

must be satisfied; if thermal diffusion is predominant,

$$\frac{l d(\ln T)}{dx}, \frac{l^2 d^2(\ln T)}{dx^2}, \frac{l^2 d^3(\ln T)/dx^3}{d(\ln T)/dx} \ll 1 \quad (\text{A9})$$

must be satisfied.

To test whether terms containing $f_z(E, x)$ can be

neglected in a particular case, it is necessary to evaluate the various derivatives in inequalities (A5), (A8), and (A9) from the computed solutions and see if the inequalities are satisfied. For scattering mechanisms with an energy-dependent mean free path, the conditions will remain essentially unaltered with l evaluated for the average electron energy kT .

Theory of Superconductivity. I. Electron-Lattice Interaction

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(Received April 21, 1961)

The electron-lattice interaction responsible for electrical resistivity in perfect metallic crystals is shown to be a form of Jahn-Teller effect. It does not occur in the Born-Oppenheimer (adiabatic) approximation even when the electron-electron interaction is taken fully into account. The matrix elements that describe corrections to the Born-Oppenheimer approximation are derived by a general argument that can be applied to metals with arbitrary electronic energy band structure, and the case of monatomic metals is worked out in detail in the effective mass approximation. Two types of physical phenomena are attributed to these matrix elements. The first is ordinary electrical resistivity due to electron-phonon scattering. The present derivation leads to the same formal structure as the usual theory, but should give quantitatively different results when applied to specific metals. The second type of physical phenomenon is a modification to the stationary states of the electron-lattice system that can significantly alter the total energy spectrum at low energies, and mixes states of electron excitation and lattice excitation. An effect of this kind can account qualitatively for the disappearance of electrical resistivity at finite temperatures in superconductors. Other special properties of superconductors should follow from consideration of the stationary states modified by the Jahn-Teller effect.

I. INTRODUCTION

THE theory of superconductivity¹ developed by Bardeen, Cooper, and Schrieffer and by Bogoliubov successfully accounts for the thermodynamic behavior of superconductors at low temperatures, the dependence of critical temperature on isotopic mass, and other properties dependent upon the existence and magnitude of an energy gap for electron excitations. However, the Meissner effect (expulsion of the magnetic field) follows from an argument that has been the subject of considerable controversy² and cannot be said to be an immediate intuitive result of the theory. The phenomenon of superconductivity itself (vanishing resistivity at a finite temperature) is not explained by the theory.² The theory is based on a highly simplified form of the Hamiltonian, which, although representing the most important terms in the complete Hamiltonian, leaves out most of the structure both of the phonon frequency spectrum and of the electronic energy bands.

It has been pointed out by several authors³ that the electron-lattice interaction must be thought of as a correction to the Born-Oppenheimer or adiabatic approximation, and that this must affect the theory of superconductivity. Matrix elements for transitions described as electron-phonon scattering are unchanged to first order from those of the Bloch theory.³ However, matrix elements also occur between nondegenerate Born-Oppenheimer states. The present paper will derive these matrix elements in more detail than did the authors cited, in order to establish a basis for discussion of the stationary (or metastable) states of the interacting electron-lattice system. This leads to a reformulation of the theory of superconductivity that includes a more realistic description of the phonon energy spectrum and the electronic band structure than is possible in the Bardeen-Cooper-Schrieffer theory. Since the field-theoretical formalism does not lend itself to a detailed discussion of the degeneracies that occur, which are qualitatively very important in treating the electron-phonon interaction, the present analysis will be carried out in terms of the Schrödinger wave functions of the system.

The exact nonrelativistic Hamiltonian for a metal

¹ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957); N. N. Bogoliubov, *Nuovo cimento* (10) **7**, 794 (1958); *J. Exptl. Theoret. Phys. (U.S.S.R.)* **34**, 58 (1958); N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in the Theory of Superconductivity* (Academy of Sciences of U.S.S.R., Moscow, 1958).

² M. R. Schafroth, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, pp. 293-498.

³ J. M. Ziman, *Proc. Cambridge Phil. Soc.* **51**, 707 (1955); H. Stumpf, *Z. Naturforschung* **11a**, 259 (1956); A. Haug, *Z. Physik* **146**, 75 (1956); B. Goodman, *Phys. Rev.* **110**, 888 (1958).

contains three types of terms: H_e , the kinetic energy and mutual Coulomb repulsion of the electrons; H_n , the kinetic energy and mutual repulsion of the nuclei; and H_{ne} , the Coulomb attraction between nuclei and electrons. In the theory of molecular structure, of which the theory of solids is a special case, the first stage of an *ab initio* calculation of the molecular energy levels would consist of calculation of the low-lying electronic wave functions as eigenfunctions of the partial Hamiltonian, $H_e + H_{ne}$, for each set of values of the nuclear coordinates. The eigenvalues of this Hamiltonian are electronic energies, but they are parametric functions of the nuclear coordinates. The corresponding electronic wave functions are also parametric functions of the nuclear coordinates. In the Born-Oppenheimer approximation,⁴ each electronic state leads to a potential energy hypersurface in the nuclear coordinates when the Coulomb repulsion between nuclei, part of H_n , is added to the electronic energies. The nuclear Hamiltonian for each electronic state is obtained by adding the kinetic energy part of H_n to this. In general the potential energy hypersurface for a bound state has a well-defined absolute minimum. The nuclear motion is most conveniently described by coordinates measuring displacement from the potential minimum, transformed to normal coordinates by diagonalizing the quadratic part of the potential energy function of the displacement coordinates. Except for the degrees of freedom describing rotation or displacement of the entire system, this leads to a vibrational spectrum of energies describing the nuclear motion, added to the potential energy at the minimum point of the potential hypersurface for each electronic state. The wave function is a product of the nuclear wave function and an electronic wave function that is parametrically dependent upon the nuclear coordinates.

This wave function is not, however, an exact eigenfunction of the original Hamiltonian, $H_n + H_e = H_{ne}$. Corrections to the Born-Oppenheimer approximation arise from the action of the nuclear Hamiltonian H_n on the nuclear coordinates that occur parametrically in the assumed electronic wave function. It has been shown by Born,⁵ and in a more recent article by Bratoz,⁶ that an interaction between wave functions is introduced in the form of matrix elements of H_n between electronic wave functions that describe different states in the Born-Oppenheimer approximation. Ordinarily these effects are small, in the ratio of the electronic mass to the nuclear mass, but they cannot be ignored when there is a degeneracy or near-degeneracy between different electronic states. In such cases the interaction between these states is

described as a dynamical Jahn-Teller effect, and leads to special vibronic states of the system.⁷

The argument of the present work is simply to apply the above analysis to the case of electrons in metals, interacting with the lattice vibrations. Because of the degeneracy or near degeneracy of the low-lying electronic states, there are interactions physically described as scattering of electrons by lattice excitations, that are a form of the dynamical Jahn-Teller effect. Since these interactions do not occur in the Born-Oppenheimer approximation (adiabatic approximation), they have nothing to do either with the parametric dependence of the Born-Oppenheimer electronic wave function on the nuclear coordinates, or with the question of electron correlation. On the contrary, the electronic wave function in the adiabatic approximation can in principle be calculated exactly, including correlation, as a smooth parametric function of the nuclear displacement coordinates. One must distinguish clearly between this dependence on nuclear coordinates, which does not describe anything corresponding to a physical scattering phenomenon (a statistically irreversible transition between distinct states), and the more subtle dynamical Jahn-Teller effect, which does describe scattering in the physical sense, and must be identified with the effect responsible for resistivity in perfect crystals of ordinary metals.

In addition to the interaction between degenerate electron-lattice states, there will also be a systematic change in the nature of the eigenstates of the system, which become linear combinations of the Born-Oppenheimer electron-lattice states. Electron excitations of finite wave vector are mixed with the lattice zero-point oscillations. The electric current vector due to this admixture of electronic states is found to be finite for each lattice mode, when there is an external electromagnetic field. In agreement with Bloch's theorem, the net electric current density vanishes in the absence of an electromagnetic field. This electric current density provides a qualitative explanation of the Meissner effect and of the absence of electrical resistivity at finite temperatures in superconductors, which will be discussed in more detail in separate papers.

II. ADIABATIC APPROXIMATION AND THE JAHN-TELLER EFFECT

For each set of values of nuclear coordinates, there will be a complete set of electronic wave functions. In particular it is convenient to consider this complete set for the nuclear coordinates corresponding to the minimum of the lowest potential energy hypersurface

⁴ M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

⁵ M. Born, Nachr. Akad. Wiss. Göttingen Math. Phys. Kl., No. 6, 1 (1951).

⁶ S. Bratoz, Colloq. intern. centre natl. recherche sci. Paris **82**, 127 (1958).

⁷ H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937); A. D. Liehr and W. Moffitt, J. Chem. Phys. **25**, 1074 (1956); W. Moffitt and A. D. Liehr, Phys. Rev. **106**, 1195 (1957); H. C. Longuet-Higgins, U. Opik, M. H. L. Pryce, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958); W. Moffitt and W. Thorson, Colloq. intern. centre natl. recherche sci. Paris **82**, 141 (1958); A. D. Liehr, Revs. Modern Phys. **32**, 436 (1960).

(electronic energy plus Coulomb repulsion between the nuclei). Then the electronic wave functions for displaced positions of the nuclei can be expanded as linear combinations of this particular complete set. As far as the electronic wave function is concerned this potential minimum has no special properties—it is determined by the balance between the electronic energy, which in general has no minimum at this point, and the repulsion between the nuclei. Hence, a Taylor expansion of both electronic energy and wave functions should be possible, with the nuclear displacements or normal coordinates as variables. For low excitations, where anharmonic contributions to the nuclear potential surfaces can be neglected, it should be sufficient to expand the electronic wave function to first order in the normal coordinates.

If Ψ_μ is an electronic wave function at the potential minimum, the corresponding wave function for general values of the normal coordinates q_f will be

$$\Psi_\mu(n) = \sum_\nu \Psi_\nu U_{\nu\mu}(q_f), \quad (1)$$

or up to linear terms in the normal coordinates

$$\Psi_\mu(n) = \Psi_\mu + \sum_\nu \sum_f \Psi_\nu i S_{\nu\mu}(f) q_f. \quad (2)$$

Here $U_{\nu\mu}$ is a unitary matrix, which can be expressed as $(\exp iS)_{\nu\mu}$ where S is an Hermitian matrix of the form

$$S_{\nu\mu} = \sum_f S_{\nu\mu}(f) q_f + \dots, \quad (3)$$

expanded in the normal coordinates, if states ν and μ are not degenerate.

Now if all of the wave functions $\Psi_\mu(n)$ were known, as a result of solving the electronic Schrödinger equation, including correlation of the electrons, the coefficients $S_{\nu\mu}(f)$ could be evaluated. This would give a complete description of the adiabatic change of the electronic wave function, following the nuclear motion. It does not describe scattering from one electronic state to another due to this nuclear motion, because the electronic wave function is inherently dependent upon the nuclear coordinates. The function of Eq. (1) describes a single electronic state only.

The scattering phenomenon that occurs as a correction to the Born-Oppenheimer approximation arises from the commutator of H_n with the electronic wave function of Eq. (1). Since

$$H_n = \frac{1}{2} \sum_f (\dot{p}_f \dot{p}_f^* + \omega_f^2 q_f q_f^*), \quad (4)$$

it follows that

$$[H_n, \Psi_\mu(n)] = \sum_\nu \sum_f \Psi_\nu S_{\nu\mu}(f) \hbar \dot{p}_f^*. \quad (5)$$

The electronic part of the interaction matrix element⁶ between two electron-lattice states that are uncoupled in the Born-Oppenheimer approximation, to first order in the normal coordinates or momenta, is just the coefficient of Ψ_ν in Eq. (5),

$$(H_n)_{\nu\mu} = \sum_f S_{\nu\mu}(f) \hbar \dot{p}_f^*. \quad (6)$$

This will have nonvanishing matrix elements only between lattice states that differ by a single quantum in just one normal mode. Hence, the scattering theory is formally the same as is usually assumed,⁸ but the normal mode momentum replaces the corresponding coordinate, and the matrix element $S_{\nu\mu}(f)$ occurs in place of the matrix element of the scattering potential of the usual theory.

Since matrix elements of this kind occur between electron-lattice states that are not degenerate in the Born-Oppenheimer approximation, there will be corrections to the energy spectrum and stationary state wave functions of the electron-lattice system, in addition to the phenomenon of scattering between degenerate states.

It is clear that the form of the interaction matrix element of Eq. (6) is not dependent upon any approximate description of the electronic wave function or of the spectrum of electronic excited states. However, to estimate the coefficient $S_{\nu\mu}(f)$, it is helpful to make several simplifying assumptions. In particular, the electronic correlation energy can be expected to be insensitive to small displacements of the nuclei, and it should be adequate to describe the electronic ground state by the Hartree-Fock approximation, and to approximate to the low-lying excited states by simple replacement of occupied Hartree-Fock orbitals by unoccupied orbitals. This is the description of these states postulated in the band theory of metals, and in the application of Fermi-Dirac statistical mechanics to the electrons.

There will be a different Hartree-Fock electronic ground-state wave function for each value of the nuclear coordinates. This implies that the effective one-electron Hamiltonian depends parametrically on the nuclear coordinates. Since there is no reason for a singularity to occur at the potential energy minimum, this effective one-electron Hamiltonian can also be expanded to first order in the normal coordinates

$$\mathcal{H}(n) = \mathcal{H}_0 + \sum_f V(f) q_f + \dots. \quad (7)$$

The operator \mathcal{H}_0 is the Hartree-Fock effective Hamiltonian for the electronic ground state at the equilibrium nuclear configuration. The electronic states are approximated for each nuclear configuration by the collection of Slater determinants, for N electrons, constructed from any N of the Hartree-Fock orbitals $\phi_i(n)$, eigenfunctions of $\mathcal{H}(n)$. These orbitals can be assumed to form a complete orthonormal set for each nuclear configuration.

The relationship between the orbitals $\phi_i(n)$ and the Hartree-Fock orbitals at the equilibrium nuclear configuration, ϕ_i , will be given by a unitary transformation analogous to Eqs. (1) and (2). To first

⁸ A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), 2nd ed.

order in the normal coordinates,

$$\phi_i(n) = \phi_i + \sum_j \sum_f \phi_j i s_{ji}(f) q_f + \dots, \quad (8)$$

from

$$\phi_i(n) = \sum_j \phi_j u_{ji}(n) = \sum_j \phi_j (\exp i s)_{ji}, \quad (9)$$

where

$$s_{ji} = \sum_f s_{ji}(f) q_f + \dots, \quad (10)$$

if orbitals ϕ_i and ϕ_j are not degenerate.

This unitary transformation of the Hartree-Fock orbitals induces a unitary transformation of the Slater determinants constructed from them, which will be an approximation to the unitary transformation, Eq. (1), of the electronic wave functions. For example, if Φ_0 is the Hartree-Fock ground-state wave function, the perturbed function to first order is

$$\Phi_0(n) = \Phi_0 + \sum_j \sum_i \sum_a \Phi_i^a (i s_{ai} q_j) + \dots, \quad i < N < a, \quad (11)$$

where Φ_i^a is a Slater determinant obtained from Φ_0 by replacing an occupied orbital ϕ_i by an unoccupied orbital ϕ_a . Comparing this with Eq. (2), the coefficients S_{i0} differ from zero only when Φ_i differs from Φ_0 by the change of a single orbital (ϕ_a replacing ϕ_i), and are equal to s_{ai} in this case.

If the coefficients $V(f)$ of Eq. (7) are known, then, by first-order perturbation theory,

$$s_{ai}(f) = i V_{ai}(f) / (\epsilon_a - \epsilon_i). \quad (12)$$

This formula must be modified to account for the degeneracy when ϵ_a and ϵ_i approach each other, unless $V_{ai}(f)$ vanishes. In describing the ground state, this degeneracy only occurs at the Fermi surface.

The analysis up to this point is compatible with the band theory of solids. If the coefficients $V(f)$ could be estimated the formalism could be applied to systems with arbitrary band structure. In particular, the separation between valence electrons and electrons in ion cores does not have to be made in this argument. In the following sections, more restrictive assumptions will be made, in order to examine the implications of this formalism in more detail.

III. MATRIX ELEMENTS IN THE EFFECTIVE MASS APPROXIMATION

If the idea of ion cores of charge Ze and mass M is introduced, with only the conduction electrons considered in detail by the band theory, then the perturbing part of $\mathcal{H}(n)$, Eq. (7), represents the change in effective potential due to displacement of the ion cores from equilibrium. This will consist of the change in potential due to the ion cores themselves reduced by the screening effect of the electrons, since $\mathcal{H}(n)$ is the self-consistent field acting on the electrons. In the region outside the ion cores, the net perturbing potential can be assumed to be the derivative of a screened Coulomb potential due to charge Ze at each ion, screened by a factor $\exp(-\lambda r)$. If the electronic orbitals ϕ_i at the equilibrium nuclear configuration are represented simply

as plane waves, normalized in volume V ,

$$\phi_i = V^{-1/2} \exp(i \sigma_i \cdot \mathbf{x}), \quad (13)$$

then the matrix elements of the coefficients of Eq. (12) can easily be evaluated to be

$$V_{ai}(f) = i \xi_f \cdot (\kappa_f + \mathbf{K}_a) (NM)^{-1/2} \frac{4\pi Z e^2}{|\kappa_f + \mathbf{K}_a|^2 + \lambda^2} \frac{N}{V}, \quad (14)$$

where $\kappa_f = \sigma_a - \sigma_i - \mathbf{K}_a$ and \mathbf{K}_a is a reciprocal lattice vector. Here ξ_f is a polarization vector, and κ_f is restricted to values as indicated that lie in the first Brillouin zone. N is the number of ion cores of charge Ze in a crystal of volume V . This form is clearly limited to monatomic lattices, and the assumption of Eq. (13) limits this expression except for qualitative purposes to the alkali metals. For discussing low-temperature phenomena, it is convenient to neglect Umklapp transitions, and thus to consider only the terms with $\mathbf{K}_a = 0$. This is partially justified by the occurrence of $|\kappa + \mathbf{K}_a|^2$ in the denominator in Eq. (14), if the empirical parameter λ is not too large. If the unit polarization vectors ξ_f for each normal mode are chosen so that one is parallel to κ_f and the others orthogonal to it, the latter do not occur in Eq. (14) except for nonvanishing \mathbf{K}_a . Hence, neglecting the Umklapp transitions has the effect of limiting the electron-lattice interaction to longitudinal lattice modes only. This reduces Eq. (14) to

$$V_{ai}(\kappa) = i \kappa (NM)^{-1/2} \left(\frac{4\pi Z e^2}{\kappa^2 + \lambda^2} \right) \frac{N}{V}, \quad (15)$$

where $\kappa = \sigma_a - \sigma_i$, in the first Brillouin zone.

The screening constant λ is to be considered as an empirical parameter. Its value can be estimated by an argument due to Bohm and Staver,⁹ quoted by Bardeen and Pines,¹⁰ who show that the argument is consistent with both the earlier self-consistent field derivation of Bardeen¹¹ and with a more sophisticated field theoretical derivation that takes the electron correlation into account. The argument of Bohm and Staver leads also to a relationship between the electron velocity at the Fermi surface, v , and the velocity of longitudinal acoustic waves, s , found to be empirically reasonable even for polyvalent metals.

The argument, as given by Bardeen and Pines, is to consider the dynamics of the ion cores, oscillating about their equilibrium configuration with the plasma frequency for classical particles of charge Ze ,

$$\Omega^2 = 4\pi Z^2 e^2 N / M V, \quad (16)$$

in interaction with the density fluctuations of a perfect Fermi gas through a scattering potential with Fourier components $q_\kappa v_{-\kappa} \rho_\kappa$, where ρ_κ is a Fourier component of

⁹ D. Bohm and T. Staver, Phys. Rev. **84**, 836 (1952).

¹⁰ J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955).

¹¹ J. Bardeen, Phys. Rev. **52**, 688 (1937).

the electron density. The Thomas-Fermi equation establishes a linear relationship between the perturbing potential and the perturbation of electron density. Hence the increment to ρ_κ is proportional to the nuclear displacement q_κ , since the net perturbing potential is proportional to q_κ . This then contributes to the term linear in q_κ in the equation of motion for the ion cores, and amounts to a renormalization of the frequencies of the normal modes. By this argument, the net perturbing potential acting on the electrons is the sum of the potential $v_\kappa^i q_\kappa$ due to the displacement q_κ , and, from Poisson's equation, the potential due to the induced change in electron density, of the form

$$v_\kappa^p q_\kappa = (4\pi e^2/\kappa^2)\delta\rho_\kappa. \quad (17)$$

But the Thomas-Fermi equation implies that

$$v_\kappa q_\kappa = (v_\kappa^i + v_\kappa^p)q_\kappa = -(2\epsilon_F/3n_0)\delta\rho_\kappa, \quad (18)$$

for orbitals near the Fermi level, ϵ_F measured from the bottom of the conduction band, if there are n_0 conduction electrons per unit volume. Equations (17) and (18) can be solved for the screened interaction coefficient

$$v_\kappa = \left(1 + \frac{3}{2} \frac{4\pi e^2 n_0}{\kappa^2 \epsilon_F}\right)^{-1} v_\kappa^i. \quad (19)$$

The renormalized lattice frequencies corresponding to this are

$$\omega_\kappa^2 = \Omega^2 + \frac{\kappa^2}{4\pi e^2} v_{-\kappa}^i v_\kappa^p. \quad (20)$$

For a pure Coulomb potential, following the derivation of Eq. (15), we have

$$v_\kappa^i = i\kappa(N/MV)^{1/2}(4\pi Ze^2/\kappa^2). \quad (21)$$

Then from Eq. (19),

$$v_\kappa = i\kappa(N/MV)^{1/2}4\pi Ze^2/(\kappa^2 + \lambda^2), \quad (22)$$

with

$$\lambda^2 = \frac{3}{2}(4\pi e^2 n_0/\epsilon_F), \quad (23)$$

determining the constant λ^2 in Eq. (15). This can also be expressed in terms of the electron plasma frequency,

$$\omega^2 = 4\pi e^2 n_0/m, \quad (24)$$

and in the effective-mass approximation becomes

$$\lambda^2 = 3\omega^2/v^2, \quad (25)$$

where ω is the plasma frequency for the effective mass, not the true electron mass, and v is the electron velocity at the Fermi surface. In terms of these constants, from Eq. (20),

$$\begin{aligned} \omega_\kappa^2 &= \Omega^2 \kappa^2 / (\kappa^2 + \lambda^2) \\ &\cong \Omega^2 (\kappa^2 / \lambda^2) = \kappa^2 (\Omega^2 v^2 / 3\omega^2), \end{aligned} \quad (26)$$

for small κ . This is of the form $\omega_\kappa^2 = \kappa^2 s^2$, determining a constant velocity s for longitudinal acoustic waves. The empirical relationship checked by Bohm and Staver

then follows as

$$s^2/v^2 = \frac{1}{3}\Omega^2/\omega^2 = \frac{1}{3}mZ/M, \quad (27)$$

using the fact that $NZ = n_0 V$ for electrical neutrality. Again, m is the effective mass of the electrons at the Fermi surface. Thus the specific form, Eq. (15), postulated for the perturbation to the electronic self-consistent field is part of the same general argument that leads to the empirical relationship of Eq. (27), and the corresponding value of the parameter λ^2 is that of Eq. (23) or (25).

The matrix elements that lead to corrections to the Born-Oppenheimer approximation are of the form⁶

$$(\Phi_\mu(n)\chi(\{n_\kappa\}_\mu), H\Phi_\nu(n)\chi(\{n_\kappa\}_\nu)), \quad (28)$$

where the vibrational wave function χ is determined by specifying the number of quanta, n_κ , in each normal mode. Combining Eqs. (6), (11), (12), and (15), to the approximations involved in these equations, the only nondiagonal matrix elements involving the electronic ground state, with arbitrary phonon excitation, are of the form

$$\begin{aligned} &(\Phi_i^a(n)\chi(\cdots n_\kappa - 1 \cdots), H\Phi_0(n)\chi(\cdots n_\kappa \cdots)) \\ &= -\hbar\kappa(NM)^{-1/2}(\epsilon_a - \epsilon_i)^{-1} \frac{4\pi Ze^2 N}{\kappa^2 + \lambda^2 V} \\ &\quad \times (\cdots n_\kappa - 1 \cdots | p_{-\kappa} | \cdots n_\kappa \cdots) \\ &= -(n_\kappa \hbar\omega_\kappa / 2NM)^{1/2} \hbar\kappa(\epsilon_a - \epsilon_i)^{-1} \frac{4\pi Ze^2 N}{\kappa^2 + \lambda^2 V}, \end{aligned} \quad (29)$$

if

$$\sigma_a = \sigma_i + \kappa.$$

There is a similar matrix element between states $\Phi_i^a(n)\chi(\cdots n_{-\kappa} \cdots)$ and $\Phi_0(n)\chi(\cdots n_{-\kappa} - 1 \cdots)$, substituting $n_{-\kappa}$ for n_κ in the last line of Eq. (29). The apparent singularity as $\epsilon_a \rightarrow \epsilon_i$ will be considered in the next section.

IV. SCATTERING NEAR THE FERMI SURFACE

The resolvent operator formalism of Van Hove and Hugenholtz¹² can be used to develop a rigorous perturbation theory for the electron continuum. For the one-electron problem, this formalism becomes similar to the more familiar Brillouin-Wigner perturbation theory, except that sums of products of matrix elements occurring in higher order terms are combined wherever possible into a simpler form. In the lowest orders, the most important effect is a change in the energy denominators of the perturbation formulas. It should be noted that the perturbed wave functions correspond to metastable states, not to true stationary states, in the limit of infinite volume. This must be taken into

¹² L. Van Hove, *Physica* **21**, 901 (1955); **22**, 343 (1956); N. M. Hugenholtz, *ibid.* **23**, 481 (1957).

account in the theory of transport processes based on the present formalism, but will not be discussed here.

Following Van Hove and Hugenholtz, it is convenient to define the operator $G(z)$, diagonal in the unperturbed basis, as the sum of all possible products of matrix elements connecting a given unperturbed state with itself in the perturbation formulas. The unperturbed energy ϵ_i is replaced by a complex variable z . The imaginary part of $G(z)$ will be called $\delta(z)$ here. Then the perturbed wave function is expressed in terms of a complex diagonal operator $D(z)$. To the lowest non-vanishing order, the formula corresponding to Eq. (12) is

$$s_{ai}(f) = \lim_{z \rightarrow \epsilon_i + i0} D_a(z) i V_{ai}(f) = i V_{ai}(f) / (\epsilon_a - \zeta_i), \quad (30)$$

where

$$D_a(z) = [\epsilon_a - z - G_a(z)]^{-1},$$

and

$$\zeta_i = \lim_{z \rightarrow \epsilon_i + i0} [z + G_a(z)] \cong \epsilon_i + i\delta_i.$$

The index a of $G_a(z)$ can be replaced by i , since $G_a(\epsilon_i)$ is evaluated by integration of the second-order perturbation formula along a contour just below the real axis of energy, and is determined primarily by the residue at ζ_i . The imaginary part is found to be finite and has the important effect of making $s_{ai}(f)$ a continuous bounded function (presumably analytic) of the energy ϵ_a . The real part has no qualitative effect, representing a small shift of the energies in the continuum, and will be neglected. Since the magnitude of $\epsilon_i - \zeta_i$ is small, it can be neglected in the denominator of the second-order perturbation formula. Then the imaginary part is given by the formula

$$\delta_i = -\text{Im}(\epsilon_i - \zeta_i) = \text{Im} \sum_{\kappa} |q_{\kappa}|^2 |V_{ji}|^2 / (\epsilon_j - \epsilon_i), \quad (31)$$

where $\sigma_j = \sigma_i + \kappa$, and the sum is replaced by a contour integral in the complex variable ϵ_j , passing below the singularity at ϵ_i .

To make it possible to derive a definite result, δ_i will be calculated taking into account the zero-point motion of the lattice only. Thus the terms $|q_{\kappa}|^2$ will be replaced by their zero-point mean values, $\hbar/2\omega_{\kappa}$. However, the normal mode coordinates q_{κ} which multiply the coefficients calculated by Eq. (30) are retained as dynamical variables, leading to the basic formulas of Eqs. (6) and (29). These should be valid for low-energy processes under this approximation.

Replacing $|q_{\kappa}|^2$ by the zero-point mean value for each κ , and using Eq. (15) for the matrix element $V_{ji}(\kappa)$, Eq. (31) becomes

$$\delta_i = A\pi \text{Res}_{\rho=\sigma} \int_{-1}^{+1} d\mu \frac{\rho^2(\rho^2 + \sigma^2 - 2\rho\sigma\mu)^{\frac{1}{2}}}{(\rho^2 - \sigma^2)(\rho^2 + \sigma^2 + \lambda^2 - 2\rho\sigma\mu)^2}, \quad (32)$$

where

$$A = 4mNZ^2e^4/\hbar M V s. \quad (33)$$

Here σ is the magnitude of σ_i , ρ is the magnitude of σ_j , and μ is the direction cosine between these two

vectors. Then

$$\kappa^2 = \rho^2 + \sigma^2 - 2\rho\sigma\mu. \quad (34)$$

The limits of integration should limit κ to the first Brillouin zone, but this does not affect δ_i , which depends only on the residue at $\rho = \sigma$.

Now, estimating the inner integral by the formula

$$\int_{-1}^{+1} f(\mu) d\mu \cong 2f(0), \quad (35)$$

$$\delta_i \cong \sqrt{2}\pi A \sigma^2 / (2\sigma^2 + \lambda^2)^2 \quad (36)$$

$$= \frac{s}{v} \frac{\sqrt{2}\pi\lambda^4}{(2\sigma^2 + \lambda^2)^2} \frac{\sigma_F^3 V}{6\pi^2 N Z}, \quad (37)$$

from Eqs. (23), (27), and (33). For monovalent metals the last factor, evaluated at the Fermi surface, is

$$\sigma_F^3 V / 6\pi^2 N = \frac{1}{2}, \quad (38)$$

since this is just the ratio of the volume of the Fermi sphere to that of the first Brillouin zone. Hence in general the ratio δ_i/ϵ_i is of the order s/v , since the screening constant λ is comparable in magnitude to σ_F .

The final result for the scattering matrix element is Eq. (29), with the denominator $\epsilon_a - \epsilon_i$ replaced by $\epsilon_a - \epsilon_i - i\delta_i$. This matrix element characterizes an interaction between the electronic ground state, in the lattice state such that n_{κ} phonons are in the longitudinal normal mode κ , and a state in which an electron has been excited from orbital ϕ_i to orbital ϕ_a , with only $n_{\kappa}-1$ phonons remaining in mode κ . If these Born-Oppenheimer states are degenerate, with

$$\hbar\omega_{\kappa} = \epsilon_a - \epsilon_i, \quad (39)$$

this matrix element results in a finite rate of transition between the two states. The transition is described physically as the scattering of an electron from σ_i to σ_a , with absorption of a phonon of longitudinal mode κ . There is an analogous process with emission of a phonon of mode $-\kappa$. Since they occur between nondegenerate Born-Oppenheimer states as well, the scattering matrix elements will also modify the stationary states of the electron-lattice system.

Equation (29) is valid in exactly the same form for matrix elements between any electronic excited state in which orbital ϕ_i is occupied, and another state in which orbital ϕ_i is replaced by ϕ_a . For states near the ground state, the change in the denominator is approximated by $-i\delta_i$, from Eq. (37), and with this the formula of Eq. (29) describes the electron-lattice interaction in all states of importance at low temperatures.

V. DISCUSSION

The quantum theory of the electrical conductivity of metals is reviewed in detail in the book by Wilson.⁸ One conclusion that can be drawn is that even for the

monovalent metals the quantitative agreement between theory and experiment is poor. Part of this discrepancy can be corrected by a more consistent treatment of the departure from thermal equilibrium of both electrons and lattice, as in recent work by Hanna and Sondheimer.¹³ However, it is clear that the form of the electron-lattice interaction, on which detailed calculations have been based, must be modified as indicated in the present paper. This interaction, as developed in the classical paper by Bardeen,¹¹ and used for calculations of electrical resistivity,¹⁴ is attributed directly to the matrix elements of Eq. (15). This is incorrect, since these matrix elements describe only the adiabatic changes in the electronic wave function, following the lattice motion, not the Jahn-Teller effect that describes a physical scattering phenomenon.

Since q_k occurs in one equation and p_k in the other, the ratio between the correct matrix elements, Eq. (29), and those used in the usual theory is

$$\hbar\omega_k/(\epsilon_a - \epsilon_i - i\delta_i). \quad (40)$$

As a result of the energy conservation condition, Eq. (39), this ratio is unity for scattering matrix elements unless $\epsilon_a - \epsilon_i$ is small. When $\epsilon_a - \epsilon_i$ is small, however, the magnitude of the ratio given in Eq. (40) can become smaller than unity. This can be expected to have a significant effect on the quantitative results of calculations of electrical resistivity due to the electron-lattice interaction.

It should be pointed out that there is a close relationship between the present derivation and the field theoretical derivation by Bardeen and Pines.¹⁰ Following Fröhlich¹⁵ and Nakajima,¹⁶ Bardeen and Pines carry

out a canonical transformation of the electron and electron-lattice Hamiltonian ($H_e + H_{ne}$ here), using a unitary operator that depends on both coordinates and momenta of the lattice modes. The transformation removes the electron-lattice coupling term and modifies the nuclear Hamiltonian and electron-electron interaction. They include an electron-electron Coulomb interaction as a separate term, and conclude that its effect should be small. Their transformation cannot be carried through exactly, and terms arising from degenerate states are omitted. The physical scattering responsible for electrical resistivity is attributed to these terms and is not treated in detail.

The present treatment can also be considered as a canonical transformation of $H_e + H_{ne}$, but with a unitary operator, given by Eqs. (1) and (2), that depends on the normal mode coordinates only. The electron-electron interaction is included in H_e . Effects that arise from the normal mode momenta are evaluated by perturbation theory, after the original canonical transformation. The physical scattering of electrons by lattice vibrations can be examined in detail, and leads to the matrix elements of Eq. (29).

The additional phenomena peculiar to superconductors at low temperatures, that follow from the development of Bardeen and Pines, must also be expected to follow from the present formalism. Such effects will be examined in later papers, where the modification of the stationary states of the electron-lattice system due to the electron-lattice interaction of Eq. (29) will be investigated.

ACKNOWLEDGMENTS

The author is indebted to Professor R. Daudel for his hospitality during a prolonged visit to the Centre de Mécanique Ondulatoire Appliquée in Paris, to the National Cancer Institute for a fellowship, and to Dr. S. Bratoz for several valuable discussions.

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