Density Matrix Formulation of Small-Polaron Motion*

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A density-matrix treatment of small-polaron motion is presented for the case in which the electronic overlap term of the total Hamiltonian is a small perturbation. The principal result of the density matrix formalism is that total small-polaron mobility can be expressed as the sum of a band part $\langle v_o^2\tau\rangle$, characteristic of the low-temperature regime ($T<T_t$), plus a part ($W_T a^2$) describing the hopping motion dominant at high temperatures ($T>T_t$). This verifies the separation of the above two types of motion made on the basis of physical arguments. In addition, the present treatment avoids certain formal divergences in the integrals for the jump probabilities. Furthermore, the hopping contribution does not require localization of the polaron at a particular site, but follows from a translationally invariant formulation. These results are obtained, in part, from lowest order Boltzmann equations which are derived both in the local-site and polaron-band representations. The principal contributions to the scattering terms of the Boltzmann equations are determined by interference effects between the matrix elements, which are examined in some detail.

INTRODUCTION

DURING the past several years, there has been considerable theoretical interest in the basic mechanisms of small-polaron transport. The small-polaron concept applies to semiconductors of sufficiently narrow electronic-conduction bandwidth (or valence bandwidths, in the case of hole conduction) for which the interaction of the charge carrier with the lattice vibrations is particularly strong. In such a situation, the charge carrier gets essentially self-trapped in the immediate neighborhood of one of a large number of crystallographically equivalent atomic sites. The existence of a nonvanishing electronic overlap then gives rise to occasional transfers among these sites. The unit consisting of the charge carrier and surrounding induced lattice deformation—the latter serving as a potential well in which the carrier is self-trapped—is designated as the small polaron.

Conventional (large) polaron theories[1,2] are based on a continuum model in which: (a) the ionic dipole moments arising from the displacements of the discrete lattice particles are replaced by a continuous polarization field, and (b) the motion of the charge carrier is formulated in terms of an effective mass approximation. Such a model is clearly inadequate in describing the small polaron, whose dimensions are of the order of the lattice spacing. Rather, the periodicity of the discrete lattice structure must be taken into account explicitly.

This distinction was first recognized and treated by Tyablikov.[3] Employing a tight-binding approach in which the electronic overlap part of the total Hamiltonian was treated as a small perturbation,[4] he showed that band spectrum of the small polaron is characterized by a width which is exponentially smaller than the purely electronic bandwidth by a factor depending on the overlap of neighboring vibrational wavefunctions. His treatment of the "polaron-band" is limited to the absolute zero of temperature, however, thereby precluding any consideration of the hopping-type conduction prevalent at high temperatures.

The finite temperature case was next investigated by Yamashita and Kurosawa.[5,6] Using a discrete description of the crystal lattice, but treating the electron-lattice interaction by a continuum approximation, these authors were the first to note that the polaron bandwidth, already very small at $T=0$, decreases even further (in particular, exponentially) with increasing temperature. As a consequence, they point out that the corresponding small-polaron mass (which varies inversely with bandwidth) is exponentially large. They therefore argue that a localized description is more appropriate than polaron-band motion, and then go on to calculate the lowest-order elementary jump rate between local sites. They do not, however, make clear the criteria which distinguish the two regimes. The polaron-band motion and its temperature dependence was also carefully formulated and studied by Sewell[7];

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[1] S. I. Pekar, Issledovaniya po Electronnoi Teorii Kristallov, Gosudarstvennoe Izdatel'stvo Tekhniko-Teoreticheskoi Literatury, Moskva, 1951 [English transl.: AEC-tr-5575, Feb. (1963), Office of Technical Services, Department of Commerce, Washington, D. C.].

[2] H. Fröhlich, Advan. Phys. **3**, 325 (1954).

[3] S. V. Tyablikov, Zh. Eksperim. i Teor. Fiz. **23**, 381 (1952).

[4] It should be pointed out that all of the references to be discussed, as well as the treatment of the present paper, are largely confined to the case in which the electronic overlap term of the total Hamiltonian can be treated as a small perturbation. However, it should be noted that there is a remaining (adiabatic) regime in which the polaron is small, but perturbation theory does not apply (see Refs. 6, 8, and footnote 22).

[5] J. Yamashita and T. Kurosawa, Phys. Chem. Solids **5**, 34 (1958). These authors employ an Einstein spectrum and an arbitrary cutoff $t\leq 2\pi/\omega_0$ of the type discussed in footnote 11.

[6] J. Yamashita and T. Kurosawa, J. Phys. Soc. Japan **15**, 802 (1960). This paper considers the practical consequences of including a small, fluctuating potential (due to a random distribution of impurities) on small-polaron motion, and, in particular, on the "washing out" of the polaron-band motion. In the present paper, it is shown that the dominance of the hopping motion for $T>T_t$ is an automatic consequence of the theory, even for the ideal, periodic case.

[7] G. L. Sewell, Phil. Mag. **3**, 1361 (1958).

however, he gave no consideration to the hopping-type motion prevalent at high temperatures.

A more satisfactory resolution of the above two types of small-polaron motion was given by Holstein.[8] It was here pointed out that the basic distinction between the two regimes is determined by two basic classes of matrix elements which describe site-jump transitions. As will be made explicit later in the paper, the low-temperature polaron mobility is dominated by the so-called "diagonal" matrix elements, in which the totality of vibrational quantum numbers accompanying a site-jump transition remains precisely unchanged.[9] These matrix elements give rise to the previously described temperature-dependent polaron bandwidth. In this regime, the role of the "nondiagonal" matrix elements, defined as those in which some of the vibrational quantum numbers change by ± 1, is to provide scattering between polaron-band states, and therefore to determine their lifetimes in the absence of other scattering mechanisms (which is the condition we shall assume to apply). It was then argued that above a certain transition temperature[10] T_t the energy broadening of the polaron-band states exceeds the (exponentially decreasing) polaron bandwidth, the band approach clearly breaks down, and a localized basis becomes the more appropriate starting point. In this high-temperature regime, the nondiagonal matrix elements now play the dominant role, giving rise to a diffusion-type motion of the charge carrier, in which the basic steps are random jumps between local sites.

Recent investigators have essentially confirmed the above picture of small-polaron motion.[11] Klinger,[12] by a resolvent technique which introduces collision damping of the polaron-band motion, finds that the criteria for summing certain term sequences of diagonal transitions [cf. later text and footnote 20] are essentially the same as those cited above, with some differences in detail. Lang and Firsov[13] have provided a systematic perturbation development of small-polaron mobility, in which the smallness parameter [η_2, defined in footnote 22] is just that obtained in Ref. (8). In the high-temperature regime, the leading term for the mobility is gain the same as that given in Ref. (8). In addition, two alternating and rapidly decreasing sequences of terms for the mobility are obtained in increasing powers of the smallness parameter. However, in the low-temperature polaron-band regime, using an alternate Boltzmann equation treatment derived by diagrammatic techniques, these authors point out that a higher order contribution[14] to the scattering between polaron band states, not considered in Ref. (8), can compete with or dominate the lowest-order contribution, and therefore serve to limit the band contribution to polaron mobility. Nagaev[15] has adopted an alternate approach which is basically different from those of the previous authors. He constructs his basic wave functions from plane-wave combinations of states which, in turn, are superpositions of localized states with varying distributions of the vibrational quantum numbers, but with a fixed number of total excitations. From such a basis, the mean-square dispersion of the polaron bandwidth is found to increase with increasing temperature. Thus, he concludes that the increase in small-polaron mobility with temperature follows from the band motion alone, and is not associated with site-jump transitions (in this connection, see the discussion of Sec. VI). While plausible for the case of an Einstein spectrum, where all states in the above linear combination are strictly degenerate, such a recipe becomes ambiguous for a finite vibrational dispersion which lifts this degeneracy. For this case, the above states are chosen to lie within some energy intervale L of arbitrary width. Indeed, it is pointed out that in the limit $L \to 0$, the mean-square dispersion now decreases with temperature as predicted in Ref. 8 and in the present paper. Moreover, the density-matrix treatment of the present paper, which is invariant to the choice of representation, gives no evidence for any increase of bandwidth with temperature [c.f. (4.5), (4.9), (4.11), and Sec. VI].

[8] T. Holstein, Ann. Phys. (N.Y.), **8**, 343 (1959).

[9] These matrix elements therefore provide *exact* energy conservation.

[10] In practice, T_t turns out to be $\sim\frac{1}{2}\Theta_D$, where Θ_D is the optical, Debye theta.

[11] R. R. Dogonadze and Yu. A. Chizmadzhev, Fiz. Tverd. Tela **3**, 3712 (1961) [English transl.: Soviet Phys.—Solid State **3**, 2693 (1962)]; R. R. Dogonadze, A. A. Chernenko, and Yu. A. Chizmadzhev, Fiz. Tverd. Tela **3**, 3720 (1961) English transl.: Soviet Phys.—Solid State **3**, 2698 (1962)]. These authors also obtain the dual aspect of small-polaron motion found in Ref. 8 and the present paper (viz., the scattering probabilities between band states, and the site-jump transition rates), with some differences in detail. These differences appear to be due to the fact that account is not taken of dispersion of the vibrational spectrum which, in the opinion of the present author, is essential in obtaining convergent expressions for the transition probabilities. These authors apparently obviate this difficulty by arbitrarily restricting the limits on the time integrations to $t \leqslant 2\pi/\omega_0$, where ω_0 is the Einstein frequency.

[12] M. J. Klinger, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 205; Fiz. Tverd. Tela **4**, 3074 and 3086 (1962) [English transl.: Soviet Phys.—Solid State **4**, 2252 and 2260 (1963)].

[13] I. G. Lang and Y. A. Firsov, Zh. Eksperim. i Teor. Fiz. **43**, 1843 (1962) [English transl.: Soviet Phys.—JETP **16**, 1301 (1963)].

[14] As pointed out by T. Holstein (private communication), this additional contribution corresponds to processes of the type p, N_{k_1}, $N_{k_2} \to p \pm 1$, $N_{k_1} \pm 1$, $N_{k_2} \to p$, $N_{k_1} \pm 1$, $N_{k_2} \pm 1$, in which the polaron eventually remains on site p, but the vibrational state changes. These processes are therefore scattering events between polaron-band states which do not constitute site-jump transitions ($p \nleftrightarrow p \pm 1$). That they make an important contribution is principally due to the fact that, though smaller than the first-order nondiagonal process by a factor $\sim J^2$, they do not contain an activation-type factor, since the above intermediate state is virtual. Processes of this type can, in principal, be treated as higher order effects within the density-matrix formalism of the present paper. Although a proper accounting of such terms will affect the transition temperature T_t, it is felt that this will not alter the essential features of the present paper, in particular the additivity of our final result (4.17).

[15] E. L. Nagaev, Fiz. Tverd. Tela **4**, 2201 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1611 (1963)].

Reik[16] has recently shown that the high-temperature drift mobility formula of Ref. 8 also follows directly from the Kubo formula. He does not consider the low-temperature mobility due to polaron-band motion. His approach has the advantage of being translationally invariant, as is the density-matrix treatment of the present paper. However, in the opinion of the present author, Reik's final result, given by Eq. (10) of his paper, is not correct in detail. Specifically, it is correctly pointed out that this result is essentially equivalent to Eq. (57) of Ref. 8. However, in the text following Eq. (57) of Ref. 8, it is established in some detail that (57) diverges linearly with t, and therefore cannot represent a conventional transition rate. [This can be seen qualitatively from the argument of the exponential appearing in the integrand. For large τ and some dispersion of the vibrational spectrum ω_k, the sum over k of the terms proportional to $\cos(\omega_k\tau)$ tends to oscillate about a mean value of zero. It is not surprising, therefore, that this sum turns out to vary as an inverse power of τ for large τ (specifically, as $\tau^{-1/2}$). The integral therefore exhibits a linear divergence in the limit of infinite interaction time t. It might also be remarked that the adiabatic factor $\exp(\epsilon\tau)$ is not sufficient to provide convergence in the limit that $\epsilon \to 0$.] This difficulty is due to the tacit inclusion of the diagonal matrix elements in the treatment, and is rectified in Ref. 8 by a suitable subtraction recipe (see footnote 20). In the present paper, the contributions of the diagonal elements are rigorously excluded from the jump probabilities, thereby avoiding this difficulty.

In a research note, Fröhlich and Sewell[17] have discussed the breakdown of conventional band theory in narrow-band semiconductors, and the alternate applicability of small-polaron theory. They discuss a number of scattering mechanisms in the polaron-band regime, in addition to the nondiagonal processes operative in the ideal case. They also note the site-jump transitions operative at high temperatures, and calculate the mobility appropriate to a two-phonon hopping process; however, they note the larger weight which must be given to multiphonon[5,8] transitions when the electron-phonon coupling is strong. Fröhlich, Machlup, and Mitra[18] have recently called attention to an additional aspect of the small-polaron problem which has thus far not been taken into account: namely, the dependence of the electronic overlap integrals on the vibrational displacement coordinates (via their dependence on the local electronic wave functions appropriate to the *instantaneous* ion positions). While this is a real physical effect which would tend to broaden the *electronic* overlap with increasing temperature, a question remains as to whether its temperature dependence would be sufficiently rapid to appreciably affect the strong exponential decrease of the polaron bandwidth arising from the *vibrational* overlap factor. As far as the effect of this dependence on the hopping motion is concerned, it should be pointed out that, as has been shown by a classical treatment of the lattice motions,[8] the site jumps occur for a more or less particular value of the overlap: namely, that appropriate to a vibrational configuration corresponding to a momentary coincidence of the electronic energies of neighboring sites. Thus, from this point of view, variations in overlap with relative displacement would not be expected to basically alter the form of the hopping mobility obtained on the basis of a constant overlap evaluated for the above coincidence configuration.

The purpose of the present study is to present an alternate formulation of small-polaron motion which serves to treat both the band motion and the hopping motion in a more unified fashion, and also serves to remove some of the formal objections to the theory. This approach is a density-matrix formulation of small-polaron motion, analogous to (but differing in important ways from) the well-known density-matrix treatment of Kohn and Luttinger.[19] The use of such an approach is strongly suggested by the previously described distinction between the diagonal and nondiagonal matrix elements of the perturbation: the density matrix approach provides such a separation in a natural and straightforward fashion. By the general procedures of Ref. 19, a "Boltzmann" equation is obtained to lowest order in the overlap J (which plays the role of the dimensionless parameter λ in the work of Kohn and Luttinger). The time rate of change of the density matrix is essentially given by a part which wholly describes the band motion, plus a scattering term which provides damping of the band propagation. In this connection, a formal difficulty of the theory is avoided: namely, that the diagonal matrix elements of the perturbation are rigorously absent from the expression for the jump rate, and do not have to be subtracted out by physical arguments.[20] The principal result of the present paper, given by Eq. (4.17), is that, to lowest order in J, the expectation value of velocity is given by a band part $\langle v_\sigma^2\tau_\sigma\rangle$, *plus* a contribution due the hopping motion $\sim W_T a^2$. (Here, v_σ is the polaron velocity in Bloch state σ, τ_σ is its lifetime, $\langle\cdots\rangle$ indicates a statistical average over the polaron band, W_T is the thermal average jump rate between nearest neighbor sites, and "a" is the lattice constant.) The density-matrix treatment therefore confirms the

[16] H. G. Reik, Phys. Letters **5**, 236 (1963).
[17] H. Fröhlich and G. L. Sewell, Proc. Phys. Soc. (London) **74**, 643 (1959).
[18] H. Fröhlich, S. Machlup, and T. K. Mitra, Phys. Kondens Materie **1**, 359 (1963).
[19] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).
[20] As pointed out in Ref. 8, the diagonal matrix elements provide exact energy conservation and therefore lead to a transition probability which increases quadratically (rather than linearly) with time. However, the time over which the diagonal transitions can occur is limited by the lifetime of the localized states, and by the very definition of the site-jump regime, the probability of such a transition in such a time turns out to be much less than unity. Hence, this is a purely formal, rather than a basic physical difficulty.

separation of the two types of small-polaron mobility according to the criteria given in Ref. 8. The present approach also overcomes another objection to the theory: namely, that localization of the carrier at a given site (which is made in order to compute the jump probability) is inconsistent with the translational invariance of the system. In the density-matrix approach, the site-jump term is obtained on the basis of a zeroth-order density matrix [cf. (4.6)] (which applies for zero electric field and zero overlap) which represent a uniform probability distribution of the carrier over the lattice.[16]

In deriving the lowest-order Boltzmann equation, we also exhibit certain interference effects among the matrix elements which determine the scattering processes of importance, and the form of the Boltzmann equation. Although the final expectation value of velocity is independent of the choice of basis functions, the above described program is also carried out in the polaron-band representation, since this emphasizes characteristic differences between the Boltzmann equations in the two representations. Finally, we note that only the lowest-order Boltzmann equation is obtained. We do not carry out the iterative procedure by which higher order corrections to the current can be obtained from the density-matrix equations of motion. A systematic treatment of this type should agree with the perturbation development[14] given in Ref. 13.

II. BASIC HAMILTONIAN AND DENSITY-MATRIX EQUATIONS OF MOTION

The starting point of the density-matrix formulation is the Hamiltonian appropriate to a single excess electron in a one-dimensional molecular crystal in the presence of a weak, externally applied, electric field. This model has been described in detail in Ref. 8 and elsewhere,[21] and so will not be reiterated here. We shall simply write down the basic Hamiltonian, attempting to make clear the physical significance of its various parts. The basic equation of motion reads:

$$i\hbar(\partial a(n,\cdots q_k\cdots)/\partial t)=\{\sum_k H_k^{(n)}+E_b+eFn\}\times a(n,\cdots q_k\cdots)-J\{a(n+1,\cdots q_k\cdots)+a(n-1,\cdots q_k\cdots)\}. \quad (2.1)$$

In this equation, the $a(n,\cdots q_k\cdots)$ are the amplitudes of the total wave function of the system in a tight-binding expansion of the form

$$\Psi(\mathbf{r},\cdots x_i\cdots)=\sum_n a(n,\cdots x_i\cdots)\phi(\mathbf{r}-n\mathbf{a},x_n), \quad (2.2)$$

in which the ϕ are the set of local electronic wavefunctions centered at the various lattice sites n,$\mathbf{r}$ is the electronic coordinate, and the x_i are the vibrational displacement coordinates. In going from (2.2) to (2.1), the x_i have been transformed to the normal mode coordinates, q_k, of the host crystal.

The quantities $H_k^{(n)}$ are displaced oscillator Hamiltonians, given by

$$H_k^{(n)}=-(\hbar^2/2M)(\partial^2/\partial q_k^2)+\tfrac{1}{2}M\omega_k^2(q_k-q_k^{(n)})^2, \quad (2.3)$$

where M is the (reduced) mass of the lattice particles, $\omega_k^2=\omega_0^2+\omega_1^2\cos k$ gives the dispersion of the vibrational spectrum, and the $q_k^{(n)}$ represent the displacements of the normal mode coordinates which occurs as a result of incorporating the linear electron-lattice interaction in zeroth order. Finally, $E_b(<0)$ is the corresponding small-polaron binding energy, F is the applied electric field strength, and $(-J)$ is the standard electronic overlap integral of tight-binding theory (assumed to be a constant[18] for all pairs of nearest-neighbor sites).

The present treatment is based on the so-called jump-perturbation approximation, in which the J-proportional term of (2.1) can be treated as a small perturbation.[22] In the absence of this term (and also for zero electric field), the electron is confined to a particular site, say $n=p$. The corresponding eigenstates of (2.1) are given by

$$a_{p,\cdots N_k\cdots}(n,\cdots q_k\cdots)=\delta_{np}\prod_k \Phi_{N_k}[(M\omega_k/\hbar)^{1/2}(q_k-q_k^{(p)})], \quad (2.4)$$

where the $\Phi_{N_k}(z)$ are normalized harmonic oscillator eigenfunctions of vibrational quantum number N_k.

To keep clear the later treatment, it is important to point out that the a's should be though of as "wavefunctions" satisfying (2.1); they are functions of the dynamical variables n and $(\cdots q_k\cdots)$, and are specified (in zeroth order) by the quantum numbers p and $(\cdots N_k\cdots)$. Also, since the latter notation will occur frequently in the remainder of the paper, the *totality* of vibrational quantum numbers will henceforth be abbreviated by N: thus, $N\equiv(\cdots N_k\cdots)$, $N'\equiv(\cdots N_k'\cdots)$, etc. The total number of sites will be distinguished by a capital script $\mathfrak{N}$.

The eigenvalues corresponding to (2.4) are

$$E_N=\sum_k \hbar\omega_k(N_k+\tfrac{1}{2})+E_b. \quad (2.5)$$

The perturbation development proceeds according to standard time-dependent perturbation theory: The total wave function of (2.1) is expanded in the inter-

[21] L. Friedman and T. Holstein, Ann. Phys. (N. Y.) **21**, 494 (1963). This reference contains the generalization for the case of an applied magnetic field. The present density-matrix method can also be generalized to treat the correlation effects discussed in this reference which are responsible for the existence of the Hall effect in the multiphonon site-jump regime.

[22] As pointed out in Ref. 8, the small-polaron condition $J<E_b$ is not sufficient for the applicability of the jump-perturbation approximation. Rather, the more stringent condition

$$\eta_2\equiv J/(\hbar\omega_0)^{1/2}(kTE_a)^{1/4}\ll 1,$$

where E_a is the activation energy, is required (for the case $T>T_t$ of principal interest). The adiabatic regime referred to in footnote 4 is defined by $J<E_b$, $\eta_2\gtrsim 1$.

action picture in the basis provided by (2.4):

$$a(n,\cdots q_k\cdots;t)=\sum_{p'N'}C(p',N';t)\times a_{p'N'}(n,\cdots q_k\cdots)e^{-(it/\hbar)E_{N'}}. \quad (2.6)$$

The C's are then found to obey the equations

$$i\hbar(\partial C(p,N;t)/\partial t)=eFpC(p,N;t)+\sum_{p'N'}\langle pN|V|p'N'\rangle C(p'N';t)e^{(it/\hbar)(E_N-E_{N'})}. \quad (2.7)$$

The $\langle pN|V|p'N'\rangle$ are the basic matrix elements of the perturbation [i.e., of the J-proportional term of (2.1)]. They are different from zero only if p and p' are nearest-neighbor sites. Their explicit form is given in Ref. 8 and is written down here for future reference:

$$\langle p'N'|V|pN\rangle=-J\sum_{\epsilon=\pm1}\delta_{p',p\pm1}\prod_k\{[1-(4/\mathfrak{N})\times(N_k+\tfrac{1}{2})\gamma_k\cos^2(k(p+\tfrac{1}{2}\epsilon)+\tfrac{1}{4}\pi)]\delta_{N_{k'},N_k}\mp[(8/\mathfrak{N})^{1/2}\epsilon\mu_k\gamma_k^{1/2}((N_k+\tfrac{1}{2}\pm\tfrac{1}{2}))^{1/2}\times\cos(k(p+\tfrac{1}{2}\epsilon)+\tfrac{1}{4}\pi)]\delta_{N_{k'},N_k\pm1}\}, \quad (2.8)$$

where $\mu_k=\pm1$ according to whether k is positive or negative, and the γ_k's are the characteristic coupling constants of the theory, given essentially by the ratio of the polaron binding energy to the vibrational quantum $\hbar\omega_k$.

From the above form, it is furthermore clear that the nondiagonal matrix elements are smaller than the diagonal ones (which are $\sim\mathfrak{N}^0$) by the factor $\mathfrak{N}^{-S/2}$, where S is the number of quantum numbers in the set N' which differ from the corresponding ones in N by ±1. As discussed in the Introduction, this distinction is of fundamental importance.

Having completed the discussion of the Hamiltonian, we now consider a statistical ensemble of noninteracting small polarons, each moving under the action of the identical Hamiltonian (2.1). In terms of the C's defined by (2.6), the total density matrix in the local-site representation is defined by

$$(\rho_T)_{p'N',pN}\equiv\langle C(p'N')C^*(pN)e^{-(it/\hbar)(E_{N'}-E_N)}\rangle, \quad (2.9)$$

where the brackets denote an average over the statistical ensemble[23] of small polarons. It is rather important to make clear that the distinction between the diagonal and nondiagonal elements of the density matrix is made only with respect to N and not with respect to p (or other additional quantum numbers), unless specifically so stated.[24]

The equation of motion for the total density matrix is readily obtained by taking the time derivative of (2.9), and making use of (2.7) and its complex conjugate. We get

$$i\hbar(\partial(\rho_T)_{p'N',pN}/\partial t)=eF(p'-p)(\rho_T)_{p'N',pN}+(E_{N'}-E_N)(\rho_T)_{p'N',pN}+\sum_{p''N''}[\langle p'N'|V|p''N''\rangle(\rho_T)_{p''N'',pN}-(\rho_T)_{p'N',p''N''}\langle p''N''|V|pN\rangle], \quad (2.10)$$

where the $\langle p'N'|V|pN\rangle$ are given by (2.8). This result can also be straightforwardly obtained by taking matrix elements of the equation of motion of the density operator

$$i\hbar(\partial\rho_T/\partial t)=[(H_0+V+H_F),\rho_T]$$

in the local site representation, $|pN\rangle$. Here H_0 is the zeroth order ($J=F=0$) Hamiltonian, V is the overlap part of the Hamiltonian, and $H_F=eFn$ is the electric-field part.

As usual, we are interested in the linear response of the system, and therefore set

$$\rho_T=\rho+\rho_F, \quad (2.11)$$

where ρ represents the equilibrium density matrix, and ρ_F is a small additional part linearly proportional to F. (Here and in what follows, we follow the notation of Kohn and Luttinger, Ref. 19, as much as possible.) Substituting (2.11) into (2.10), one gets

$$i\hbar(\partial\rho_{p'N',pN}/\partial t)=(E_{N'}-E_N)\rho_{p'N',pN}+\sum_{p''N''}[\langle p'N'|V|p''N''\rangle\rho_{p''N'',pN}-\rho_{p'N',p''N''}\langle p''N''|V|pN\rangle], \quad (2.12)$$

as the equation of motion[25] obeyed by ρ, and

$$i\hbar(\partial(\rho_F)_{p'N',pN}/\partial t)=eF(p'-p)\rho_{p'N',pN}+(E_{N'}-E_N)(\rho_F)_{p'N',pN}+\sum_{p''N''}[\langle p'N'|V|p''N''\rangle(\rho_F)_{p''N'',pN}-(\rho_F)_{p'N',p''N''}\langle p''N''|V|pN\rangle], \quad (2.13)$$

describing the linearized response.

In accordance with the adiabatic hypothesis, the system is taken to be in thermal equilibrium at $t=-\infty$. It is then isolated from the heat bath, and the electric field is turned on adiabatically according to

$$F=F_0e^{st}, \quad -\infty<t\leq0. \quad (2.14)$$

One seeks solutions of (2.13) for which the induced currents are at all times proportional to the applied field, that is,

$$\rho_F=fe^{st}. \quad (2.15)$$

[23] R. C. Tolman, *Principles of Statistical Mechanics* (Oxford University Press, New York, 1930), p. 327.

[24] The reason, as will be shown later, is that the velocity operator is nondiagonal in p, so that the only elements of the density matrix which contribute to the current are those for which $p'\neq p$.

[25] This equation will in practice be solved at $t=-\infty$ under equilibrium conditions ($\partial/\partial t=0$) (see footnote 34).

Equations (2.14) and (2.15) are now substituted into (2.13). With respect to the sum over N'' in (2.13), those terms involving diagonal elements of V and f are specifically separated out from the sum. The diagonal elements of ρ and f are designated by

$$\rho_{p'N,pN}\equiv\rho_{p'p}(N), \quad f_{p'N,pN}\equiv f_{p'p}(N).$$

In addition, we define the frequency differences

$$\omega_{N'N}\equiv(E_{N'}-E_N)/\hbar.$$

Incorporating the above definitions, the nondiagonal ($N'\neq N$) and diagonal ($N'=N$) forms of (2.13) are given by

$$\begin{aligned}-\hbar(\omega_{N'N}-is)f_{p'N',pN}&=eF_0(p'-p)\rho_{p'N',pN}\\&+\sum_{p''}[\langle p'N'|V|p''N\rangle f_{p''p}(N)\\&-f_{p'p''}(N')\langle p''N'|V|pN\rangle]\\&+\sum_{p''}[\langle p'N'|V|p''N'\rangle f_{p''N',pN}\\&-f_{p'N',p''N}\langle p''N|V|pN\rangle]\\&+\sum_{p'',N''\neq N,N'}[\langle p'N'|V|p''N''\rangle f_{p''N'',pN}\\&-f_{p'N',p''N''}\langle p''N''|V|pN\rangle],\\&\qquad(N'\neq N),\end{aligned}\tag{2.16}$$

and

$$\begin{aligned}i\hbar s f_{p'p}(N)&=eF_0(p'-p)\rho_{p'p}(N)\\&\sum_{p''}[\langle p'N|V|p''N\rangle f_{p''p}(N)\\&-f_{p'p''}(N)\langle p''N|V|pN\rangle]\\&+\sum_{p'',N''\neq N}[\langle p'N|V|p''N''\rangle f_{p''N'',pN}\\&-f_{p'N,p''N''}\langle p''N''|V|pN\rangle],\\&\qquad(N'=N).\end{aligned}\tag{2.17}$$

Equations (2.16) and (2.17) provide the starting point for the derivation of the lowest-order (in J) Boltzmann equation, presented in the following section.

III. BOLTZMANN EQUATION IN THE LOCAL-SITE REPRESENTATION

In the present section, we present the derivation of the lowest order Boltzmann equation obeyed by the diagonal density-matrix elements, $f_{pp'}(N)$. The formal procedure is the usual one of developing the nondiagonal elements $f_{p'N',pN}$ of (2.16) in a power series in J, and then eliminating these in (2.17) in favor of the diagonal elements.

Let us first consider (2.16). The first (driving) term on the right-hand side[26] is proportional to the nondiagonal elements of ρ which will be shown later to be of the order J^1 or higher. In the iterative procedure, the last two terms of (2.16) are proportional to $J\times f_{p'N',pN}$, and can therefore be neglected in lowest order. The lowest order diagonal elements $f_{pp'}(N)$ will be later shown to be of the order[27] J^{-1}, and, thus, the second term on the right-hand side of (2.16) dominates. We thus obtain

$$\begin{aligned}f_{p'N',pN}=&-(1/\hbar)[1/(\omega_{N'N}-is)]\\&\times\sum_{p''}[\langle p'N'|V|p''N\rangle f_{p''p}(N)\\&-f_{p'p''}(N')\langle p''N'|V|pN\rangle].\end{aligned}\tag{3.1}$$

With respect to the second term on the right-hand side of (2.17), it is shown in Ref. 8 that the diagonal matrix elements of V can be put into the form

$$\langle p'N|V|pN\rangle=-Je^{-S(N)}\sum_{\epsilon=\pm1}\delta_{p',p+\epsilon},\tag{3.2}$$

where

$$S(N)=\sum_k(1+2N_k)\gamma_k/\mathfrak{N}.\tag{3.3}$$

Substituting (3.1) and (3.2) into (2.17), we obtain the equation

$$\begin{aligned}i\hbar s f_{p'p}(N)&=eF_0(p'-p)\rho_{p'p}(N)\\&-Je^{-S(N)}\{[f_{p'+1,p}(N)+f_{p'-1,p}(N)]\\&-[f_{p',p+1}(N)+f_{p',p-1}(N)]\}+P-D.\end{aligned}\tag{3.4}$$

The first term on the right-hand side plays the role of a driving term, while P and D, as discussed below, will ultimately become the scattering terms. The second term on the right-hand side is proportional to the diagonal matrix elements, and will be later shown to entirely characterize the polaron-band motion. The term P is a population-like contribution which, after introducing irreversibility at a later stage in the calculation, will ultimately become the population term in the Boltzmann equation for certain of the elements $f_{p'p}$. It consists of two of the terms gotten by substituting (3.1) into (2.17) which, after some minor algebra and interchange of summation indices, can be written in the form:

$$\begin{aligned}P=&\sum_{p'',p''',N''}{}'\langle p'N|V|p''N''\rangle\\&\times\langle p'''N''|V|pN\rangle(1/\hbar)[(1/\omega_{NN''}-is)\\&-(1/\omega_{NN''}+is)]f_{p''p'''}(N''),\end{aligned}\tag{3.5}$$

where the prime denotes that the diagonal contributions ($N''=N$) are strictly absent from the sum.

The remaining two terms, D, are the depopulation

[26] This term [as well as the corresponding term in (2.17)] is perhaps more familiar as the matrix element of the commutator of the field Hamiltonian, $H_F=eFn$, and the equilibrium density matrix, ρ.

[27] In the treatment of Kohn and Luttinger, Ref. 19, the corresponding lowest order diagonal elements $f_k\sim\lambda^{-2}$, where λ is the strength of the scattering interaction and plays a role analogous to J of the present treatment. The reason for this difference is that in their treatment, the lowest order "driving term" $C_{kk}^{(0)}\sim\lambda^0$, whereas, in the present case, it $\sim J^1$, as we shall later show.

terms, and are given by

$$D=D_1+D_2,$$

where

$$D_1=\sum_{p'',p''',N'}{}' \frac{1}{\hbar}\frac{\langle p'N|V|p''N''\rangle\langle p''N''|V|p'''N\rangle}{\omega_{N''N}-is}\times f_{p'''p}(N), \quad (3.6)$$

and

$$D_2=\sum_{p'',p''',N'}{}' \frac{1}{\hbar}\frac{\langle p'''N|V|p''N''\rangle\langle p''N''|V|p'N\rangle}{\omega_{NN''}-is}\times f_{p'p'''}(N). \quad (3.7)$$

Let us first focus on the population term, (3.5). Our general procedure will be to manipulate this term for fixed s, and then let s become small with respect to the characteristic frequencies of the problem in order to obtain irreversible behavior.[28]

It proves convenient to replace the difference of energy denominators by their integral representation

$$\left(\frac{1}{\omega_{NN''}-is}-\frac{1}{\omega_{NN''}+is}\right)=i\int_{-\infty}^{\infty}dt'e^{i\omega_{NN''}t'}e^{-s|t'|}, \quad (3.8)$$

which can be readily verified.

To make further progress with (3.5), it is clear that the N'' dependence of $f_{p''p'''}(N'')$ must be specified. It is first assumed that the *diagonal* elements are factorable[29]

$$f_{p''p'''}(N'')=\mathfrak{f}_{p''p'''}\times g(N''). \quad (3.9)$$

In addition, we make the "Stosszahlansatz" that $g(N'')$ is given by its equilibrium form[30]

$$g(N'')=Z^{-1}e^{-\beta E_{N''}}, \quad \beta=(1/kT), \quad (3.10)$$

where

$$Z=\sum_N e^{-\beta E_N}$$

is the vibrational partition function. These assumptions will be discussed in Sec. VI.

We now substitute the expressions for the matrix elements, (2.8), into (3.5). Also using (3.8)–(3.10), the sum over N'' becomes a product of sums, one for each allowable value of k, and can be readily carried out. In this connection, the assumption (3.10) works out rather simply: namely, it is found to simply add an imaginary part $-i\beta\hbar$ to the times multiplying the frequencies of (3.8), while the remaining N dependence factors out, and is just the equilibrium function $Z^{-1}e^{-\beta E_N}$. The latter then cancels the corresponding factors which multiply the remaining terms of (3.4) [the diagonal elements of ρ are also written in product form]. Following the general methods of Ref. 8, and replacing the N_k's by their thermal average values, we obtain

$$P=i\frac{J^2}{\hbar}\sum_{\substack{\epsilon''=\pm1\\ \epsilon'''=\pm1}}\mathfrak{f}_{p'-\epsilon'',p+\epsilon'''}\times\exp\left\{\sum_k\left[-\frac{2}{\mathfrak{N}}\gamma_k\coth\frac{\beta\hbar\omega_k}{2}\right]\right\}\times\int_{-\infty-i\beta\hbar/2}^{\infty-i\beta\hbar/2}d\tau e^{-s|\tau|}e^{is\beta\hbar/2}\times\left[\exp\left\{\frac{2}{\mathfrak{N}}\sum_k I_P{}^{(k)}(p'-p,\epsilon'',\epsilon''')\times\gamma_k\operatorname{csch}\frac{\beta\hbar\omega_k}{2}\cos\omega_k\tau\right\}-1\right]. \quad (3.11)$$

The (-1) appearing in the square brackets represents the elimination of the diagonal elements $(N''=N)$, which are rigorously excluded from the sum over N''. Its presence removes the linear divergence of the integrand for large τ discussed in Ref. 8.

The quantity

$$I_P{}^{(k)}(p'-p,\epsilon'',\epsilon''')=-\epsilon''\epsilon'''\cos[k(p'-p-\tfrac{1}{2}(\epsilon''+\epsilon'''))] \quad (3.12)$$

represents spatial interference effects in the population (P) term arising from the matrix elements, and is of crucial importance. In particular, it is found that

$$I_P{}^{(k)}(\pm1,\pm1,\pm1)=-1,$$
$$I_P{}^{(k)}(\pm1,\mp1,\mp1)=-\cos2k,$$
$$I_P{}^{(k)}(\pm1,\pm1,\mp1)=\cos k,$$
$$I_P{}^{(k)}(0,\pm1,\pm1)=-\cos k,$$
$$I_P{}^{(k)}(0,\pm1,\mp1)=+1.$$

Now, (3.11) can be considered in the two cases that

$$\textstyle\sum_k F(k)=(2/\mathfrak{N})\sum_k\gamma_k\operatorname{csch}(\beta\hbar\omega_k/2), \quad (3.13)$$

is much less than or much greater than unity. The latter case is the one of principal interest.[31] In this case, the integrand is an oscillatory and rapidly damped function of τ, and the method of steepest descents is applicable. For the case $I_P=+1$, the principal con-

[28] It has been pointed out that this limiting process, in addition to the usual "Stosszahlansatz", is an essential feature of irreversible behavior. See E. N. Adams, Phys. Rev. **120**, 675 (1960).

[29] This, of course, does not mean that the entire matrix f is diagonal.

[30] This stosszahlansatz is analogous to that made in the kinetic theory of gases, in which the distribution of particles about to collide with a given center is characterized by the equilibrium distribution function. Classically, this corresponds to the neglect of position-velocity correlation. See D. Ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, New York, 1954), p. 13. In addition, such an assumption implies that the density matrix is sufficiently slowly varying in N'' space so as to permit, in effect, the replacement of energy denominators by Dirac delta functions.

[31] This latter case, in fact, defines the multiphonon site-jump regime which takes the form of a classical, thermally activated, diffusion process at sufficiently high temperatures ($kT\gg\hbar\omega_0$). The former case defines the regime in which a small number of phonons are emitted and absorbed in a site jump. The density-matrix treatment has not been examined in detail for this regime.

tribution occurs in the neighborhood of $\tau=0$, and gives just the standard expression for the two-site jump rate. However, for the case $I_P=-1$, the saddle points occurs at $\tau\approx\pi/\omega_0$ where the contribution can be shown to be very small because of dispersion of the vibrational spectrum. Finally, for the cases $I_P=(\pm\cos k, \cos 2k)$, the sum appearing in the exponential would vanish for an Einstein spectrum, and otherwise gives a very small contribution depending on ω_1, the vibrational bandwidth. It is clear that the contributions for $|p'-p|>1$ are likewise negligibly small. The final conclusion is that only the case $p'=p$, $\epsilon''=\pm1$, $\epsilon'''=\mp1$ gives the usual integral for the jump probability. Thus, the population term contributes for $p'=p$, but is absent for $p'\neq p$. The absence of a term for $p'\neq p$ insures the existence of a relaxation time which will later be identified as the reciprocal jump rate, W_T^{-1}.

Finally, s is taken to be small with respect to the characteristic frequencies of the problem, specifically,[32]

$$s\ll(kT/\hbar),\quad \omega_0,\quad W_T^{-1}.$$

The integral over τ can then be carried out in the complex plane by the methods given in Ref. 8. The final result is that

$$P=i\mathfrak{f}_{p\pm1,p\pm1}\hbar W_T, \tag{3.14}$$

where

$$W_T=\frac{J^2}{\hbar^2}\left[\frac{2\pi}{\pi^{-1}\int_0^\pi 2\gamma_k\omega_k^2\,\mathrm{csch}\dfrac{\beta\hbar\omega_k}{2}dk}\right]^{1/2}\times\exp\left\{\pi^{-1}\int_0^\pi 2\gamma_k\tanh\frac{\beta\hbar\omega_k}{4}dk\right\} \tag{3.15}$$

is the thermal average (T) jump rate [cf. Ref. 8, Eq. (77)].

Having treated the population term in some detail, the depopulation terms of (3.4) will now be described in a more cursory fashion. For D_1, defined by (3.6), we get

$$D_1=i\frac{J^2}{\hbar}\sum_{\substack{\epsilon''=\pm1\\ \epsilon'''=\pm1}}\mathfrak{f}_{p'-\epsilon''-\epsilon''',p}\int_{-\infty-i\beta\hbar/2}^{0-i\beta\hbar/2}d\tau e^{s\tau}e^{is\beta\hbar/2}\times\exp\left\{-\sum_k\frac{2}{\mathfrak{N}}\gamma_k\coth\frac{\beta\hbar\omega_k}{2}\right\}\times\left[\exp\left\{\frac{2}{\mathfrak{N}}\sum_k\gamma_k I_D{}^{(k)}(\epsilon'',\epsilon''')\times\mathrm{csch}\frac{\beta\hbar\omega_k}{2}\cos\omega_k\tau\right\}-1\right], \tag{3.16}$$

where

$$I_D{}^{(k)}(\epsilon'',\epsilon''')=-\epsilon''\epsilon'''\cos\left[k\left(\frac{\epsilon''+\epsilon'''}{2}\right)\right]. \tag{3.17}$$

One sees that $I_D{}^{(k)}(\pm1,\pm1)=-\cos k$, and hence gives a negligible contribution as discussed previously. Physically, this choice corresponds to the process $(p'N\to p''N''\to p'\pm2, N)$, and represents a higher order contribution to the band motion, since N is exactly conserved. The principal contribution occurs for the choice $I_D(\pm1,\mp1)=+1$, and corresponds to the process $\sum_{p''N''}(p'N\to p''N'')$, that is, a simple scattering-out or depopulation contribution.

A basic difficulty with regard to (3.16) is that the τ-integration extends from $(-\infty-i\beta\hbar/2)$ to only $(0-i\beta\hbar/2)$, rather than to $(+\infty-i\beta\hbar/2)$. This is traceable to the appearance of only a single energy denominator in (3.6). If this were the final result, one would *not* get the usual integral for W_T, but would instead have an addition contribution from the segment along the imaginary axis $(0-i\beta\hbar/2)$ to (0,0). However, if one now considers the term D_2, given by (3.7), one can cast the result in the form

$$D_2=i\frac{J^2}{\hbar}\sum_{\substack{\epsilon''=\pm1\\ \epsilon'''=\pm1}}\mathfrak{f}_{p',p+\epsilon''+\epsilon'''}\int_{0-i\beta\hbar/2}^{\infty-i\beta\hbar/2}d\tau e^{s\tau}e^{-is\beta\hbar/2}\times\exp\left\{-\frac{2}{\mathfrak{N}}\sum_k\gamma_k\coth\frac{\beta\hbar\omega_k}{2}\right\}\times\left[\exp\left\{\frac{2}{\mathfrak{N}}\sum_k I_D{}^{(k)}(\epsilon'',\epsilon''')\gamma_k\times\mathrm{csch}\frac{\beta\hbar\omega_k}{2}\cos\omega_k\tau\right\}-1\right]. \tag{3.18}$$

Again, $I_D(\pm1,\pm1)$ gives a negligibly small propagation contribution, while $I_D(\pm1,\mp1)$ makes the principal contribution. One now sees that the principal contributions of D_1 and D_2 add, after taking the limit of small s, to give the integral $(-\infty-i\beta\hbar/2)$ to $(+\infty-i\beta\hbar/2)$, and

$$D=D_1+D_2=i\mathfrak{f}_{p'p}\hbar W_T. \tag{3.19}$$

Combining the results (3.4), (3.14), and (3.19), the steady-state Boltzmann equation[33] in the local-site representation reads

$$0=eF_0(p'-p)\rho_{p'p}-Je^{-S_T}\{[\mathfrak{f}_{p'+1,p}+\mathfrak{f}_{p'-1,p}]-[\mathfrak{f}_{p',p+1}+\mathfrak{f}_{p',p-1}]\}+i\mathfrak{f}_{p\pm1,p\pm1}\hbar W_T\delta_{p'p}-i\mathfrak{f}_{p'p}\hbar W_T, \tag{3.20}$$

where $S_T=\sum_k(\gamma_k/\mathfrak{N})\coth(\beta\hbar\omega_k/2)$ is the thermal average of $S(N)$, given by (3.3).

[32] In addition, s must be small compared to the reciprocal interval over which the dominant contribution to the integral (3.11) occurs. This implies the condition $s\ll\omega_0(\pi^{-1}\int_0^\pi dkF(k))^{1/2}$, where $F(k)$ is given by (3.13). However, since the square root factor is $\gg1$, this inequality is automatically obeyed if $s\ll\omega_0$. It might also be remarked that (3.5) would seem to imply the more stringent condition $s\ll\omega_1$, since $\langle\omega_{NN''}\rangle\sim\omega_1$. However, this condition does not appear to be required by (3.11).

[33] The usefulness of a Boltzmann equation for the nondiagonal (in p, for this case) elements of the density matrix occurs in other areas of quantum transport. See P. N. Argyres, Phys. Rev. **117**, 315 (1960).

In the next section, (3.20) will be solved in order to evaluate the expectational value of small-polaron mobility.

IV. CALCULATION OF THE CURRENT IN THE LOCAL-SITE REPRESENTATION

As described in the introduction, the principal motivation of the present paper is to show that the expectation value of small-polaron mobility (in lowest order) is just the *sum* of a band part, in which the role of the nondiagonal matrix elements is to limit the lifetimes of the band states, plus a thermally assisted diffusion contribution due to hopping between local sites.

The expectation value of the velocity, to first order in the electric field strength, is given by

$$\langle v\rangle=\mathrm{tr}\{v_{\mathrm{op}}f\}=\sum_{\substack{pN\\p'N'}}\langle pN|v_{\mathrm{op}}|p'N'\rangle f_{p'N',pN}, \quad (4.1)$$

where $\langle pN|v_{\mathrm{op}}|p'N'\rangle$ is the matrix element of the velocity operator in the local-site representation, and will be calculated shortly. Equation (4.1) is more conveniently written

$$\langle v\rangle=\langle v\rangle_{\mathrm{d}}+\langle v\rangle_{\mathrm{nd}},$$

where the diagonal (d) part is given by

$$\langle v\rangle_{\mathrm{d}}=\sum_{p,p',N}\langle pN|v_{\mathrm{op}}|p'N\rangle f_{p'p}(N), \quad (4.2)$$

and the nondiagonal (nd) part by

$$\langle v\rangle_{\mathrm{nd}}=\sum_{\substack{pN\\p',N'\neq N}}\langle pN|v_{\mathrm{op}}|p'N'\rangle f_{p'N',pN}. \quad (4.3)$$

The matrix elements of the velocity operator are straightforwardly gotten from the Heisenberg operator equation of motion

$$v_{\mathrm{op}}=dn/dt=(i/\hbar)[H_T,n]=(i/\hbar)[H,n],$$

where the last equality follows from the fact that the commutator of $H_F=eFn$ and n vanishes. Taking matrix elements between localized states, one gets

$$\langle p'N'|v_{\mathrm{op}}|pN\rangle=(i/\hbar)\langle p'N'|V|pN\rangle(p'-p), \quad (4.4)$$

and is therefore entirely nondiagonal in p, as one would intuitively expect. Making use of (3.2), the diagonal elements of v_{op} are given by

$$\langle p'N|v_{\mathrm{op}}|pN\rangle=-i(J/\hbar)e^{-S(N)}(p'-p)\times\sum_{\epsilon=\pm1}\delta_{p',p+\epsilon}. \quad (4.5)$$

We next must solve (3.20) for $f_{p'p}$. In order to do this, however, one must know the elements $\rho_{p'p}$ of the equilibrium density matrix. Now, ρ is the appropriate stationary density matrix at $t=-\infty$ when $F=0$. However, since $J\neq0$ at $t=-\infty$, it will depend on V, and may be developed in a power series in J. This expansion is most unambiguously carried out by the method of Karplus and Schwinger.[34] Thus, with the density operator given by $\rho=Z^{-1}\exp[-\beta(H_0+V)]$ [these symbols are defined in the text following (2.10)], one has

$$\langle pN|\exp[-\beta(H_0+V)]|p'N'\rangle=Z^{-1}e^{-\beta E_N}\delta_{NN'}\mathfrak{N}^{-1}\delta_{pp'}-Z^{-1}\frac{e^{-\beta E_N}-e^{-\beta E_{N'}}}{\hbar\omega_{NN'}}\mathfrak{N}^{-1}\langle pN|V|p'N'\rangle+\sum_{p''N''}\mathfrak{N}^{-1}\frac{\langle pN|V|p''N''\rangle\langle p''N''|V|p'N'\rangle}{\hbar\omega_{N''N'}}\times Z^{-1}\left[\frac{e^{-\beta E_{N'}}-e^{-\beta E_N}}{\hbar\omega_{NN'}}-\frac{e^{-\beta E_{N''}}-e^{-\beta E_N}}{\hbar\omega_{NN''}}\right]+\cdots.$$

Of particular interest is the leading term of the expansion

$$\rho_{p'p}{}^{(0)}(N)=Z^{-1}e^{-\beta E_N}\delta_{NN'}\mathfrak{N}^{-1}\delta_{pp'}, \quad (4.6)$$

which is diagonal both in N *and in* p. This form reflects the translational invariance of the problem in that it gives an equal *a priori* probability for the polaron being at any site on the linear chain. Thus, in this respect, the random-phase approximation is made at the initial time ($t=-\infty$), but is *not* repeated at later times. Since $\rho^{(0)}$ is diagonal in p, it clearly will not contribute to the driving term of (3.20). The first such nonvanishing contribution is made by the second term of the above expansion, which is written

$$\rho_{p'N',pN}{}^{(1)}=-\mathfrak{N}^{-1}\langle p'N'|V|p_N\rangle Z^{-1}e^{-\beta E_N}\times(1-e^{-\beta\hbar\omega_{NN'}}/\hbar\omega_{N'N}). \quad (4.7)$$

Thus, the first nonvanishing driving term of (3.20) is a mixed field-scattering term ($\sim J\times F_0$).

The corresponding diagonal elements are obtained by taking the limit as $\omega_{NN'}\to0$ smoothly. Using (3.2), the result is

$$\rho_{p'p}{}^{(1)}(N)=\beta Je^{-S(N)}Z^{-1}e^{-\beta E_N}\sum_{\epsilon=\pm1}\delta_{p',p+\epsilon}. \quad (4.8)$$

These results suffice for our present purposes. Although we will not consider higher-order approximations, it is of interest to note from the products of matrix elements appearing in the expansion, that only for the odd terms of the series will $p'=p\pm1$. (For the second-order term, for example, it is clear that $p'=p$, $p\pm2$.) Hence, only these can "drive" the $f_{p,p\pm1}$ which alone contribute to the net current, as will be later shown.

We are now in a position to solve (3.20) for $f_{p'p}$ and obtain $\langle v\rangle_d$. The homogeneous solution of (3.20) is gotten by setting the driving (F_0-proportional) term equal to

[34] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1949), Appendix I; also see Ref. 19, Appendix C. The expansion of the density operator can alternately be gotten by direct iteration of (2.12) under the equilibrium conditions ($\partial/\partial t=0$) applicable at $t=-\infty$.

zero, and is shown in Appendix A to entirely characterize the polaron-band motion, and not to contribution to the net current. The homogeneous solution can be shown to be orthogonal to the driving term, insuring the existence of the inhomogeneous solution given by

$$\mathfrak{f}_{p'p}=-i\frac{eF_0}{kT}\frac{Je^{-S_T}}{\hbar W_T}(p'-p)\sum_{\epsilon=\pm1}\delta_{p',p+\epsilon}. \quad (4.9)$$

This is indeed of order J^{-1}, as claimed earlier. One sees that (4.5) and (4.9) are both properly odd in p space, in analogy with the properties of v_k and f_k in the usual transport integral expression for the current of conventional band theory. Substituting (4.9) and (4.5) into (4.2), and recalling that $f_{p'p}(N)=\mathfrak{f}_{p'p}Z^{-1}e^{-\beta E_N}$, one obtains the first half of our result, namely, that

$$\langle v\rangle_{\rm d}=-F_0\mu_B, \quad (4.10)$$

where the band contribution to the mobility, μ_B, is given by the Einstein relation

$$\mu_B=\frac{e}{kT}\left[\frac{2J^2e^{-2S_T}}{\hbar^2}\tau_T\right], \quad (4.11)$$

and where $\tau_T=W_T^{-1}$. The quantity in square brackets is just the band-diffusivity, and is identical with equation (100) of Ref. 8.

Next, let us consider $\langle v\rangle_{\rm nd}$, defined by (4.3). The lowest order $f_{p'N',pN}$ which could contribute to the sum is gotten by substituting (4.9) into (3.1). Dimensionally, one sees that this $f_{p'N',pN}\sim J^0$. and since $v_{\rm op}\sim J^1$, this would lead to $\langle v\rangle_{\rm nd}\sim J^1$. However, it is shown immediately below that this contribution in fact vanishes, and that one must go to the next order in $f_{p'N',pN}$ to obtain a finite contribution. To show this, we substitute (4.9), (3.1), and (4.4) into (4.3). Interchanging summation indices here and there, the result can be written:

$$\langle v\rangle_{\rm nd}{}^{(1)}=-\frac{i}{\hbar^2}\sum_{p'N,p''N'',p'''}(p''-p')f_{p'''p'}(N)\times\langle p'N|V|p''N''\rangle\langle p''N''|V|p'''N\rangle\times\left(\frac{1}{\omega_{N''N}-is}-\frac{1}{\omega_{N''N}+is}\right).$$

By the previous arguments, the only choice giving a finite result is $p'''=p'$. In any case, however, some addition manipulation shows that the two choices $p''-p'=\pm1$ exactly cancel, with the result that $\langle v\rangle_{\rm nd}{}^{(1)}\equiv0$. The first nonvanishing contribution to $\langle v\rangle_{\rm nd}$ occurs if we use the $f_{p'N',pN}$ which is "driven" directly by the field term, namely [cf. (2.16)],

$$f_{p'N',pN}=-\frac{1}{\hbar}\frac{1}{\omega_{N'N}-is}eF_0(p'-p)\rho^{(1)}{}_{p'N',pN}. \quad (4.12)$$

The above quantity[35] $\sim J^1$, and leads to $\langle v\rangle_{\rm nd}{}^{(2)}\sim J^2$, which dimensionally is of the order of W_T, as desired. We now substitute (4.7) for $\rho^{(1)}{}_{p'N',pN}$ into (4.12), and then, in turn, substitute (4.12) and (4.4) into (4.3). In addition, it proves convenient to symmetrize the resulting expression by adding the trace gotten by interchanging (p,N) and (p',N') in (4.3), and then dividing by two. The result reads

$$\langle v\rangle_{\rm nd}{}^{(2)}=i\frac{eF_0}{2\hbar^2}\sum_{pN,p'N'}\frac{(p'-p)^2}{\mathfrak{N}}|\langle pN|V|p'N'\rangle|^2\times\left(\frac{1}{\omega_{N'N}-is}-\frac{1}{\omega_{N'N}+is}\right)Z^{-1}e^{-\beta E_N}\times\left[\frac{1-e^{-\beta\hbar\omega_{NN'}}}{\hbar\omega_{N'N}}\right]. \quad (4.13)$$

In principal, there is some difficulty in carrying out the sum over N' due to the presence of the last factor in square brackets, which cannot be expressed as a product over the individual vibrational modes. However, noticing that

$$\left(\frac{1}{\omega_{N'N}-is}-\frac{1}{\omega_{N'N}+is}\right)=i\int_{-\infty}^{\infty}dt'e^{i\omega_{N'N}t'}e^{-s|t'|}\xrightarrow[s\to0^+]{}i2\pi\delta(\omega_{N'N}), \quad (4.14)$$

one sees that energy conservation applies (in the sense of time-dependent perturbation theory), and that the square bracket can be replaced by its limit as $\omega_{N'N}\to0$, i.e.,

$$\lim_{\omega_{NN'}\to0}\left[\frac{1-e^{-\beta\hbar\omega_{N'N}}}{\hbar\omega_{N'N}}\right]\to\beta=\frac{1}{kT}.$$

Using the first equality of (4.14), Eq. (4.13) can be written

$$\langle v\rangle_{\rm nd}{}^{(2)}=\frac{eF_0}{kT}\frac{1}{\mathfrak{N}}\sum_p\tfrac{1}{2}\sum_{p'}(p'-p)^2\left\{\sum_N Z^{-1}e^{-\beta E_N}\times\sum_{N'}\frac{2}{\hbar^2}\int_{-\infty}^{\infty}|\langle pN|V|p'N'\rangle|^2\frac{e^{-i\omega_{N'N}t'}}{2}e^{-s|t'|}dt'\right\}.$$

The factor in curly brackets is precisely W_T as defined by Eqs. (47)–(49), and (51) of Ref. 8. Since this is independent of p, the summation over p just cancels the $(1/\mathfrak{N})$ factor, while the two cases $p'=p\pm1$ cancel the factor of $\frac{1}{2}$. The final result can be put in the form

$$\langle v\rangle_{\rm nd}{}^{(2)}=-F_0\mu_H, \quad (4.15)$$

[35] There is an additional contribution to $f_{p'N',pN}$ also of order J^1 which is gotten by once iterating (2.16): specifically, by resubstituting (3.1) into (2.16), where $f_{p'p}$ is given by (4.9). Some examination shows that this term makes a negligibly small contribution to the net current because of incoherence of the matrix elements of the type discussed in the text.

where the "hopping" mobility is given by

$$\mu_H=(e/kT)W_T a^2, \tag{4.16}$$

where a ($|a|=1$) is the lattice constant of the linear chain.

To summarize the principal results of this section: Total small-polaron mobility, within the jump-perturbation approximation, takes the form of a sum

$$\mu_T=\mu_B+\mu_H, \tag{4.17}$$

where the band part, (4.11), arises from the diagonal part of the trace for the expectation value of velocity, while the hopping contribution (4.16) arises from the nondiagonal part. Thus, the present treatment verifies the separation of the two types of small-polaron motion made in Ref. 8 on the basis of physically reasonable considerations. In particular, the concept of the transition temperature, T_t, as approximately defining the domain of validity of the two regimes, follows immediately. In addition, the result (4.16) reflects the translational invariance of the problem as expressed by (4.6). Further discussion of (4.17) is given in Sec. VI.

V. POLARON MOBILITY IN THE POLARON-BAND REPRESENTATION

Some additional insight can be gained by reformulating the density-matrix treatment in the polaron-band representation of small-polaron motion. Since this development is in many ways similar to that given for the local-site representation, the results will be stated more briefly, with particular emphasis given to the differences[36] between the two cases.

Just as the local-site representation is the appropriate choice at high temperatures ($T>T_t$), the polaron-band representation is more appropriate in the low-temperature regime ($0<T<T_t$). In the latter case, as discussed in Ref. 8, the diagonal matrix elements play the dominant role. If these alone are taken into account in (2.7), it is found that the stationary solutions to the latter equation are of the form

$$C_p=e^{ip\sigma}\exp[i(t/\hbar)]2Je^{-S(N)}\cos\sigma, \tag{5.1}$$

where σ, the polaron wave vector, takes on the usual values imposed by periodic boundary conditions. The corresponding eigenstates and eigenvalues are then given by

$$a_{\sigma,N}(n,\cdots q_k\cdots)=e^{in\sigma}\prod_k \Phi_{N_k}[(M\omega_k/\hbar)^{1/2}(q_k-q_k{}^{(n)})], \tag{5.2}$$

and

$$E_{\sigma,N}=E_N+\Delta E_{\sigma,N}, \tag{5.3}$$

respectively, where as before, N stands for $(\cdots N_k\cdots)$, E_N is given by (2.5), and

$$\Delta E_{\sigma,N}=-2Je^{-S(N)}\cos\sigma. \tag{5.4}$$

Thus, in incorporating the diagonal matrix elements in zeroth order, the basic states (5.2) are Bloch-type plane-wave combinations of localized states, while the energy spectrum (5.3) is manifestly of a band-type character.

The residual interaction due to the nondiagonal matrix elements is taken into account by expanding the total "wave function" $a(n,\cdots q_k\cdots)$ in the basis provided by the polaron-band states

$$a(n,\cdots q_k\cdots)=\sum_{\sigma'N'} C(\sigma'N';t)a_{\sigma'N'}e^{-i(t/\hbar)E_{\sigma'N'}}, \tag{5.5}$$

and then substituting this into the full Hamiltonian (2.1). In analogy with (2.7), the equations obeyed by the $C(\sigma N)$ are[37]

$$i\hbar\frac{\partial C(\sigma N)}{\partial t}=ieF\frac{\partial C(\sigma N)}{\partial\sigma}+\sum_{\sigma'N'}\langle\sigma N|V|\sigma'N'\rangle\times C(\sigma'N')e^{i(t/\hbar)(E_{\sigma N}-E_{\sigma'N'})}, \tag{5.6}$$

where the $\langle\sigma N|V|\sigma'N'\rangle$ are the matrix elements of the perturbation in the polaron-band representation, and are given as plane-wave combinations of those in the local-site representation, i.e.,

$$\langle\sigma N|V|\sigma'N'\rangle=(1/\mathfrak{N})\sum_{pp'}e^{i(p'\sigma'-p\sigma)}\langle pN|V|p'N'\rangle. \tag{5.7}$$

As a consequence of writing (5.5) in the interaction picture, the sum (5.6) excludes the term for which $\sigma'=\sigma$ and $N'=N$. Hence, (5.6) describes only nondiagonal transitions between polaron-band states. Using (3.2), the above neglected diagonal matrix elements can in fact be shown to be of the form

$$\langle\sigma N|V|\sigma'N\rangle=-2Je^{-S(N)}\cos\sigma\delta_{\sigma'\sigma}, \tag{5.8}$$

that is, the diagonal (in N) matrix elements are diagonal in σ as well, a result which will be of needed in connection with the evaluation of the velocity operator in the polaron-band representation.

With the replacements

$$p\rightarrow\sigma$$

$$\langle pN|V|p'N'\rangle\rightarrow\langle\sigma N|V|\sigma'N'\rangle$$

$$E_N\rightarrow E_{\sigma N},\ \omega_{NN'}\rightarrow\omega_{\sigma N,\sigma'N'}$$

$$(\rho_T)_{pN,p'N'}\rightarrow(\rho_T)_{\sigma N,\sigma'N'}$$

$$eF(p'-p)(\rho)_{p'N',pN}\rightarrow eF\left(\frac{\partial}{\partial\sigma'}+\frac{\partial}{\partial\sigma}\right)(\rho)_{\sigma'N',\sigma N},$$

[36] These differences will not, of course, affect the final expectation value of velocity which is independent of representation.

[37] The form of the electric field term follows from the standard procedure of replacing $ne^{in\sigma}$ by $-i(\partial/\partial\sigma)e^{in\sigma}$, integrating over σ by parts, and applying the periodic boundary conditions.

the equations of motion for the density matrix are closely analogous to (2.16) and (2.17) in the p representation. The only difference is the absence of diagonal elements of V in the sums over intermediate states $(\sigma''N'')$, this being compensated for in the analog of (2.17) by the appearance of an additional term $(\Delta E_{\sigma N}-\Delta E_{\sigma' N})\times \mathfrak{f}_{\sigma'\sigma}(N)$ in the zeroth-order energies.

Consider first the analog of the population term (3.5). One substitutes (5.7) expressing the matrix elements in terms of those in the local-site regions. The summations are again restricted to those for which the interference factor [cf. (3.12)] gives a finite contribution. After some considerable algebra, one gets[38]

$$P_{\sigma\sigma'}=(2\cos(\sigma'-\sigma)/\mathfrak{N})W_T\sum_{\Delta\sigma}\mathfrak{f}_{\sigma'+\Delta\sigma,\sigma+\Delta\sigma}. \quad (5.9)$$

Of particular interest will be the case $\sigma'=\sigma$. Here,

$$P_{\sigma\sigma}=(2/\mathfrak{N})W_T\sum_{\Delta\sigma}\mathfrak{f}_{\sigma+\Delta\sigma,\sigma+\Delta\sigma}. \quad (5.10)$$

Now, it can be easily shown that the density matrices in the two representations are related by

$$\mathfrak{f}_{\sigma'\sigma}=(1/\mathfrak{N}^2)\sum_{p'p}e^{-i(\sigma' p'-\sigma p)}\mathfrak{f}_{p'p}.$$

From this, one can easily show that

$$\sum_{\Delta\sigma}\mathfrak{f}_{\sigma'+\Delta\sigma,\sigma+\Delta\sigma}=(1/\mathfrak{N})\sum_{p}e^{-i(\sigma'-\sigma)p}\mathfrak{f}_{pp},$$

and, in particular,

$$\sum_{\Delta\sigma}\mathfrak{f}_{\sigma+\Delta\sigma,\sigma+\Delta\sigma}=(1/\mathfrak{N})\sum_{p}\mathfrak{f}_{pp}.$$

However, summing (2.17) over (pN), and interchanging (pN) with $(p''N'')$ in the last terms of the sum, one sees that for any finite $s>0$,

$$\sum_{pN}\mathfrak{f}_{pp}(N)\equiv 0,$$

and therefore,

$$\sum_{p}\mathfrak{f}_{pp}\equiv 0. \quad (5.11)$$

This simply expresses particle conservation given by the invariance of the trace of ρ: namely, that the electron must be somewhere in the crystal and that this is unchanged by the application of an electric field. The final result of these arguments is that

$$P_{\sigma\sigma}=0. \quad (5.12)$$

This result corresponds to the vanishing of the population term in the local-site representation for $p'\neq p$. [cf. (3.20) and text following (3.13).] Both results are consequences of the independence of W_T on the initial and final states (this being characteristic of multiphonon processes).

[38] In getting this expression, we neglect the time-dependent exponentials of the type $\exp\{(it'/\hbar)(\Delta E_{\sigma',N}-\Delta E_{\sigma,N})\}$, in view of the smallness of $E_{\sigma,N}$ with respect to $\hbar\omega_k$.

With respect to the depopulation terms, one again finds that the two analogs of D_1 and D_2 add to give a conventional depopulation term of the form

$$D_{\sigma'\sigma}=-i\mathfrak{f}_{\sigma'\sigma}\hbar W_T. \quad (5.13)$$

It will be seen immediately below that the case of interest is $\sigma'=\sigma$. In this case, using (5.12) and (5.13), one gets the Boltzmann equation

$$0=(eF_0/\hbar)(\partial\rho_{\sigma\sigma}/\partial\sigma)-W_T\mathfrak{f}_{\sigma\sigma}. \quad (5.14)$$

This equation is quite analogous to the Boltzmann equation of conventional band theory, the first term representing a standard acceleration term, and the second a depopulation term characterized by a relaxation time $\tau_T=W_T^{-1}$ [the population term is absent by virtue of (5.12)]. In particular, a term analogous to the second term on the right-hand side of (3.4) is missing in (5.14). This term is shown in Appendix A to describe the polaron-band motion, and its absence in (5.14) simply reflects the fact that the latter is already accounted for in the basic states (for $\sigma'=\sigma$).

The reason for the particular interest in the case $\sigma'=\sigma$ can be seen from the form of the matrix elements of the velocity operator. Using (5.2) for the polaron-band states, one straightforwardly finds that

$$\langle\sigma'N'|v_{\rm op}|\sigma N\rangle=\frac{1}{\hbar}\left(\frac{\partial}{\partial\sigma'}+\frac{\partial}{\partial\sigma}\right)\langle\sigma'N'|V|\sigma N\rangle, \quad N'\neq N, \quad (5.15)$$

while

$$\langle\sigma'N|v_{\rm op}|\sigma N\rangle=(2Je^{-S(N)}/\hbar)\sin\sigma\delta_{\sigma'\sigma}, \quad (5.16)$$

i.e., that the diagonal elements of $v_{\rm op}$ are diagonal in σ as well, this being a consequence of (5.8).

One can also show that

$$\rho_{\sigma\sigma}^{(1)}=(\beta Je^{-S_T}/\mathfrak{N})2\cos\sigma. \quad (5.17)$$

Substituting (5.17) into (5.14), solving for $\mathfrak{f}_{\sigma\sigma}$, and taking into account (5.16), one finds that

$$\langle v\rangle_{\rm d}=\sum_{\sigma}v_{\sigma\sigma}f_{\sigma\sigma}=-(eF_0/kT)(2Je^{-ST}/\hbar)^2\tau_T(1/\mathfrak{N})\times\sum_{\sigma}\sin^2\sigma$$
$$=-(eF_0/kT)[(2J^2e^{-2S_T}/\hbar^2)\tau_T], \quad (5.18)$$

a result identical with (4.11).

Finally, from the nondiagonal density-matrix equation, one has that

$$f_{\sigma'N',\sigma N}=-i\frac{1}{\hbar}\frac{1}{\omega_{\sigma'N',\sigma N}-is}eF_0\left(\frac{\partial}{\partial\sigma'}+\frac{\partial}{\partial\sigma}\right)\times\rho_{\sigma'N',\sigma N}^{(1)}, \quad (5.19)$$

where

$$\rho_{\sigma'N',\sigma N}^{(1)}=-\frac{1}{\mathfrak{N}^2}Z^{-1}e^{-\beta E_N}\frac{1-e^{-\beta\hbar\omega_{NN'}}}{\hbar\omega_{NN'}}\times\langle\sigma'N'|V|\sigma N\rangle. \quad (5.20)$$

From (5.19), and (5.15), one can establish that

$$\langle v\rangle_{\rm nd}=\sum_{\sigma N,\sigma' N'} v_{\sigma N,\sigma' N'} f_{\sigma' N',\sigma N}=\sum_{pN,p' N'} v_{pN,p' N'} f_{p' N',pN},$$

and is, therefore, identical with the result

$$\langle v\rangle_{\rm nd}=-\frac{eF_0}{kT}W_T a^2, \tag{5.21}$$

obtained in the local-site regime. This establishes the equivalence of our final result in the two representations.

VI. SUMMARY AND DISCUSSION OF RESULTS

In this section, we present some discussion of the physical significance of our results. Our final result (4.17) states that, to lowest order in the density-matrix treatment, the two contributions to the mobility are additive. Thus, both mechanisms are operative at any given temperature, although one of the two dominates at temperatures far from the transition region (which, to lowest order, is now entirely characterized by the above additivity of our result). In particular, the theory predicts no discontinuous change from band-like behavior to a localized description of the mobility. It might (hopefully) serve to clarify this point by contrasting our result with the well-known predictions of Mott.[39] Mott considered the conductivity of a crystalline array of atoms as a function of their interatomic spacing. He presented arguments to the effect that, at some critical value of the interatomic spacing, there should be an abrupt transition from a localized, real (and therefore nonconducting) state, to nonlocalized current-carrying state. For an array of monovalent atoms,[40] he emphasizes that these are not alternate zeroth order descriptions of the ground-state wave function, but rather correspond to physically different states, the one assumed by the system being the one of lower energy. In the present paper we are not, of course, comparing *conventional* band theory with a localized treatment of the charge carrier. The parameters of the theory are assumed to be such as to favor localization and small-polaron formation ($J<E_b$, $\eta_2\ll 1$). Rather, we are studying the question of whether small-polaron motion occurs predominantly by polaron-band motion, or via site-jump transitions. The thesis of the present paper is that this question is decided by the simultaneous action of the two basic classes of matrix elements, and their relative importance as a function of temperature. In particular, the effects of the diagonal and nondiagonal matrix elements, essentially contained in the polaron bandwidth and site-jump rates, respectively, are continuous (albeit exponential) functions of the temperature; there is therefore no reason to expect any discontinuity. Thus, the persistence of some small residual amount of band motion for $T>T_t$, in the opinion of the present author, is simply a manifestation of the fact that band motion will always exist and contribute to the conductivity whenever one has periodicity, as indeed one has in the present case. The fact that its contribution is small, simply means that, from one point of view, the time for the polaron to move a lattice spacing via band motion ($\sim\hbar/\Delta E_{\sigma,\langle N\rangle}$) is much larger than the time between multiphonon site-jump transitions (W_T^{-1}). The latter therefore dominate the charge transport in this regime ($T>T_t$). For $T<T_t$, the diagonal matrix elements dominate, and polaron-band motion, described by the alternate Boltzmann Eqs. (3.20) and (5.14), is the principal conduction mechanism. Here, the nondiagonal transitions provide scattering between polaron-band states, and, as shown by (4.17), also make a small contribution of their own to the hopping mobility. The particular choice[15] of band states appropriate to this regime, it should be emphasized, plays no essential role, since $\langle v\rangle$ is independent of representation.

In conclusion, the following additional points should be noted with respect to the specific treatment of the present paper. First, the iteration procedures employed on Eqs. (2.16) and (2.17) are essentially the same as those of other more conventional treatments of quantum transport.[19,33] In this connection, the use of perturbation theory is strictly valid, since it has been assumed that $\eta_2\ll 1$ (cf. footnote 22). Turning next to the separability assumption (3.9), this simply expresses the fact that the thermal excitation of the many degrees of freedom of the lattice is insensitive to the location of the single excess electron (or hole). With regard to the stosszahlansatz (3.10), it should be pointed out that such an assumption is a necessary ingredient of any theory which obtains irreversible behavior from entirely time-reversible density-matrix equations of motion, as far as is known to the present author [in this connection, see the discussion following Eq. (42) of Ref. 19]. This assumption should not basically affect the structure of the final results, specifically, the additivity of the two contributions to small polaron mobility which, as emphasized earlier, depends basically on the decomposition of $\langle v\rangle$ into parts depending on the diagonal and nondiagonal matrix elements of the perturbation.

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APPENDIX A

In this Appendix, we discuss the physical significance of the homogeneous solution of the difference Eq. (3.20) (which obtains for zero driving term, i.e., $F_0=0$). It is instructive to first consider the solution of (3.20) which applies in the absence of damping, that is for $W_T=0$

[39] N. F. Mott, Can. J. Phys. 34, 1356 (1956).

[40] For divalent atoms, the two representations (i.e., Heitler-London and Bloch) are equivalent; however, Mott gives additional arguments for the abrupt transition. Thus, in this respect, this contrast is not entirely appropriate.

(i.e., to order J^1). For this case, a possible solution is of the form[41]

$$\mathfrak{f}_{p'p}=e^{i(p'\sigma_r'-p\sigma_r)},$$

where, for reasons which will be evident shortly, σ_r denotes the *real* part of the wave vector, σ. For f to be Hermitian,

$$\mathfrak{f}_{p'p}{}^*=\mathfrak{f}_{pp'},$$

it follows that $\sigma_r'=\sigma_r$, and

$$\mathfrak{f}_{p'p}=e^{i(p'-p)\sigma_r} \tag{A1}$$

satisfies (3.4) (for $W_T=0$) identically.[42]

This is a propagating type solution describing the polaron-band motion in the absence of damping. The contribution made by (A1) to the expectation value of the velocity is

$$\langle v\rangle_\sigma=\sum_{p'pN} f_{p'p}(N)v_{pp'}(N),$$

where

$$f_{p'p}(N)=Z^{-1}e^{-\beta E_N}\mathfrak{f}_{p'p}$$

where $\mathfrak{f}_{p'p}$ is given by (A1), and $v_{p'p}(N)$ by (4.5). One straightforwardly finds that

$$\langle v\rangle_\sigma=\frac{Je^{-S_T}}{\hbar\mathfrak{N}}\frac{1}{i}\sum_{p,\epsilon=\pm1}\epsilon e^{i\epsilon\sigma_r}$$
$$=(2Je^{-S_T}/\hbar)\sin\sigma_r, \tag{A2}$$

that is, the expectation value of velocity in polaron-band state σ_r.

However, instead of (A1), one should really have the superposition[43]

$$\mathfrak{f}_{p'p}=(1/\mathfrak{N})\sum_{\sigma_r} e^{i(p'-p)\sigma_r}\tilde{\mathfrak{f}}_{\sigma_r}. \tag{A3}$$

Letting $\sigma_r\rightarrow-\sigma_r$ in (A3) and again using the Hermeticity condition $f_{p'p}{}^*=f_{pp'}$, one finds that

$$\tilde{\mathfrak{f}}_{\sigma_r}=\tilde{\mathfrak{f}}_{-\sigma_r}. \tag{A4}$$

Hence, the net current due to the homogeneous solution in the absence of damping is

$$\langle v\rangle_h=\sum_{\sigma_r}\langle v\rangle_{\sigma_r}=\frac{2Je^{-S_T}}{\hbar}\frac{1}{\mathfrak{N}}\sum_{\sigma_r}\tilde{\mathfrak{f}}_{\sigma_r}\sin\sigma_r=0, \tag{A5}$$

because of (A4). This simply verifies that the unperturbed polaron-band motion (in the absence of both scattering and the electric field) carries no net current.

A somewhat more interesting case occurs for nonvanishing damping ($W_T\neq0$). Since the coefficients of (3.20) are constants, a representative solution is again of the form (A1); however, it is clear that (3.20) cannot be satisfied by σ pure real. Rather, one must have

$$\sigma=\sigma_r-i\sigma_i/2,\quad \sigma'=\sigma_r'-i\sigma_i'/2.$$

Again from the Hermiticity condition, one gets that

$$\sigma_r'=\sigma_r,\quad \sigma_i'=-\sigma_i,$$

and

$$\mathfrak{f}_{p'p}=e^{i(p'-p)\sigma_r}e^{-\frac{1}{2}(p'+p)\sigma_i} \tag{A6}$$

Thus, in addition to the propagating part depending on the difference $(p'-p)$, there is an additional part depending on the centroid $[(p'+p)/2]$, which describes damping of the polaron-band motion due to the nondiagonal transitions. The relation between σ_i and the amount of damping may be obtained by substituting (A6) into (3.20); one finds that

$$\sinh\left(\frac{\sigma_i}{2}\right)=\frac{\hbar W_T}{4Je^{-S_T}\sin\sigma_r}. \tag{A7}$$

It may be noted that the damping becomes infinite for $\sin\sigma_r=0$, i.e., for zero velocity of propagation; however, this causes no formal difficulties. Finally, one can show that the expectation value of velocity $\langle v\rangle$ is identically zero for the state (A6), as it must be.

[41] This form also follows directly from the definition (2.9) together with (5.1).

[42] Substituting (A1) into (3.20) (for $F_0=0$, $W_T=0$) gives $-2Je^{-S_T}(\cos\sigma-\cos\sigma)\equiv0$.

[43] This is, of course, nothing more than the transformation of the density matrix from the local-site (p) to the polaron-band (σ) representation.