal Structures Handbook* (Interscience Publishers, Inc., New York, 1958).