

Electron-Vibration Interactions and Superconductivity

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I. INTRODUCTION

THE isotope effect, discovered independently by E. Maxwell¹ of the National Bureau of Standards and by Reynolds, Serin, Wright, and Nesbitt² of Rutgers University, indicates that superconductivity arises from interactions between electrons and vibrations of the crystal lattice. Using separated isotopes, both groups found that the temperature, T_c , of the transition between the normal and superconducting phases of mercury depends markedly on the isotopic mass, M . The Rutgers group³ showed that T_c varies approximately as $M^{-\frac{1}{2}}$ and this result has since been confirmed from measurements on separated isotopes of tin⁴ and thallium⁵. These later measurements showed that the critical field, H_c , varies in the same way with M as T_c . Plots of H_c versus T for different isotopes can be superimposed if both field and temperatures are multiplied by a factor proportional to $M^{\frac{1}{2}}$.

The vibrational frequencies and, thus, the mean square amplitude of zero-point motion of the lattice also varies as $M^{\frac{1}{2}}$. Prior to his knowledge of the isotope effect, Fröhlich⁶ developed a theory of superconductivity based on the self-energy of the electrons arising from interactions with the phonon field. He found an effective interaction between electrons, called the S -interaction, which comes from application of the exclusion principle. This interaction is repulsive for small distances in \mathbf{k} -space and attractive for larger distances. If the interaction is sufficiently strong, there is a state of lower free energy at low temperatures which is formed by displacing a shell of electrons with energies near the Fermi surface outward a small distance in \mathbf{k} -space. This modified distribution is identified by Fröhlich with the superconducting phase. It is lower in energy than the normal phase at $T=0^\circ\text{K}$ by an amount which is inversely proportional to M . Since this energy difference is equal to $H_c^2/8\pi$, for unit volume it follows that H_c , and presumably also T_c , varies as $M^{-\frac{1}{2}}$, in agreement with the isotope effect.

Independently, the writer⁷ has also proposed a theory of superconductivity based on interactions between electrons and lattice vibrations. We have used a model based on energies of the individual electrons as affected by interactions with the vibrations. It was proposed that in the superconducting phase electrons with energies within $\sim \kappa T_c$ of the Fermi surface are lowered in energy by an amount also $\sim \kappa T_c$. This energy decrease, summed over all of the electrons, is of the order of

$$W_n - W_s \sim 2n(\kappa T_c)^2/E_F, \quad (1.1)$$

where $2n$ is the concentration of conduction electrons (n of each spin) and E_F is the Fermi energy. This expression gives values of the correct order of magnitude.

The calculations which we have made so far have been very crude and have served mainly to estimate orders of magnitude. The problem is complicated by the fact that most of the electron-vibration interaction energy occurs in the normal phase; only a small additional amount is involved in the transition to the superconducting phase. In the normal phase, there is a small decrease in energy of the electrons which does not depend strongly on the wave vector \mathbf{k} nor on the distribution of electrons in \mathbf{k} -space. The additional decrease in the transition to the superconducting phase presumably involves only those electrons with energies near the Fermi surface and depends markedly on the distribution of electrons in \mathbf{k} -space. This dependence on distribution is equivalent to an effective interaction between electrons in \mathbf{k} -space, as in Fröhlich's theory.

Both theories are subject to mathematical difficulties. Fröhlich uses an expression based on second-order perturbation theory in a range where its validity is uncertain. In our theory, we have not distinguished sufficiently well between interactions which occur in the normal state and those which are peculiar to superconductivity.

In view of these difficulties, a discussion of various approximate methods of calculation of the interaction energy appears to be warranted, even though none of them has as yet been carried out in a satisfactory way. The problem is introduced in Sec. II. The sections which follow are concerned with Fröhlich's method, with an extension of the adiabatic method used by the author, with an application of Tomonaga's one-dimensional theory of plasma oscillations, which has been discussed

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¹ E. Maxwell, Phys. Rev. **78**, 477 (1950); **79**, 173 (1950).

² Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. **78**, 487 (1950).

³ Serin, Reynolds, and Nesbitt, Phys. Rev. **78**, 813 (1950).

⁴ Reported by D. Sheenber, by K. Mendelssohn, by E. Maxwell and by Reynolds, Serin, and Nesbitt at the Low Temperature Symposium of the National Bureau of Standards, March 27-29 (1951).

⁵ Reported by E. Maxwell at the Low Temperature Symposium of the National Bureau of Standards, March 27-29 (1951).

⁶ H. Fröhlich, Phys. Rev. **79**, 845 (1950).

⁷ J. Bardeen, (a) Phys. Rev. **79**, 167 (1950); (b) **80**, 567 (1950); (c) **81**, 829 (1951); (d) **82**, 978 (1951).

by Wentzel⁸ and by Dresden,⁹ and finally with the use of a canonical transformation of the type used by Bloch and Nordsieck to eliminate the interaction terms in radiation theory.

We shall be concerned solely with the calculation of the interaction energy and shall not discuss how the typical superconducting properties—infinite conductivity and a perfect diamagnetism—follow from the model. It is believed that the explanation is to be found along the lines suggested by F. London:¹⁰ A magnetic field will not penetrate if the wave functions of the electrons are only slightly modified by the field. We have attempted to explain the superconducting properties in terms of a small effective mass for the superconducting electrons which have energies near the Fermi surface.⁷ When the effective mass is very small, the magnetic field is confined to a thin surface layer corresponding to the penetration depth of the London theory and this field is insufficient to provide bound quantum states corresponding to either the classical circular orbits of a free electron in the interior or to the boundary orbits. The conditions for the London theory are thus satisfied.

II. THE HAMILTONIAN AND METHODS OF SOLUTION

The complete hamiltonian¹¹ for the system of electrons plus lattice vibrations may be expressed in the form:

$$H = H_e + H_L + H_I, \quad (2.1)$$

where H_e is that for the electrons with the ions in their equilibrium positions, H_L is that for the lattice vibrations, and H_I represents the interaction between them. These terms are not completely independent. For example, the frequencies of the lattice vibrations are determined in part by energies which come from the interaction terms. Furthermore, to determine the interaction terms one must consider the coulomb energy between electrons which occurs in H_e .

The hamiltonian H_e includes the kinetic energy of the electrons, the coulomb interaction between electrons the interaction between electrons and ions, and the, interaction terms, including the long-range coulomb interactions, between the ions in their equilibrium positions. We need not give an explicit expression as we shall be concerned mainly with the Bloch approximation in which correlation effects are neglected and it is assumed that each electron moves in the periodic field of the ions and the average space charge of the valence electrons. Then we may take

$$H_e = \sum_i H_{ei} \quad i = 1, 2, \dots, 2n, \quad (2.2)$$

⁸ G. Wentzel, Phys. Rev. **83**, 168 (1951).

⁹ M. Dresden, report at the Low Temperature Conference of the National Bureau of Standards, March 27–29 (1951).

¹⁰ F. London, Proc. Roy. Soc. (London) **A152**, 24 (1935); Phys. Rev. **74**, 562 (1948). See also, J. Bardeen, Phys. Rev. **81**, 469 (1951).

¹¹ The formulation and notation are similar to those of the author in reference 7a.

where

$$H_{ei} = (\hbar^2/2m)\Delta_i + U(x_i). \quad (2.3)$$

The wave functions of the individual electrons are the Bloch functions, $\psi_k(x_i)$, with energy E_k , specified by the wave vector k .

The hamiltonian for the lattice, H_L , can be expressed in the form,

$$H_L = \sum_s [-(\hbar^2/2\mu)(\partial^2/\partial q_s^2) + \frac{1}{2}K_s q_s^2], \quad (2.4)$$

where μ is proportional to the mass of the atoms. The exact value of μ depends on how the displacement coordinate, q_s , is defined. The sum is over the various normal modes which may be specified by the wave vector \mathbf{s} and a polarization. The allowed values of \mathbf{s} lie on one side of a plane through the origin so that if \mathbf{s} is included $-\mathbf{s}$ is not. It is the longitudinal modes which interact most strongly with the electrons.

The interaction terms are linear in the displacements and may be taken to be of the form,

$$H_I = \sum_{i,s} V_s(x_i)q_s, \quad (2.5)$$

the interaction potential $V_s q_s$ has matrix elements connecting two states \mathbf{k} and \mathbf{k}' only if

$$\pm \mathbf{s} = \mathbf{k} - \mathbf{k}' + \mathbf{K}, \quad (2.6)$$

where \mathbf{K} is a lattice vector of the reciprocal lattice space. As in reference 3, we shall denote the matrix element which connects the states \mathbf{k} and \mathbf{k}' by

$$M_{kk'} = \mathfrak{M}_{kk'} q_{kk'}, \quad (2.7)$$

where $q_{kk'}$ is the amplitude of the vibration which connects the states \mathbf{k} and \mathbf{k}' and

$$\mathfrak{M}_{kk'} = \int \psi_{k'}^* V_{kk'} \psi_k d\tau. \quad (2.8)$$

It is the interaction terms which determine the effect of the conduction electrons on the motion of the ions and vice versa. A longitudinal wave, for example, gives a varying electrostatic potential. In a region of compression, where the ions are closer together than normal, the potential is more positive, giving a lower than normal energy for the electrons. Where they are farther apart, the potential is higher. There is a compensating shift in the density of conduction electrons. The interaction potential acting on an electron is the sum of the changes in the potential of the ions and the self-consistent field of the electrons resulting from the lattice vibrations. The second part tends to cancel the first, particularly for waves of long wavelength, and must be taken into consideration. In a discussion of the theory of conductivity of monovalent metals,¹² we have determined the matrix elements of the interaction potential by such a self-consistent field method.

¹² J. Bardeen, Phys. Rev. **52**, 688 (1937).

The shift in density of the electrons must also be taken into account in calculating the frequencies of the normal modes. Such frequencies are usually determined in the adiabatic approximation in which it is assumed that the motion of the electrons is sufficiently rapid to follow the motion of the ions. One first supposes that the ions are in fixed positions and calculates the wave function and energy of the electrons. The coordinates of the ions, which we shall take to be those of the normal modes, are treated as parameters.

$$(H_e + H_I)\varphi(x, q) = E(q)\varphi(x, q). \quad (2.9)$$

Here x stands for the coordinates of all of the electrons and q for the coordinates of all of the normal modes. The frequencies of the normal modes are then obtained by solving

$$(H_L + E(q))Q(q) = WQ(q). \quad (2.10)$$

The wave function for the complete system is of the form:

$$\Phi(x, q) = \varphi(x, q)Q(q). \quad (2.11)$$

In general, the energy $E(q)$ depends so strongly on q that it is not sufficiently accurate to determine the normal modes from H_L alone and then average over $E(q)$ by use of first-order perturbation theory.¹³

By far the largest part of the interaction energy occurs in the normal phase, only a small additional amount occurs in the transition to the superconducting phase. To determine the latter, it should usually be sufficiently accurate to determine the normal modes for the normal state as above and then average the superconducting energy over these. Similar considerations apply to the calculation of the matrix elements of the interaction potential. The shift in charge density associated with the superconducting transition should generally have a negligible effect on the self-consistent field. This point is discussed at greater length in Sec. IV.

While the adiabatic procedure previously outlined should be satisfactory for most of the interaction energy occurring in the normal phase, one must go beyond it in the discussion of superconductivity. There are several approximate methods that can be used:

(a) Fröhlich uses an expression for the interaction energy, W_I , based on second-order perturbation theory:⁶

$$\Delta W = 2 \sum_{k, k'} \frac{|M_{kk'}|^2 f_k (1 - f_{k'})}{E_k - E_{k'} - \hbar\omega_{kk'}}. \quad (2.12)$$

The factor of two accounts for the two possible values of electron spin. Here f_k represents the probability that the state \mathbf{k} is occupied. The normal state at $T=0^\circ\text{K}$ is that for which $f_k = 1$ for $E_k < E_F$ and $f_k = 0$ for $E_k > E_F$. He finds that if the interaction is sufficiently strong (and this is the criterion for superconductivity) there is a state of lower energy for which $f_k = 1$ for $E_k < E_F - \epsilon_1$ and for $E_F < E_k < E_F + \epsilon_1$ and $f_k = 0$ for $E_F - \epsilon_1 < E_k < E_F$

¹³ In molecular theory, H_L includes the terms from $E(q)$ and so takes into account the displacement of the electrons with the motion of the ions.

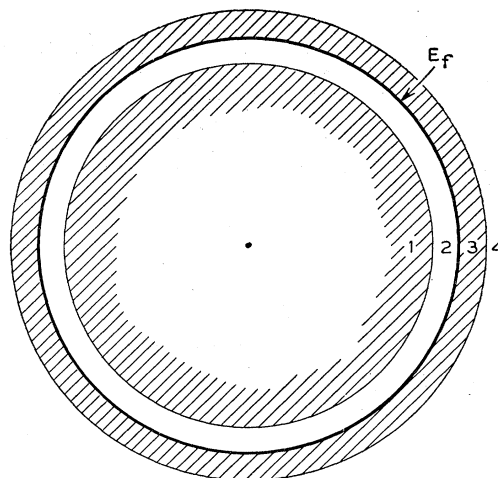


FIG. 1. Schematic diagram showing the occupied states in k -space according to Fröhlich's theory. In the normal phase, electrons occupy regions 1 and 2 within the Fermi sphere of energy E_F . In the superconducting phase, as a result of electron vibration interactions, a lower energy at $T=0^\circ\text{K}$ is obtained by filling regions 1 and 3, leaving 2 and 4 vacant. The thickness of the "shell," region 3, is greatly exaggerated.

and $E_k > E_F + \epsilon_1$, where $\epsilon_1 \sim (\hbar\omega_{kk'})_{av}$. This "shell" distribution (see Fig. 1) is identified with the superconducting phase.

(b) We have used a wave function of the form (2.11) in which $\varphi(x, q)$ is approximated by determinantal wave functions of the Slater-Fock type. In the calculation of the kinetic energy corresponding to the normal modes, it is necessary to take into account derivatives of $\varphi(x, q)$ with respect to the q which do not appear in the strict adiabatic approximation already given. The application of this method to the calculation of the interaction energy in an approximation corresponding to second-order perturbation theory will be discussed in Sec. III.

(c) Wentzel⁸ and Dresden⁹ have suggested using an approach based on use of collective coordinates for the electrons corresponding to "plasma oscillations." Both have used the method of Tomonaga which is restricted to the one-dimensional case. If an approximate expression can be used for the kinetic energy operator, an exact solution can be obtained and it is even possible to take into account the coulomb interactions between electrons if so desired. Bohm and Pines have developed a theory of plasma oscillations for conduction electrons in metals which can be used for the three-dimensional case, at least for oscillations of sufficiently long wavelengths, and have suggested that the theory could be applied to superconductivity. We shall discuss the Tomonaga theory in Sec. V.

(d) It has been suggested to the author in private communications by Fierz and by Drell¹⁴ that a trans-

¹⁴ S. D. Drell, Phys. Rev. **83**, 838 (1951). The author does not agree with Drell's conclusions in regard to a lack of a critical dependence of interaction energy on the distribution of electrons in k -space.

formation such as that used by Bloch and Nordsieck¹⁵ in radiation theory might be useful. In this method one attempts to find a canonical transformation involving coordinates of both the electrons and normal modes in such a way as to eliminate the interaction terms. In effect, one uses in place of (2.11) a wave function of the form:

$$\Phi(x, q) = \psi(x)Q(q, x), \quad (2.13)$$

in which the coordinates of the electrons appear in the wave function for the normal modes. We have been successful in applying this method in the limiting case in which the wavelengths of the lattice vibrations are long compared with the electron waves, but the general case appears to be difficult. We shall discuss this method in Sec. VI and show how it is related to the other methods.

III. FRÖHLICH'S THEORY

We shall give here a simplified account of Fröhlich's theory in order to show the conditions under which one may expect the shell distribution (identified with the superconducting state) to have lower energy than the normal distribution. The shell distribution is shown schematically in Fig. 1. Regions 1 and 3 are occupied; 2 and 4 are unoccupied. In the normal distribution, 1 and 2 are occupied, 3 and 4 are unoccupied. The difference in interaction energy for the two distributions is

$$(W_s - W_n)_I = 2 \sum_{1+3} \sum'_{2+4} - 2 \sum_{1+2} \sum'_{3+4}. \quad (3.1)$$

The sums are overexpressions of the form (2.12); the prime indicates the sum over the unoccupied states. We shall assume that the interaction energy for the configurations in which the inner regions are occupied, the rest unoccupied, is approximately the same as that for the normal distribution:

$$2 \sum_{1,2,3} \sum'_{4} \simeq 2 \sum_{1+2} \sum'_{3+4} \simeq 2 \sum_{1} \sum'_{2+3+4}. \quad (3.2)$$

If (3.2) is used to simplify the summation in (3.1), we find after expanding out the sums and canceling the common terms that

$$(W_s - W_n)_I = 2 \sum_{2} \sum'_{3} + 2 \sum_{3} \sum'_{2}. \quad (3.3)$$

This is very nearly the same as Fröhlich's expression for the energy difference. It should be noted that the only interactions which occur are those between the inner and outer shells.

If we now introduce the summand (2.12) into (3.3), we find

$$(W_s - W_n)_I = 4 \sum_{k \text{ in } 2} \sum_{k' \text{ in } 3} \frac{\hbar\omega_{kk'} |M_{kk'}|^2}{(\epsilon_k - \epsilon_{k'}) - (\hbar\omega_{kk'})^2}. \quad (3.4)$$

¹⁵ F. Bloch and A. Nordsieck, Phys. Rev. **52**, 54 (1937).

The contribution to the interaction energy is negative if

$$(\epsilon_k - \epsilon_{k'}) < \hbar\omega_{kk'}. \quad (3.5)$$

Accordingly, we shall assume that energy difference, ϵ_1 , between the inner sphere and the shell is of the order of

$$\epsilon_1 = (\epsilon_k - \epsilon_{k'})_{Av} \sim (\hbar\omega_{kk'})_{Av}. \quad (3.6)$$

The number of states in the shell is $\epsilon_1 N(\epsilon)$, where $N(\epsilon)$ is the density of states in energy at the Fermi surface. The number of possible interactions is the square of this, so that the net difference in interaction energies is of the order of

$$(W_s - W_n)_I \simeq -4(N(\epsilon))^2 (\hbar\omega_{kk'})_{Av} |M_{kk'}|^2_{Av}. \quad (3.7)$$

The difference in energies of the initial Bloch states for the two distributions is of the order of

$$(W_s - W_n)_e = 2N(\epsilon)\epsilon_1(\epsilon_k - \epsilon_{k'})_{Av} \sim 2N(\epsilon)(\hbar\omega_{kk'})_{Av}^2. \quad (3.8)$$

The shell distribution will have a net lower energy if

$$4(N(\epsilon))^2 (\hbar\omega_{kk'})_{Av} |M_{kk'}|^2_{Av} > 2N(\epsilon)(\hbar\omega_{kk'})_{Av}^2, \quad (3.9)$$

or if

$$N(\epsilon) |M_{kk'}|^2_{Av} > \frac{1}{2} (\hbar\omega_{kk'})_{Av}. \quad (3.10)$$

Except for a numerical factor which depends in part on the particular assumptions made regarding the model, this condition is the same as Fröhlich's criterion for superconductivity. The criterion is identical with the one given in reference 7a.

The energy difference calculated in this way, of the order of

$$W_s - W_n \sim n(\hbar\omega_{kk'})_{Av}^2 / E_F, \quad (3.11)$$

is too large. Equation (3.11) is similar to Eq. (1.1) except that $(\hbar\omega_{kk'})_{Av}$ replaces κT_e and the former is generally considerably larger than the latter.

There is considerable doubt as to the validity of these calculations because the criterion (3.10) for superconductivity is essentially the same as the condition that the second-order perturbation theory break down. Thus (2.12) is used in a region where it is not expected to be valid.

It is not believed, however, that the specific objections of Wentzel⁸ and of Kohn and Vachaspati¹⁶ to Fröhlich's theory are valid. Wentzel calculates the self-energy of a phonon from interaction with the electrons, with use of second-order perturbation theory, and finds a value which may be written

$$-\frac{1}{2} K_s^{(2)} q^2. \quad (3.12)$$

The total potential energy of the lattice vibration is then

$$\frac{1}{2} (K_s - K_s^{(2)}) q^2, \quad (3.13)$$

where K_s comes from other terms. As Wentzel points out, the criterion (3.10) is essentially equivalent to

$$K_s^{(2)} > \mu_s^2 \omega_s^2. \quad (3.14)$$

¹⁶ W. Kohn and Vachaspati, Phys. Rev. **83**, 462 (1951).

Thus if K_s is calculated from the *observed* frequency, and is set equal to $\mu_s^2\omega_s^2$, Eq. (3.13) indicates that the lattice becomes unstable when the interaction is so large as to satisfy the criterion for superconductivity. The objection of Kohn and Vachaspati is similar, although reached from a somewhat different point of view.

According to the argument given in Sec. II it is $K_s - K_s^{(2)}$ rather than K_s , which is related to the observed frequency:

$$\mu_s^2\omega_s^2 = K_s - K_s^{(2)}. \quad (3.15)$$

Since $K_s^{(2)}$ involves ω_s , Eq. (3.15) is to be regarded as an implicit equation for ω_s . Actually, $K_s^{(2)}$ does not depend strongly on ω_s . Rather than (3.14), the condition that the lattice be unstable is

$$K_s^{(2)} > K_s. \quad (3.16)$$

If K_s is sufficiently large, the lattice is stable regardless of the strength of the interaction. Second-order perturbation theory might be satisfactory for the calculation of $E(q)$ in Eq. (2.0) and thus of $K_s^{(2)}$ even when the term has a large effect on the vibrational frequency. It is not surprising that it may be necessary to take the displacement of the electrons into account in a calculation of the frequencies of the vibrational modes.

It is correct to take the interaction energy as

$$-\frac{1}{2}K_s^{(2)}(q^2)_{\text{av}},$$

where the average is calculated for the *observed* frequency, and one should not worry if this energy correction is comparable to $\hbar\omega_s$. The energy involved in the transition from the normal to the superconducting phase is only a small part of the total interaction energy and should generally have only a small effect on the vibrational frequencies.

From a discussion of an application of a method due to Tomonaga to the corresponding one-dimensional problem, Wentzel concludes that the hamiltonian (2.1) requires modification when there is strong coupling between electrons and lattice vibrations. For reasons given in Sec. V, where Tomonaga's method is treated in detail, we do not agree with this conclusion.

IV. DETERMINENTAL WAVE FUNCTIONS

We shall discuss here wave functions of the form (2.11) in which the wave function for the electrons $\varphi(x, q)$ is approximated by Slater-Fock determinants of one-electron functions. Since interaction with the lattice does not change the spin, we may consider each spin system separately. Let $x_1 \cdots x_n$ represent the coordinates of the half of the $2n$ electrons which have parallel spins. We want to find the best determinental wave function of the form,

$$\varphi(x, q) = \frac{1}{(n!)^{\frac{1}{2}}} \begin{vmatrix} \Psi_1(x_1, q) & \cdots & \Psi_1(x_n, q) \\ \vdots & & \vdots \\ \Psi_n(x_1, q) & \cdots & \Psi_n(x_n, q) \end{vmatrix} Q(q). \quad (4.1)$$

Here q represents the coordinates of all the normal modes with wave function $Q(q)$. It is supposed that the electronic wave functions are normal and orthogonal for all values of the q 's:

$$\int \Psi_i^*(x, q) \Psi_j(x, q) dx = \delta_{ij}. \quad (4.2)$$

We shall omit correlation effects which arise from the coulomb terms and take H_s to be of the form (2.2). The total energy corresponding to the wave function (4.1)

is then

$$\begin{aligned} W = & \sum_i \int \int |Q|^2 \Psi_i^* H_i \Psi_i dx dq \\ & + \sum_s \int \int |Q|^2 \Psi_i^*(x) V_s(x) q_s \Psi_i(x) dx dq \\ & + \sum_s \int Q^* \sum_s \left(-\frac{\hbar^2}{2\mu_s} \frac{\partial^2}{\partial q_s^2} + \frac{1}{2} K_s q_s^2 \right) Q dq \\ & + \sum_{i,s} \int \int |Q|^2 \Psi_i^* \left(-\frac{\hbar^2}{2\mu_s} \frac{\partial^2}{\partial q_s^2} \right) \Psi_i dx dq \\ & - \sum_{i,j,s} \frac{\hbar^2}{2\mu_s} \int \int \int |Q|^2 [\Psi_i^*(x_i) \Psi_j^*(x_j) \\ & - \Psi_i^*(x_j) \Psi_j^*(x_i)] \frac{\partial \Psi_i(x_i)}{\partial q_s} \frac{\partial \Psi_j(x_j)}{\partial q_s} dq dx_i dx_j. \quad (4.3) \end{aligned}$$

The sums over i and j are over all occupied states.

The last two terms come from the derivatives of the determinant with respect to the q 's; the last is the exchange term. These terms can be simplified by using the orthogonality relations if it is assumed that if Ψ_i is in the determinant so is Ψ_i^* . This will certainly be true for the lowest state. The terms which come from the derivatives of $\varphi(x, q)$ with respect to the q 's, then become

$$\begin{aligned} \sum_{i,s} \int \int |Q|^2 \frac{\hbar^2}{2\mu_s} \left| \frac{\partial \Psi_i}{\partial q_s} \right|^2 dx_i dq \\ - \sum_{i,j,s} \int |Q|^2 \frac{\hbar^2}{2\mu_s} \left| \int \Psi_i^* \frac{\partial \Psi_j}{\partial q_s} dx \right| dq. \quad (4.4) \end{aligned}$$

The expression for the energy is similar to that used by Wigner and Seitz and by Wigner¹⁷ in a calculation of the correlation energy of an electron gas.

The two terms in (4.4) tend to cancel for the normally occupied states. Let us consider a complete orthonormal set of $\Psi_i (i=1, 2, \dots, \infty)$ of which n occur in the determinant. One may expand $\partial \Psi_i / \partial q_s$ in terms of the Ψ_i :

$$\partial \Psi_i / \partial q_s = \sum_{j=1}^{\infty} a_{ijs} \Psi_j, \quad (4.5)$$

in which the a_{ijs} are functions of the q 's. On introducing (4.5) into (4.4), we get

$$\begin{aligned} \sum_{i=1}^n \left[\sum_{j=1}^{\infty} \sum_s \frac{\hbar^2}{2\mu_s} \int |Q|^2 |a_{ijs}|^2 dq \right. \\ \left. - \sum_{j=1}^n \sum_s \frac{\hbar^2}{2\mu_s} \int |Q|^2 |a_{ijs}|^2 dq \right] \\ = \sum_{i=1}^n \sum_{j=n+1}^{\infty} \sum_s \frac{\hbar^2}{2\mu_s} \int |Q|^2 |a_{ijs}|^2 dq. \quad (4.6) \end{aligned}$$

¹⁷ E. Wigner and F. Seitz, Phys. Rev. 46, 509 (1933), E. Wigner, Phys. Rev. 46, 1002 (1934).

The sum is over the a_{ijs} which connect occupied with unoccupied states.

Although it is not difficult to write out the equations for the Ψ_i , the solution for the general case appears to be difficult and has not been obtained. A solution can be found for the limiting case for which the interaction is small. The various states can be specified by the wave vector \mathbf{k} , and one need consider only the terms linear in the q 's:

$$\Psi_k = \psi_k + \sum_{k'} b_{kk'} q_{kk'} \psi_{k'} + \dots \quad (4.7)$$

Orthogonality requires that

$$b_{kk'}^* = -b_{k'k}. \quad (4.8)$$

Inserting (4.7) into (4.5), we find

$$\begin{aligned} a_{kk's} &= b_{kk'} \quad \text{for } q_s = q_{kk'} \\ &= 0 \quad \text{otherwise.} \end{aligned} \quad (4.9)$$

This gives for (4.6) the energy

$$\sum_{k \text{ occ.}} \sum_{k' \text{ unocc.}} \sum_{2\mu_s} \frac{\hbar^2}{2\mu_s} |b_{kk'}|^2. \quad (4.10)$$

This expression may be interpreted as follows. If $(q_{kk'}^2)_{Av}$ represents an average over zero-point vibrations, we have

$$(\hbar^2/2\mu)(q_{kk'}^2)_{Av} = \hbar\omega_{kk'}(q_{kk'}^2)_{Av}, \quad (4.11)$$

so that (4.10) may be written

$$\sum_{k \text{ occ.}} \sum_{k' \text{ unocc.}} \hbar\omega_{kk'} |b_{kk'}|^2 (q_{kk'}^2)_{Av}. \quad (4.12)$$

This means that an energy $\hbar\omega_{kk'}$ (representing an excited phonon) is to be added to the energy associated with the wave function $q_{kk'}\psi_{k'}$ only if the state \mathbf{k}' is normally unoccupied. If both \mathbf{k} and \mathbf{k}' are occupied there is no energy associated with the virtual phonon. The reason for this is as follows. One may take linear combinations of any of the functions included in the determinant without changing its value, and this is true even if the coefficients depend on the $q_{kk'}$. The determinant itself is independent of the coefficients, and thus of the $q_{kk'}$ which connect occupied states. There can thus be no additional energy from derivatives with respect to the $q_{kk'}$.

Let us now determine the value of the $b_{kk'}$ which give a minimum free energy for a Fermi distribution for which the probability that a state \mathbf{k} is occupied is the Fermi function:

$$f_k = 1/(1 + \exp((\epsilon_k - E_F)/\kappa T)). \quad (4.13)$$

We shall impose the condition (4.8) and write out the total energy associated with $b_{kk'}$ and $b_{k'k}$. From H_e and the energy (4.12) we have

$$\begin{aligned} |b_{kk'}|^2 q_{kk'}^2 (f_k(\epsilon_k - \epsilon_{k'}) + f_{k'}(1 - f_{k'})\hbar\omega_{kk'}) \\ + f_{k'}(\epsilon_k - \epsilon_{k'}) + f_{k'}(1 - f_k)\hbar\omega_{kk'}. \end{aligned} \quad (4.14)$$

The interaction terms which come from the states Ψ_k and $\Psi_{k'}$ are

$$\begin{aligned} f_k(b_{kk'}\mathfrak{M}_{k'k} + b_{kk'}^*\mathfrak{M}_{kk'})q_{kk'}^2 \\ + f_{k'}(b_{k'k}\mathfrak{M}_{kk'} + b_{k'k}^*\mathfrak{M}_{k'k})q_{kk'}^2 \\ = (f_k - f_{k'})(b_{kk'}\mathfrak{M}_{k'k} + b_{kk'}^*\mathfrak{M}_{kk'})q_{kk'}^2. \end{aligned} \quad (4.15)$$

We want to choose $b_{kk'}$ in such a way as to make the total energy, the sum of (4.14) and (4.15), a minimum. This gives

$$b_{kk'} = \frac{(f_k - f_{k'})\mathfrak{M}_{k'k}}{(f_k - f_{k'})(\epsilon_k - \epsilon_{k'}) - \hbar\omega_{kk'}(f_k + f_{k'} - 2f_k f_{k'})}. \quad (4.16)$$

If now we use (4.13) for f_k , which is legitimate as long as the interactions are not so large as to affect the energies very much, we find after some reduction that

$$b_{kk'} = \frac{\mathfrak{M}_{k'k}}{\epsilon_k - \epsilon_{k'} + \hbar\omega_{kk'} \coth((\epsilon_k - \epsilon_{k'})/2\kappa T)}. \quad (4.17)$$

The change in energy of an electron in the state \mathbf{k} resulting from the interaction is¹⁸

$$\Delta W_k = \sum_{k'} \frac{|\mathfrak{M}_{kk'}|^2 q_{kk'}^2}{\epsilon_k - \epsilon_{k'} + \hbar\omega_{kk'} \coth((\epsilon_k - \epsilon_{k'})/2\kappa T)}. \quad (4.18)$$

and the total energy change, including electrons of both spins, is

$$\Delta W = 2 \sum_k f_k \Delta W_k. \quad (4.19)$$

The sum (4.18) is over-all \mathbf{k}' , including occupied as well as unoccupied states. The denominator is odd for interchange of \mathbf{k} and \mathbf{k}' and has a minimum value of $\hbar\omega_{kk'}$ when $\epsilon_k \simeq \epsilon_{k'}$ and $T \rightarrow 0$. The energy change does not depend markedly on the state \mathbf{k} , and does not change rapidly as one approaches the Fermi surface. In fact, the Fermi level E_F does not appear in (4.18). This means that the density of states in energy, and thus the entropy terms are not affected very much by the interaction. Thus the change in free energy is very nearly equal to the energy change (4.19).

The expressions (4.18) and (4.19) reduce to Fröhlich's in the limit $T=0$ but give a lower free energy at higher temperatures. Not only is ΔW lower, but the entropy is higher since our expression gives a smaller spread in energy for states near the Fermi level.

The aforementioned approximations break down when the matrix elements of the interaction are so large that

$$\sum |b_{kk'}|^2 > \sim 1. \quad (4.20)$$

The large terms come for $\epsilon_k \simeq \epsilon_{k'}$. The denominator is small only if the temperature is low; otherwise the hyperbolic cotangent term is large. At $T=0^\circ\text{K}$, condition (4.20) is equivalent to the criterion (3.10) of Fröhlich's theory.

We have attempted⁷ to extend the theory to cover

¹⁸ This result was given without proof in reference 7(d).

large interactions by introducing a normalization factor in (4.7):

$$\Psi_k = N_k(q)(\psi_k + \sum b_{kk'} q_{kk'} \psi_{k'}). \quad (4.21)$$

The energy (4.18) is reduced by a factor $(N_k^2)_{Av}$. The normalization factor is larger and the energy lower if the sum over k' runs only over the *unoccupied* states rather than over all states as in (4.18). This makes the energy reduction depend markedly on \mathbf{k} and gives a small effective mass for electrons near the Fermi surface. However, the normalization factor includes only a part of the higher order terms, and it is not clear under what conditions a small effective mass will be obtained if all higher order terms are included.

Presumably most of the interaction energy is of the sort given by (4.18) which is characteristic of the normal phase. The terms responsible for superconductivity are those for which $\epsilon_k \cong \epsilon_{k'}$ and for which the matrix elements are large. We have previously assumed that interactions for which $|\epsilon_k - \epsilon_{k'}| < \Delta E$, where ΔE is the energy reduction per electron at the Fermi surface, occur only in the superconducting phase, not in the normal phase. This assumption is too drastic. The calculated energy difference is too large, and furthermore, the dynamic nature of the interaction, which is undoubtedly important, does not play a role. Thus the theory in this form is not satisfactory.

V. APPLICATION OF TOMONAGA'S THEORY

Tomonaga¹⁹ has recently given a theory of a one-dimensional Fermi-Dirac gas which takes into account interactions between the particles provided they are of sufficiently long range and provided that the excitations are not too large. The coordinates used are those of plasma oscillations of the gas rather than those of the individual particles. A less rigorous theory which can be applied to an actual three-dimensional gas has been developed by Bohm and Pines.²⁰

Wentzel⁸ and Dresden⁹ have independently applied the Tomonaga theory to the problem of superconductivity. The hamiltonian reduces to that of a system of coupled oscillators so that the problem can be solved exactly. Let dE/dn represent the spacing of the levels of the individual electrons in the vicinity of the Fermi level. Let a_n^* and a_n represent creation and destruction operators for electron-hole pairs which are separated by an n levels corresponding to an energy $n(dE/dn)$.¹⁹ The hamiltonian for the electrons alone is then

$$H_e = (dE/dn) \sum_n n a_n^* a_n. \quad (5.1)$$

Let ω_n be the vibrational frequency for the lattice vibration which connects levels separated by n . We may take

$$H_L = \sum \frac{1}{2} (p_n^2 + \omega_n^2 q_n^2) \quad (5.2)$$

$$H_I = \sum n^{\frac{1}{2}} q_n (\mathfrak{M}_n a_n + \mathfrak{M}_n^* a_n^*), \quad (5.3)$$

where \mathfrak{M}_n is the matrix element for an individual interaction as defined by (2.8).

For simplicity and without loss of any generality, we shall suppose that \mathfrak{M}_n is real. Let

$$\hbar\Omega_n = n(dE/dn) \quad (5.4)$$

and let

$$a_n^* = (2\hbar)^{-\frac{1}{2}} (\Omega_n^{\frac{1}{2}} Q_n + i\Omega_n^{-\frac{1}{2}} P_n), \quad (5.5a)$$

$$a_n = (2\hbar)^{-\frac{1}{2}} (\Omega_n^{\frac{1}{2}} Q_n - i\Omega_n^{-\frac{1}{2}} P_n). \quad (5.5b)$$

Then,

$$H = \sum_n \left[\frac{1}{2} (P_n^2 + \Omega_n^2 Q_n^2) - \frac{1}{2} \hbar\Omega_n + \frac{1}{2} (p_n^2 + \omega_n^2 q_n^2) + C_n q_n Q_n \right], \quad (5.6)$$

where

$$C_n^2 = (2n\Omega_n/\hbar) \mathfrak{M}_n^2 = (4n/\hbar^2) M_n^2 \Omega_n \omega_n. \quad (5.7)$$

The latter follows from

$$M_n^2 = \mathfrak{M}_n^2 (q_n^2)_{Av} = (\hbar/2\omega_n) \mathfrak{M}_n^2. \quad (5.8)$$

To transform to principal form, we need the roots of

$$(\lambda^2 - \Omega_n^2)(\lambda^2 - \omega_n^2) = C_n^2. \quad (5.9)$$

The solution is

$$\lambda_n = 2^{-\frac{1}{2}} (\Omega_n^2 + \omega_n^2 \pm [(\Omega_n^2 - \omega_n^2)^2 + 4C_n^2]^{\frac{1}{2}})^{\frac{1}{2}}, \quad (5.10)$$

as first obtained by Wentzel. One root becomes imaginary when the interaction is sufficiently large. The condition for this is

$$C_n^2 > \Omega_n^2 \omega_n^2,$$

or

$$(nM_n^2/\hbar\Omega_n) > \hbar\omega_n/4. \quad (5.11)$$

This equation may be written

$$N(E)M_n^2 > \hbar\omega_n/4. \quad (5.12)$$

Except for a factor of two, this condition is the same as the criterion for superconductivity given previously (see Eq. (3.10)).

The lattice becomes unstable in this approximation if $\omega_n < \Omega_n$, as it is the root which is lowest to start with which is pushed down by the interaction. On the other hand, the electrons become unstable²¹ if $\Omega_n < \omega_n$. This latter corresponds to the condition (3.5) of Fröhlich's theory. The interactions important for superconductivity are those for which the differences in energies of the electron states are less than the phonon energy. Presumably, this instability of the electrons is associated with the onset of superconductivity, but without going beyond the description in terms of plasma oscillations one cannot tell what will actually occur.

The Tomonaga theory is restricted to the case of one dimension. It may be supposed, however, that the ac-

²¹ Wentzel (reference 8) did not take this possibility into account; he presumed that it is always the lattice which becomes unstable. An instability of the electrons does not imply that the initial hamiltonian (2.1) is inadequate, but that the excitations are so large that (5.1) is not a good approximation.

¹⁹ S. Tomonaga, Prog. Theor. Phys. 5, 544 (1950).

²⁰ D. Bohm and D. Pines, Phys. Rev. 82, 625 (1951).

tual three-dimensional case would be similar. The formulation of Bohm and Pines is valid for long wavelengths which may be the important ones for superconductivity. One would expect, however, that in any case the three-dimensional model would behave qualitatively in the same way as the one-dimensional model of Tomonaga.

The description in terms of plasma oscillations has the advantage that one can include the coulomb interaction between electrons. However, some care must be taken to include all of the coulomb interactions. One must consider also the self-energy of the charge distribution of the positive ions, ρ_+ , and the interaction between the electrons and ions. These two distributions tend to compensate, particularly for waves of long wavelength:

$$\rho_- + \rho_+ \cong 0.$$

In this case the energies also tend to compensate; the negative interaction energy is almost equal in magnitude to the sum of the self-energies of the negative and positive charge distributions. In the formulation given, Ω_n , ω_n , and C_n would be large but nearly equal for waves of long length. One root of (5.10) would be small and would describe a lattice oscillation in which the displacement of the ions is compensated by motion of the electrons. While this method would presumably give the correct frequency for the lattice vibrations, it would not describe the excitations of the electrons.

Instead of following this procedure, we believe that for a discussion of superconductivity it is better to avoid an explicit introduction of the coulomb interactions and to calculate the matrix elements for the normal state by a self-consistent field procedure. The transition to the superconducting phase involves such a small number of electrons that it has a negligible effect on the self-consistent field and thus on the matrix elements.

VI. BLOCH-NORDSIECK TRANSFORMATION

Bloch and Nordsieck¹⁵ have shown that it is possible to eliminate the interaction terms between electrons and the radiation field by a suitable canonical transformation. The approximation made is essentially the neglect of electron recoil during radiation. It is then possible to replace the kinetic energy operator, $\hat{p}^2/2m$, by $\mathbf{v} \cdot \mathbf{p}$, where \mathbf{v} is the average velocity of the electron. The transformation requires that the kinetic energy operator be linear in the momentum. It has been suggested to the author in private communications from M. Fierz and from S. D. Drell¹⁴ that a transformation of the Bloch-Nordsieck type might be useful for calculating the interaction energy of electrons and lattice vibrations.

The approximation of neglecting electron recoil is not a good one for our problem because interaction with the lattice can cause real or virtual transitions in which there are large changes in both the magnitude and

direction of the momentum or wave vector. It is satisfactory only for lattice waves of such long wavelength that their wave vectors are small compared with those of the electrons. This will be true, for example, in the one-dimensional case if the excitations are small compared with the Fermi energy. Let \mathbf{V} represent the velocity vector for an electron with energy near the Fermi surface and consider the interaction of a group of electrons with velocities near \mathbf{V} . One may measure the momentum relative to $m\mathbf{V}$ and take

$$\begin{aligned} \mathbf{P} &= \mathbf{p} - m\mathbf{V} \\ \text{K.E.} &= \frac{1}{2}mV^2 + \mathbf{V} \cdot \mathbf{P}. \end{aligned} \quad (6.1)$$

We neglect the term in P^2 .

With this approximation, the hamiltonian may be expressed in the form:

$$\begin{aligned} H &= \sum \mathbf{V} \cdot \mathbf{P}_i + \sum_i q_s (\mathfrak{N}_s e^{i\mathbf{s} \cdot \mathbf{x}_i} + \mathfrak{N}_s^* e^{-i\mathbf{s} \cdot \mathbf{x}_i}) \\ &\quad + \sum \frac{1}{2} (p_s^2 + \omega_s^2 q_s^2). \end{aligned} \quad (6.2)$$

The canonical transformation which eliminates the interaction terms is obtained as follows. Let

$$f_{si} = \mathfrak{N}_s e^{i\mathbf{s} \cdot \mathbf{x}_i} + \mathfrak{N}_s^* e^{-i\mathbf{s} \cdot \mathbf{x}_i}. \quad (6.3)$$

Introduce the new coordinates,

$$\begin{aligned} q_s' &= q_s + \sum_i \alpha_s f_{si}, \\ \mathbf{x}_i' &= \mathbf{x}_i, \end{aligned} \quad (6.4)$$

and take the wave function for the system in the form,

$$\Phi(\mathbf{x}, q) = \exp[iS(\mathbf{x}', q')/\hbar] \Phi'(\mathbf{x}', q'). \quad (6.5)$$

The operators p_s and \mathbf{P}_i acting on Φ give

$$p_s \Phi = \exp(iS/\hbar) [(\partial S/\partial q_s') + p_s'] \Phi'; \quad (6.6)$$

$$\begin{aligned} \mathbf{P}_i \Phi &= \exp(iS/\hbar) \\ &\quad \times \{ \sum_s [(\partial S/\partial q_s') + p_s'] \nabla_i q_s' + \nabla_i S + \mathbf{P}_i' \} \Phi'; \end{aligned} \quad (6.7)$$

$$\nabla_i q_s' = \alpha_s \nabla_i f_{si}.$$

We take S in the form,

$$S = - \sum_{is} q_s' \alpha_s (\mathbf{V} \cdot \nabla_i) f_{si}, \quad (6.9)$$

so that

$$\partial S/\partial q_s' = - \sum_i \alpha_s (\mathbf{V} \cdot \nabla_i) f_{si}$$

and

$$\begin{aligned} \sum_i (\mathbf{V} \cdot \nabla_i) S &= - \sum_{si} \alpha_s q_s' (\mathbf{V} \cdot \nabla_i)^2 f_{si} \\ &= \sum_s \alpha_s (\mathbf{V} \cdot \mathbf{s})^2 q_s' \sum_i f_{si}. \end{aligned} \quad (6.10)$$

The coefficient α_s , chosen in such a way as to eliminate the interaction terms, is

$$\alpha_s = 1/(\omega_s^2 - (\mathbf{V} \cdot \mathbf{s})^2). \quad (6.11)$$

The transformed hamiltonian operating on Φ' is

$$H' = \sum \mathbf{V} \cdot \mathbf{P}' - \frac{1}{2} \sum_{sij} [\alpha_s^2 (\mathbf{V} \cdot \nabla_i f_{si}) (\mathbf{V} \cdot \nabla_j f_{sj}) + (2\alpha_s - \omega_s^2 \alpha_s^2) f_{si} f_{sj}] + \sum_s \frac{1}{2} [(p_s')^2 + \omega_s^2 (q_s')^2]. \quad (6.12)$$

An interaction between electrons replaces the interaction between electrons and lattice vibrations. With

$$\sum_{sij} \frac{\frac{1}{2} (3(\mathbf{V} \cdot \mathbf{s})^2 - W_s^2) \{ \mathfrak{N}_s^2 \exp[i\mathbf{s} \cdot (\mathbf{x}_i + \mathbf{x}_j)] + \mathfrak{N}_s^{*2} \exp[-i\mathbf{s} \cdot (\mathbf{x}_i + \mathbf{x}_j)] \}}{(\omega_s^2 - (\mathbf{V} \cdot \mathbf{s})^2)}. \quad (6.14)$$

The first of these interaction terms, (6.13), contributes to the energy in the first order, the second (6.14), only in higher orders.

The wave function for the system is of the form,

$$\Phi(x, q) = \exp(iS/\hbar) \varphi(x) Q(q_s + \sum_{si} \alpha_s f_{si}). \quad (6.15)$$

It should be noted that in (2.11) the vibrational coordinates appear in the electron wave function while here the electron coordinates appear in the vibrational wave function.

One may calculate the interaction energy in the first order by using a determinantal wave function for $\varphi(x)$ in (6.15). The terms with $i=j$ in (6.13) give

$$-\sum_{is} \sum \frac{|\mathfrak{N}_s|^2}{\omega_s^2 - (\mathbf{V} \cdot \mathbf{s})^2} = -\frac{1}{2} \sum_{i\pm s} \sum \frac{|\mathfrak{N}_s|^2}{\omega_s(\omega_s - (\mathbf{V} \cdot \mathbf{s}))}. \quad (6.16)$$

The sum on the left includes s values of only one sign (lying in one hemisphere) while the sum on the right is over both positive and negative values.

It is only the exchange terms which contribute when $i \neq j$; the direct terms average to zero. The exchange terms give

$$\sum_{k, k'} \int \int \Psi_k^*(x_2) \Psi_{k'}^*(x_1) \frac{|\mathfrak{N}_s|^2 \cos \mathbf{s} \cdot (\mathbf{x}_1 - \mathbf{x}_2)}{\omega_s^2 - (\mathbf{V} \cdot \mathbf{s})^2} \Psi_k(x_1) \Psi_{k'}(x_2) dx_1 dx_2. \quad (6.17)$$

The sum is over occupied states. The integral is equal to

$$\frac{1}{2} [|\mathfrak{N}_s|^2 / \omega_s^2 - (\mathbf{V} \cdot \mathbf{s})^2] \quad (6.18)$$

if

$$\mathbf{k}' = \mathbf{k} \pm \mathbf{s} \quad (6.19)$$

and is equal to zero otherwise.

Suppose that the state $\mathbf{k} = \mathbf{k}_1$ is occupied. If $\mathbf{k}' = \mathbf{k}_1 + \mathbf{s}$ is also occupied, there are two terms in the sum over \mathbf{k} and \mathbf{k}' which give (6.18) and the sum of these two just cancels the corresponding terms in (6.16). If $\mathbf{k}_1 + \mathbf{s}$ is not occupied, the exchange terms vanish and the terms remain in (6.16).

The expression for the interaction energy is identical with Eq. (2.12) used by Fröhlich and obtained from second-order perturbation theory. The relation between

use of (6.3) for f_{si} , the second summation reduces to the sum of two terms, one of which depends on $\mathbf{x}_i - \mathbf{x}_j$:

$$U_1(x) = -\sum_{sij} \frac{|\mathfrak{N}_s|^2 \cos \mathbf{s} \cdot (\mathbf{x}_i - \mathbf{x}_j)}{\omega_s^2 - (\mathbf{V} \cdot \mathbf{s})^2}, \quad (6.13)$$

and the other on $\mathbf{x}_i + \mathbf{x}_j$:

the matrix elements is

$$|M_{kk'}|^2 = |\mathfrak{N}_{kk'}|^2 (q_{kk'})_{k'}^2 = |\mathfrak{N}_{kk'}|^2 (\hbar/2\omega_{kk'}). \quad (6.20)$$

Furthermore,

$$\epsilon_k - \epsilon_{k'} = \hbar V \cdot (k - k'). \quad (6.21)$$

With $\mathbf{k}' = \mathbf{k} + \mathbf{s}$, the right-hand side of (6.16) is therefore equivalent to

$$\sum_k \sum_{k'} \frac{f_k |M_{kk'}|^2}{\epsilon_k - \epsilon_{k'} - \hbar\omega_{kk'}}. \quad (6.22)$$

The exchange terms may be expressed in the form,

$$\frac{1}{2} \sum_k \sum_{k'} \frac{f_k f_{k'} |M_{kk'}|^2 2\hbar\omega_{kk'}}{(\hbar\omega_{kk'})^2 - (\epsilon_k - \epsilon_{k'})^2} = -\sum_k \sum_{k'} \frac{f_k f_{k'} |M_{kk'}|^2}{\epsilon_k - \epsilon_{k'} - \hbar\omega_{kk'}}. \quad (6.23)$$

The sum of (6.23) and (6.22) is just (2.12).

This procedure thus gives some justification for use of Fröhlich's expression beyond the limits set by second-order perturbation theory. We have an explicit wave function which gives (2.12) regardless of how large the interaction may be. However, it is undoubtedly a poor approximation when the interaction is so large as to give superconductivity.

Unfortunately the proof as given is limited to interactions with lattice waves of long wavelength. While the situation is by no means certain, present theoretical indications are that it is short rather than the long wavelengths which predominate in giving the superconducting transitions. However, present theories give energies for the transition which are much too large, and it may be that the longer waves are actually the important ones. Attempts to carry through the theory without the restriction to long wavelengths have not been successful.

VII. CONCLUSIONS

The dependence of specific heat and conductivity of the normal phase on temperature is given correctly by the one-electron or Bloch model in which it is assumed that the energies of the electrons are not greatly de-

pendent on the distribution of electrons in \mathbf{k} -space. There must be some sort of a one-to-one correspondence between the wave functions for the metal formed from Bloch functions and the true many-particle wave functions. Interactions between electrons and lattice vibrations characteristic of the normal phase are included in these functions.

There remains a degeneracy corresponding to electrons of the same or nearly the same energy moving in different directions. Transitions between these states via the lattice vibrations are possible. Presumably the onset of superconductivity is associated with a resolution of this degeneracy. Condition (3.5) suggests that the interactions responsible are such that $|\epsilon_k - \epsilon_{k'}| < \hbar\omega_{kk'}$. Superconductivity occurs in metals for which the matrix elements of the interaction are so large that the criterion (3.10) is satisfied. This criterion does in

fact distinguish pretty well between superconductors and non-superconductors.^{6,7a}

It is not as yet clear how best to characterize superconductivity. The various approaches we have described indicate a marked change in the wave functions and energies of the electrons when the criterion (3.10) is satisfied. A really good description of superconductivity undoubtedly requires the use of many-electron wave functions. Unfortunately coordinates representing plasma oscillations of the electron gas are not suitable. It is uncertain whether the best "one-electron" approximation is a shell distribution as Fröhlich suggests or gives simply a reduction in energy and small effective mass of electrons in states near the Fermi surface. The best wave functions of the form (4.1) may yield a lower energy than (6.15) provided that $\varphi(x)$ in the latter is approximated by determinantal wave functions.