STOCHASTIC ASPECTS OF LOW MOBILITY THEORY

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A new method for calculating the electric conductivity is formulated in the Wannier (site) representation. An equation similar to the Boltzmann equation and describing electron motion in the space of lattice sites is derived by using the Kubo formula. As an illustration, the case of narrow bands and strong electron-phonon interaction is investigated; it is shown that in this case the motion of an electron in the lattice may be regarded as comprising non-Markoffian random jumps between lattice sites. Under certain conditions this random walk process becomes Markoffian and the problem reduces to calculation of the site-jump probabilities per unit time. A possible way of extending the limits of applicability of the present low-mobility theory is indicated.

1. INTRODUCTION

IN the first papers on low mobility theory [1-3] it was postulated that the motion of small-radius polarons can be regarded as jumps from site to site. It is necessary to assume for this purpose the possibility of object localization within a unit cell. The localized state is not stationary, by virtue of Bloch's theorem, according to which the object is smeared out over the entire lattice and is characterized by a quasimomentum $\mathbf{k}$. For semiconductors with broad bands (bands of width $\Delta E \gg T$), the characteristic length is $\lambda_T \approx \hbar/(m^*T)^{1/2} \gg a_0$ (m^*—effective mass, a_0—lattice constant), so that packets with dimensions smaller than λ_T will spread out very rapidly. In the case of narrow bands ($\Delta E \ll T$), a characteristic value of the quasimomentum will be a_0^{-1}, i.e., the characteristic length will be a_0. If we localize the electron within one unit cell, then in the case when the lattice polarization produced by it is large (polaron), the most probable process (at sufficiently high temperatures) is the following [1,2,4]: a polarization well, centered about the neighboring site, is created by fluctuation, one electron tunnels through to the neighboring site and fixes the produced polarization, and the old well is disintegrated. The probability of such a process (site jump) depends exponentially on the temperature ($w_H \sim \exp(-E_a/T)$, where $E_a \gg \hbar\omega_0$; ω_0 is the limiting frequency of the polarization photon), and when $T > \hbar\omega_0/2$ it exceeds the probability of the tunneling in the absence of fluctuations; the electron executes the jump before the wave packet spreads out.

We can expect the site (Wannier) representation (the m-representation) to be convenient in such problems. Indeed, rigorous calculations carried out by the density-matrix method in the k-representation [4-5], where the polaron band enters in explicit form, confirm many of the results of Holstein [2], who calculated w_H in the site representation. The site representation is natural also in such problems as the impurity conductivity, the conductivity in a narrow band $\Delta E \lesssim \hbar w$ (where w is the characteristic scattering probability), the ionic conductivity, etc. We note that in many of these cases the mobility is small, and the kinetic equation cannot be used.

In the present paper we develop a consistent method of calculating the electric conductivity in the m-representation [1)]. By way of illustration we analyze the case of a small-radius polaron. The proposed method affords a deeper insight into the physical essence of the problem and permits a generalization of known results [1,2,4,5]. It is shown that the motion of a polaron is described by a function $P(\mathbf{mm}'t)$, which has the meaning of a probability of finding a polaron at site $\mathbf{m}$ at the instant of time $t > 0$, if it was situated at the site $\mathbf{m}'$ at $t = 0$. The time evolution of $P(\mathbf{mm}'t)$ is described by an equation of the Kolmogorov-

[1)] We do not touch upon Mott's problem [6,7] (which is also usually formulated in the site representation) concerning the realization of the current states for narrow partially-filled bands, and confine ourselves to the case when the substance is a dielectric and contains no impurities.

Feller type [8], and is a Markoffian stochastic process. The equation obtained plays the same role in m-space as Boltzmann's equation in k-space. It follows from it that the spreading of the inhomogeneity in m-space is described by a diffusion equation with a diffusion coefficient

$$D = \lim_{t\to\infty} \frac{1}{t} \sum_{\mathbf{m}} \mathbf{R}_{\mathbf{m}}^2 P(\mathbf{m}, 0, t) = \lim_{t\to\infty} \frac{\langle R^2 \rangle}{t},$$

where $\langle R^2 \rangle$ is the mean-square displacement of the polaron within a time t. The mobility is $u = eD/T$. In the general case the carrier motion is also described by the function $P(\mathbf{mm}'t)$, but the equation is integro-differential with respect to time, and the process of variation of $P(\mathbf{mm}'t)$ is interpreted as a stochastic non-Markoffian process.

The proposed method may be useful in an analysis of kinetic problems under conditions of spatial inhomogeneity of microscopic scale, and can also be used in the microscopic theory of Brownian motion for the derivation of an equation for the conditional probability function (analogous to $P(\mathbf{mm}'t)$).

2. GENERAL EXPRESSION FOR THE ELECTRIC CONDUCTIVITY

According to [9], the expression for the electric conductivity is

$$\sigma \equiv \sigma_{xx} = \frac{\beta}{V} \operatorname{Re} \int_0^\infty e^{-st} \langle j_x(t) j_x(0) \rangle \, dt,$$

$$s \to 0, \quad \beta = \frac{1}{T} \tag{1}$$

(V—volume of the crystal). Since in the m-representation it is the dipole moment d_x which is diagonal, and not the current j_x, we change over in (1) to the operators d_x. We obtain (we leave out the subscript x of d_x and j_x and use the relation $j_x(t) = \dot{d}_x(t) = dd_x(t)/dt$)

$$VT\sigma = -\operatorname{Re} \langle d(0) j(0) \rangle + s \langle d^2 \rangle - s^2 \int_0^\infty e^{-st} \langle d(t) d(0) \rangle \, dt. \tag{2}$$

The operator d is of the following form:

$$d \equiv d_x = e \sum_{\mathbf{m}} X_{\mathbf{m}} a_{\mathbf{m}}^+ a_{\mathbf{m}} \tag{3}$$

(m numbers the lattice sites, and X_m is the x-component of the radius vector R_m of site m). Since $\langle d_j \rangle$ is pure imaginary, we have

$$\frac{VT\sigma}{e^2} = -\frac{s}{2} \sum_{\mathbf{mm}'} (X_{\mathbf{m}} - X_{\mathbf{m}'})^2 \langle a_{\mathbf{m}}^+ a_{\mathbf{m}} a_{\mathbf{m}'}^+ a_{\mathbf{m}'} \rangle + \frac{s^2}{2} \int_0^\infty e^{-st} \sum_{\mathbf{mm}'} (X_{\mathbf{m}} - X_{\mathbf{m}'})^2 \langle (a_{\mathbf{m}}^+ a_{\mathbf{m}})_t \, a_{\mathbf{m}'}^+ a_{\mathbf{m}'} \rangle \, dt. \tag{4}$$

In the lowest order in the electron density n_0 we have

$$\sigma = \frac{e^2}{VT} \frac{s^2}{2} \int_0^\infty e^{-st} \sum_{\mathbf{mm}'} (X_{\mathbf{m}} - X_{\mathbf{m}'})^2 \langle (a_{\mathbf{m}}^+ a_{\mathbf{m}})_t \, a_{\mathbf{m}'}^+ a_{\mathbf{m}'} \rangle \, dt. \tag{5}$$

The correlator in (5) is diagonal in the m-representation. We note that (5) can be represented in the form

$$\sigma = \frac{e^2}{VT} \lim_{t\to\infty} \frac{1}{2t} \sum_{\mathbf{mm}'} (X_{\mathbf{m}} - X_{\mathbf{m}'})^2 \langle (a_{\mathbf{m}}^+ a_{\mathbf{m}})_t \, a_{\mathbf{m}'}^+ a_{\mathbf{m}'} \rangle, \tag{6}$$

if the limit exists. Setting V equal to the volume per electron, i.e., $V = n_0^{-1}$, we obtain

$$\sigma = n_0 e^2 T^{-1} D;$$

$$D = \lim_{t\to\infty} \frac{1}{2t} \sum_{\mathbf{mm}'} (X_{\mathbf{m}} - X_{\mathbf{m}'})^2 \langle (a_{\mathbf{m}}^+ a_{\mathbf{m}})_t \, a_{\mathbf{m}'}^+ a_{\mathbf{m}'} \rangle \tag{7}$$

(the average in (7) is taken over the single-electron states), where D has the meaning of a diffusion coefficient.

3. CARRIER MOTION OVER THE LATTICE SITES

Let the electron band be narrow ($\Delta E \ll T$), and let the electron-lattice interaction be weak. When $t < 0$ there are no electrons in the lattice. At the instant $t = 0$ an electron occupies the site m. What is the probability of finding it at the site m′ when $t > 0$? The Hamiltonian has the following form:

$$H = H_0 + H_e + U, \qquad H_e = \sum_{\mathbf{m};\,\mathbf{g}} J(\mathbf{g}) \, a_{\mathbf{m}+\mathbf{g}}^+ a_{\mathbf{m}}, \tag{8}$$

where H_0 is the phonon part of the Hamiltonian, H_e the electronic part, U the electron-phonon interaction, J(g) the overlap integral between the nearest neighbors, and summation over g means summation over the nearest neighbors. The electronic part of the Hamiltonian H_e is responsible for the transitions of the electron from site to site.

Assume that when $t < 0$ the lattice was in one of the stationary states $\Phi_M(\xi)$ of the Hamiltonian H_0 (M is the number of the stationary state and ξ the aggregate of normal coordinates of the lattice). When $t = 0$ the system is described by the

wave function

$$\psi_{Mm}(\xi; t)|_{t=0} = a_m^+ |0\rangle \Phi_M(\xi); \quad (9)$$

$|0\rangle$ is the state of electronic vacuum. When $t > 0$, the time development of the system is described by the wave function

$$\psi_{Mm}(\xi; t) = e^{-iHt/\hbar} \Phi_M(\xi) a_m^+ |0\rangle. \quad (10)$$

We represent $\psi_{Mm}(t)$ in the form

$$\psi_{Mm}(\xi; t) = \sum_{m'} A_{Mm}(\xi; m'; t) a_{m'}^+ |0\rangle. \quad (11)$$

Obviously, $A_{Mm}(\xi; m', t)$ is the amplitude of the probability of finding the electron at the site m' at the instant t for specified ξ. We have

$$A_{Mm}(\xi; m', t)|0\rangle = a_{m'} \psi_{Mm}(\xi, t)$$

$$= a_{m'} e^{-iHt/\hbar} a_m^+ |0\rangle \Phi_M(\xi). \quad (12)$$

The probability of finding an electron at the site m' if at the instant $t = 0$ its position was at m, and the phonons were in the state M, is

$$\int d\xi \langle 0 | a_m \Phi_M^*(\xi) (a_{m'}^+ a_{m'})_t a_m^+ \Phi_M(\xi) | 0\rangle. \quad (13)$$

Averaging (13) over the Gibbs distribution, we obtain

$$P(m'mt) = \left(\sum_M e^{-\beta E_M}\right)^{-1}$$

$$\times \sum_M e^{-\beta E_M} \langle 0M | a_m (a_{m'}^+ a_{m'})_t a_m^+ | M0\rangle. \quad (14)$$

The function $P(m'mt)$ is the (conditional) probability of finding an electron in the site m' at the instant t, if its location at $t = 0$ was the site m and if the lattice temperature was T. $P(m'mt)$ is real and satisfies the relation

$$\sum_{m'} P(m'mt) = 1. \quad (15)$$

Let us find $P(m'mt)$ with interaction neglected. According to (14),

$$P_0(m'mt) = \langle 0 | a_m e^{iH_e t/\hbar} a_{m'}^+ a_{m'} e^{-iH_e t/\hbar} a_m^+ | 0\rangle$$

$$\equiv P_0(m' - m; t). \quad (16)$$

We go over to the k-representation (N is the number of sites in the lattice):

$$a_m = \frac{1}{\sqrt{N}} \sum_k e^{ikR_m} a_k; \qquad H_e = \sum \varepsilon_0(k) a_k^+ a_k;$$

$$\varepsilon_0(k) = \sum_g J(g) e^{ikg}. \quad (17)$$

Simple calculations yield

$$P_0(m; t) = \frac{1}{N^2} \sum_{k;\, \varkappa} \exp(-i\varkappa R_m)$$

$$\times \exp\left\{\frac{it}{\hbar}\left[\varepsilon_0\left(k + \frac{\varkappa}{2}\right) - \varepsilon_0\left(k - \frac{\varkappa}{2}\right)\right]\right\}. \quad (18)$$

For a primitive cubic lattice the dispersion law is

$$\varepsilon_0(k) = 2J[\cos(k_x a_0) + \cos(k_y a_0) + \cos(k_z a_0)];$$

$$|g| = a_0. \quad (19)$$

After integrating with respect to k and $\varkappa$ we obtain

$$P_0(m; t) = J_{m_x}^2(2Jt/\hbar) J_{m_y}^2(2Jt/\hbar) J_{m_z}^2(2Jt/\hbar), \quad (20)$$

where $J_m(z)$ is a Bessel function.

Let us find the rms displacement of the electron during the time t:

$$\langle R^2(t)\rangle_0 = \sum_m R_m^2 P_0(m; t) = \frac{1}{N^2} \sum_{m;k;\varkappa} R_m^2 \exp\left\{-i\varkappa R_m + \frac{it}{\hbar}\left[\varepsilon_0\left(k + \frac{\varkappa}{2}\right) - \varepsilon_0\left(k - \frac{\varkappa}{2}\right)\right]\right\}$$

$$= \frac{-1}{N^2} \sum_{k;\varkappa} \left[\nabla_\varkappa^2 \sum_m \exp(-i\varkappa R_m)\right]$$

$$\times \exp\left\{\frac{it}{\hbar}\left[\varepsilon_0\left(k + \frac{\varkappa}{2}\right) - \varepsilon_0\left(k - \frac{\varkappa}{2}\right)\right]\right\}. \quad (21)$$

After going over from summation to integration, and after integrating twice by parts with respect to $\varkappa$, we obtain

$$\langle R^2(t)\rangle_0 = t^2 \frac{V}{(2\pi)^3 N} \int dk \sum_{i=1}^3 v_i^2(k) = t^2 \sum_{i=1}^3 \langle v_i^2\rangle,$$

$$v_i(k) = \frac{1}{\hbar} \frac{\partial \varepsilon_0(k)}{\partial k_i}, \quad (22)$$

where $\langle v_i^2 \rangle$ is the rms value of the i-th component of the electron velocity in the band; for the dispersion law (2) we have $\langle v_i^2 \rangle = (Ja_0/\hbar)^2/2$.

The motion of the electron in an ideal lattice is a process involving the spreading out of the wave packet, but not a random walk over the sites; in the latter case we would obtain $\langle R^2 \rangle \sim t$.[10] We note that when interaction is taken into account, the proportionality to t^2 holds for small times (see Sec. 5).

We proceed to the analogous problem for the small-radius polaron. In this case the Hamiltonian takes the form [4]

$$H_0 = \sum_q \hbar\omega_q b_q^+ b_q, \qquad H_e = \sum_{m;g} J(g) a_{m+g}^+ a_m;$$

$$u_{\mathbf{qm}} = \gamma_{\mathbf{q}} \exp(i\mathbf{q}\mathbf{R}_{\mathbf{m}}),$$

$$U = \frac{1}{\sqrt{N}} \sum_{\mathbf{m}} a_{\mathbf{m}}^{+} a_{\mathbf{m}} \sum_{\mathbf{q}} \hbar\omega_{\mathbf{q}} (u_{\mathbf{qm}} b_{\mathbf{q}}^{+} + u_{\mathbf{qm}}^{*} b_{\mathbf{q}})$$

$$\equiv \sum_{\mathbf{m}} U_{\mathbf{m}} a_{\mathbf{m}}^{+} a_{\mathbf{m}}; \qquad (23)$$

$\gamma_{\mathbf{q}}$ is the dimensionless constant of the interaction, which we consider to be strong:

$$\bar{\gamma} \equiv \frac{1}{N} \sum_{\mathbf{q}} |\gamma_{\mathbf{q}}|^2 \gg 1.$$

At the instant t = 0 a polaron is placed in an undeformed lattice, the state of which is $\Phi_{\mathbf{M}}(\xi)$. At t = 0 the wave function of the system is

$$\psi|_{t=0} = e^{-S_{\mathbf{m}}} a_{\mathbf{m}}^{+} |0\rangle \Phi_{M}(\xi),$$

$$S_{\mathbf{m}} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} (b_{\mathbf{q}}^{+} u_{\mathbf{qm}} - b_{\mathbf{q}} u_{\mathbf{qm}}^{*}); \qquad (24)$$

here $\exp(-S_{\mathbf{m}})$ is the operator for the production of a polaron well at site m. The expressions in (24) can also be written in the form

$$\psi|_{t=0} = e^{-S} a_{\mathbf{m}}^{+} |0\rangle \Phi_{M}(\xi), \qquad S = \sum_{\mathbf{m}} S_{\mathbf{m}} a_{\mathbf{m}}^{+} a_{\mathbf{m}}, \quad (25)$$

where e^{-S} is the canonical-transformation operator introduced in [4] [2)].

Reasoning as before, we find that the probability of finding the polaron at the site m′ at the instant of time t, if it was situated at the site m at t = 0, is

$$P(\mathbf{m}'\mathbf{m}t) = (\mathrm{Sp}\, e^{-\beta H_0})^{-1}$$

$$\times \langle 0 | \mathrm{Sp}\, e^{-\beta H_0} a_{\mathbf{m}} e^{i\tilde{H}t/\hbar} a_{\mathbf{m}'}^{+} a_{\mathbf{m}'} e^{-i\tilde{H}t/\hbar} a_{\mathbf{m}}^{+} | 0 \rangle \qquad (26)$$

(the trace is taken only over the phonon operators). Here

$$\tilde{H} = e^{S} H e^{-S} = \tilde{H}_0 + \tilde{U}, \qquad \tilde{H}_0 = \sum_{q} \hbar\omega_q b_q^{+} b_q,$$

$$\tilde{U} = \sum_{\mathbf{m};\,\mathbf{g}} J(\mathbf{g})\, a_{\mathbf{m}+\mathbf{g}}^{+} a_{\mathbf{m}} \exp(S_{\mathbf{m}+\mathbf{g}} - S_{\mathbf{m}})$$

$$\equiv \sum_{\mathbf{m};\,\mathbf{g}} a_{\mathbf{m}+\mathbf{g}}^{+} a_{\mathbf{m}} \tilde{U}_{\mathbf{m};\,\mathbf{g}}. \qquad (27)$$

It will be shown later that knowledge of the function P(m′mt) is sufficient for the calculation of the static conductivity.

[2)] It has the meaning of a transition from the states of a "bare" electron localized at the site to the state of a polaron at the same site. In other words, e^{-S} diagonalizes $H_0 + U$.

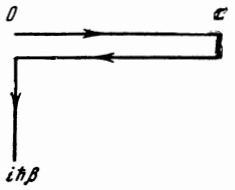

FIG. 1

4. DIAGRAM TECHNIQUE IN THE SITE REPRESENTATION

We proceed to calculate the quantity M(m′; m; s) in (5):

$$M(\mathbf{m}'; \mathbf{m}; s) = \int_0^{\infty} e^{-st} M(\mathbf{m}'; \mathbf{m}; t)\, dt.$$

$$= \int_0^{\infty} e^{-st} \langle (a_{\mathbf{m}'}^{+} a_{\mathbf{m}'})_t\, a_{\mathbf{m}}^{+} a_{\mathbf{m}} \rangle\, dt. \qquad (28)$$

Using the Hamiltonian (27), we shall seek (28) in the form of a series in $\tilde{U}$. We employ the device of Konstantinov and Perel' [11] [3)], which makes it possible to represent M(s) in the form of an integral over a contour in the complex time plane (Fig. 1). The terms of the series for M are best calculated with the aid of a diagram technique in the m-representation [4)].

The analytic rules for the calculation of the phonon averages of the type $\langle \tilde{U}_{\mathbf{m}_1\mathbf{g}_1}(\tau_1) \ldots \tilde{U}_{\mathbf{m}_i\mathbf{g}_i}(\tau_i) \rangle$ are given in Appendix I of [4]. Each diagram is characterized by a definite arrangement of the points relative to one another on the contour C. All the points are numbered in their sequence on the contour, starting with the upper left part. The point with number i is assigned a time τ_i, the $\mathbf{m}_i$ which enters in it and the $\mathbf{m}_i + \mathbf{g}_i$ which leaves it are the site indices. Unlike the usual single-phonon interaction [13], in this case each of the n points of the n-th order diagram is connected by n − 1 phonon lines with the remaining n − 1 points. The phonon line joining the points i and k (i < k) corresponds to the expression

$$Z_{ik}(\tau_i - \tau_k), \qquad (29)$$

where

$$Z_{ik}(\tau) = \exp\left\{ \frac{1}{N} \sum_{\mathbf{q}} \Gamma_{\mathbf{q}} a_{ik}(\mathbf{q}) \cos(\omega\ (\tau + i\alpha)) \right\},$$

[3)] The contour C differs from that introduced in [11], since (1) does not contain an integral with respect to λ, and the direction of τ is reversed.

[4)] The technique for single-particle correlators is developed in [12].

$$\alpha = \frac{\hbar}{2T}, \qquad \Gamma_{\mathbf{q}} = \frac{|\gamma_{\mathbf{q}}|^2}{\mathrm{sh}\,(\alpha\omega_{\mathbf{q}})}; \tag{30}*$$

$$2a_{ik}(\mathbf{q}) = \cos(\mathbf{q}(\mathbf{m}_i + \mathbf{g}_i - \mathbf{m}_k)) + \cos(\mathbf{q}(\mathbf{m}_i - \mathbf{m}_k - \mathbf{g}_k)) - \cos(\mathbf{q}(\mathbf{m}_i - \mathbf{m}_k)) - \cos(\mathbf{q}(\mathbf{m}_i + \mathbf{g}_i - \mathbf{m}_k - \mathbf{g}_k)). \tag{31}$$

We introduce

$$S_T(\mathbf{g}_i) = \frac{1}{N}\sum_{\mathbf{q}} \Gamma_{\mathbf{q}}\,\mathrm{ch}\,(\alpha\omega_{\mathbf{q}})\,a_i(\mathbf{q}),$$

$$2a_i(\mathbf{q}) = 1 - \cos(\mathbf{q}\mathbf{g}_i), \qquad (S_T)_{T=0} \equiv S_0. \tag{32}\dagger$$

When taking the trace over the electronic variables, we confine ourselves to the lowest-order terms in the electron density[5], as a result of which we obtain the connection between the neighboring site indices. Namely, the site index leaving a certain point (which can also be a bracket), is equal to that entering the neighboring point from the right. Summation is carried out over all the site indices (with the exception of the corresponding brackets). We integrate over all the intermediate times in the order corresponding to the arrangement of the points on the contour, the extreme right point being integrated from 0 to t; the result is integrated with respect to t from 0 to ∞ with a factor e^{-st}. The final expression is multiplied by

$$(-1)^{n_1}\prod_{i=1}^{n}\frac{iJ(\mathbf{g}_i)}{\hbar}\exp[-S_T(\mathbf{g}_i)],$$

where n_1 is the number of points on the upper part of the contour. Summing the contributions from all the n-th order diagrams with all the possible arrangements of the points on the contour C, we obtain the n-th term of the expansion for M(s)[6].

In view of the fact that $Z(\tau) \to 1$ as $\tau \to \infty$ (i.e., $Z(\infty) = 1$), the contribution of each diagram with n points is of the order of $1/s^{n+1}$ (see [4]), corresponding to a divergence of the free section type. Noting that the divergences are connected with the asymptotic behavior of $Z(\tau)$, we can

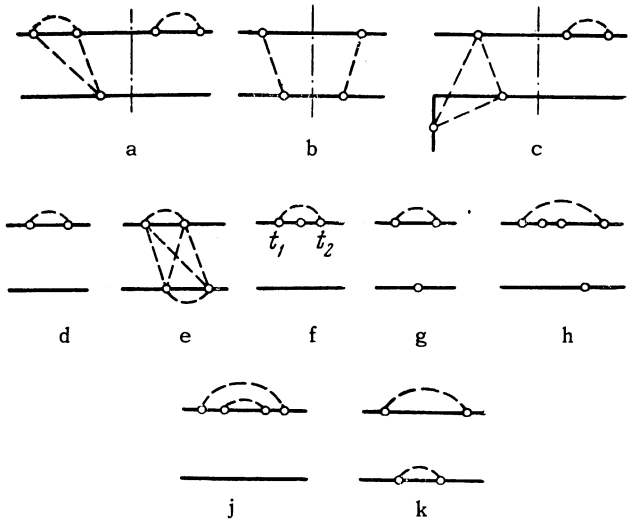

FIG. 2

separate them in simpler form, by writing for Z

$$Z_{ik}(\tau) = [Z_{ik}(\tau) - Z_{ik}(\infty)] + Z_{ik}(\infty) \equiv \tilde{Z}_{ik}(\tau) + 1. \tag{33}$$

This enables us to introduce the concept of the free section. Replacing in each diagram all the Z by $\tilde{Z} + 1$, we have

$$\prod_{i<k} Z_{ik} = \prod_{i<k}(\tilde{Z}_{ik} + 1), \tag{34}$$

from which we see that each preceding diagram can be represented in the form of a sum of new diagrams, in which the phonon line corresponds to $\tilde{Z}_{ik}$; namely, in place of the diagram ΠZ_{ik} it is necessary to take a similar one, in which each line corresponds to $\tilde{Z}_{ik}$, add to it the sum of the contributions obtained from it by removal of each line, each pair, each three, ...k, ..., n lines.

Each M(s) is represented by a sum of diagrams, each of which consists of compact parts joined by free sections. A free section is defined as that part of the diagram, which is subdivided by a vertical line into two parts that are not connected by phonon lines (see Figs. 2a, b, c). The compact parts (blocks), by definition, contain no free sections (see Fig. 2, d, e.) They contain divergences of the 1/s type, due to the appearance inside the blocks of points containing no phonon lines (see Figs. 2f, g, h), and also internal blocks not connected with them, constituting the "skeleton" of the diagram (see Fig. 2j, k; a "skeleton" diagram is obtained from a given diagram by removing from it all the points and internal blocks).

It is shown in Appendix I that summation of diagrams that are identical in structure but differ

*sh ≡ sinh.

†ch ≡ cosh.

[5]The pairing of the extreme right and extreme left electronic operators under the trace sign yields n_0, and the remaining pairings (only the nearest neighbors are paired) yield unity.

[6]Unlike[4,5], where the current correlator is calculated, in the diagrams for M(s) the brackets do not contain the phonon operators and consequently do not contain phonon lines.

in the number of "empty" points, can be carried out and yields an expression of the type $\exp[-i\tau\epsilon(\mathbf{k})/\hbar]$, where $\epsilon(\mathbf{k})$ is the band energy of the polaron. Inasmuch as $\epsilon(\mathbf{k}) \sim J\exp(-S_T)$ is exponentially small, all the $\exp[-i\epsilon(\mathbf{k})\tau/\hbar]$ can be replaced by unity within the limits of computational accuracy. Such arguments are obtained in the exponentials also in the k-representation, where the polaron band is introduced from the very outset [4]. Summation of the blocks also changes the behavior of the "skeleton" parts only over times $t \sim w^{-1}$ ($w \ll w_0$) which are appreciably larger than those which determine the main contribution of the "skeleton" ($t \lesssim \omega_0^{-1}$).

The compact part containing the left bracket will be called the angle part and denoted $\Gamma_{\mathbf{mm}}^{\mathbf{mm}_1}$. The internal compact part will be denoted by $W_{\mathbf{m}_2\mathbf{m}_4}^{\mathbf{m}_1\mathbf{m}_3}$.

As a result of translational symmetry we have

$$\Gamma_{\mathbf{m}+\mathbf{m}'\,\mathbf{m}_2+\mathbf{m}'}^{\mathbf{m}+\mathbf{m}'\,\mathbf{m}_1+\mathbf{m}'} = \Gamma_{\mathbf{m}\mathbf{m}_2}^{\mathbf{m}\mathbf{m}_1}, \qquad W_{\mathbf{m}_2+\mathbf{m}'\,\mathbf{m}_4+\mathbf{m}'}^{\mathbf{m}_1+\mathbf{m}'\,\mathbf{m}_3+\mathbf{m}'} = W_{\mathbf{m}_2\mathbf{m}_4}^{\mathbf{m}_1\mathbf{m}_3}. \quad (35)$$

From the structure of the series for $M(s)$ it follows that

$$M(\mathbf{m}'\mathbf{m}s) = \sum_{\mathbf{m}_1;\ \mathbf{m}_2} \Gamma_{\mathbf{m}\mathbf{m}_2}^{\mathbf{m}\mathbf{m}_1}(s)\, P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}(s), \quad (36)$$

$$P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}(s) \equiv \int_0^\infty e^{-st} P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}(t)\, dt$$

$$= \int_0^\infty e^{-st}\, \frac{\langle 0 \,|\, \mathrm{Sp}\exp(-\widetilde{\beta H}_0)\, a_{\mathbf{m}_2}(a_{\mathbf{m}'}^+ a_{\mathbf{m}'})_t a_{\mathbf{m}_1}^+ \,|\, 0\rangle}{\mathrm{Sp}\,[\exp(-\beta\widetilde{H}_0)]}\, dt. \quad (37)$$

when $\mathbf{m}_1 = \mathbf{m}_2$, Eq. (37) goes over into the function considered in Sec. 3.

5. EQUATION FOR THE FUNCTION $P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}$

The system of equations for $P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}(s)$ has the following form:

$$sP_{\mathbf{m}\mathbf{m}'}^{\mathbf{m}\mathbf{m}'}(s) = \delta_{\mathbf{m}\mathbf{m}'} + W_{\mathbf{m}\mathbf{m}}^{\mathbf{m}\mathbf{m}} P_{\mathbf{m}\mathbf{m}'}^{\mathbf{m}\mathbf{m}'} + \sum_{\mathbf{m}_1\neq\mathbf{m}} W_{\mathbf{m}\mathbf{m}_1}^{\mathbf{m}\mathbf{m}_1} P_{\mathbf{m}_1\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}$$

$$+ \sum_{\mathbf{m}_1\neq\mathbf{m}_2} W_{\mathbf{m}\mathbf{m}_2}^{\mathbf{m}\mathbf{m}_1} P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}, \quad (38)$$

$$sP_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}(s)$$

$$= W_{\mathbf{m}_2\mathbf{m}_2}^{\mathbf{m}_1\mathbf{m}_1} P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'} + \sum_{\mathbf{m}_3} W_{\mathbf{m}_2\mathbf{m}_3}^{\mathbf{m}_1\mathbf{m}_3} P_{\mathbf{m}_3\mathbf{m}'}^{\mathbf{m}_3\mathbf{m}'} + \sum{}' W_{\mathbf{m}_2\mathbf{m}_4}^{\mathbf{m}_1\mathbf{m}_3} P_{\mathbf{m}_4\mathbf{m}'}^{\mathbf{m}_3\mathbf{m}'} \quad (39)$$

(the prime at the summation sign in the last term of (39) denotes that $\mathbf{m}_3 \neq \mathbf{m}_4$, $\mathbf{m}_1 \neq \mathbf{m}_2$, and $\mathbf{m}_2 \neq \mathbf{m}_4$). From the definition of (37) it follows that

$$\sum_{\mathbf{m}'} P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}(s) = \frac{1}{s}\delta_{\mathbf{m}_1\mathbf{m}_2}. \quad (40)$$

Summing both parts of (38) and (39) over $\mathbf{m}'$, we obtain, with account of (40),

$$-W_{\mathbf{m}\mathbf{m}}^{\mathbf{m}\mathbf{m}} = \sum_{\mathbf{m}_1\neq\mathbf{m}_2} W_{\mathbf{m}\mathbf{m}_1}^{\mathbf{m}\mathbf{m}_1}, \qquad \sum_{\mathbf{m}_3} W_{\mathbf{m}_2\mathbf{m}_3}^{\mathbf{m}_1\mathbf{m}_3} = 0 \quad (\mathbf{m}_1 \neq \mathbf{m}_2). \quad (41)$$

Using the explicit expressions for $W_{\mathbf{m}_2\mathbf{m}_4}^{\mathbf{m}_1\mathbf{m}_3}$ with

$$T > T_0 \equiv \hbar\omega_0 / 2\ln S_0, \quad \eta_1 = \frac{J}{E_a} < 1,$$

$$\eta_2 = \frac{J^2}{\hbar\omega_0 (E_a T)^{1/2}} < 1, \qquad \eta_3 = \frac{J^2}{E_a T} < 1,$$

$$E_a = \frac{1}{N}\sum_{\mathbf{q}} |\gamma_{\mathbf{q}}|^2 \hbar\omega_{\mathbf{q}} a(\mathbf{q})$$

(see [4]) we can verify that when $\mathbf{m}_1 \neq \mathbf{m}_2$ the quantities $W_{\mathbf{m}_2\mathbf{m}_2}^{\mathbf{m}_1\mathbf{m}_1}$ contain no exponentially small term and are represented by a series in powers of η_1, η_2, and η_3. The largest term of the series is equal to

$$W_{\mathbf{m}_2\mathbf{m}_2}^{\mathbf{m}_1\mathbf{m}_1} \sim \frac{\eta_1^4 \omega_0^2}{\mathrm{sh}^2(\alpha\omega_0)\,\Delta\omega} \quad (42)$$

($\Delta\omega$ is the phonon dispersion width).

The diagonal probabilities ($\mathbf{m}_1 = \mathbf{m}_2$, $\mathbf{m}_3 = \mathbf{m}_4$, $s = 0$) are proportional to $\exp(-E_a/T)$ [7]. The first term of the series for w_0 (diagram with two points) coincides with that calculated in [4] and is equal to $\omega_0\eta_2\exp(-E_a/T)$. The nondiagonal small terms ($\mathbf{m}_1 - \mathbf{m}_2 \neq \mathbf{m}_3 - \mathbf{m}_4$) are at least as small as $\exp(-\mu S_T)$, where $\mu \sim 1$. Inasmuch as $W_{\mathbf{m}_2\mathbf{m}_2}^{\mathbf{m}_1\mathbf{m}_1}$ are the largest when $\mathbf{m}_1 \neq \mathbf{m}_2$, the nondiagonal parts relax more rapidly than the diagonal ones.

It follows from the foregoing that the probabilities through which the systems (38) and (39) become coupled are small, and in the lowest approximation this coupling can be neglected:

$$sP_{\mathbf{m}\mathbf{m}'}^{\mathbf{m}\mathbf{m}'}(s) = \delta_{\mathbf{m}\mathbf{m}'} + W_{\mathbf{m}\mathbf{m}}^{\mathbf{m}\mathbf{m}} P_{\mathbf{m}\mathbf{m}'}^{\mathbf{m}\mathbf{m}'} + \sum_{\mathbf{m}_1\neq\mathbf{m}} W_{\mathbf{m}\mathbf{m}_1}^{\mathbf{m}\mathbf{m}_1} P_{\mathbf{m}_1\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}. \quad (43)$$

Owing to translational symmetry we have

$$P_{\mathbf{m}\mathbf{m}'}^{\mathbf{m}\mathbf{m}'} \equiv P(\mathbf{m} - \mathbf{m}'), \qquad W_{\mathbf{m}\mathbf{m}_1}^{\mathbf{m}\mathbf{m}_1} \equiv W(\mathbf{m} - \mathbf{m}_1). \quad (44)$$

Going over in (43) to the Fourier representation

$$P(\mathbf{m}) = \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{R}_{\mathbf{m}}} P(\mathbf{k}), \qquad P(\mathbf{k}) = \frac{1}{N}\sum_{\mathbf{m}} e^{-i\mathbf{k}\mathbf{R}_{\mathbf{m}}} P(\mathbf{m}), \quad (45)$$

[7] This property is demonstrated in Appendix II using three-point diagrams as examples.

we obtain

$$P(\mathbf{k}) = \{N[s + W_0(\mathbf{k}; s)]\}^{-1},$$
$$W_0(\mathbf{k}; s) = \sum_{\mathbf{m}} (1 - e^{-i\mathbf{k}\mathbf{R}_\mathbf{m}}) W(\mathbf{m}; s). \quad (46)$$

Taking the inverse Laplace transform, we get

$$P(\mathbf{m}; t) = \frac{1}{N} \sum_{\mathbf{k}} e^{-i\mathbf{k}\mathbf{R}_\mathbf{m}} \frac{1}{2\pi i} \int_{l-i\infty}^{l+i\infty} \frac{e^{st} dt}{s + W_0(\mathbf{k}; s)}. \quad (47)$$

Inversion of (43) yields

$$\frac{dP(\mathbf{m}; t)}{dt} = -\int_0^t d\tau \sum_{\Delta\mathbf{m} \neq 0} W(\Delta\mathbf{m}; t - \tau)$$
$$\times [P(\mathbf{m}; \tau) - P(\mathbf{m} + \Delta\mathbf{m}; \tau)] \quad (48)$$

with initial condition $P(\mathbf{m}, 0) = \delta_{\mathbf{m};0}$. The quantities $W(\tau)$ are real and non-negative. Expression (47) is a formal solution of (43) or (48); to determine it we must know $W_0(\mathbf{k}; s)$ as a function of s. Equations (48) describe the motion of the electron over the lattice sites (in accordance with the definition given for $P(\mathbf{mm}'t)$ in Sec. 3) as a random-walk process with aftereffect. However, if we use the fact that $W(\tau)$ is essentially different from zero in the interval $\tau < t_0$ ($t_0 = \hbar/(E_a T)^{1/2} \ll 1/\omega_0$), and $P(\mathbf{m}; t)$ varies slightly over intervals $\sim t_0$ (see above), then (48) takes the form

$$\frac{dP(\mathbf{m}; t)}{dt} = -\sum_{\Delta\mathbf{m}} \overline{W}(\Delta\mathbf{m}) [P(\mathbf{m}; t) - P(\mathbf{m} + \Delta\mathbf{m}; t)], \quad (49)$$

$$\overline{W}(\Delta\mathbf{m}) = \int_0^\infty W(\Delta\mathbf{m}; \tau) d\tau \equiv \lim_{s \to 0} W(\Delta\mathbf{m}; s). \quad (50)$$

The solution of (49) is of the form

$$P(\mathbf{m}; t) = \frac{1}{N} \sum_{\mathbf{k}} \exp\{i\mathbf{k}\mathbf{R}_\mathbf{m} - t[W_0(\mathbf{k}; s)]_{s=0}\}. \quad (51)$$

Equation (49) is of the Kolmogorov-Feller type, and describes a Markoffian stochastic process. The motion of the electron can therefore also be interpreted as a Markoffian wandering process over the sites, with $\overline{W}(\Delta\mathbf{m})$ having the meaning of the probability of executing a jump $\Delta\mathbf{m}$ in a unit time. It was found earlier [4] that the main contribution is made by jumps to the nearest sites ($\Delta\mathbf{m} = \mathbf{g}$). Namely, for $\eta_2 < 1$ we have

$$\overline{W}(\Delta\mathbf{m}) = \sum_{\mathbf{g}} \delta_{\Delta\mathbf{m};\,\mathbf{g}} [\overline{w}(\mathbf{g})]_{s=0}, \quad F(z) = \frac{1}{N} \sum_{\mathbf{q}} \Gamma_\mathbf{q} a(\mathbf{q}) \cos(\omega_\mathbf{q} z),$$

$$\overline{w}(\mathbf{g}) = \frac{1}{2} \frac{J^2}{\hbar^2} e^{-2S_T} \int_0^\infty e^{-st} [e^{F(t+i\alpha)} + e^{F(t-i\alpha)} - 2]\, dt. \quad (52)$$

For a simple cubic lattice $\overline{w}(\mathbf{g}) = w_0$ and we obtain

$$[W(\mathbf{k}; s)]_{s=0} = 2w_0\{[1 - \cos(k_x a_0)] + [1 - \cos(k_y a_0)]$$
$$+ [1 - \cos(k_z a_0)]\}. \quad (53)$$

Substituting (53) in (51) and integrating with respect to $\mathbf{k}$ we obtain

$$P(\mathbf{m}; t) = p(m_x; t) p(m_y; t) p(m_z; t),$$
$$p(m; t) = e^{-2tw_0} I_m(2tw_0) \quad (54)$$

($I_m(z)$ is a Bessel function of imaginary argument).

The condition for the validity of (49) is $t_0 w_0 \ll 1$, i.e., the jump time t_0 must be much shorter than the time between jumps w_0^{-1}. Taking (52) into account, we obtain the criterion for the process to be Markoffian [8]:

$$\hbar\omega_0 (E_a T)^{-1/2} \eta_2 e^{-E_a/T} \equiv \eta_3 e^{-E_a/T} \ll 1. \quad (55)$$

Let us find $P(\mathbf{m} - \mathbf{m}')$ in the next approximation, discarding the last term in (39). In this case the non-diagonal part is expressed in terms of the diagonal part as follows:

$$P^{\mathbf{m}_1\mathbf{m}'}_{\mathbf{m}_2\mathbf{m}'}(s) = (s - W^{\mathbf{m}_1\mathbf{m}_1}_{\mathbf{m}_2\mathbf{m}_2})^{-1} \sum_{\mathbf{m}_3} W^{\mathbf{m}_1\mathbf{m}_3}_{\mathbf{m}_2\mathbf{m}_3} P^{\mathbf{m}_3\mathbf{m}'}_{\mathbf{m}_3\mathbf{m}'}. \quad (56)$$

As a result we obtain

$$P(\mathbf{k}; s) = \{N[s + \widetilde{W}(\mathbf{k}; s)]\}^{-1};$$
$$\widetilde{W}(\mathbf{k}, s) \equiv W(\mathbf{k}) + W_1(\mathbf{k}) =$$
$$\sum_{\mathbf{m}} [1 - \exp(-i\mathbf{k}\mathbf{R}_\mathbf{m})]\, \widetilde{W}(\mathbf{m}; s), \quad (57)$$

$$\widetilde{W}(\mathbf{m}; s) = W(\mathbf{m}; s)$$
$$+ \sum_{\mathbf{m}_1 \neq \mathbf{m}_2} W^{\mathbf{m}\mathbf{m}_1}_{\mathbf{m}\mathbf{m}_2} W^{\mathbf{m}_1 0}_{\mathbf{m}_2 0} [s - W^{\mathbf{m}_1\mathbf{m}_1}_{\mathbf{m}_2\mathbf{m}_2}(s)]^{-1}. \quad (58)$$

The first and second terms in (58) correspond to the Holstein and the Boltzmann contributions to the mobility [4], the second term being small compared with the first when $T > T_0$. [9]

[8] There are grounds for assuming that $w_0 \sim \omega_0 f(\eta_2) \times \exp(-E_a/T)$ for arbitrary η_2, where $f(\eta_2) \sim \eta_2$ for $\eta_2 \ll 1$ and $f(\eta_2) \sim 1$ for $\eta_2 \geq 1$ [2,4]. In this case (55) takes the form

$$\hbar\omega_0 (E_a T)^{-1/2} \exp(-E_a/T) \ll 1.$$

[9] An account of the last term in (39) leads in this case to the appearance of factors of the type $1 + |\eta|$ in front of each term in (58), with

$$|\eta| \sim \Big| \sum_{\mathbf{m}_1 \neq \mathbf{m}_2} W^{\mathbf{m}\mathbf{m}_1}_{\mathbf{m}\mathbf{m}_2} W^{\mathbf{m}_1 0}_{\mathbf{m}_2 0} \{W^{\mathbf{m}\mathbf{m}}_{\mathbf{m}\mathbf{m}} W^{\mathbf{m}_1\mathbf{m}_1}_{\mathbf{m}_2\mathbf{m}_2}\}^{-1} \Big| \ll 1.$$

Let us investigate the time dependence of the rms displacement. Using (45) and (46), we easily obtain

$$\langle X^2(s)\rangle \equiv \int_0^\infty e^{-st}\langle X^2(t)\rangle\, dt = -N\,[\nabla^2_{k_x} P(\mathbf{k};\, s)]_{\mathbf{k}=0}$$

$$= \frac{1}{s^2}\sum_{\mathbf{m}} X_{\mathbf{m}}^2 W(\mathbf{m};\, s), \tag{59}$$

whence

$$\langle X^2(t)\rangle = \sum_{\mathbf{m}} X_{\mathbf{m}}^2 \int_0^t d\tau\,(t-\tau)\,W(\mathbf{m};\,\tau), \tag{60}$$

$$W(\mathbf{m};\,\tau) = \frac{1}{2\pi i}\int_{l-i\infty}^{l+i\infty} e^{s\tau} W(\mathbf{m};\, s)\, ds. \tag{61}$$

We use expression (52) for $W(\mathbf{m};\, s)$. Let us consider first the variation of $\langle X^2(t)\rangle$ for small times $t < t_0 \ll \omega_0^{-1}$. Then the function $F(t \pm i\alpha)$ in the exponentials can be expanded in t, retaining terms $\sim t$ and t^2. Since $E_a/T \gg 1$, we have

$$\langle X^2(t)\rangle = 2\left(\frac{a_0 J}{\hbar}\right)^2 \left\{ t_1^2\left[1-\cos\frac{t}{t_1}\right] - \frac{1}{2}\, t^2 e^{-2S_T}\right\}, \tag{62}$$

where $t_1 \sim \hbar/E_a$. An account of the contribution from the polaron band eliminates the second term in the curly bracket of (62), after which we have

$$\langle X^2(t)\rangle = 2(Ja_0 t_1/\hbar)^2[1-\cos(t/t_1)]. \tag{63}$$

For times $t \ll t_1$ this yields

$$\langle X^2(t)\rangle \approx (Jta_0/\hbar)^2. \tag{64}$$

When $t \gg t_0$ we obtain

$$\langle X^2(t)\rangle \approx a_0^2 w_0 t \equiv a_0^2 t\omega_0\eta_2 \exp(-E_a/T). \tag{65}$$

Relations (63)—(65) admit of an intuitive interpretation. At first, when $t \ll t_1$, the electron placed in the well does not "feel" the polarization and behaves like a "bare" electron: $\langle X^2(t)\rangle \sim (Jta_0/\hbar)^2$ (see Sec. 3). When $t_1 \lesssim t < t_0$, it executes "vibrational motion" about the site with frequency t_1^{-1} and amplitude $r_0 \sim Ja_0 t_1/\hbar$. When $t > t_0$, the relation $\langle X^2(t)\rangle \sim t$, which is characteristic of jumps, holds true. Allowance for W_1 adds to $\langle R^2(t)\rangle$ a term

$$\sum_{\mathbf{m}}\sum_{\mathbf{m}_1\neq\mathbf{m}_2} R_{\mathbf{m}}^2 \frac{W_{\mathbf{mm}_2}^{\mathbf{mm}_1} W_{\mathbf{m}_2 0}^{\mathbf{m}_1 0}}{W_{\mathbf{m}_2\mathbf{m}_2}^{\mathbf{m}_1\mathbf{m}_1}} \times \left\{ t - \frac{1}{W_{\mathbf{m}_2\mathbf{m}_2}^{\mathbf{m}_1\mathbf{m}_1}}\left[1-\exp\left(-tW_{\mathbf{m}_2\mathbf{m}_2}^{\mathbf{m}_1\mathbf{m}_1}\right)\right]\right\}. \tag{66}$$

A similar time variation is a characteristic of Brownian motion [10].

6. EXPRESSION FOR THE ELECTRIC CONDUCTIVITY

According to (36), the quantity $M(\mathbf{m}';\, \mathbf{m};\, t)$ in (5) is expressed in terms of the quantities $\Gamma_{\mathbf{mm}_2}^{\mathbf{mm}_1}$ and $P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}$, which, by definition, contain no free sections, i.e., contain no singularities of the type s^{-1}. We shall show that for the determination of σ it is sufficient to know only the quantities P. Solving the linear system of equations (39) with respect to the nondiagonal $P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}(s)$ $(\mathbf{m}_1 \neq \mathbf{m}_2)$, we obtain

$$P_{\mathbf{m}_2\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}(s) = \sum_{\mathbf{m}_3} L_{\mathbf{m}_2\mathbf{m}_3}^{\mathbf{m}_1\mathbf{m}_3}(s)\, P_{\mathbf{m}_3\mathbf{m}'}^{\mathbf{m}_3\mathbf{m}'}(s) \tag{67}$$

(the concrete form of L is of no importance to us; it is important that, generally speaking, they have no singularities when $s = 0$). Substituting (67) in (38), we obtain a system for the diagonal $P_{\mathbf{mm}'}^{\mathbf{mm}'}(s)$:

$$sP_{\mathbf{mm}'}^{\mathbf{mm}'}(s) = \delta_{\mathbf{mm}'} + \overline{\overline{W}}_{\mathbf{mm}}^{\mathbf{mm}} P_{\mathbf{mm}'}^{\mathbf{mm}'} + \sum_{\mathbf{m}_1\neq\mathbf{m}} \overline{\overline{W}}_{\mathbf{mm}_1}^{\mathbf{mm}_1} P_{\mathbf{m}_1\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}, \tag{68}$$

$$\overline{\overline{W}}_{\mathbf{mm}_1}^{\mathbf{mm}_1} = \overline{\overline{W}}(\mathbf{m}-\mathbf{m}_1) = W_{\mathbf{mm}_1}^{\mathbf{mm}_1} + \sum_{\mathbf{m}_2\neq\mathbf{m}_3} W_{\mathbf{mm}_3}^{\mathbf{mm}_2} L_{\mathbf{m}_3\mathbf{m}_1}^{\mathbf{m}_2\mathbf{m}_1}. \tag{68a}$$

The quantities $\overline{\overline{W}}$ also possess the properties (44), so that the $P_{\mathbf{mm}'}^{\mathbf{mm}'}(s)$ satisfy Eq. (46), in which W is replaced by $\overline{\overline{W}}$:

$$P_{\mathbf{mm}'}^{\mathbf{mm}'}(s) = \frac{1}{N}\sum_{\mathbf{k}} \frac{\exp[i\mathbf{k}(\mathbf{R}_{\mathbf{m}}-\mathbf{R}_{\mathbf{m}'})]}{s+\overline{\overline{W}}(\mathbf{k};\, s)}. \tag{69}$$

Using (67), we can write (36) in the form

$$M(\mathbf{m}';\, \mathbf{m};\, s) = \sum_{\mathbf{m}_1} \tilde{\Gamma}_{\mathbf{mm}_1}^{\mathbf{mm}_1} P_{\mathbf{m}_1\mathbf{m}'}^{\mathbf{m}_1\mathbf{m}'}, \tag{70}$$

$$\tilde{\Gamma}_{\mathbf{mm}_1}^{\mathbf{mm}_1} = \Gamma_{\mathbf{mm}_1}^{\mathbf{mm}_1} + \sum_{\mathbf{m}_2\neq\mathbf{m}_3} \Gamma_{\mathbf{mm}_3}^{\mathbf{mm}_2} L_{\mathbf{m}_3\mathbf{m}_1}^{\mathbf{m}_2\mathbf{m}_1}. \tag{71}$$

From (28) we obtain the following relation (accurate to $O(n_0^2)$)

$$\sum_{\mathbf{m}} M(\mathbf{m}';\, \mathbf{m};\, s) = \frac{1}{s}\frac{N_e}{N}. \tag{72}$$

Here N_e is the number of electrons in the volume V. Summing both sides of (69) with respect to $\mathbf{m}'$, we obtain, to the same accuracy,

$$\sum_{\mathbf{m}_1} \tilde{\Gamma}_{\mathbf{mm}_1}^{\mathbf{mm}_1} = N_e/N. \tag{73}$$

According to (5) we can show, using (69) and (72), that

$$\sigma = -\frac{e^2}{2T}\frac{N}{V} s^2 \left\{\frac{d^2}{dk_x^2}\left[\frac{\tilde{\Gamma}(\mathbf{k})}{s+\overline{\overline{W}}(\mathbf{k})}\right]\right\}_{\mathbf{k}=0}$$

$$\tilde{\Gamma}(\mathbf{k}) = \sum_{\mathbf{m}} \exp(-i\mathbf{k}\mathbf{R}_{\mathbf{m}})\, \tilde{\Gamma}_{\mathbf{m}0}^{\mathbf{m}0}. \tag{74}$$

Carrying out the differentiation and letting first $\mathbf{k} \to 0$ and then $s \to 0$, we obtain, neglecting corrections $\sim \exp(-\mu S_T)$

$$\sigma = \frac{e^2 n_0}{2T} \sum_{\mathbf{m}} X_{\mathbf{m}}^2 [\overline{\overline{W}}(\mathbf{R}_{\mathbf{m}}; s)]_{s\to 0}. \quad (75)$$

(We have put $\tilde{\Gamma}(\mathbf{k})|_{\mathbf{k}=0} = N_e/N$.) We see from (75) that $\tilde{\Gamma}$ is not contained in the final result; thus, formula (5) is equivalent to

$$\sigma = \frac{e^2 n_0}{T} \frac{s^2}{2} \frac{1}{N} \sum_{\mathbf{m}\mathbf{m}'} (X_{\mathbf{m}} - X_{\mathbf{m}'})^2 P_{\mathbf{m}\mathbf{m}'}^{\mathbf{m}\mathbf{m}'}(s); \qquad s \to 0. \quad (76)$$

It is easy to understand why $\tilde{\Gamma}$ is absent from the final result. According to (6), when $t \to \infty$ σ is determined by the asymptotic behavior of some process which starts at $t = 0$. The quantity $\tilde{\Gamma}$ is determined by the initial stage of the process, the "memory" of which vanishes in the limit. For a small-radius polaron we obtain, starting from (58),

$$\sigma = \frac{e^2 n_0}{2T} v a_0^2 [\overline{w}_0(\mathbf{g}) + W_B(\mathbf{g})] = \sigma_H + \sigma_B, \quad (77)$$

we have assumed here

$$W_B(\mathbf{g}) = \sum_{\mathbf{m}_1 \neq \mathbf{m}_2} W_{\mathbf{g}\mathbf{m}_2}^{\mathbf{g}\mathbf{m}_1} W_{\mathbf{m}_2 0}^{\mathbf{m}_1 0} |W_{\mathbf{m}_2\mathbf{m}_2}^{\mathbf{m}_1\mathbf{m}_1}|^{-1} \quad (78)$$

(ν is the number of nearest neighbors). We note that $W_{\mathbf{m}_2\mathbf{m}_2}^{\mathbf{m}_1\mathbf{m}_1} < 0$.[5]

7. THE MARKOFFIAN CASE

Expression (75) for the electric conductivity is quite general, but the determination of $\overline{\overline{W}}(\mathbf{R}_{\mathbf{m}})$ is a difficult task. In the case when the "Markoffian" condition is satisfied, i.e., when the time dependence of $P(\mathbf{m}; t)$ is described by equations of the type (49), a different approach is possible, which facilitates the solution of the problem. In this case

$$P(\mathbf{m}; t) = \frac{1}{N} \sum_{\mathbf{k}} \exp[i\mathbf{k}\mathbf{R}_{\mathbf{m}} - t\overline{\overline{W}}(\mathbf{k})]. \quad (79)$$

For times $t \ll \overline{\overline{W}}^{-1}$ we can write

$$P(\mathbf{m}; t) = \frac{1}{N} \sum_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{R}_{\mathbf{m}}) [1 - t\overline{\overline{W}}(\mathbf{k})]$$

$$= \delta_{\mathbf{m};0} + t\overline{\overline{W}}(\mathbf{m}). \quad (80)$$

Hence

$$\overline{\overline{W}}(\mathbf{m}) = t^{-1} P(\mathbf{m}; t), \quad \mathbf{m} \neq 0, \quad (81)$$

i.e., to find $\overline{\overline{W}}(\mathbf{m})$ it is sufficient to know $P(\mathbf{m}; t)$ for small times, where $P(\mathbf{m}; t)$ depends linearly on t.[10] t should be bounded from below in this case, $t \gg t_0$ (t_0 is the jump time), since the linear dependence of $P(t)$ begins with $t \gg t_0$.

The foregoing considerations allow us to generalize the well-known results of [2,4] to the case of arbitrary η_2, using the method used in a paper by the authors [14] to calculate short-time correlators. Then, for $\eta_3 < 1$, the main contribution is made by terms with $\mathbf{m} = \mathbf{g}$, i.e., it is sufficient to calculate (79) with $\mathbf{m} = \mathbf{g}$. It follows from [14] that

$$P(\mathbf{g}; t) = \langle \Phi^+(\mathbf{g}; i)\, \Phi(\mathbf{g}; t) \rangle$$

(the average is taken over the phonons). The quantities $\Phi(\mathbf{g}; t)$, which have the meaning of amplitudes of the transition from site $\mathbf{m}$ to $\mathbf{m} + \mathbf{g}$, were obtained earlier [14] for $\omega_0 t < 1$ (quasi-classical case) and for arbitrary η_2 and $\eta_3 < 1$; the latter condition leads to the absence of interference in $\Phi(\mathbf{g}; t)$ between transitions with different $\mathbf{g}$, i.e., the problem reduces to a "two-site" problem. In this region of times $P(\mathbf{g}; t) = At$, and the coefficient A can be calculated.

Let us consider the problem of the equalization of the inhomogeneous distribution of the particles over the sites. Assume that at $t = 0$ such a distribution is specified by the function $\varphi(\mathbf{m}; 0)$. For the instant $t > 0$ we have

$$\varphi(\mathbf{m}; t) = \sum_{\mathbf{m}'} P(\mathbf{m} - \mathbf{m}'; t)\, \varphi(\mathbf{m}'; 0). \quad (82)$$

We see therefore that $\varphi(\mathbf{m}, t)$ satisfies an equation of the type (48). In the Markoffian case $\varphi(\mathbf{m}, t)$ satisfies Eq. (49), and we can show that it follows from it that

$$\varphi(\mathbf{m}; t + \Delta t) = \sum_{\Delta\mathbf{m}} P(\Delta\mathbf{m}; \Delta t)\, \varphi(\mathbf{m} + \Delta\mathbf{m}; t). \quad (83)$$

If the inhomogeneity is weak (its scale is $L \gg a_0$), and $\Delta t \gg t_0$ then, expanding $\varphi(\mathbf{m} + \Delta\mathbf{m})$ in powers of $\Delta\mathbf{m}$ (replacing the discrete variable $\mathbf{R}_{\mathbf{m}}$ by the continuous variable $\mathbf{r}$), we obtain the diffusion equation

$$\partial\varphi(\mathbf{r}; t)/\partial t = D\nabla_{\mathbf{r}}^2 \varphi(\mathbf{r}; t),$$

$$D = \frac{1}{2\Delta t} \sum_{\Delta\mathbf{m}} R_{\Delta\mathbf{m}}^2 P(\Delta\mathbf{m}; \Delta t). \quad (84)$$

[10] The foregoing justifies the calculation method used by Holstein[2], who found the probability $w_0(\mathbf{g})$ of jumping to the neighboring site and substituted this value of w_0 in a formula similar to (75).

Equation (84) is meaningful for time intervals $\Delta t \gg t_0$.

8. CONCLUSION

It follows from the form of (48) that the motion of the carrier in the lattice can be regarded as a sequence of individual jumps (generally speaking, non-Markoffian). The quantity $\overline{\overline{W}}(\mathbf{m}; s)$ characterizes the individual properties of the jump, and the equation indicates the method of summing the individual jumps. The mathematical expression of the fact that the process proceeds like a sequence of individual acts is the presence in the expansion of correlators of the divergences of the free-section type. In the case when (79) is valid (Markoffian case), the individual characteristic will be $\overline{\overline{W}}(\mathbf{m})$—the probability that in a unit time the particle will jump from site $\mathbf{m}_1$ to site $\mathbf{m}_1 + \mathbf{m}$, and individual jumps are summed as the acts of a Markoffian process (random walk). A Markoffian condition of the type (55) signifies that the jump is completed within a time short compared with the time between jumps. The problem of finding $\overline{\overline{W}}(\mathbf{m})$ then reduces to a calculation of $P(\mathbf{m}; t)$ for small times, and is not connected directly with the solution of the kinetic problem. (In the non-Markoffian case there is generally speaking no such independent method of obtaining $\overline{\overline{W}}$.)

The present considerations justify the procedure used by Holstein [2] to calculate the mobility, and point to a way of extending the previously obtained results [2,4,5] to include the case when it is not sufficient to confine oneself to the lowest perturbation-theory approximations (for details see Sec. 7). We note that in the derivation of (38), (39), and the main results of Sec. 6, we made use of no properties of the model in question whatever. Therefore all the arguments based on them, and also expression (76) for σ (containing no angle parts), are quite general (in the lowest order in the density, $\Delta E < T$ for narrow bands)[17].

Let us consider the results pertaining to the theory of the small polaron. The first term in (77) coincides with the Holstein term σ_H obtained in [2,4]. The second term in (77) corresponds to the Boltzmann term σ_B from [4]. Its calculation for $T > T_0$ is difficult, and we can only estimate the order of magnitude (see [4]). The result for $T < T_0$, is given in [5] and can be obtained from (77) and (78) by recognizing that in this case

$$W_{gm_2}^{gm_1} \sim (iJ/\hbar)\,\delta_{m_1 g}\,\delta_{m_2 0},$$

and $W_{m_2 m_2}^{m_1 m_1}$ coincides with $W(0) - W(g)$ from [5] [11].

In conclusion the authors are grateful to A. I. Ansel'm for a useful discussion.

APPENDIX I

ELIMINATION OF POINTS INSIDE A BLOCK

By way of an example let us sum the diagrams with "empty" points shown in Figs. 2f, g, h. All contain a line joining points 1 and 2, and differ in the number and distribution of the "empty" points in the interval t_2, t_1 on the upper and lower parts of the contour. The contribution from the sum of such diagrams can be written

$$W_{nn'}^{mm'}(t_2 - t_1) = \sum_{gg'} Z(t_2 - t_1; \mathbf{m} - \mathbf{m}'; \mathbf{g}; \mathbf{g}')\,\tilde{P}_{n\,n'}^{m+g\;m'-g'}(t_2 - t_1), \quad (A.1)$$

where $\tilde{P}$ satisfies the equation

$$\frac{d\tilde{P}_{n\,n'}^{m+g\;m'-g'}(t)}{dt} = \frac{i}{\hbar}\sum_{g_1} J(\mathbf{g}_1)\, e^{-S_T(g_1)}\,[\tilde{P}_{n\,n'}^{m+g\;m'-g'-g_1'} - \tilde{P}_{n\,n'-g_1}^{m+g\;m'-g'}];$$

$$\tilde{P}_{nn'}^{mm'}(t)\big|_{t=0} = \delta_{mm'}\delta_{nn'}. \quad (A.2)$$

Its solution can be sought in the form

$$P_{n\,n'}^{m+g\;m'-g'}(t) = \sum_{k_1 k_2} P_{k_2}^{k_1}(t)\exp\{i\mathbf{k}_1(\mathbf{m} + \mathbf{g}' - \mathbf{m}' + \mathbf{g}') - i\mathbf{k}_2(\mathbf{m} - \mathbf{m}')\}. \quad (A.3)$$

From (A.2), taking (A.3) into account, we obtain

$$P_{k_2}^{k_1}(t) = \frac{1}{N^2}\sum_{k_1 k_2}\exp\left\{\frac{i}{\hbar}[\varepsilon(\mathbf{k}_1) - \varepsilon(\mathbf{k}_2)]\,t\right\};$$
$$\varepsilon(\mathbf{k}) = \sum_{g} e^{-i\mathbf{k}g} J(\mathbf{g})\, e^{-S_T(g)}. \quad (A.4)$$

Then

$$W_{nn'}^{mm'}(t_2 - t_1) = \sum_{gg'}\frac{1}{N^2}\sum_{k_1 k_2} Z_{12}(t_2 - t_1; \mathbf{m} - \mathbf{m}'; \mathbf{g}; \mathbf{g}') \times \exp\left\{\frac{i}{\hbar}[\varepsilon(\mathbf{k}_1) - \varepsilon(\mathbf{k}_2)](t_2 - t_1)\right\} \times \exp[i\mathbf{k}_1(\mathbf{m} + \mathbf{g} - \mathbf{m}' + \mathbf{g}') - i\mathbf{k}_2(\mathbf{n} - \mathbf{n}')]. \quad (A.5)$$

In our case all the characteristic times are much

[11] Friedmann [15] also reached the conclusion that $\sigma = \sigma_H + \sigma_B$, but since he confined himself to the lowest order in J his expression for σ_B differs from that obtained in [4] and above. An account of the succeeding approximations within the framework of his method causes σ_B to coincide with the result in [4].

shorter than $[J \exp(-S_T)/\hbar]^{-1}$, and we can neglect $\epsilon(k)$ in the exponentials; this yields

$$W_{nn'}^{mm'}(t_2 - t_1) = \sum_{gg'} Z_{12}(t_2 - t_1)\,\delta_{nn'}\,\delta_{m+g;\,m'-g'}. \quad (A.6)$$

Thus, if we are not interested in corrections of the order $\exp(-S_T)$, we can take into account only the "skeleton" diagrams without "empty" points.

APPENDIX II

PROPERTIES OF THE PROBABILITIES (BLOCKS)

Let us demonstrate, using third-order diagrams as an example, some properties of the probabilities mentioned in Sec. 5. A typical diagram is shown in Fig. 3a.

A. Diagonal probability $W_{\mathbf{mm}+\mathbf{g}_1+\mathbf{g}_2}^{\mathbf{mm}+\mathbf{g}_1+\mathbf{g}_2}$ for $s = 0$ and $\mathbf{g}_1 + \mathbf{g}_2 + \mathbf{g}_3 = 0$. We are summing the diagrams shown in Figs. 3b, c, d, (and their complex conjugates). According to the rules of Sec. 4, the contribution from diagram 3b is

$$A_1 = (-1)^2\left(\prod_{i=1}^{3}\frac{iJ(\mathbf{g}_i)\exp[-S_T(\mathbf{g}_i)]}{\hbar}\right)\int_0^\infty d\tau_2 \times \int_0^{\tau_2} d\tau_1\, Z_{12}(\tau_1-\tau_2)Z_{23}(\tau_2)Z_{13}(\tau_1) \quad (A.7)$$

(in the calculation of the compact parts the number of integrations is one less than the number of points, and one integration is used to obtain the free section, so that we can set the value of τ farthest on the left equal to zero). The contributions from the diagrams 3c and d are respectively

$$A_2 = \prod\left(\frac{iJe^{-S_T}}{\hbar}\right)\int_0^\infty d\tau_2 \int_0^{\tau_2} d\tau_3\, Z_{12}(-\tau_2)Z_{23}(\tau_2-\tau_3)Z_{13}(-\tau_3),$$

$$A_3 = \prod\left(\frac{iJe^{-S_T}}{\hbar}\right)\int_0^\infty d\tau_3 \int_0^{\tau_3} d\tau_2\, Z_{12}(-\tau_2)Z_{23}(\tau_2-\tau_3)Z_{13}(-\tau_3). \quad (A.8)$$

For $A_2 + A_3$ we have

$$A_2 + A_3 = \prod\left(\frac{iJe^{-S_T}}{\hbar}\right)\int_0^\infty d\tau_2 \int_0^\infty d\tau_3\, Z_{12}(-\tau_2)Z_{23}(\tau_2-\tau_3)Z_{13}(-\tau_3). \quad (A.9)$$

In A_1 we put $\tau_2 = z_1 + z_2$ and $\tau_1 = z_1$. After some transformations we obtain

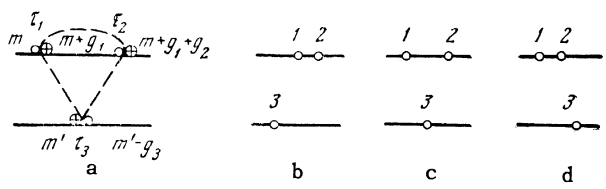

FIG. 3

$$A_1 + A_2 + A_3 = \prod\left(\frac{iJe^{-S_T}}{\hbar}\right)\int_0^\infty d\tau_2 \int_{-\infty}^{+\infty} d\tau_1\, Z_{12}(-\tau_2)Z_{23}(\tau_2-\tau_1)Z_{13}(-\tau_1). \quad (A.10)$$

Substituting the explicit expressions for Z_{ik} and replacing $\tau_1 - i\alpha$ by τ_1', we get

$$A_1 + A_2 + A_3 = \left(\frac{iJ}{\hbar}\right)^3 \int_0^\infty d\tau_2 \int_{-\infty}^{+\infty} d\tau_1 \exp\left\{-\frac{1}{N}\sum_{\mathbf{q}}\Gamma_{\mathbf{q}}a(\mathbf{q})\{3\,\mathrm{ch}(\alpha\omega_{\mathbf{q}}) - \cos(\omega_{\mathbf{q}}\tau_1) - \cos(\omega_{\mathbf{q}}(\tau_1-\tau_2)) - \cos(\omega_{\mathbf{q}}(\tau_2 - i\alpha))\}\right\}, \quad (A.11)$$

We see therefore that in the most favorable case, $\tau_1 = \tau_2 = 0$, the integrand is not smaller than

$$\exp\left\{-\frac{2}{N}\sum\Gamma_{\mathbf{q}}a(\mathbf{q})[\mathrm{ch}(\alpha\omega_{\mathbf{q}}) - 1]\right\},$$

i.e., the contribution to the diagonal probability is small like $\exp(-E_a/T)$. We can show [16] that this is true in any order.

B. Nondiagonal block $W_{\mathbf{m}'\mathbf{m}-\mathbf{g}_3}^{\mathbf{mm}+\mathbf{g}_1+\mathbf{g}_2}(s)$; $\mathbf{g}_1 + \mathbf{g}_2 + \mathbf{g}_3 \neq 0$ or $\mathbf{m} \neq \mathbf{m}'$. We shall verify that the small factor $\exp(-3S_T)$ (preceding the integral) is not cancelled even when $t_1 = t_2 = 0$. In this case

$$e^{-3S_T}Z_{12}(0)Z_{23}(0)Z_{13}(0) = -\frac{1}{2N}\sum_{\mathbf{q}}|\gamma_{\mathbf{q}}|^2\coth(\alpha\omega_{\mathbf{q}}) \times [3 - \cos(\mathbf{qg}) - a_{12} - a_{13} - a_{23}]. \quad (A.12)$$

Writing out a_{ik} in explicit form, in accordance with the rules of Sec. 4, we find that the expression in the square bracket is

$$Y_{\mathbf{q}} \equiv 2 - \cos(\mathbf{qg}_3) - \cos(\mathbf{q}(\mathbf{g}_1+\mathbf{g}_2)) + \cos(\mathbf{q}(\mathbf{G}+\mathbf{g}_3)) - \cos(\mathbf{qG}) + \cos(\mathbf{q}(\mathbf{G}+\mathbf{g}_1+\mathbf{g}_2)) - \cos(\mathbf{q}(\mathbf{G}+\mathbf{g}_1+\mathbf{g}_2+\mathbf{g}_3)); \quad \mathbf{G} = \mathbf{R}_{\mathbf{m}} - \mathbf{R}_{\mathbf{m}'}. \quad (A.13)$$

Let us consider some particular cases:

a) $\mathbf{G} = 0$; $\mathbf{g}_1 + \mathbf{g}_2 + \mathbf{g}_3 \neq 0$;

$$Y_{\mathbf{q}} = -1/2\{1 - \cos[\mathbf{q}(\mathbf{g}_1 + \mathbf{g}_2 + \mathbf{g}_3)]\};$$

b $\mathbf{G} \neq 0$; $\mathbf{g}_1 + \mathbf{g}_2 = 0$; $Y_{\mathbf{q}} = -1/2[1 - \cos(\mathbf{q}\mathbf{g}_3)]$;

c $\mathbf{G} \neq 0$; $\mathbf{g}_1 + \mathbf{g}_2 + \mathbf{g}_3 = 0$;

$$Y_{\mathbf{q}} = -[1 - \cos(\mathbf{q}\mathbf{G})][1 - \cos(\mathbf{q}\mathbf{g}_3)].$$

In all these cases the expression for W is proportional to $\exp(-N^{-1}\Sigma\Gamma_{\mathbf{q}}Y_{\mathbf{q}})$, i.e., the exponential contains a quantity $\sim \epsilon S_T$ with $\epsilon \sim 1$. We can show [16] that for any choice of $\mathbf{G}$, $\mathbf{g}_1$, $\mathbf{g}_2$, or $\mathbf{g}_3$ the exponential small factor is not cancelled for the nondiagonal block.

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115