

Adiabatic perturbation theory for metals and the problem of lattice stability

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Electron-phonon interaction in metals is considered on the basis of quantum-mechanical perturbation theory, which is fully equivalent to the adiabatic expansion. An appropriate diagram technique is used. The dependence of the electron-phonon matrix elements on the phonon momentum is analyzed in various models. Results of calculations are presented for corrections to the vertices, for the energy spectra of the electrons and phonons, and for the phonon damping. It is shown that even though the adiabatic phonon frequency is renormalized very little as a result of nonadiabatic and anharmonic terms, its value depends significantly on the electron-phonon interaction. This dependence, however, does not lead to a possible lattice instability at a sufficiently large value of the electron-phonon interaction parameter, as in the Fröhlich model, since it corresponds only to a transition from an optical dispersion law, in the absence of interaction of the electron and phonons, to an acoustic dispersion law when this interaction is taken into account. The Fröhlich model in its literal form cannot be obtained from the exact Hamiltonian of the system, but it is possible to choose a zero-order Hamiltonian such that the form of the electron-phonon interaction Hamiltonian coincides, accurate to small terms, with the form of this operator in the Fröhlich model. It turns out here that the nonrenormalized phonon frequency is described not by an acoustic dispersion law, as postulated in the Fröhlich model, but by an optical law, and is equal to the ion plasma frequency, as in the Bohm-Staver model of "bare" ions. Therefore even in this model allowance for the electron-phonon interaction leads only to a transformation of the optical dispersion law into an acoustic one, and cannot lead to lattice instability, i.e., to a decrease of the acoustic frequency all the way to zero.

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1. INTRODUCTION

As is well known, the adiabatic approximation, which is a regular expansion in the small parameter $\kappa = (m/M)^{1/4}$, is the most rigorous method not only in the theory of molecules, but also in the theory of metals (m and M are the masses of the electron and ion, respectively)^[1]. However, the adiabatic perturbation theory is much more complicated than ordinary quantum-mechanical perturbation theory, and its use in practical calculations entails great difficulties. Consequently, the Bloch-Fröhlich model is customarily used in different particular calculations in metal theory. This theory has no rigorous foundation, but offers great conveniences in the calculations, since it was formulated as an ordinary quantum-mechanical perturbation theory. In this model, the Hamiltonian of the electron-phonon system is assumed equal to the sum of the Hamiltonians of the free electron and phonon fields \mathcal{H}_0 , i.e., to the sum of the Hamiltonians of the noninteracting electrons moving in the periodic potential of the lattice and the Hamiltonian of the harmonic oscillations of the ions, as well as the Hamiltonian of the interaction between the ions, which is equated to the change of the potential acting on the electrons as a result of the displacement of the ions:

$$\mathcal{H}' = \sum_i [V(\mathbf{r} - \mathbf{R}_{0i} - \Delta \mathbf{R}_i) - V(\mathbf{r} - \mathbf{R}_{0i})] = \sum_i (\nabla_r V(\mathbf{r} - \mathbf{R}_{0i}), \Delta \mathbf{R}_i),$$

where $V(\mathbf{r} - \mathbf{R}_{0i})$ is the potential with which the i -th ion with equilibrium coordinate \mathbf{R}_{0i} acts on an electron with coordinate \mathbf{r} , and $\Delta \mathbf{R}_i$ is the displacement of the ion from the equilibrium position. In the Fröhlich model it is postulated that the nonrenormalized frequency of the phonons, i.e., the frequency of the free phonon field $\omega_0(\mathbf{q})$ at small phonon wave vectors \mathbf{q} , is described by an acoustic dispersion law. Ziman^[2] proved back in 1955 that the Bloch-Fröhlich model in conductivity theory, i.e., in the calculation of the matrix element of the transition of an electron from a state with momentum \mathbf{k} to a state with momentum \mathbf{k}' followed by emission or absorption of a phonon, is equivalent to the adiabatic theory. Subsequently, the question of the energy of the electron-phonon system and of the energy spectra of excitations in this system has attracted particularly great interest. Attempts were made to prove the equivalence of both theories also in this respect, but actually there is no such equivalence, as will be explained below. An exact calculation within the framework of the Fröhlich model, based on summation of all the essential diagrams^[3] (approximate perturbation-theory estimates were given in^[4-6]) has led to two

important results: 1) the initial electron velocity v_0 on the Fermi surface, owing to the electron-phonon interaction \mathcal{H}'_F , is changed (renormalized) by the amount $1 + \zeta_0$: $v = v_0 / (1 + \zeta_0)$, where ζ_0 is the dimensionless Fröhlich parameter characterizing the electron-phonon interaction, $\zeta_0 < 1$; at the same time, a renormalization takes place in the chemical potential $\mu - \Delta\mu \sim \zeta_0 \omega_D$, where ω_D is the Debye frequency; 2) at small q (for simplicity, only the interaction of the electrons with longitudinal phonons and an acoustic dispersion for $\omega_0(q)$ were considered) the phonon frequency with allowance for interaction, $\omega(q)$, is expressed in terms of the nonrenormalized (zereth) frequency $\omega_0(q)$ in accordance with the formula $\omega(q) = \omega_0(q) \sqrt{1 - 2\zeta_0}$. Obviously, the velocity of the longitudinal sound $u_l = u_{l0} \sqrt{1 - 2\zeta_0}$, is expressed in the same manner. Therefore $\omega(q)$ becomes pure imaginary at $\zeta_0 > 1/2$, i.e., the lattice becomes unstable. Thus, the maximum possible value of ζ_0 turns out to be $1/2$. Within the framework of the Bardeen model, according to the microscopic theory of superconductivity (the so-called weak-coupling theory), the critical temperature of the superconductor T_C is determined by the well-known formula $T_C = 1.14\hbar\omega_D \exp(-1/\zeta_0)$. Therefore the maximum possible value of T_C for a given ω_D is $T_C \max = 1.14\hbar\omega_D e^{-2}$. The existence of this limiting value of T_C is in qualitative agreement with the experimental facts.

However, this concept of limiting value of ζ_0 , connected with the onset of lattice instability, has soon encountered two contradictions.

1) In the more exact formula obtained in^[7] for T_C , the electron-phonon interaction parameter, designated λ in^[7], enters in a more complicated manner. It turned out here that for certain superconductors λ greatly exceeds $1/2$, for example $\lambda = 1.1-1.3$ for Pb, $\lambda = 1.6$ for Hg, and $\lambda = 2.25$ for Ga; of course, the experimental data indicating that T_C has a certain upper bound still remain in force.

2) It was shown in^[8] that if we start with a consistent adiabatic theory, rather than the intuitive Fröhlich model, then the result concerning the renormalization of v_0 remains valid, and the renormalization of the phonon frequency turns out to be negligibly small, $\sim \kappa^4$. It was therefore deduced that the conclusions made in^[8] with respect to a possible instability of the lattice in the case of strong electron-phonon interaction is unfounded.

This was followed by the question of the extent to which the other results obtained on the basis of the Fröhlich model can be trusted, and whether the Fröhlich-Bloch Hamiltonian can be rigorously obtained from the complete Hamiltonian of this system of electrons and ions. To this end it was necessary to compare the Fröhlich model with adiabatic perturbation theory. But whereas the Fröhlich model constitutes an ordinary quantum-mechanical perturbation theory, the adiabatic theory, as is well known, has an essentially different structure, and consequently a direct comparison of the two theories is quite difficult. It was possible, however, to construct on the basis of the adiabatic theory an ordinary quantum-mechanical perturbation theory with a zero-order Hamiltonian that depends, in contrast to the adiabatic theory, simultaneously on the electron and on the ion variables^[9]. Although this theory is quite different in structure from the adiabatic

theory in its canonical form, the two theories are quite equivalent in their results. The adiabatic approximation in the form of a quantum-mechanical perturbation theory permits the use of a standard diagram technique, but one characterized by the presence of vertices with not only one but with two and more phonon ends. In particular, this gives rise, besides the corrections to the vertex with one phonon and, obtained in^[3], also to additional corrections that have the same order of smallness $\sim \kappa^2$. The perturbation operator \mathcal{H}' has a peculiar form and differs noticeably from the perturbation operator \mathcal{H}'_F in the Fröhlich model. Therefore, although the phonon frequency, to the extent that it coincides with the adiabatic value even in the zeroth-order approximation, is very little renormalized (if account is taken of the anharmonicity, then the renormalization is of the order of κ^2 and not κ^4), but the interaction forces between the electrons turns out to be large, on the order of ζ_0 .

In this article, which is devoted to a clarification of the theory of metals, are presented the main results of the papers devoted to this question; principal attention is paid to the question of the limits of applicability of the Fröhlich model in the theory of metals.

It is shown in^[9] that the Fröhlich model with $\mathcal{H}' = \mathcal{H}'_F$ cannot be obtained from the exact complete Hamiltonian of the system regardless of the choice of the zero-order operator. The perturbation operator closest to \mathcal{H}'_F can be obtained nevertheless for a definite form of the potential energy $U_i(\Delta\mathbf{R})$ of the ion oscillations in \mathcal{H}_0 , which differs significantly from the form of U_i in the adiabatic theory (see formulas (27) and (28) in the Fröhlich model, the form of U_i remains unknown). This potential energy, however, corresponds to a zero-point frequency equal to the ion plasma frequency, and not to the acoustic frequency as postulated in the Fröhlich model. Therefore, although allowance for the perturbation, which in this theory is not small (close to \mathcal{H}'_F) yields for the renormalized (i.e., adiabatic) frequency a formula of the same type as in the Fröhlich model, namely $\omega_{ad}(q) = \omega_0(q) \sqrt{1 - (\overline{\omega}^2/\omega_0^2)}$, this leads only to a transition from an optical to an acoustic dispersion law for arbitrary ζ_0 , inasmuch as ω_0 is the ion plasma frequency (this was already known earlier in the so-called model of "bare" ions^[10-13], and not to a vanishing of the frequency. Thus, the conclusion that the lattice may become unstable via such a mechanism is unfounded in the Fröhlich model.

Of course, this conclusion does not concern other possible instability mechanisms, such as the so-called Peierls doubling, martensitic transformations in compounds of the A-15 type, Mott transition, etc.

In spite of the fact that the Fröhlich model in its literal form does not agree with the complete Hamiltonian of the system of electrons and ions, many important results obtained within the framework of the Fröhlich model and determined directly by the perturbation \mathcal{H}'_F still turn out to be correct. These include the equation of the pairing self-energy part Σ_2 and the superconducting gap, the value of the matrix element for the transition of an electron with emission or absorption of a phonon in the theory of the conductivity of metals, the value of the energy-dependent part of the mass operator Σ_1 , the renormalization of the electron velocity v_0 , and the magnitude of the electron-electron forces due to exchange of virtual phonons. All these quantities

contain only the real phonon frequency $\omega(\mathbf{q})$ in place of the zero-point frequency $\omega_0(\mathbf{q})$.

An essential role in the calculation of the corrections to the energy of the electron and phonon is played by the form of the electron-phonon matrix elements and their dependence on the phonon momentum. This article contains an analysis of this dependence and an explanation of the disparities between the relative forms of the matrix elements in different models.

It is also shown in the article that the upper limit for the critical temperature T_c of the superconductor is connected with the fact that there exists a value ξ_0 max, equal to $\frac{1}{2}$, since the formula for T_c contains not ξ_0 but ξ (or $\lambda = \xi \langle \sum_{\nu=1}^3 u_\nu^2 q^2 \gamma_\nu \omega_\nu^{-2}(\mathbf{q}) \rangle_{av}$ for a real dispersion law; see (31)), which can assume arbitrary values. The upper limit for T_c is connected with the renormalization of the pairing self-energy part Σ_2 and the gap. An investigation of the ordinary and pairing self-energy parts Σ_1 and Σ_2 shows that they (and consequently also the electron effective mass and the critical temperature) have a noticeable singularity as functions of the Fermi momentum $p_F \approx \hbar n^{1/3}$, and consequently of the electron density n at $2p_F = q_0$ (q_0 is the maximum phonon momentum).

2. ADIABATIC EXPANSION FOR METALS

We consider first the usual adiabatic perturbation theory^[1].

The Schrödinger equation for a system of electrons with coordinates \mathbf{r}_i and of ions with coordinates \mathbf{R}_i takes the symbolic form

$$\begin{aligned} (\mathcal{H}_e + \mathcal{H}_i + \mathcal{H}_{ei}) \Psi(\mathbf{r}, \mathbf{R}) &= E \Psi(\mathbf{r}, \mathbf{R}); \\ \mathcal{H}_e &= \sum_i^N \frac{p_i^2}{2m}, \quad \mathcal{H}_i = \sum_j^N \frac{p_j^2}{2M}, \\ \mathcal{H}_{ei}(\mathbf{r}, \mathbf{R}) &= V(\mathbf{r}, \mathbf{r}) + V(\mathbf{R}, \mathbf{R}) + V(\mathbf{r}, \mathbf{R}) \end{aligned} \quad (1)$$

is the total potential energy. We assume that $V(\mathbf{R}, \mathbf{R})$ and $V(\mathbf{r}, \mathbf{R})$ take into account the potential of the ions with the electrons of the filled shells. We neglect here the reaction of the conduction electrons on the inner electrons, which are rigidly bound to the nuclei within the framework of the adiabatic theory. This approximation is sufficiently accurate because of the presence of a forbidden band.

Since the ion kinetic energy \mathcal{H}_i is smaller by a factor κ^2 than the electron energy, it is neglected in the zeroth approximation of the adiabatic theory, and the following equation is considered^[1]:

$$(\mathcal{H}_e + \mathcal{H}_{ei}) \psi_m(\mathbf{r}, \mathbf{R}) = E_m(\mathbf{R}) \psi_m(\mathbf{r}, \mathbf{R}). \quad (2)$$

The complete Ψ function can be sought in the form of an expansion in a complete orthogonal system of functions $\psi_m(\mathbf{r}, \mathbf{R})$; $\Psi_n(\mathbf{r}, \mathbf{R}) = \sum_m \Phi_{nm}(\mathbf{R}) \psi_m(\mathbf{r}, \mathbf{R})$; the symbol n indicates that we are seeking the complete Ψ function pertaining to the n -th electronic state, in which the term with $m = n$ is the principal one.

Substituting this series for Ψ_n in (1), multiplying by ψ_n^* , and integrating with respect to \mathbf{r} , we obtain

$$\begin{aligned} (\mathcal{H}_e + E_n^0) \Phi_n + \sum_m C_{nm} \Phi_m &= E_n \Phi_n, \\ \Phi_n &= \Phi_{nn}, \quad E_n^0 = E_n(\mathbf{R}), \quad C_{nm} = A_{nm} + B_{nm}, \\ A_{nm} &= -\frac{\hbar^2}{M} \sum_j^N \sum_\alpha^3 A_{nm\alpha}^j \frac{\partial}{\partial X_{j\alpha}}, \quad B_{nm} = -\frac{\hbar^2}{2M} \sum_j^N B_{nm}^j, \end{aligned} \quad (3)$$

$$A_{sm\alpha}^j = \int \psi_s^* \frac{\partial \psi_m}{\partial X_{j\alpha}} d\mathbf{r}, \quad B_{sm}^j = \int \psi_s^* \Delta_{R_j} \psi_m d\mathbf{r}, \quad d\mathbf{r} = \prod_i^N d\mathbf{r}_i.$$

Assuming that $\Phi_n \psi_n \ll \sum_{m \neq n} \Phi_m \psi_m$, we obtain by successive approximations an expression for Φ_n , with arbitrary accuracy^[1,8].

The equation for $\Phi_n \equiv \Phi_{n\nu}$ takes the form

$$\begin{aligned} (\mathcal{H}_i + U_{2n} + \mathcal{H}'_{pn}) \Phi_{n\nu} &= [E_{n\nu} - E_n(\mathbf{R}_0)] \Phi_{n\nu}, \\ \mathcal{H}'_{pn} &= (C_{nn} + \sum_{s \neq n} C_{ns} D_{sn} + \sum_{m \neq n} C_{ns} D_{sm} D_{mn} + \dots) \\ &\quad + (U_{3n} + U_{4n} + \dots), \quad D_{sm} = (E_n - \mathcal{H}_i - E_s^0)^{-1} C_{sm}, \\ U_{2n} &= \frac{1}{2} \sum_{ij}^N \sum_{\alpha\beta}^3 \frac{\partial^2 E_n(\mathbf{R})}{\partial X_{i\alpha} \partial X_{j\beta}} \Big|_{\mathbf{R}=\mathbf{R}_0} \Delta X_{i\alpha} \Delta X_{j\beta}, \\ U_{3n} &= \frac{1}{6} \sum_{ijk}^N \sum_{\alpha\beta\gamma}^3 \frac{\partial^3 E_n(\mathbf{R})}{\partial X_{i\alpha} \partial X_{j\beta} \partial X_{k\gamma}} \Big|_{\mathbf{R}=\mathbf{R}_0} \Delta X_{i\alpha} \Delta X_{j\beta} \Delta X_{k\gamma}, \end{aligned} \quad (4)$$

$\Delta X_{i\alpha} = X_{i\alpha} - X_{0i\alpha}$, and ν is the aggregate of the phonon quantum numbers. The expression for \mathcal{H}'_{pn} is given in^[8].

It is expedient to expand $\psi_n(\mathbf{r}, \mathbf{R})$ in (2) also in a series^[1] in powers of $\Delta X_{i\alpha}$ near the equilibrium positions \mathbf{R}_{0i} :

$$\psi_n(\mathbf{r}, \mathbf{R}) = \psi_n(\mathbf{r}, \mathbf{R}_0) + \sum_{i\alpha} \frac{\partial \psi_n(\mathbf{r}, \mathbf{R})}{\partial X_{i\alpha}} \Big|_{\mathbf{R}=\mathbf{R}_0} \Delta X_{i\alpha} + \dots = \psi_n^0(\mathbf{r}) + \psi_n^1(\mathbf{r}, \mathbf{R}).$$

Since $\partial \psi_n / \partial X_{i\alpha} \sim \psi_n / a$, a $[(\Delta X_{i\alpha})^2 / a^2]^{1/2} \sim a_0$, the second term is of the order of $a_0/d \sim \kappa$, the third of the order of κ^2 , etc., d is the lattice constant, $a_0 \sim \sqrt{\hbar/M\omega D}$ is the amplitude of the zero-point oscillations, and ωD is the Debye frequency. Therefore the corresponding terms in the expression for the Ψ function of the system must be included in the correction $\psi_{n\nu}^1$ to the Ψ function $\psi_{n\nu}^0$ of the zero-order approximation.

Then $\psi_{n\nu}^0 = \Phi_{n\nu}^0(\mathbf{R}) \psi_n(\mathbf{r}, \mathbf{R}_0)$, and the correction is

$$\begin{aligned} \psi_{n\nu}^1 &= \sum_{m \neq n} \Phi_{m\nu}(\mathbf{R}) \psi_m(\mathbf{r}, \mathbf{R}) + \Phi_{n\nu}^1(\mathbf{R}) \psi_n^1(\mathbf{r}, \mathbf{R}) \\ &\quad + \Phi_{n\nu}^2 \psi_n(\mathbf{r}, \mathbf{R}_0) + \Phi_{n\nu}^3 \psi_n^1(\mathbf{r}, \mathbf{R}), \quad \Phi_{n\nu}^1 = \Phi_{n\nu} - \Phi_{n\nu}^0 \sim \kappa \Phi_{n\nu}^0. \end{aligned}$$

Differentiating Eq. (2) with respect to $X_{j\alpha}$, multiplying then by ψ_n^* , and integrating with respect to \mathbf{r} , we obtain for $s \neq m$

$$A_{sm}^j = |\nabla_{R_j} \mathcal{H}_{ei}(\mathbf{r}, \mathbf{R})|_{sm} (E_m^0 - E_s^0)^{-1} \quad (5)$$

and using (5), we obtain

$$\begin{aligned} B_{sm}^j &= |\Delta_{R_j} \mathcal{H}_{ei}(\mathbf{r}, \mathbf{R})|_{sm} (E_m^0 - E_s^0)^{-1} \\ &\quad + 2 \sum_{r \neq m} [|\nabla_{R_j} \mathcal{H}_{ei}|_{sr} | \nabla_{R_j} \mathcal{H}_{ei}|_{rm} (E_m^0 - E_r^0)^{-1} (E_m^0 - E_s^0)^{-1} \\ &\quad + 2 \left(\left[\int \psi_m^* \nabla_{R_j} \psi_m d\mathbf{r} - |\nabla_{R_j} \mathcal{H}_{ei}|_{mm} (E_m^0 - E_s^0)^{-1} \right] | \nabla_{R_j} \mathcal{H}_{ei}|_{sm} \right). \end{aligned} \quad (6)$$

For $m = n$ we get

$$\begin{aligned} \frac{\partial^2 E_n(\mathbf{R})}{\partial X_{i\alpha} \partial X_{j\beta}} &= \left| \frac{\partial^2 \mathcal{H}_{ei}}{\partial X_{i\alpha} \partial X_{j\beta}} \right|_{nn} + \sum_{m \neq n} \left[\left| \frac{\partial \mathcal{H}_{ei}}{\partial X_{i\alpha}} \right|_{nm} \left| \frac{\partial \mathcal{H}_{ei}}{\partial X_{j\beta}} \right|_{mn} \right. \\ &\quad \left. + \left| \frac{\partial \mathcal{H}_{ei}}{\partial X_{j\beta}} \right|_{nm} \left| \frac{\partial \mathcal{H}_{ei}}{\partial X_{i\alpha}} \right|_{mn} \right] (E_n^0 - E_m^0)^{-1}. \end{aligned} \quad (7)$$

If we use the representation of the single-particle Bloch electron ψ functions $\psi_{\mathbf{k}} = e^{i(\mathbf{k}, \mathbf{r})} u_{\mathbf{k}}(\mathbf{r})$ ($u_{\mathbf{k}}(\mathbf{r})$ is a periodic function; the question of taking the Coulomb interaction into account will be considered later on), then

$$\begin{aligned} |\nabla_{R_j} \mathcal{H}_{ei}(\mathbf{r}, \mathbf{R}_0)|_{nm} &= |\nabla_{R_j} \sum_s V(\mathbf{r}_s - \mathbf{R}_{0j})|_{nm} = \mathbf{U}_{\mathbf{k}\mathbf{k}'}^j = e^{i(\mathbf{k}' - \mathbf{k}, \mathbf{R}_{0j})} \mathbf{U}_{\mathbf{k}\mathbf{k}'}, \\ \mathbf{U}_{\mathbf{k}\mathbf{k}'} &= - \int \psi_{\mathbf{k}}^*(\mathbf{r}_j) \nabla_{\mathbf{r}_j} V(\mathbf{r}_j) \psi_{\mathbf{k}'}(\mathbf{r}_j) d\mathbf{r}_j, \quad \mathbf{r}_j = \mathbf{r} - \mathbf{R}_{0j}. \end{aligned} \quad (8)$$

In the representation of single-particle functions,

expression (7) takes the form (for $R = R_0$)

$$\frac{\partial^2 E_n(R)}{\partial X_{i\alpha} \partial X_{j\beta}} \Big|_{R=R_0} = \sum_{\mathbf{k}} \left| \frac{\partial^2 V(\mathbf{r}-R_j)}{\partial X_{i\alpha} \partial X_{j\beta}} \right|_{\mathbf{k}\mathbf{k}'} \Big|_{R=R_0} \delta_{ij} n_{\mathbf{k}} \quad (9)$$

$$+ \frac{\partial^2 V(R_i - R_j)}{\partial X_{i\alpha} \partial X_{j\beta}} \Big|_{R=R_0} + \sum_{\mathbf{k}\mathbf{k}'} [U_{\mathbf{k}\mathbf{k}'}^i U_{\mathbf{k}'\mathbf{k}}^j + U_{\mathbf{k}\mathbf{k}'}^j U_{\mathbf{k}'\mathbf{k}}^i] (\varepsilon_{\mathbf{k}} - \varepsilon_{\mathbf{k}'})^{-1} n_{\mathbf{k}} (1 - n_{\mathbf{k}'})$$

where $E_n(R)$ is an eigenvalue of (2) and $n_{\mathbf{k}}$ are the electron occupation numbers.

In the last term of (9), the factor $n_{\mathbf{k}} - n_{\mathbf{k}'} n_{\mathbf{k}'}$ under the summation sign can be replaced by $n_{\mathbf{k}}$ or, in the usual symmetrical form, by $(n_{\mathbf{k}} - n_{\mathbf{k}'})/2$, since the sum in the symmetrical term $n_{\mathbf{k}} n_{\mathbf{k}'}$ is obviously equal to zero, for when \mathbf{k} is replaced by \mathbf{k}' the denominator of the summed expression reverses sign, while the numerator remains unchanged.

3. ORDINARY PERTURBATION THEORY BASED ON THE ADIABATIC EXPANSION

The main practical shortcoming of the adiabatic theory is the impossibility of separating the zeroth-approximation Hamiltonian \mathcal{H}_0 , which depends simultaneously on \mathbf{r} and \mathbf{R} (and on \mathbf{R} not as on the parameters), to obtain its eigenfunctions, which take the form of the products $\psi_m(\mathbf{r}) \Phi_\nu(\mathbf{R})$, and to separate the perturbation operator $\mathcal{H}'(\mathbf{r}, \mathbf{R})$ in explicit form. This makes it impossible to develop an ordinary quantum-mechanical perturbation theory and to employ the standard diagram technique.

It is easily seen that this ordinary perturbation theory can be developed on the basis of the results of the adiabatic approximation^[9]. We seek the complete Ψ function pertaining to the n -th electronic state. The adiabatic zeroth-approximation function in this case (in the harmonic approximation for phonons) is known to us: $\Psi_{n\nu}^0 = \psi_n(\mathbf{r}, \mathbf{R}_0) \Phi_{n\nu}^0(\mathbf{R})$. Let us find a Hamiltonian that depends on \mathbf{r} and \mathbf{R} , one of the eigenfunctions of which is equal to $\Psi_{n\nu}^0$, and use it as the zeroth-approximation Hamiltonian.

Obviously,

$$\mathcal{H}_0(\mathbf{r}, \mathbf{R}) = \mathcal{H}_{0e}(\mathbf{r}) + \mathcal{H}_{0i}(\mathbf{R}),$$

$$\mathcal{H}_{0e} = \mathcal{H}_e + \mathcal{H}_{ei}(\mathbf{r}, \mathbf{R}_0), \quad \mathcal{H}_{0i} = \mathcal{H}_i + \frac{1}{2} \sum_{\substack{i\alpha \\ j\beta}} \frac{\partial^2 E_n(\mathbf{R})}{\partial X_{i\alpha} \partial X_{j\beta}} \Big|_{R=R_0} \Delta X_{i\alpha} \Delta X_{j\beta}, \quad (10)$$

$$\mathcal{H}_0(\mathbf{r}, \mathbf{R}) \Psi_{m\mu}^0(\mathbf{r}, \mathbf{R}) = E_{m\mu}^0 \Psi_{m\mu}^0(\mathbf{r}, \mathbf{R}), \quad \mathbf{R}_0 \equiv \mathbf{R}_{0n}.$$

As usual, the Fourier component of the Coulomb interaction potential $V_C(\mathbf{k})$ with $\mathbf{k} = 0$ can be set equal to zero, since it is cancelled out by the potential of the ions. Generally speaking, the remaining eigenfunctions $\Psi_{m\mu}^0$ of the complete orthogonal system, with the exception of $\Psi_{n\nu}^0$, have no real meaning, since the coordinates in (10) are equal to \mathbf{R}_{0n} for all m (and not to \mathbf{R}_{0m}), while the frequencies $\omega(\mathbf{q})$ are equal to $\omega^n(\mathbf{q})$ (and not to $\omega^m(\mathbf{q})$); but if two electronic functions differ from each other in that the momenta of s electrons have changed from \mathbf{k}_s to \mathbf{k}'_s , then the values of \mathbf{R}_{0m} and $\omega^m(\mathbf{q})$ for these will differ by an amount on the order of s/N , so that for states close to the ground state the dependence of \mathbf{R}_{0n} and of $\omega^n(\mathbf{q})$ on n can be neglected, and consequently all the $\Psi_{m\mu}^0$ have a direct physical meaning.

The perturbation operator \mathcal{H}' is obviously equal to

$$\mathcal{H}' = \mathcal{H} - \mathcal{H}_0 = -U_{2n} + \mathcal{H}_{ei}(\mathbf{r}, \mathbf{R}) - \mathcal{H}_{ei}(\mathbf{r}, \mathbf{R}_0) \quad (11)$$

$$= -U_{2n} + \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3 + \dots,$$

where

$$\mathcal{H}_1 = \sum_{i\alpha} \frac{\partial \mathcal{H}_{ei}}{\partial X_{i\alpha}} \Big|_{R=R_0} \Delta X_{i\alpha}, \quad \mathcal{H}_2 = \frac{1}{2} \sum_{\substack{i\alpha \\ j\beta}} \frac{\partial^2 \mathcal{H}_{ei}}{\partial X_{i\alpha} \partial X_{j\beta}} \Big|_{R=R_0} \Delta X_{i\alpha} \Delta X_{j\beta}$$

etc.

Using (7), we get

$$U_{2n} = |\mathcal{H}_2|_{nn} + \mathcal{H}_{2n}, \quad \mathcal{H}_{2n} = \sum_m |\mathcal{H}_1|_{nm}^2 (E_{0n} - E_{0m})^{-1}, \quad (12)$$

$$E_{0m} = E_m(\mathbf{R}_0).$$

Substituting (12) in (11), we obtain

$$\mathcal{H}' = \mathcal{H}_1 + \overline{\mathcal{H}}_2 - \mathcal{H}_{2n} + \sum_{m=3}^{\infty} \mathcal{H}_m, \quad (13)$$

here $\overline{\mathcal{H}}_2 = \mathcal{H}_2 - |\mathcal{H}_2|_{nn}$; $|\mathcal{H}_1|_{nn} = 0$, since

$$\frac{\partial E_n}{\partial X_{i\alpha}} \Big|_{R=R_0} = \left| \frac{\partial \mathcal{H}_{ei}}{\partial X_{i\alpha}} \right|_{R=R_0} = 0.$$

$|\mathcal{H}_2|_{nn}$ and \mathcal{H}_{2n} are operators with respect to the phonon degrees of freedom and are classical quantities with respect to the electron variables. The perturbation theory for \mathcal{H}' is obviously fully equivalent in its results to the adiabatic perturbation theory, although the two theories are different in structure. We note that the considered perturbation theory with \mathcal{H}' in the form (11) is perfectly applicable also in the case of overlapping bands, for unlike in the theory of molecules (the Jahn-Teller effect), the degeneracy for a metal, as is well known, is lifted already within the framework of the electronic problem alone (in the case of tight binding for the electrons see^[14,15]), and $E_n(\mathbf{R})$ is determined by the electrons of all the overlapping bands. As is well known, in the Fröhlich model the perturbation operator is equal to $\mathcal{H}' = \sum_{i\alpha} (\partial V(\mathbf{r}, \mathbf{R}) / \partial X_{0i\alpha}) \Delta X_{i\alpha}$, i.e., to the operator \mathcal{H}_1 without the term $\sum_{i\alpha} (\partial V(\mathbf{r}, \mathbf{R}) / \partial X_{0i\alpha}) \Delta X_{i\alpha}$,

which, however, is equal to zero in the presence of a symmetry center. Thus, (11) corresponds to the corrected Fröhlich-Bloch model, since now \mathcal{H}' is equal not simply to \mathcal{H}_1 but to $\mathcal{H}_1 + \overline{\mathcal{H}}_2 - \mathcal{H}_{2n} + \mathcal{H}_3 + \dots$, and the frequencies $\omega(\mathbf{q})$ in (10) are equal to the frequencies in the Debye approximation, since the potential energy of the oscillations $U_1(\Delta \mathbf{R})$ is equal to

$$\frac{1}{2} \sum_{\substack{i\alpha \\ j\beta}} \frac{\partial^2 E_n}{\partial X_{i\alpha} \partial X_{j\beta}} \Big|_{R=R_0} \Delta X_{i\alpha} \Delta X_{j\beta}$$

in accordance with the zeroth approximation of the adiabatic theory. Let us estimate the order of magnitude of the terms contained in \mathcal{H}' : $\mathcal{H}_2 \sim \mathcal{H}_{2n} \sim |\mathcal{H}_2|_{nn} \sim \hbar \omega_D$, like \mathcal{H}_1 ; $\mathcal{H}_1 \sim \hbar \omega_D / \kappa$; and further $\mathcal{H}_3 \sim \kappa \mathcal{H}_{s-1}$. The corrections to the energy $E_{m\mu}^0$ are calculated from the formulas of ordinary perturbation theory. It is easily seen that although $\mathcal{H}_1 \sim \hbar \omega_D / \kappa$ and $\overline{\mathcal{H}}_2 \sim \mathcal{H}_{2n} \sim \hbar \omega_D$, the first correction to the energy $E_{n\nu}^0$ is of the order of $\kappa^2 \hbar \omega_D$, just as in the adiabatic expansion. Indeed, we first take into account the correction from the terms \mathcal{H}_1 , $\overline{\mathcal{H}}_2$, and \mathcal{H}_{2n} . It is equal to the diagonal matrix element of $\overline{\mathcal{H}}_2$ and $-\mathcal{H}_{2n}$ and the second approximation of H_1 , since

$$|\mathcal{H}_1|_{n\nu}; n\nu = 0:$$

$$E_{n\nu}^I = |\overline{\mathcal{H}}_2|_{n\nu}; n\nu - |\mathcal{H}_{2n}|_{n\nu}; n\nu + \sum_{m, \mu} |\mathcal{H}_1|_{n\nu}; m\mu (E_{0n}^0 - E_{0m}^0)^{-1}.$$

From the definition of $\overline{\mathcal{H}}_2$ it follows that $|\overline{\mathcal{H}}_2|_{n\nu}; n\nu = 0$. Therefore

$$E_{n\nu}^I = \sum_{m, \mu} |\mathcal{H}_1|_{n\nu}; m\mu (E_{0n}^0 - E_{0m}^0)^{-1} - \sum_m |\mathcal{H}_1|_{n\nu}; m\nu (E_{0n}^0 - E_{0m}^0)^{-1}$$

$$= |\mathcal{H}_1 (E_{0n}^0 - \mathcal{H}_0)^{-1} \mathcal{H}_1|_{n\nu}; n\nu - \sum_m |\mathcal{H}_1|_{n\nu}; m\nu (E_{0n}^0 - E_{0m}^0)^{-1}. \quad (14)$$

Since the matrix elements of \mathcal{H}_1 are not diagonal in ν ,

the energy denominators of the first term in (14) will contain, in addition to the differences $E_{0n}^0 - E_{0m}^0$, also the terms $\pm \hbar\omega_{\mathbf{q}}$. Therefore $E_{n\nu 1}^I$ will be of the order of $\hbar\omega_{\mathbf{D}} |\mathcal{H}_{2n}|_{\nu\nu} / \epsilon_F \sim \kappa^2 \hbar\omega_{\mathbf{D}}$ ($\epsilon_F = p_F^2 / 2m$ is the Fermi energy). Indeed, substituting in (14) the formula (8) and the known expressions for ΔR_i in terms of the phonon amplitudes $b_{\mathbf{q}\lambda}$ [14, 16]

$$\Delta R_i = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}\lambda} e_{\mathbf{q}\lambda} (b_{\mathbf{q}\lambda} e^{i(\mathbf{q}, \mathbf{R}_{0i})} + \text{h.c.}) \sqrt{\frac{\hbar}{2M\omega_{\mathbf{q}\lambda}}},$$

$$[b_{\mathbf{q}\lambda}, b_{\mathbf{q}'\lambda'}^\dagger] = \delta_{\lambda\lambda'} \delta_{\mathbf{q}\mathbf{q}'}$$

($e_{\mathbf{q}\lambda}$ is the unit vector of the phonon polarization; N is the number of ions per unit volume), we obtain the first term in formula (14):

$$E_{n\nu 1}^I = \sum_{\mathbf{k}\mathbf{q}\lambda} |M_{\mathbf{k}\mathbf{q}\lambda}|^2 [(N_{\mathbf{q}\lambda} + 1) (e_{\mathbf{k}} - e_{\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\lambda})^{-1} + N_{\mathbf{q}\lambda} (e_{\mathbf{k}} - e_{\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\lambda})^{-1}] n_{\mathbf{k}} (1 - n_{\mathbf{k}+\mathbf{q}}) \quad (15)$$

and the second term

$$E_{n\nu 1}^{II} = - \sum_{\mathbf{k}\mathbf{q}\lambda} |M_{\mathbf{k}\mathbf{q}\lambda}|^2 (2N_{\mathbf{q}\lambda} + 1) (e_{\mathbf{k}} - e_{\mathbf{k}+\mathbf{q}})^{-1} n_{\mathbf{k}} (1 - n_{\mathbf{k}+\mathbf{q}}). \quad (16)$$

The summation over \mathbf{R}_{0i} yields $\delta_{\mathbf{k}' - \mathbf{k} + \mathbf{q} + \mathbf{g}}$; \mathbf{g} is the integer reciprocal-lattice vector multiplied by 2π ; we shall assume $\mathbf{g} = 0$.

It should be noted that (15) takes into account the electron-phonon interaction, and therefore the $n_{\mathbf{k}}$ in (16) can differ from (15) by an amount $\sim \kappa^2$, which we neglect here (see Appendix II).

In (15) and (16) we have introduced the Bloch matrix element $M_{\mathbf{k}\mathbf{q}\lambda}$:

$$M_{\mathbf{k}\mathbf{q}\lambda} = - \sqrt{\frac{\hbar N}{2M\omega_{\mathbf{q}\lambda}}} (e_{\mathbf{q}\lambda}, \mathbf{U}_{\mathbf{k}, \mathbf{k}+\mathbf{q}}). \quad (17)$$

This yields

$$E_{n\nu 1}^I = \sum_{\mathbf{k}\mathbf{q}\lambda} |M_{\mathbf{k}\mathbf{q}\lambda}|^2 n_{\mathbf{k}} (1 - n_{\mathbf{k}+\mathbf{q}}) (e_{\mathbf{k}} - e_{\mathbf{k}+\mathbf{q}})^{-1} (\hbar\omega_{\mathbf{q}\lambda} (e_{\mathbf{k}+\mathbf{q}} - e_{\mathbf{k}} + \hbar\omega_{\mathbf{q}\lambda})^{-1} - 2N_{\mathbf{q}\lambda} \hbar^2 \omega_{\mathbf{q}\lambda}^2 [(e_{\mathbf{k}+\mathbf{q}} - e_{\mathbf{k}})^2 - \hbar^2 \omega_{\mathbf{q}\lambda}^2]^{-1}), \quad (18)$$

$$E_{n\nu 1}^{II} \sim \kappa^2 \hbar\omega_{\mathbf{D}},$$

since

$$M_{\mathbf{k}\mathbf{q}\lambda} \sim \epsilon_F a_0 d \sim \kappa \epsilon_F, \quad \hbar\omega_{\mathbf{q}\lambda} (e_{\mathbf{k}} - e_{\mathbf{k}+\mathbf{q}})^{-1} (e_{\mathbf{k}+\mathbf{q}} - e_{\mathbf{k}} + \hbar\omega_{\mathbf{q}\lambda})^{-1} \sim \hbar\omega_{\mathbf{D}} \epsilon_F^2.$$

Thus, although each term in $E_{n\nu 1}^I$ is of the order of $\hbar\omega_{\mathbf{D}}$, their mutual cancellation causes $E_{n\nu 1}^I$ to be of the order of $\kappa^2 \hbar\omega_{\mathbf{D}}$, as in the adiabatic perturbation theory (see above). This cancellation of \mathcal{H}_{2n} and $|\mathcal{H}_{2n}|_{nn}$, and also of \mathcal{H}_{1n} and \mathcal{H}_{2n} , plays an essential role not only in the first-order perturbation-theory approximation, but also in the higher ones. If the energy denominators do not contain the electron energies but only the phonon energy, i.e., are of the order of $\hbar\omega_{\mathbf{D}}$ and not ϵ_F , then, inasmuch as $\mathcal{H}_{1n} \sim \hbar\omega_{\mathbf{D}} / \kappa$, and $\mathcal{H}_{2n} \sim \mathcal{H}_{2n} \sim \hbar\omega_{\mathbf{D}}$, the corrections in the next higher approximations for \mathcal{H}_{2n} and \mathcal{H}_{1n} may turn out to be of the order of $\hbar\omega_{\mathbf{D}}$. The energy denominators can be of the order of $\hbar\omega_{\mathbf{D}}$ only in the case when there exist nonzero matrix elements \mathcal{H}_{2n} and \mathcal{H}_{1n} which are diagonal in the electron quantum numbers n and are not diagonal in ν . From the definition of \mathcal{H}_{2n} it is seen that $|\mathcal{H}_{2n}|_{nn} = 0$; $|\mathcal{H}_{1n}|_{nn}$ is also equal to zero. However, the second-approximation operator of \mathcal{H}_{1n} , equal to $\mathcal{H}_{1n}^I (E_{n\nu}^0 - \mathcal{H}_{0n})^{-1} \mathcal{H}_{1n}$, which is of the order of $\hbar\omega_{\mathbf{D}}$ (since $E_{n\nu}^0 - \mathcal{H}_{0n} \sim \epsilon_F$), can have nonzero matrix elements that are diagonal in n and not diagonal in ν . But such a matrix element enters in any approximation, as can be readily seen, only in the form of the difference $|\mathcal{H}_{1n}^I (E_{n\nu}^0 - \mathcal{H}_{0n})^{-1} \mathcal{H}_{1n}|_{nn} - \mathcal{H}_{2n}$, which we have seen to be of the order of $\kappa^2 \hbar\omega_{\mathbf{D}}$. Consequently, in the

higher approximations the energy denominators for \mathcal{H}_{2n} and \mathcal{H}_{1n} will be of the order of ϵ_F . As to the higher approximations of \mathcal{H}_{3n} , \mathcal{H}_{4n} , etc., they cannot yield corrections of the order of $\hbar\omega_{\mathbf{D}}$, since $\mathcal{H}_{3n} \sim \kappa \hbar\omega_{\mathbf{D}}$, $\mathcal{H}_{4n} \sim \kappa^2 \hbar\omega_{\mathbf{D}}$, etc. Thus, the subtraction of \mathcal{H}_{2n} from $\mathcal{H}_{1n} + \mathcal{H}_{2n} + \mathcal{H}_{3n} + \dots$ in the expression for \mathcal{H}_{1n} plays a very important role.

We have calculated $E_{n\nu 1}^I$. The second term $E_{n\nu 1}^{II} \sim \kappa^2 \hbar\omega_{\mathbf{D}}$ consists of five terms:

1) First approximation of \mathcal{H}_{4n} ; $|\mathcal{H}_{4n}|_{n\nu}$; 2) second approximation of \mathcal{H}_{2n} ; 3) first approximation in \mathcal{H}_{1n} and first in \mathcal{H}_{3n} ; 4) first approximation in \mathcal{H}_{1n} (with subtraction of \mathcal{H}_{2n} ; see above) and first approximation in \mathcal{H}_{2n} ; 5) fourth approximation in \mathcal{H}_{1n} (also with the corresponding subtraction of \mathcal{H}_{2n} (see [9])). The next corrections of $E_{n\nu 1}$ are of the order of $\kappa^4 \hbar\omega_{\mathbf{D}}$ and higher. We shall see that to calculate the energy $E_{n\nu}$ with accuracy $\kappa^2 \hbar\omega_{\mathbf{D}}$ we must take into account in \mathcal{H}' [Eq. (13)] all the \mathcal{H}_{5n} up to \mathcal{H}_{4n} .

Variation of $E_{n\nu 1}$ with respect to $N_{\mathbf{q}\lambda}$ determines the nonadiabatic correction to the phonon frequency $\omega_{\mathbf{q}\lambda} - \Delta\omega_{\mathbf{q}\lambda}$. It is easily seen that $\Delta E_{n\nu 1}^{II}$ yields $\Delta\omega_{\mathbf{q}\lambda} / \omega_{\mathbf{q}\lambda} \sim \kappa^2$ even though $E_{n\nu 1}^I$ yields for $\Delta\omega_{\mathbf{q}\lambda} / \omega_{\mathbf{q}\lambda}$ a value of order κ^4 . It is also easily seen that the correction to the electron velocity v on the Fermi surface $\partial\Delta\epsilon_F / \partial p|_{p=p_F}$ due to the first term of (15) in $E_{n\nu 1}^I$ turns out to be of the order of ζv_0 both in calculations based on the Fröhlich model [3] and in the ordinary adiabatic theory [6]; here p_F is the Fermi momentum and ζ is the so-called Fröhlich parameter, defined by the formula

$$\zeta_{\lambda} = |M_{\mathbf{k}\mathbf{q}\lambda}^{\text{sc}}|^2 \frac{V m p_F}{2\pi^2 \hbar^4 \omega_{\mathbf{q}\lambda}}, \quad (19)$$

$M_{\mathbf{k}\mathbf{q}\lambda}^{\text{sc}} = M_{\mathbf{k}\mathbf{q}\lambda}$ with allowance for screening (see (23)); for an acoustic dispersion law we have $\zeta_l \equiv \zeta = \text{const}$, where the subscript l corresponds to the longitudinal branch.

So large a correction is due to the fact that the energy denominators in (15) contain $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} \pm \hbar\omega_{\mathbf{q}\lambda}$ and the region $|\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}}| < \hbar\omega_{\mathbf{D}}$ makes an appreciable contribution to v .

The interaction forces between the electrons via the phonons can be obtained in the usual manner within the framework of perturbation theory. The matrix element of the interaction of two electrons with initial momenta \mathbf{p}_1 and \mathbf{p}_2 and with final momenta \mathbf{p}_3 and \mathbf{p}_4 , due to exchange of virtual phonons (if the number of phonons is initially equal to zero), is equal to

$$M_{\mathbf{p}_1 \mathbf{p}_2; \mathbf{p}_3 \mathbf{p}_4} = M_1 + M_2,$$

$$M_1 = |\mathcal{H}_{1n}|_{\mathbf{p}_1 \mathbf{p}_2 N_{\mathbf{q}\lambda}=0; \mathbf{p}_3 \mathbf{p}_4 N_{\mathbf{q}\lambda}=1} \frac{|\mathcal{H}_{2n}|_{\mathbf{p}_3 \mathbf{p}_2 N_{\mathbf{q}\lambda}=1; \mathbf{p}_2 \mathbf{p}_1 N_{\mathbf{q}\lambda}=0}}{e_{\mathbf{p}_1} - e_{\mathbf{p}_3} - \hbar\omega_{\mathbf{q}\lambda}} + \frac{|\mathcal{H}_{1n}|_{\mathbf{p}_1 \mathbf{p}_2 N_{\mathbf{q}\lambda}=0; \mathbf{p}_1 \mathbf{p}_1 N_{\mathbf{q}\lambda}=1} |\mathcal{H}_{2n}|_{\mathbf{p}_1 \mathbf{p}_4 N_{\mathbf{q}\lambda}=1; \mathbf{p}_2 \mathbf{p}_4 N_{\mathbf{q}\lambda}=0}}{e_{\mathbf{p}_2} - e_{\mathbf{p}_4} - \hbar\omega_{\mathbf{q}\lambda}}, \quad (20)$$

$$\mathbf{p}_3 - \mathbf{p}_1 = \mathbf{p}_2 - \mathbf{p}_4 = \mathbf{q}, \quad e_{\mathbf{p}_1} - e_{\mathbf{p}_3} = e_{\mathbf{p}_2} - e_{\mathbf{p}_4},$$

$$M_2 = \frac{\sum_{\mu\nu} |\mathcal{H}_{1n}|_{\nu\nu; \mu\mu} |\mathcal{H}_{2n}|_{\mu\mu; \nu\nu}}{E_{n\nu}^0 - E_{n\mu}^0} + \sum_{\mu\nu} \left[\frac{|\mathcal{H}_{1n}|_{\nu\nu; \mu\mu} |\mathcal{H}_{2n}|_{\mu\mu; \nu\nu} |\mathcal{H}_{1n}|_{\mu\mu; \nu\nu}}{(E_{n\nu}^0 - E_{n\mu}^0) (E_{n\nu}^0 - E_{\mu\nu}^0)} + 2 \mp 1, 1 \right]$$

The terms $|\mathcal{H}_{2n}|_{nn}$ and $-\mathcal{H}_{2n}$ in \mathcal{H}' , which are numbers

in terms of the electron variables, make no contribution whatever to $M_{p_1 p_2; p_3 p_4}$. In the case of M there is no cancellation of the different terms, similar to that which existed for the correction to the energy of the system. The second term, which is connected with $\overline{\mathcal{H}}_2$, is smaller by a factor κ^2 than M_1 and can be neglected. On the other hand, the first term M_1 coincides with the matrix element obtained in the usual Fröhlich model. If the energy transfer is $|\epsilon_{p_1} - \epsilon_{p_3}| < \hbar\omega_D$, then M_1 is very large, on the order of ϵ_F , i.e., the interaction of the electrons turns out to be an essentially nonadiabatic effect. We consider below the electron interaction exactly, and not by perturbation theory (see expressions (22) and (23)).

In the matrix elements $|\mathcal{H}_S|_{mn}$, and in particular in M_{kq} it is necessary to take into account the Coulomb interaction between the electrons in the single-particle representation. Since the Coulomb interaction is not small, it cannot be accounted for by perturbation theory. The easiest way is to use a diagram technique. As shown in Appendix I (formulas (A.1)–(A.3)), it is necessary to put in this case in formulas (8), (9), and (15)–(18)

$$|M_{kq\lambda}|^2 = \frac{|M_{kq\lambda}^n|^2}{\epsilon(q, \omega_{q\lambda})}, \quad M_{kq\lambda}^n = -i \frac{4\pi Ze^2}{q} \sqrt{\frac{\hbar N}{2M\omega_{q\lambda}}} \left(e_{q\lambda}, \frac{q}{q} \right), \quad (21)$$

where $M_{kq\lambda}^n$ is the matrix element without allowance for screening, and $\epsilon(q, \omega) = 1 - V_{C0}(q)P(q, \omega)$ is the dielectric constant, where $V_{C0} \underset{q \rightarrow 0}{=} 4\pi e^2/q^2$; $P(q, \omega)$ is the so-called polarization loop, Z is the ion charge, and the crystal volume V is set equal to unity. In (21) it is possible to replace $\epsilon(q, \omega_{q\lambda})$ approximately by $\epsilon(q, 0) = 1 + (\kappa_D^2/q^2)$. Thus, one factor in the product $M_{kq\lambda}^* M_{kq\lambda}$ should be taken with allowance for screening, and the other without allowance for screening. The expression for the matrix element $|\mathcal{H}_2|_{mn}$ is given in Appendix I (A.8).

We have calculated the correction that must be introduced into the system energy to account for the electron-phonon interaction. The Coulomb repulsion between the electrons was considered only as the cause of the screening of the electron-phonon interaction. But the Coulomb repulsion makes, of course, also a direct contribution to the system energy. To calculate this contribution it is easiest to find the total effective interaction between the electrons, the so-called four-pole term, V_{eff} . As shown in Appendix I (formulas (A.4)–(A.6)), it is equal to the sum of the interaction V'_{ep} via the phonons, described by the expression for M_1 in (20), the screened Coulomb repulsion V_C , and the mixed term V_{epc} :

$$V_{\text{eff}} = V'_{ep} + V_C + V_{epc}, \quad V'_{ep} = \sum_{\lambda} [|M_{kq\lambda}^n|^2 D_{\lambda}(\omega, q)/\epsilon(q, \omega)], \quad (22)$$

$$V_C = V_{C0}(q)/\epsilon(q, \omega), \quad V_{epc} = V'_{ep} P(q, \omega) V_C,$$

$$D_{\lambda}(\omega, q) = \frac{2\omega_{q\lambda}}{\omega^2 - \omega_{q\lambda}^2 + i\delta}. \quad (23)$$

Since

$$V'_{ep} + V_{epc} = V_{ep} = \sum_{\lambda} |M_{kq\lambda}^{sc}|^2 (D_{\lambda}(\omega, q)),$$

it follows that

$$V_{\text{eff}} = V_C + V_{ep}, \quad M_{kq\lambda}^{sc} = \frac{M_{kq\lambda}^n}{\epsilon(q, \omega)};$$

D_{λ} is the phonon Green's function.

Thus, owing to the presence of a mixed term, both the total electron-phonon interaction obtained from the four-pole term after subtracting the screened Coulomb repulsion and the correction to the electron energy contain a factor $|M^n|^2/\epsilon^2$, which behaves like q^2/ω_q as $q \rightarrow 0$, rather than $|M^n|^2/\epsilon$, as in the correction $\Pi = |M^n|^2 P/\epsilon$ to the phonon energy (see (A.2)).

On the basis of the ordinary perturbation theory developed above, which is based on an adiabatic expansion, we can construct a standard diagram technique; it is described in Appendix II.

Although in the adiabatic theory, as we have seen, the corrections to the system energy and to the vertices (see Appendix II) are expansions in powers of κ^2 , nevertheless, owing to the nonadiabatic behavior of the electrons in a thin layer of thickness on the order of $\hbar\omega_D$ near the Fermi surface, the correction to the total Ψ function of the system may not turn out to be small. This is the cause of such nonadiabatic effects as the large value of the constant for the interaction of the electrons via phonons and the renormalization of the electron velocity on the Fermi surface, on the order of ξ .

We have seen that the perturbation operator \mathcal{H}' in our perturbation theory [Eqs. (11) and (13)] has a complicated structure and constitutes a series in powers of κ , with terms describing the electron-phonon interaction and the pure phonon interaction. The peculiarity of the operator \mathcal{H}' is that its leading term $-\mathcal{H}_1$ is of the order of $\hbar\omega_D/\kappa$, and only the next term is of the order of $\hbar\omega_D$, whereas the energy of the lattice vibrations in the zero-order Hamiltonian is of the order of $\hbar\omega_D$. Although the largest correction to the system energy turns out to be, nevertheless, of the order $\kappa^2 \hbar\omega_D$, while the next terms are of order $\kappa^4 \hbar\omega_D$, etc., i.e., they do not contain nonadiabatic terms, nevertheless the more subtle characteristics of a metal, which are determined directly by the operator \mathcal{H}_1 in \mathcal{H}' , namely the correction Ψ' to the Ψ function, the matrix element $M_{kq\lambda}$ for the transition of an electron with emission of a phonon ($\sim \hbar\omega_D/\kappa$), the electron-electron interaction via virtual phonons ($\sim \epsilon_F$ at $|\epsilon_{p_3} - \epsilon_{p_1}| < \hbar\omega_D$), the self-energy part Σ_1 ($\sim \hbar\omega_D$), and the renormalization of the electron velocity on the Fermi surface ($\sim \xi$), all turn out to be large (see Appendix II). The values of these nonadiabatic quantities increase additionally if they are not determined by integrals over the entire Fermi sphere, but the principal contribution to them is made by a layer of nonadiabatic electrons of thickness $\hbar\omega_D$ near the Fermi surface.

4. THE FRÖHLICH MODEL AND LATTICE STABILITY

As is well known, from calculations based on the Fröhlich model it follows that at small q the renormalized frequency $\omega_l(q)$ for longitudinal phonons is given by $\omega_l(q) = \omega_l 0(q) \sqrt{1 - 2\xi_0}$, where ξ_0 is defined by formula (19) with $\omega(q)$ replaced by $\omega_0(q)$, where $\omega_0(q)$ is the nonrenormalized frequency; it is assumed here that $\omega_0 = u_0 q$ as $q \rightarrow 0$, i.e., that $\omega_0(q)$ is described by an acoustic dispersion law. The lattice should thus become unstable at $\xi_0 \geq 1/2$. We have seen above, however, that within the framework of the adiabatic theory the phonon frequency is renormalized as a result of the nonadiabatic and anharmonic terms only by a small amount, on the order of κ^2 .

We can therefore conclude that the deduced lattice instability at $\zeta_0 \geq 1/2$ is illusory^[8]. However, this conclusion must not be regarded as fully warranted beforehand, since the nonrenormalizing adiabatic frequency itself can depend significantly on the parameter ζ_0 and can vanish at sufficiently large ζ_0 .

Indeed, it follows from (7) that the adiabatic force matrix $(\partial^2 E_n^0 / \partial X_{0i\alpha} \partial X_{0j\beta})$ is equal to the sum of the positive-definite matrix $\{\mathcal{H}_2\}_{nn} / (\Delta X_{i\alpha} \Delta X_{j\beta})$ and the negative-definite matrix $\mathcal{H}_2 n / (\Delta X_{i\alpha} \Delta X_{j\beta})$ (the denominators $E_{0n}^0 - E_{0m}^0$ are negative, since E_n^0 is the energy of the ground state). Using (9) and the known formula for the frequency^[16]

$$\omega_{q\lambda}^2 = \sum_{\alpha\beta} e_{q\lambda\alpha} D_{\alpha\beta}(q) e_{q\lambda\beta}, \quad D_{\alpha\beta}(q) = \frac{1}{M} \sum_{R_{0ij}} \Phi_{\alpha\beta}(R_{0ij}) e^{-i(q, R_{0ij})}, \quad (24)$$

$$\Phi_{\alpha\beta}(R_{0ij}) = \frac{\partial^2 E_n^0}{\partial X_{0i\alpha} \partial X_{0j\beta}},$$

we obtain for the longitudinal frequency the expression

$$\omega_l(q) = \omega_{l0}(q) \sqrt{1 - (\bar{\omega}^2 / \omega_{l0}^2)}, \quad (25)$$

i.e., an expression of the same type as in the Fröhlich model with $2\zeta_0 = \bar{\omega}^2 / \omega_{l0}^2$. In this case

$$\bar{\omega}^2 = \sum_k \frac{2\omega_{q\lambda}}{\hbar} |M_{kq\lambda}|^2 (n_k - n_{k+q}) (\epsilon_{k+q} - \epsilon_k)^{-1} > 0$$

and is proportional to the square of the modulus of the matrix element of the electron-phonon interaction. However, ω_{l0}^2 is determined in accordance with (9) by the force matrix

$$\left| \frac{\partial^2 \mathcal{H}_{ei}}{\partial X_{0i\alpha} \partial X_{0j\beta}} \right|_{nn} = \sum_k \left| \frac{\partial^2 V(r-R_j)}{\partial X_{0i\alpha} \partial X_{0j\beta}} \right|_{kk} \delta_{ij} n_k + \frac{\partial^2 V(R_{0i} - R_{0j})}{\partial X_{0i\alpha} \partial X_{0j\beta}},$$

i.e., at $R_{0ij} \neq 0$ this matrix is determined only by the Coulomb repulsion of the ions alone. Since $V(R_{ij})_{R_{ij} \rightarrow \infty} = Z^2 e^2 / R_{ij}$, we obtain from (24) for ω_{l0} at small q , as in the model of "bare" ions^[10-13, 17-20],

$$\omega_{l0}^2 = \frac{4\pi Z^2 e^2 N}{M} + a^2 q^2 \quad (26)$$

(the term $a^2 q^2$ is connected with the behavior of $V(R_{ij})$ at small R_{ij}). Consequently, ω_{l0} is the plasma ion frequency and is thus described not by the acoustic dispersion law, as in the Fröhlich model, but by the optical dispersion law as $q \rightarrow 0$. Whether this can lead to a vanishing of $\omega_l(q)$ at large values of ζ_0 and to instability of the lattice can be easily resolved by calculating $\omega_l(q)$ from formula (25). We perform this calculation in a somewhat different manner, which makes it possible simultaneously to ascertain whether the Fröhlich model is justified.

A comparison of the Fröhlich model with the adiabatic approximation in its canonical form is difficult, but the task becomes easier if we use in (10)–(13) adiabatic theory in the form of ordinary quantum-mechanical perturbation theory.

We have seen that according to (13) the perturbation operator \mathcal{H}' for the adiabatic theory differs significantly from $\mathcal{H}' = \mathcal{H}_1$ in the Fröhlich model. Can we nevertheless find a zero-order Hamiltonian \mathcal{H}_0 , equal to the sum of the Hamiltonians of the noninteracting electron and phonon fields, such that the perturbation operator \mathcal{H}' (which is the difference between the exact Hamiltonian (1) and \mathcal{H}_0) is equal to \mathcal{H}_1 ? It is seen from (1), (10), and (13) that this is impossible, i.e., that the Fröhlich model in its literal form cannot be obtained from the exact Hamiltonian (1). It is possible, however, to choose \mathcal{H}_0 in such a way that the corrections to the system en-

ergy and the energy of the excitations, which are of the order of $\hbar\omega_D$, are determined only by the term \mathcal{H}_1 , just as in the Fröhlich model; the corrections of order $\kappa^2 \hbar\omega_D$ will be determined also by other terms in \mathcal{H}' . It is easy to see that in this case \mathcal{H}_0 should take the form^[9]

$$\tilde{\mathcal{H}}_0 = \mathcal{H}_e + \mathcal{H}_{ei}(r, R_0) + \tilde{\mathcal{H}}_{0i}, \quad \tilde{\mathcal{H}}_{0i} = \mathcal{H}_i + |\mathcal{H}_2\}_{nn}, \quad (27)$$

which corresponds to the choice of an entirely different force matrix in \mathcal{H}_{0i} than in (10). The perturbation operator is then

$$\tilde{\mathcal{H}}' = \mathcal{H} - \tilde{\mathcal{H}}_0 = \mathcal{H}_i + \mathcal{H}_2 + \sum_{s=3}^{\infty} \mathcal{H}_s, \quad (28)$$

and consequently, the correction to the energy is $E_{n\nu 1} = \sum_{\mu} |\mathcal{H}'_{1}|_{\nu\mu} \langle E_{n\nu}^0 - E_{n\mu}^0 \rangle^{-1} \sim \hbar\omega_D$, i.e., actually the

principal correction $\sim \hbar\omega_D$ is determined by the term \mathcal{H}_1 in $\tilde{\mathcal{H}}'$; the remaining terms in (28) yield corrections $\sim \kappa^2 \hbar\omega_D$ and higher.

Since we are starting from the exact Hamiltonian \mathcal{H} (1), in contrast to the Fröhlich model, the force matrix in \mathcal{H}_0 is known and, as shown above, the nonrenormalized longitudinal frequency ω_{l0} is determined by (26). Since $\tilde{\mathcal{H}}'$, according to (28), does not contain the small parameter κ , just as in the case (13), we cannot use perturbation theory; but if we are interested in corrections of order $\hbar\omega_D$ only to the energy of the excitations and the energy of the system, then we can sum all the essential diagrams, retaining only the term \mathcal{H}_1 in $\tilde{\mathcal{H}}'$. The electronic self-energy part Σ_1 and the phonon polarization operator Π (see Appendix II) will then be determined by Figs. 6 and 7, in which only the second diagrams are retained, while Σ_2 will be determined by Fig. 8 with only the first diagram, as in the model of "bare" ions (and in the Fröhlich model). For Π_l , according to (21) and (A.2), we then obtain^[21, 22]

$$\Pi_l = |M_{kq}^n|^2 P/e(q, \omega_l) = |M_{kq}^n|^2 V_c^0(q) (e^{-1}(q, \omega_l) - 1).$$

At small q this corresponds to the so-called "jellium" model, namely, M^n is determined by the expression (A.3). In this case $|M^n|^2 / \epsilon \sim 1/\omega_0(q)$. Therefore, determining $\omega(q)$ from the condition $D^{-1} = D_0^{-1} - \Pi = 0$, we obtain^[10]

$$\omega_l^2(q) = \frac{4\pi e^2 Z^2 N}{M} \left(1 - \frac{\epsilon - 1}{\epsilon}\right) + a^2 q^2 \approx \frac{4\pi Z^2 N e^2}{M \epsilon(q, 0)} + a^2 q^2 \approx \frac{4\pi e^2 Z^2 N}{M \epsilon_b} q^2 + a^2 q^2. \quad (29)$$

We can obtain a more accurate expression for $\omega_l(q)$ by using for the calculation of M^n a more exact expression for $V(R_{ij})$ than in (A.3), without confining ourselves to the high-density approximation in the calculation of P , and by calculating M^n , V_c^0 , and P with the aid of Bloch functions rather than plane waves. The frequency determined by an expression of the type (23) then coincides, accurate to terms of order $\kappa^2 \hbar\omega_D$, with the adiabatic frequency. As is well known, Eq. (29) leads to the existence of Kohn singularities for $\omega(q)$ at $q = 2\pi F$.

We see that the model that starts out from an exact Hamiltonian of the system of electrons and ions and is closest to the usual Fröhlich model coincides with the model of "bare" ions, which was considered earlier independently of the Fröhlich model. It is easily seen that the assumption on which the Fröhlich model is based, namely an acoustic dispersion law for the nonrenormalized longitudinal frequencies, and hence the assumption concerning the form of the perturbation operator $\mathcal{H}' = \mathcal{H}_1$, is in fact based on the assumption

that it is possible to choose independently the zero-order Hamiltonian and the perturbation operator. It is clear, however, that when the complete Hamiltonian is specified it is impossible to choose \mathcal{H}_0 and \mathcal{H}' independently. Of course, the choice of the zero-order Hamiltonian in the form (27) is not rational, since the perturbation operator, just as in the Fröhlich model, does not contain the small parameter κ , and consequently the correction to $\omega_l(q)$ and to the energy $E_{n\nu}$ turns out to be of the same order as the lattice-vibration energy in the zero-order Hamiltonians, and the frequencies $\omega_0(q)$ do not correspond even to the equilibrium positions of the ions, just as in the adiabatic theory. Whereas in the adiabatic theory the phonons are "dressed" already in the zero-order approximation, they are "bare" for \mathcal{H}_0 in the form (27).

Thus, the subtraction of $\bar{\omega}^2$ from ω_{l0}^2 cannot lead, just as in the Fröhlich model, to zero or imaginary values of $\omega_l(q)$, since $\omega_{l0}(q)$ is described not by an acoustic but by an optical dispersion law. It is typical, that (29) contains $(\epsilon - 1)/(2\epsilon) = \kappa_D^2/[2(\kappa_D^2 + q^2)]$, rather than ζ_0 . The reason is that the second diagram of Fig. 7 contains $|M^n|^2/\epsilon$ and not $|M^{SC}|^2 = |M^n|^2/\epsilon^2$ as the second diagram of Fig. 6 (see the Appendix); therefore the expressions for Σ_1 and Σ_2 contain ζ or $\lambda = \zeta \langle \sum_{\nu} u_l^2 q^2 \gamma_{\nu} / \omega_{\nu}(q) \rangle_{av}$ (see (31), (32), and Appendix II).

Since allowance for the electron-phonon interaction leads at any value of ζ_0 or ζ only to a transition from an optical dispersion law to an acoustic dispersion law, and not to the vanishing of $\omega_l(q)$, the conclusion of the possible instability of the lattice in the considered three-dimensional case, at large values of ζ_0 , turns out to be unwarranted in final analysis. This result, however, is not universal. For two-dimensional or one-dimensional systems, the situation changes greatly. In the one-dimensional case the ion plasma frequency is $\omega_0 q \approx \epsilon_0 u_0 q$ and $\epsilon(q, 0)$ is approximately constant. It can be shown that at low temperatures^[24a] (see also^[24b]) we have $2P|M^n|^2/\epsilon\omega_0 \approx -\tilde{\zeta} \ln(\epsilon_F/T)$. We therefore get from (25) $\omega = \omega_0 \sqrt{1 - \tilde{\zeta} \ln(\epsilon_F/T)}$, i.e., at sufficiently low temperatures the lattice can become unstable at any value of the parameter $\tilde{\zeta}$.

As is well known, there are other perfectly realistic mechanisms of lattice instability, such as the Mott transition of a dielectric into a metal, the so-called Peierls doubling, martensitic transformation in compounds of the A-15 type, which is close in its nature, according to the Labbe-Friedel and the Garko models^[23, 24a] to the Peierls transition, etc. The transitions of the latter type are connected with the fact that when the lattice symmetry changes electron energy is gained. They correspond to the quasi-one-dimensional picture (see above), and also lead to singularities of the phonon polarization operator. However, the instabilities in structural transitions of this type are outside the scope of the present article (see^[35]).

It should be noted that even if we assume, in contradiction to the Hamiltonian (1), that $\omega_{l0} = u_l q$ as $q \rightarrow 0$, then we obtain for the renormalized frequency the expression $\omega_l(q) = \omega_{l0}(q) \sqrt{1 - (2\zeta_0 \kappa_D^2 / q^2)}$, and not $\omega_l(q) = \omega_{l0}(q) \sqrt{1 - 2\zeta_0}$, since the second diagram of Fig. 7 contains $M^n M^{SC}$ rather than $|M^{SC}|^2$ as assumed in the Fröhlich-model calculations. We see that the use of the Fröhlich model with a nonrenormalized acoustic longitudinal frequency and with an interaction

of the type $|M^{SC}|^2$ leads to incorrect results in the calculation of the phonon spectrum.

5. ELECTRON-PHONON INTERACTION IN NORMAL AND SUPERCONDUCTING METALS

We now discuss some questions connected with superconductivity of metals. As shown in Appendix II (see Fig. 8), the equation for the pairing self-energy part Σ_2 , which determines the superconducting gap, is of the same form as in the Fröhlich model^[25]

$$\Sigma_2(p, \omega_n) = \frac{T}{(2\pi)^3} \sum_{\lambda, \omega_n'} \int \Gamma_i^\lambda(p, k, p-k) D_\lambda(p-k, \omega_n - \omega_n') \times \Gamma_i^\lambda(k, p, k-p) F^*(k) dk \quad (\hbar = 1), \quad D_\lambda(q) = \frac{-2\omega_{q\lambda}}{\omega_n^2 + \omega_{q\lambda}^2}, \quad (30)$$

$$F^* = \frac{\Sigma_2}{(G_0^{-1} - \Sigma_1)(G_0^{-1} - \Sigma_{1-}) + \Sigma_2^2}, \quad \Gamma_i^\lambda = M_{kq\lambda}^2, \quad \omega_n = (2n+1)\pi T.$$

The zero-order Green's function is $G_0 = (i\omega_n - \xi)^{-1}$; ξ is the energy of the free particle reckoned from the Fermi energy; $G_0 = G_0(-\omega_n)$, and $\Sigma_{1-} = \Sigma_1(-\omega_n)$. In formula (30), the expressions for the matrix element M^{SC} and for the D function contain everywhere the real phonon frequency, which coincides, as shown above, with the adiabatic frequency. It is easily seen, however, that were we not to use the adiabatic theory, but were we to start from the Hamiltonian \mathcal{H}_0 (27), when M^{SC} contains $\omega_0(q)$ rather than $\omega(q)$, then the zero-order frequency $\omega_0(q)$ would also drop out from Eq. (30) for Σ_2 and from the corresponding equation for Σ_1 (see (32)), and therefore Σ_1 and Σ_2 will contain in this case the parameter ζ and not ζ_0 . The reason is that in this model the D function takes the form $D_F = 2\omega_0(q)/[\omega^2 - \omega^2(q) + i\delta]$, and consequently $|M^{SC}(\omega_0)|^2 D_F = |M^{SC}(\omega)|^2 D$.

We change from integration with respect to q and $|\mathbf{k}|$ to integration with respect to q and ξ . We also take into account the dependence of M^{SC} on $\omega(q)$ for a real dispersion law in accordance with^[7], and then we obtain from (21) $P_{FF} |M^{SC}|^2 / (2\pi)^2 = -\zeta \gamma_\lambda(q) u_l^2 q^2 / 2\omega_{q\lambda}$; $\gamma_\lambda = (e_{q\lambda}, q/q)^2 \varphi(q)$, φ is a slowly varying function of q , $\varphi(0) = 1$ (see^[26]), and ζ is the Fröhlich parameter defined by Eq. (19). We then obtain from (30) an equation^[9, 26] for

$$\Delta(\omega_n) = \Sigma_2(\omega_n) / [1 - i f(\omega_n) / \omega_n], \quad f(\omega_n) = \Sigma_1 |_{\omega_n=0} - \Sigma_1(\omega_n)$$

$$\Delta(\omega_n) = \frac{\zeta T}{2Z(\omega_n) P_F} \sum_{\omega_n'}^{k_1} \int_0^3 q dq \sum_{\lambda} \{ u_l^2 q^2 \gamma_\lambda(q) / \omega_\lambda^2(q) \} \times \int d\xi \frac{\omega_\lambda^2(q)}{\omega_\lambda^2(q) + (\omega_n - \omega_n')^2} \frac{\Delta(\omega_n)}{\omega_n^2 + \xi^2 + \Delta^2(\omega_n)}, \quad (31)$$

$$Z(\omega_n) = 1 - i f(\omega_n) / \omega_n, \quad k_1 = \min(q_0, 2P_F).$$

The superconducting gap $\Delta(T)$, as is well known, is determined from the equation $\Delta(\omega)|_{\omega=\Delta(T)} = \Delta(T)$, where $\Delta(\omega)$ is the analytic continuation of $\Delta(\omega_n)$ to real continuous frequencies. It is seen from (31) that the dimensionless interaction constant is

$$\lambda_{eff} = \zeta \left\langle \sum_{\nu} \frac{u_l^2 q^2 \gamma_{\nu}}{\omega_{\nu}^2(q)} \right\rangle_{av} \left(1 + \frac{f(\omega)}{\omega} \right)^{-1} \Big|_{\omega=\Delta(T)},$$

where the averaging is over the phonon spectrum, and the value of $f(\omega)/\omega|_{\omega=\Delta(T)}$ is close to $f(\omega)/\omega|_{\omega=0}$, since $\Delta(T) \ll \omega_D$.

In the case of an acoustic dispersion law for $\omega_l(q)$, for a normal metal at $T = 0$, $f(\omega)$ takes the form,^[9]

$$\text{Re } f(\omega) = \frac{\zeta}{4P_F} \int_0^{k_1} \omega(q) \ln \left| \frac{\omega + \omega(q)}{\omega - \omega(q)} \right| q dq,$$

at $\omega \ll \omega_D$ $\text{Re } f = \zeta \omega k_1^2 / 4p_F^2 \equiv b\omega$, at $\omega \gg \omega_D$ $\text{Re } f = \zeta u^2 / k_1^4 / 8p_F^2 \omega$,

$$\text{Im } f = \begin{cases} \pi \zeta \omega^3 / 12 p_F^2 u^2, & \sqrt{\frac{m}{M}} \omega_D \ll |\omega| < \omega_D, \\ \pi \zeta \omega k_1^2 \text{sgn } \omega / 12 p_F^2, & |\omega| > \omega_D. \end{cases} \quad (32)$$

q_0 is the maximum phonon momentum, and u is the speed of sound. If we use the real dispersion law, then the parameter ζ is replaced by the quantity

$\lambda = \zeta \langle \sum_{\nu} u_{\nu}^2 q^2 \gamma_{\nu} / \omega_{\nu}^2(q) \rangle_{\text{av}}$.^[26,27] In the case of a superconductor, the correction for $f(\omega)$ is of the order of Δ^2 / ω_D^2 .

Thus, the dimensionless effective interaction constant turns out to be $\lambda_{\text{eff}} = \lambda / (1 + \lambda)$. This change is a consequence of the renormalization of Σ_1 and Σ_2 .

We see that inasmuch as the expression for $|M^{\text{sc}}|^2$ contains only the real phonon frequency, the parameter ζ_0 does not enter in the equation for the gap, and consequently in the equation for the critical temperature T_C . Equation (31) contains ζ for an acoustic dispersion law and λ for a real dispersion law. Therefore the upper limit of T_C can obviously not be connected with the maximum value of ζ_0 , which is equal to $1/2$, as assumed before. Besides the fact that this maximum value does not exist, even in the case of weak coupling ($\zeta \ll 1$) and in the case of an acoustic dispersion law for the phonon (real) frequency, T_C is determined by the formula $T_C = 1.14 \hbar \omega_D \exp(-\zeta^{-1})$ rather than $T_C = 1.14 \hbar \omega_D \exp(-\zeta_0^{-1})$. For a real dispersion law, ζ is replaced by the quantity $\lambda = \zeta \langle \sum_{\nu} [u_{\nu}^2 q^2 \gamma_{\nu} / \omega_{\nu}^2(q)] \rangle_{\text{av}}$ (see above). In the case of strong coupling, on the other hand, as we have seen from the renormalization of Σ_2 and Σ_1 , the interaction parameter is not λ but $\lambda_{\text{eff}} = \lambda / (1 + \lambda)$, which tends to unity even as $\lambda \rightarrow \infty$. According to^[7] it is this constant which determines the critical temperature (see also^[28]). The presence of a unity upper limit for λ_{eff} is the main cause of the upper limit of T_C . In (30) and (31) no account is taken of the Coulomb-repulsion effect, which decreases T_C , but allowance for this effect entails no difficulty (see^[7]).

Let us note one singularity in the behavior of the electron velocity on the Fermi surface and of the critical temperature as functions of the electron density n . According to (32), $\text{Re } \Sigma_1$ and $\text{Im } \Sigma_1$ have a nonanalytic behavior at the point $q_0 = 2p_F$, $p_F \sim \hbar^3 \sqrt{n}$. This singularity is of the Kohn type, but not for the polarization operator Π (and consequently for $\omega(q)$), and rather for the electron mass operator Σ_1 , and furthermore as a function of the parameter p_F rather than of the variable ω (Π , as is well known, has a singularity in the variable q). A similar dependence for Σ_1 is obtained also in the Einstein model with one frequency^[29] in the case of a real phonon spectrum, owing to the upper limit k_1 in (32). Actually, there is also Coulomb repulsion, and therefore $b = b_{\text{ph}} + b_{\text{c}}$. The nonanalytic dependence of b , and consequently also of the velocity $v = v_0 / (1 + b)$ on the Fermi surface, and of the effective mass m^* as a function of $p_F \sim \hbar n^{1/3}$, i.e., the discontinuity of the derivatives $\partial b / \partial n = \partial m^* / \partial n$, can be experimentally observed when the electron density n is varied (for example, by introducing impurities) in the tunnel experiments of Thomas and Rowell, and in measurements of the specific heat and of the cyclotron mass. A similar singularity of the Kohn type occurs also for Σ_2 in accordance with (31), owing to

the upper limit k_1 of the integral in (31), i.e., Σ_2 also has a nonanalytic dependence on n at the point $q_0 = 2p_F$. In^[28] we obtained a maximum of the critical temperature T_C as a function of n in the Einstein model; this maximum was the consequence of this singularity (see also^[29]). A similar nonanalytic dependence of Σ_2 and T_C should also be observed in the case of a real phonon spectrum. Allowance for the anisotropy and for Umklapp processes smooths this singularity out somewhat for Σ_1 and Σ_2 . It is possible that the experimentally observed^[30] nonmonotonic dependence of T_C on the pressure following introduction of impurities is connected not only with changes in the topology of the Fermi surface, but also with this Kohn-type singularity.

In conclusion, let us dwell on the conductivity of normal metals. On the basis of the canonical adiabatic perturbation theory, the matrix element A^{ad} of the transition of an electron from a state k to a state k' with absorption or emission of a phonon is given according to^[2] (see also^[8]) by

$$|A_{kk'}^{\text{ad}}|_{N_{q\lambda}, N_{q\lambda} \mp 1} = \mp \frac{\hbar \omega_{q\lambda}}{\epsilon_{k'} - \epsilon_k} M_{kq\lambda} (N_{q\lambda} + 1/2 \mp 1/2) \delta_{k', k \mp q} \quad (33) \\ = - \frac{\hbar \omega_{q\lambda}}{\epsilon_{k'} - \epsilon_k} U_{kN_{q\lambda}; k'N_{q\lambda} \pm 1}^{\text{B}}$$

where U^{B} is the matrix element in the Bloch model. Since $\epsilon_{k'} - \epsilon_k = \hbar \omega_{q\lambda}$, it follows that $A^{\text{ad}} = U^{\text{B}}$. Thus, the conductivity theory that employs the nonrigorous Bloch model turns out to be perfectly correct. The same result is obtained, of course, by using ordinary perturbation theory based on the adiabatic expansion in accordance with (10)–(13). The element $M_{kq\lambda}$ in (33) is determined by formulas (8) and (17), which correspond to the so-called rigid-ion model. As shown in Appendix II (A.7), for a real process this matrix element $M_{kq\lambda}$ is connected with the matrix element $M_{kq\lambda}^{\text{n}}$ without allowance for screening by the relation^[11,31]

$$M_{kq\lambda} = M_{kq\lambda}^{\text{n}} / \epsilon(q, \omega_q) \approx M_{kq\lambda}^{\text{n}} / \epsilon(q, 0), \\ M_{kq\lambda}^{\text{n}} \approx \frac{4\pi Z e^2}{iq} \sqrt{\frac{N\hbar}{2M\omega_{q\lambda}}} \left(e_{q\lambda}, \frac{q}{q} \right).$$

The proportionality of $M_{kq\lambda}$ to the quantity $q / \sqrt{\omega_q}$ as $q \rightarrow 0$, which is taken into account from the very beginning in the Bloch conductivity theory, is a direct consequence of the screening, i.e., of the Coulomb interaction of the electrons. Thus, the Coulomb repulsion between the electrons was in fact always taken into account in Bloch's theory, although it is customarily assumed that the interaction between the electrons is not taken into account in the usual formulation of conductivity theory.

6. APPLICATION TO MOLECULAR THEORY

The ordinary perturbation theory based on the adiabatic theory, developed in Chap. 5, and the diagram technique based on it (see Appendix II), can be fully applied to the theory of molecules, if there is no degeneracy or quasidegeneracy of the electronic states (the Jahn-Teller and Renner effects); in the latter case it is necessary to use the ordinary form of the adiabatic theory. In the case of molecules there are, however, certain differences: 1) \mathcal{H}_1 , as is well known, can be represented in the form of the sum $\mathcal{H}_1 = \mathcal{H}_{\text{vib}} + \mathcal{H}_{\text{rot}}$, where \mathcal{H}_{vib} is the kinetic energy of the vibrations and $\mathcal{H}_{\text{rot}}(\Omega, \mathbf{R})$ is the rotational energy (in a moving coordinate system; Ω is the aggregate of the Euler angles); 2) the total interaction energy \mathcal{H}_{ei} is assumed

to include the relativistic terms; 3) the role of the parameters ϵ_F and ω_D is assumed by ϵ_{el} and ω_0 ($\hbar\omega_0$ is the value of the vibrational quantum). The rotation energy can be expressed in the form of the sum $\mathcal{H}'_{rot} = \mathcal{H}'_{rot}(\Omega, \mathbf{R}_{0n}) + \mathcal{H}'_{rot}(\Omega, \Delta\mathbf{R})$ (\mathbf{R}_{0n} now depends essentially on the electronic quantum number n). Obviously, \mathcal{H}'_{rot} must be included in the zero-order Hamiltonian \mathcal{H}_0 , and \mathcal{H}'_{rot} must be included in \mathcal{H}' . Therefore, in the case of molecules Eqs. (10), (11), and (13) are replaced by

$$\mathcal{H}_0 = \mathcal{H}_e + \mathcal{H}_{el}(\mathbf{r}, \mathbf{R}_{0n}) + \mathcal{H}_{vib} + U_{2n} + \mathcal{H}'_{rot},$$

$$\mathcal{H}' = \mathcal{H}'_1 + \mathcal{H}'_2 - \mathcal{H}'_{2n} + \sum_{s=3}^{\infty} \mathcal{H}'_s + \mathcal{H}'_{rot}, \quad (34)$$

$$\mathcal{H}'_{rot} = \sum_{s=1}^{\infty} \mathcal{H}'_{rot}^{(s)}, \quad \mathcal{H}'_{rot}^{(s)} \sim \kappa \mathcal{H}'_{rot}^{(s-1)}, \quad \mathcal{H}'_{rot}^{(1)} = \sum_{i\alpha} \frac{\partial \mathcal{H}'_{rot}}{\partial X_{0i\alpha}} \Delta X_{i\alpha} \sim \kappa^3 \hbar \omega_0.$$

In view of this, the zero-order Ψ function is a product of the electronic, vibrational, and rotational functions: $\Psi_{n\nu j}^0 = \Psi_n^0(\mathbf{r}, \mathbf{R}_{0n}) \Psi_{n\nu}^0(\Delta\mathbf{R}) \Psi_{n\nu j}^0(\Omega)$. We now can use, in Chap. 3, the formalism of ordinary perturbation theory, which offers substantial advantages over the adiabatic theory in the previous form, particularly when it comes to calculating the probability of optical transitions with arbitrary accuracy, and transitions with emission of vibrational and rotational quanta. Perturbation theory in this case, just as in Chap. 3, is constructed for the n -th electronic state, and it is assumed that it corresponds to a bound state of the molecule. Since the lower section of the spectrum is discrete, in the case of molecules we do not encounter the difficulties connected in the case of a metal with the layer of non-adiabatic electrons. In particular, the correction to the Ψ function of the system, namely $\Psi'_{n\nu j} = \sum_{n', \nu', j'} |\mathcal{H}'|_{n\nu j, n'\nu'j'}$ ($E_{n\nu j}^0 - E_{n'\nu'j'}^0$) $^{-1}$ $\Psi'_{n'\nu'j'}$, will be of the order of $\kappa \Psi_0$, for even though $\mathcal{H}' \sim \mathcal{H}'_1 \sim \omega_0/\kappa$, we still have $(E_{n\nu j}^0 - E_{n'\nu'j'}^0)av \sim \epsilon_{el}$.

The perturbation theory considered above, with appropriate changes, can be used also in nuclear theory—in the so-called unified model of the nucleus for the description of the interaction of nucleonic (fast) degrees of freedom with collective vibrational and rotational (slow) degrees of freedom.

In conclusion, I am grateful to E. G. Brovman and V. Z. Kresin for an interesting discussion.

APPENDICES

I. ALLOWANCE FOR SCREENING IN ELECTRON-PHONON MATRIX ELEMENTS

On going over to the $|\mathcal{H}'_1|_{nm}$ matrix elements, and particularly to the single-particle representation in $M_{\mathbf{kq}\lambda}$, we should take exact account of the Coulomb interaction. To clear up this matter, let us find the correction that must be added to $\omega_{\mathbf{q}\lambda}$ to account for $E'_{n\nu j}$, i.e.,

$$\Delta\omega'_{\mathbf{q}\lambda} = \frac{\delta E'_{n\nu j}}{\delta N_{\mathbf{q}\lambda}} = \sum_{\mathbf{k}} |M_{\mathbf{kq}\lambda}|^2 \left[\frac{1}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} - \hbar\omega_{\mathbf{q}\lambda}} + \frac{1}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}} + \hbar\omega_{\mathbf{q}\lambda}} \right] n_{\mathbf{k}}(1 - n_{\mathbf{k}+\mathbf{q}}).$$

Replacing \mathbf{k} by $-\mathbf{k} - \mathbf{q}$ in the second term, we obtain

$$\Delta\omega'_{\mathbf{q}\lambda} = \sum_{\mathbf{k}} |M_{\mathbf{kq}\lambda}|^2 \frac{n_{\mathbf{k}+\mathbf{q}} - n_{\mathbf{k}}}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - \hbar\omega_{\mathbf{q}\lambda}}. \quad (A.1)$$

On the other hand, if we use diagram technique, $\omega_{\mathbf{q}\lambda}$ is determined as the pole of the phonon Green's function $D_{\lambda}(\omega, \mathbf{q})$ (which takes into account only the diagram corresponding to $E'_{n\nu j}$): $D_{\lambda}^{-1} = D_{\lambda 0}^{-1} - \Pi_{\lambda} = 0$,

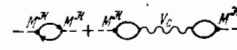


FIG. 1.

$D_{\lambda 0} = 2\omega_{\mathbf{q}\lambda} / (\omega^2 - \omega_{\mathbf{q}\lambda}^2 + i\delta)$ is the zero-order D function, i.e., at $\mathcal{H}' = 0$ and under the assumption that $\mathcal{H}' = \mathcal{H}'_1$; $\Pi_{\lambda}(\mathbf{q}, \omega)$ is the phonon polarization operator. From this we get within the framework of perturbation theory $\Delta\omega_{\mathbf{q}\lambda} = \Pi_{\lambda}(\mathbf{q}, \omega_{\mathbf{q}\lambda})$. If we introduce the matrix element $M_{\mathbf{kq}\lambda}^n$ (the vertex $\Gamma_{\mathbf{k}\lambda}^n$), in which screening connected with the Coulomb interaction of the electrons is not taken into account, then^[21,22] (Fig. 1)

$$\Pi_{\lambda} = M_{\mathbf{kq}\lambda}^{n*} P M_{\mathbf{kq}\lambda}^n + M_{\mathbf{kq}\lambda}^{n*} P V_c P M_{\mathbf{kq}\lambda}^n = M_{\mathbf{kq}\lambda}^{n*} P M_{\mathbf{kq}\lambda}^{sc}, \quad (A.2)$$

where

$$M_{\mathbf{kq}\lambda}^{sc} = \frac{M_{\mathbf{kq}\lambda}^n}{\epsilon(\mathbf{q}, \omega_{\mathbf{q}\lambda})}, \quad \epsilon(\mathbf{q}, \omega) = 1 - V_{c0}(\mathbf{q}) P(\mathbf{q}, \omega),$$

$$V_{c0} = \int \psi_{\mathbf{k}}^*(\mathbf{r}) \frac{e^2}{r} \psi_{\mathbf{k}+\mathbf{q}}(\mathbf{r}) d\mathbf{r} \approx \frac{4\pi e^2}{q^2}, \quad V_c = \frac{V_{c0}}{\epsilon(\mathbf{q}, \omega)}$$

and the polarization loop is given in the random-phase approximation (high density; G is the electron Green's function);

$$P = i \int G(p) G(p+q) \frac{d^4 p}{(2\pi)^4} = \sum_{\mathbf{k}} \frac{n_{\mathbf{k}+\mathbf{q}} - n_{\mathbf{k}}}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - \omega};$$

Comparing (A.1) and (A.2), we see that $|M_{\mathbf{kq}\lambda}^2|$ in (8), (9), and (15)–(18) should be equated to $|M_{\mathbf{kq}\lambda}^n|^2 / \epsilon(\mathbf{q}, \omega_{\mathbf{q}\lambda})$. At small $q \ll n^{1/3}$, the value of M^n will obviously be the same as for free electrons, i.e., at $u_{\mathbf{k}}(\mathbf{r}) \approx 1$ we have

$$M_{\mathbf{kq}\lambda}^n \Big|_{q \rightarrow 0} = -i \frac{4\pi Z e^2}{q} \sqrt{\frac{\hbar N}{2M\omega_{\mathbf{q}\lambda}}} \left(e_{\mathbf{q}\lambda}, \frac{\mathbf{q}}{q} \right),$$

$$\epsilon(\mathbf{q}, \omega_0) \approx \epsilon(\mathbf{q}, 0) = 1 + \frac{\kappa_j^2}{q^2}.$$

Therefore

$$\frac{|M_{\mathbf{kq}\lambda}^n|^2}{\epsilon(\mathbf{q}, \omega_{\mathbf{q}\lambda})} \Big|_{q \rightarrow 0} \rightarrow \frac{1}{\omega_{\mathbf{q}\lambda}} \quad (e_{\mathbf{q}\lambda} \parallel \mathbf{q}), \quad \frac{|M_{\mathbf{kq}\lambda}^n|^2}{\epsilon(\mathbf{q}, \omega_{\mathbf{q}\lambda})} \Big|_{q \rightarrow 0} \rightarrow 0 \quad (e_{\mathbf{q}\lambda} \perp \mathbf{q}), \quad (A.3)$$

κ_D^{-1} is the Debye radius. The same result is obtained when $\Delta\epsilon_p$ is calculated. It is easy to see that at $N_{\mathbf{q}\lambda} = 0$ we can regard $E'_{n\nu j}$ (expressed in symmetrical form) as a correction that must be introduced into the system energy because of the interaction between the electrons, in the form

$$V'_{ep} = \sum_{\lambda} |M_{\mathbf{kq}\lambda}|^2 \left[\frac{1}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} - \hbar\omega_{\mathbf{q}\lambda}} - \frac{1}{\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}} + \hbar\omega_{\mathbf{q}\lambda}} \right]$$

$$= \sum_{\lambda} |M_{\mathbf{kq}\lambda}|^2 D_{\lambda}(\epsilon_{\mathbf{k}+\mathbf{q}} - \epsilon_{\mathbf{k}}, \mathbf{q}).$$

Within the framework of the diagram technique, the four-pole V'_{ep} with allowance for screening is described by the expression (corresponding to the usual grouping of the diagrams on one side, as in (A.2))

$$V'_{ep} = \sum_{\lambda} M_{\mathbf{kq}\lambda}^{n*} D_{\lambda} M_{\mathbf{kq}\lambda}^{sc}.$$

Thus, we find again $|M_{\mathbf{kq}\lambda}|^2 = |M_{\mathbf{kq}\lambda}^n|^2 / \epsilon(\mathbf{q}, \omega_{\mathbf{q}\lambda})$. The electron mass operator in symbolic notation is equal to $\Sigma'_{ep} = (V'_{ep} G)$ (G is the electron Green's function). Obviously, it is necessary to put $|M|^2 = |M^n|^2 / \epsilon$ in both \mathcal{H}'_{2n} and $|\mathcal{H}'_2|_{nn}$.

When calculating $\Delta\epsilon_p$ and Σ_1 , however, it is customary to consider immediately not only the contribution of the electron-phonon interaction (with allowance for the Coulomb screening), but also the direct contribution of the Coulomb repulsion.

Then the complete four-pole $V = V_{eff}$ is given by

$$V = V_{ep} + V_c + V_{epc}, \quad (\text{A.4})$$

where $V_c = V_{c0}/(1 - PV_{c0})$ and the mixed term is $V_{epc} = V_{ep}PV_c$.

From (A.4) we get

$$V = V_c + V_{ep}, \quad V_{ep} = \sum_{\lambda} M_{kq\lambda}^{SC*} D_{\lambda} M_{kq\lambda}^{SC}. \quad (\text{A.5})$$

Expression (A.5) coincides with the known expression for V , which is obtained by summing the geometric progression [11,21,22]:

$$V = \frac{V_0}{1 - PV_0}, \quad V_0 = V_{c0} + \sum_{\lambda} |M_{kq\lambda}^{SC}|^2 D_{\lambda}. \quad (\text{A.6})$$

Recognizing that $D^{-1} = D_0^{-1} - \Pi$, we get (A.6) from (A.5) and (A.2). At small q we have $|M_{kq\lambda}^{SC}|^2 \sim q^2/\omega_{q\lambda}$. The mass operator is $\Sigma_1 = (VG) = \Sigma_c + \Sigma_{ep}$, $\Sigma_c = (V_c G)$, $\Sigma_{ep} = ([\sum_{\lambda} |M_{kq\lambda}^{SC}|^2 D_{\lambda}] G)$. Usually Σ_c is regarded as the contribution made to Σ_1 by the Coulomb interaction, and consequently Σ_{ep} , rather than Σ'_{ep} , is regarded as the contribution of the interaction between the electrons via the phonons. V_{ep} and Σ_{ep} , unlike V'_{ep} and Σ'_{ep} , contain not $M^{n*}M^{SC}$, but $|M^{SC}|^2$. Thus, whereas the screening is taken into account in the calculation of Π in one electron-phonon vertex, and is not taken into account in another, in the calculation of Σ_{ep} the screening should be taken into account in both vertices. In the calculation of Σ_1 and Π we have considered above only the terms connected with the term \mathcal{H}_1 in \mathcal{H}' , and did not consider the remaining terms. Of course, they should also be taken into account (see below). Conductivity theory contains the matrix element $|\mathcal{H}_1|_{n\nu; m\mu}$, or, in the single-particle representation, $M_{kq\lambda}$ for a real process—the transition of an electron from the state k to the state k' with emission or absorption of a phonon. Obviously, in this case (see [11,13,30]) we have $M^T = M^n/\epsilon(q, \omega_q)$. This result follows from the well-known equation for the electronic matrix element in a field with allowance for the interaction between electrons, which has the symbolic form [32] (Fig. 2)

$$U = U^n + \mathcal{T}GGU. \quad (\text{A.7})$$

\mathcal{T}_c is the four-pole for the Coulomb interaction between the electrons is irreducible with respect to oppositely-directed arrows, and in the high-density approximation can be assumed equal to the matrix element of the Coulomb potential V_{c0} . At small q we have $V_{c0} \approx 4\pi e^2/q^2$; U^n is the matrix element without allowance for the interaction; since $(GG) = P$, we find from (A.7) that $U = U^n/(1 - V_{c0}P)$, whence

$$M_{kq\lambda}^T = \frac{M_{kq\lambda}^n}{\epsilon(q, \omega_{q\lambda})}.$$

We see that, according to adiabatic theory, $M_{kq\lambda}$ corresponds to the rigid-ion model.

The matrix element $|\mathcal{H}_2|_{n\nu; m\mu}$ is equal to [9]

$$\frac{\hbar}{2M\sqrt{\omega_{q_1\lambda_1}\omega_{q_2\lambda_2}}} L_{kk}^{\lambda_1\lambda_2}, \quad L_{kk}^{\lambda_1\lambda_2} = \sum_{\alpha\beta} e_{q_1\lambda_1\alpha} e_{q_2\lambda_2\beta} \int \Psi_k^*(r_j) \frac{\partial^2 V(r_j)}{\partial x_{\alpha} \partial x_{\beta}} \Psi_k(r_j) dr_j.$$

From (A.7) we get $L^{SC} = L^n/\epsilon(q, \omega_q)$, $q = q_1 + q_2 + g$,

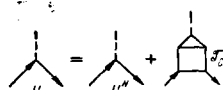


FIG. 2.

$\omega_q = \omega_{q_1\lambda_1} + \omega_{q_2\lambda_2}$, and at small q we obviously have (we put $g = 0$)

$$L_{kk}^n \approx (e_{q_1\lambda_1}, q)(e_{q_2\lambda_2}, q) \frac{4\pi Z e^4}{q^2}, \quad k' = k + q. \quad (\text{A.8})$$

II. DIAGRAM TECHNIQUE IN ADIABATIC THEORY

On the basis of ordinary perturbation theory it is easy to develop a standard diagram technique [9]. Obviously, each of the terms \mathcal{H}_S in \mathcal{H}' corresponds, as indicated in Fig. 3, by vertex parts Γ_S^{λ} in which the number of phonon ends is equal to the index s (1, 2, etc.), and with two electron ends, or else without electron ends (owing to the term $V(\mathbf{R}, \mathbf{R})$ in $\mathcal{H}_{ie}(r, \mathbf{R})$; we shall frequently omit the polarization index λ); $\Gamma_S \sim \kappa_S - 1$. Thus, $\Gamma_S = \Gamma_{S2} - \Gamma_{S0}$ (the second subscript is equal to the number of electron ends; Fig. 3 does not show the subdivision of the vertices Γ_S into Γ_{S2} and Γ_{S0}).

The term $-U_{2n}$ in \mathcal{H}' contributes not only to the phonon polarization operator Π , but also to the electronic mass operator, since $-U_{2n}$, together with its contribution to the correction to the energy $E_{n\nu i}$, is a functional of n_k and therefore makes a contribution to the correction (independent of the frequency) to the electron energy

$\Delta \epsilon_p^{(i)} = \delta E_{n\nu i} / \delta n_p$, and consequently also to Σ_1 . Thus, the contribution of $-U_{2n}$ to Σ_1 can be taken into account with the aid of the formula $\Delta \epsilon_p^{(i)} = \delta E_{n\nu i} / \delta n_p$. [9] A direct check shows that the same results are obtained for Σ_1 and π by replacing the quantity n_p in the expression (12) and (9) for U_{2n} , i.e., the mean value of the operator $a_p^+ a_p$ diagonal in the occupation numbers in the immobile-ion representation, by the operator $a_p^+ a_p$ itself. Even though, of course, $a_p^+ a_p \neq n_p \equiv \langle a_p^+ a_p \rangle_e$, this procedure leads to correct results if we disregard in the diagrams for Σ_1 and Π all the complications connected with the electron ends of the vertex Γ_2' that corresponds to the term $-\mathcal{H}_{2n}$ in \mathcal{H}' , and of the vertex Γ_2'' , that corresponds to the term $-|\mathcal{H}_2|_{nn}$. (This means that the operator $a_p^+ a_p$ is taken in the representation of immobile ions corresponding to the zero-order Hamiltonian [33].) The vertices Γ_2' and $\Gamma_2'' = \Gamma_{22} + \Gamma_{20}$ are indicated in Fig. 4. It is easy to show, using the formula [34]

$$\langle a_p^+ a_p \rangle = -2i \lim_{t \rightarrow +0} \int_{-\infty}^{\infty} G(p, \omega) e^{i\omega t} \frac{d\omega}{2\pi},$$

that

$$\langle a_p^+ a_p \rangle - \langle a_p^+ a_p \rangle_e \approx -2i \lim_{t \rightarrow +0} \int_{-\infty}^{\infty} \Sigma_1 G e^{i\omega t} \frac{d\omega}{2\pi} \sim \frac{\omega_D}{\epsilon_F} \sim \kappa^2$$

(since $\Sigma_1 \sim \omega_D$; see (32)).

In [33], for a comparison with perturbation theory and to relate similar terms in the expression for $-H_{2n}$,

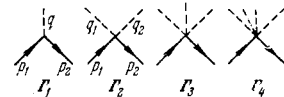


FIG. 3.

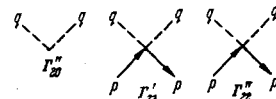


FIG. 4.

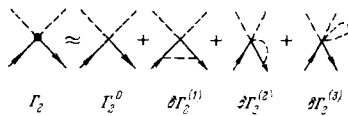
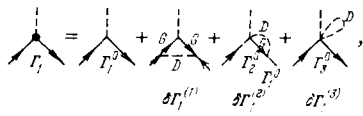


FIG. 5.

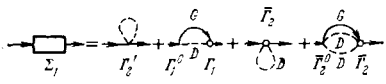


FIG. 6.

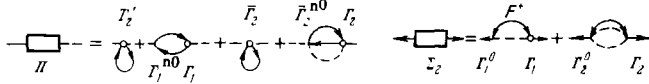


FIG. 7.

FIG. 8.

the term with $n_k n_{k'}$ was left equal to zero (see (9)), and the corresponding vertex Γ_{24} is not indicated in Fig. 4. We have combined in (13) \mathcal{H}_2 and $|\mathcal{H}_2|_{nn}$ in $\mathcal{H}_2 = \mathcal{H}_2 - |\mathcal{H}_2|_{nn}$. It is therefore useful to introduce the vertex $\bar{\Gamma}_2 = \Gamma_2 + \Gamma_2''$. If we disregard the complications of the vertex Γ_2 , i.e., use the $\hbar\omega_D$ approximation for Σ_1 and Π (these complications yield values of the order $\kappa^2 \hbar\omega_D$; as a result the third terms in the diagrams of Figs. 6 and 7 yield for Σ_1 and Π values $\sim \kappa^2 \hbar\omega_D$; see below) we have $\Gamma_2''(p, p; q, q) = -\Gamma_2(p, p; q, q)$, i.e., $\bar{\Gamma}_2(p, p; q, q) = 0$.

The graphic equations for the vertices are indicated, accurate to $\sim \kappa^2$, in Fig. 5 (the corrections to the vertices Γ_3 etc. are similar in form). It is seen from Fig. 5 that besides the correction $\delta\Gamma_1^{(1)}$ to Γ_1 , which is of order $\kappa^2 \Gamma_1$ and is considered in^[31], there arise corrections represented by the last two terms, also of order $\kappa^2 \Gamma_1$ ($\delta\Gamma_1^{(2)} \sim \Sigma_1 \Gamma_2 / \Gamma_1 \sim \kappa^2 \Gamma_1$; $\delta\Gamma_1^{(3)} \sim \Gamma_3 \sim \kappa^2 \Gamma_1$; $\delta\Gamma_2^{(2)} \sim \delta\Gamma_2^{(3)} \sim \kappa^2 \Gamma_2$), D is the phonon Green's function and F is the F-function. The equations for Σ_1 , Π , and the pairing self-energy part Σ_2 , which take the electron-phonon interaction (but not V_C) into account, are indicated in Figs. 6–8. We have confined ourselves here to the approximation $\kappa^2 \hbar\omega_D$. In Figs. 6–8, Γ_S^n is the vertex Γ_S with allowance for screening, and $\bar{\Gamma}_S \equiv \Gamma_S^{SC}$ is the vertex with allowance for screening (see above). In the fourth diagram of Fig. 6 and in the second diagram of Fig. 8 the two vertices Γ_2 are given with allowance for screening, since the corresponding electron four-pole $V_{2ep}(\Sigma_1^{(4)} = (V_{2ep}G))$, just as in (A.4), is equal to the sum $V_{2ep} = \Gamma_2 D D \Gamma_2$ of the term $V_{2ep} = \Gamma_2^n D D \Gamma_2$ with the mixed term $V_{2ep}^P V_C$. On the other hand, the fourth diagram of Fig. 7 can be expressed in the form $\Pi^{(4)} = (WD)$, with the phonon four-pole W determined by an equation analogous to (A.2).

$$W = \Gamma_2^n P \Gamma_2^n + \Gamma_2^n P V_C P \Gamma_2^n = \Gamma_2^n P \Gamma_2^n.$$

In^[9,27,33], the diagrams of order $\kappa^2 \hbar\omega_D$, which are indicated for Σ_1 in Fig. 9, were additionally included in Figs. 6–8, together with analogous diagrams for Π and Σ_2 . It was assumed there that the vertices Γ_1 and $\bar{\Gamma}_2$ do not take into account the complications connected with other vertices. When approached consistently, these complications (the last two diagrams in Fig. 5) must be taken into account together with the complications de-

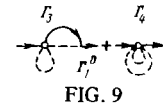


FIG. 9

scribed by the second diagrams of Fig. 5. The diagrams of Fig. 9 and the corresponding diagrams for Π and one diagram for Σ_2 turn out to be included in this case in the second and third diagrams of Figs. 6 and 7 and in the second diagram of Fig. 8.

The calculation of Σ_1 and Π , and the analysis of the equation for Σ_2 , were carried out in^[9,27]. It must be borne in mind however, that inasmuch as we are calculating Σ_{ep} and not Σ_{ep} , the constant term of the second diagram of Fig. 6, which contains $|M^{SC}|^2$, and renormalizes the chemical potential μ , is not cancelled out by the first diagram, which is proportional to $M^{n*} M^{SC}$ (see above). Therefore the renormalization of the chemical potential $\Delta\mu$ will be of the order of $\hbar\omega_D$. The cancellation of these two diagrams, which is indicated in^[9,27] with accuracy $\sim \kappa^2 \hbar\omega_D$, and the related estimate $\Delta\mu \sim \kappa^2 \hbar\omega_D$, correspond to the calculation of Σ_{ep}' and not Σ_{ep} . All the remaining results of these studies remain in force. We note also that the second term for Π in Fig. 7 contains the factor $\Gamma_1^n \Gamma_1 (M^{n*} M^{SC})$, which in the case of an acoustic dispersion law for $\omega(q)$ according to (A.3) behaves at small q like $\sim 1/q$, in contrast to Γ_1^2 , which behaves like q as $q \rightarrow 0$. However, the first term of Fig. 7, which cancels out the second with accuracy $\kappa^2 \hbar\omega_D$, also contains $\Gamma_1^n \Gamma_1$, and therefore the small difference of these two terms, $\sim \kappa^2 \hbar\omega_D$,^[9,27] has no singularities at all at small q .

As is well known, the imaginary part of Π , which is due to the second diagram of Fig. 7, is of order $\kappa^2 \hbar\omega_D$.^[3] It is easily seen that the fourth diagram of Fig. 7 also yields a quantity of the order of $\sim \kappa^2 \hbar\omega_D$.^[9,27,33] It therefore plays an important role in the calculation of $\text{Im } \Pi$.

Equations for the electron and phonon Green's functions in general form, within the framework of the most general scheme that does not use the adiabatic approximation, were obtained in^[12]. They were not used, however, to calculate the self-energy parts Σ_1 , Σ_2 , and Π .

¹⁾In^[33] the vertex Γ_2' is designated Γ_2'' , and vice versa.

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