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DYNAMICS OF SELF-LOCALIZED CHARGE-CARRIERS IN QUASI 1-D SOLIDS

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A theoretical study of the properties of large polarons in quasi one-dimensional systems, including intrachain scattering by phonons, phonon emission and absorption processes.

Quasi one-dimensional solids are often characterized by a profound anisotropy in their electronic transport properties. Concretely, within the framework of tight binding theory, the ratio of intrachain electron transfer amplitude, $J_{||}$, to interchain transfer, $J_{\perp}$, may be $\gtrsim 100$. Under these conditions, it is quite conceivable that, for non-metallic systems, an excess electron (or hole) would occur in the form of an anisotropic polaron. In particular, its intrachain dimension may be large compared to the lattice spacing, while still being confined to a single chain. Such a polaron is large as far as intrachain transport is involved, but small with respect to interchain transport. The motion of such an entity would be characterized by thermally activated hopping in the interchain direction, but would move as a quasi-free particle along the chain.

During the past one and a half years, we have developed a program of theoretical studies of the transport properties of the above described quasi one-dimensional polaron, together with preliminary surveys of the applicability of the methods to analogous properties encountered in the study of various types of solitons in quasi one-dimensional solids. Some preliminary studies on interchain hopping have been

carried out. However, the principal focus of our effort has been in the direction of developing a theory to describe intrachain transport. In particular, apart from verifying the basic quasi-free, band-type character of intrachain motion, we have developed a theoretical framework for the treatment of the different mechanisms' contribution to transport relaxation. Preliminary results on relaxation due to interaction of the polaron with the ambient phonon population of the host lattice have been obtained; in addition, the stage has been set for calculating the contribution of phonon emission and absorption process (Cherenkov processes) to said relaxation.

A detailed account of our studies in intrachain transport of quasi 1-d polarons (to be referred to as "M") will be published in an issue of Physics Reports (North Holland, 1982); a preliminary version is available upon written request to the author.

The starting point of our studies is contained in an early paper[1] which gives an explicit solution for the large 1-d polaron in the so-called molecular-crystal model, which has been used extensively in studies[2-4] focused primarily on the transport properties of the so-called small-polaron (i.e., polarons whose linear dimensions are of the order of a lattice spacing). For the case of a single electron, this model is described by the following Schrödinger equation:

$$i\hbar \frac{\partial a_n(u_1,\ldots u_m)}{\partial t} = \sum_m \left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial u_m^2} + \frac{M\omega_o^2 u_m^2}{2} \right) a_n(..u_m..)$$

$$- J(a_{n-1} + a_{n+1}) - AU_n a_n(..u_m..) \quad . \quad (1)$$

This equation describes the motions of a tight binding electron along a chain of diatomic molecules, in terms of a wave-function $a_n(u_1..u_m..)$ giving the amplitude of electron-site occupancy as a function of the vibrational coordinates, u_m (one per molecule for simplicity). The first term in the r.h.s. of Eq. (1) is manifestly associated with the purely vibrational motion of the individual molecules. The second describes intersite electron transfer in terms of an amplitude parameter J, whereas the third gives the electron-lattice interaction. The latter is assumed for simplicity to be site-diagonal and linearly dependent on the vibrational displacement coordinate u_n of the occupied site. In the previously cited studies,[2-4] the purely vibrational

component of Eq. (1) is augmented by the term of form $\sum_m M\omega_1^2 u_m u_{m+1}/2$, whose purpose is to provide a quasi-continuum of vibrational frequencies (vibrational dispersion) necessary for the discussion of hopping-type transport of small polarons. In our case, these terms will not be needed.

The basic approach, initiated in Ref. 1 and continued in this present work, is governed by the adiabatic approximation, which seeks to approximate the total amplitude function,

$$a_n(u_1..u_m..) \simeq a_n^{(ad)}(u_1..u_m..)\ \psi(u_1..u_m..)\ , \qquad (2)$$

where $a_n^{(ad)}(u_1..u_m..)$ is the adiabatic electron wave function, obtained as the eigenfunction of the stationary Schrödinger equation

$$E(u_1..u_m..)a_n^{(ad)}(u_1..u_m..) =$$

$$= \left\{(1/2)\ \sum_m M\omega_o^2 u_m^2 - Au_n\right\} a_n^{(ad)}(u_1..u_m..) - J(a_{n-1} + a_{n+1}), \qquad (3)$$

i.e., the stationary equivalent of (1), with neglect of the vibrational kinetic energy, and where $\psi(n_1..u_m..)$, describing the vibrational motion, satisfies the equation

$$i\hbar \frac{\partial \psi}{\partial t} = \left\{- \sum_m \frac{\hbar}{2M} \frac{\partial^2}{\partial u_m^2} + E(u_1..u_m..)\right\} \psi(u_1,..u_m..)\ , \qquad (4)$$

i.e., a vibrational Schrödinger equation in which the electronic energy eigenvalue, $E(u_1..u_m..)$, serves as the potential energy for vibrational motion, in accordance with standard adiabatic theory. [We should remark that a product-solution of the type given by Eq. (2) exists for each eigenfunction of Eq. (3). Here, and in what follows, we confine our attention to that eigenfunction which pertains to the lowest energy eigenvalue, i.e., the electronic ground state.]

As in analogous problems in molecular physics, Eq. (3) is too difficult to solve for arbitrary $u_1..u_m...$ The traditional procedure is first to seek the "minimal solution," $a_n^{(0)}$, for the special configuration $u_n^{(0)}..u_m^{(0)}..$, which minimizes $E(u_1..u_m..)$. This was the procedure employed in

Ref. 1. We cite, in particular, the formulae

$$a_n^{(0)} = (\gamma/2)^{1/2} \operatorname{sech} \gamma(n-\xi/a) \quad , \tag{5}$$

$$u_n^{(0)} = \frac{A}{M\omega_o^2} \gamma \operatorname{sech}^2\{\gamma(n-\xi/a)\} \quad , \tag{6}$$

$$V_o(n) = -Au_n^{(0)} = -\frac{A^2}{M\omega_o^2}\frac{\gamma}{2} \operatorname{sech}^2\gamma(n-\xi/a) \quad , \tag{7}$$

$$E_p = \frac{1}{48J}(A/M\omega_o^2)^2 = J\gamma^2/3 \quad , \tag{8}$$

which give, successively, the electron wave function, $a_n^{(0)}$, minimal distortion pattern, $u_m^{(0)}$, associated electron potential well, $V_o(n)$, and net polaron binding energy, E_p, in terms of the fundamental constants of the model. The first three quantities are functions of the site-index variable n, which is approximated by the continuous variable--appropriate for the case of the large polaron $\{\gamma \equiv A^2/4M\omega_o^2 J << 1\}$. Note especially that the argument of these functions is proportional to the combination $n - \xi/a$, where ξ is an arbitrary position variable which we designate as the polaron centroid coordinate, and "a" is the lattice spacing. This arbitrariness simply reflects the translational invariance of the physical system, so that the polaron centroid can be located "anywhere" in our one-dimensional medium.

The next stage in the adiabatic formulation is to seek solutions of the "electronic" equation, (3), for vibrational configurations $u_1..u_m..$ in the vicinity of the nominal configuration, $u_1^{(0)}..u_m^{(0)}...$ This can be done by standard perturbation theory, treating the "virtual" displacements

$$\delta u_m \equiv u_m - u_m^{(0)}$$

as small quantities. The procedure is to obtain the first-order correction to $a_n^{(0)}$ as a function of arbitrary δu_m, from which one straightforwardly obtains the vibrational potential energy

$$V(..\delta u_m..) \equiv E(..u_m^{(0)} + \delta u_m..) - E_p \quad , \tag{9}$$

to second order in the δu_m. The result [given in Sec. II of M {cf. Eqs. (2.16) - (2.18)}] reads

$$V(..\delta u_m..) = (M\omega_o^2/2)\left\{\sum_n (\delta u_n)^2 - \sum_{n,n'} \hat{G}(n-\xi/a, n'-\xi/a)\delta u_n \delta u_{n'}\right\} \quad , \qquad (10)$$

where $\hat{G}(n,n') \equiv 4\gamma^2 G(n,n')\,\mathrm{sech}\gamma n\,\mathrm{sech}\gamma n'$ and where $\hat{G}(n,n')$ is a solution of the equation

$$\frac{\partial^2 \hat{G}}{\partial n^2} + \gamma\{2\,\mathrm{sech}^2\gamma n - 1\}\hat{G} = -\delta(n-n') + \frac{\gamma}{2}\,\mathrm{sech}\gamma n\,\mathrm{sech}\gamma n' \ . \qquad (11)$$

We remark that Eq. (11) is completely equivalent to the usual perturbation-theoretic formulation for determination of the first-order correction to the electronic wave function. We note also the absence of terms linear in the δu_n in Eq. (10). This feature is expected, of course, because $V(..\delta u_m..)$ constitutes an expansion about the minimal configuration.

The next stage in the treatment is to obtain the normal vibration modes associated with the new potential energy function, $V(..\delta u_m..)$. This means obtaining the solutions of the mode eigenvalue equations:

$$-M\omega^2\delta u_n = -M\omega_o^2\{\delta u_n - \sum_{n'} \hat{G}(n-\xi/a, n'-\xi/a)\delta u_{n'}\} \ . \qquad (12)$$

This problem was, in fact, treated a few years earlier by Melnikov[5] and by Shaw and Whitfield.[6] Although a complete solution was not obtained, their results are sufficient for our purpose. Concretely, the solution of Eq. (12) yields mode functions $u_\alpha(n-\xi/a)$ (we shall refer to these as "MSW-modes"), and associated frequencies, ω_α. The latter constitute an infinite series of discretely denumerable values, ascending from zero to the host-lattice vibration frequency, ω_o, which serves as an accumulation point of the series. Of particular interest is the existence of a zero frequency mode. As emphasized in Refs. 5 and 6, this mode, whose explicit n-dependence has the form

$$u_o(n-\xi/a) \sim \mathrm{sech}^2\gamma(n-\xi/a)\,\tanh(n-\xi/a) \quad , \qquad (13)$$

is just what one obtains by considering the δu_n pattern arising from an infinitesimal displacement of the polaron centroid, as evidenced by the fact that

$$u_o(n-\xi/a) \sim \frac{\partial u_n^{(0)}(n-\xi/a)}{\partial \xi} \tag{14}$$

The existence of such a mode is just an additional manifestation of the translational invariance of the physical system.

We remark here that the existence of the zero-frequency "translational" mode also obtains in other problems; in particular, for the case of one-dimensional solitons.[7] Just as in those problems, it is inferred that one possible dynamical mode of the polaron (or soliton) consists of uniform translation; the others correspond to various types of shape-altering motions. That is, for the so-called ϕ^4-soliton,[8] there exists a discrete "breather mode," together with a continuum, which describes the interaction with "free" lattice vibrations (propagating waves). In our particular problem, in which the spectrum of free vibrations is the completely Einstein-type delta function distribution $\delta(\omega_\alpha-\omega_o)$, the MSW mode-functions, $u_\alpha(n-\xi/a)$, describe localized "bound-state" vibrations, giving rise to shape-altering motions of the polaronic distortion pattern.

It is at this point in the development that our own studies (i.e., those giving rise to new results and associated theoretical points-of-view) may be said to begin. The actual starting point is the realization of the fact that the existence of the zero-frequency mode had been established, the original procedure of computing the adiabatic potential as a function of small excursions, δu_n, about a fixed minimal pattern, $u^{(0)}(n-\xi/a)$, with fixed (though arbitrary) ξ, which lies at the basis of the treatments of Refs. 6 and 7 (as well as the corresponding treatments of the soliton problem) is manifestly inadequate whence we incorporate the vibrational kinetic energy into the problem [as is required by Eq. (4)]. The reason is simply that the amplitudes of the δu_n which occur dynamically can no longer be considered uniformly small. In particular, the amplitude of any component which contains the translational mode must be expected to get arbitrarily large. Under these circumstances, it is necessary to adopt a more flexible approach in which the centroid is no longer considered to be fixed (in zeroth order), but is permitted to assume arbitrary values, as determined ultimately by the dynamics. In other words, we propose to treat the centroid as an independent dynamical variable. We do this by writing an arbitrary displacement, u_n, in the form [cf. Eq. (3.1) of M]

$$u_n = u^{(0)}(n-\xi/a) + \sum_{\alpha=1}^{\infty} u_\alpha(n-\xi/a)Q_\alpha \qquad (15)$$

where the "mode amplitudes" Q_α are to be considered as small. Note that the mode summation excludes any contribution of the translational mode, $u_o(n-\xi/a)$. Such a contribution would be redundant since the possibility of purely translational motion is already taken into account by permitting ξ to be an arbitrary dynamical variable. Alternatively stated, the elimination of the translational mode from the α-sum automatically solves the over-counting problem which would otherwise arise from the introduction of an extra lattice dynamical variable on top of the already complete set constituted by the u_n.

We note also the important fact that, by virtue of the ξ-dependence of the mode amplitude functions, $u_\alpha(n-\xi/a)$, the translational motion is no longer decoupled from the other non-translational degrees of freedom, as in the treatment of Refs. 5, 6, and 7. This coupling gives rise to a drastic modification of the structure of the theory developed in the cited references. The modification shows up when we transform the vibrational kinetic energy operator $T \equiv (-\hbar^2/2M) \sum_m (\partial^2/\partial u_m^2)$ to the new coordinates ξ and Q_α, said transformation being defined by Eq. (15). The details of this transformation are given in Section III of M; the final result is an explicit expression for T as a function of differential operators $\partial/\partial\xi$, $\partial/\partial Q_\alpha$. When augmented by the potential energy operator

$$V(..\delta u_n..) \rightarrow \frac{1}{2} \sum_{\alpha=1}^{\infty} M\omega_\alpha^2 Q_\alpha^2$$

the total vibrational Hamiltonian is thus obtained. Before displaying the explicit expression for it, we remark that an integral feature of the treatment is the utilization of a transformed vibrational wave function

$$\chi(..Q_\alpha..\xi) = \left|1 + \frac{M}{M_p} \sum_\alpha S_\alpha Q_\alpha\right|^{1/2} \psi(..Q_\alpha..\xi)$$

$$= \left|1 + \frac{M}{M_p} \sum_\alpha S_\alpha Q_\alpha\right|^{1/2} \psi(..u_n..) \quad , \qquad (16)$$

where

$$M_p \equiv M \sum_n [\partial u^{(0)}(n-\xi/a)/\partial\xi]^2 \qquad (17)$$

plays the role of effective mass for the polaron centroid motion, and the S_α are certain coefficients given by the formula

$$S_\alpha \equiv \sum_n \frac{\partial u^{(0)}(n-\xi/a)}{\partial \xi} \frac{\partial u_\alpha(n-\xi/a)}{\partial \xi} \quad . \tag{18}$$

The basic property obeyed by the transformed wave function, $\chi(..Q_\alpha..\xi)$, is that its normalization is given by the equation

$$1 = \int |\chi(..Q_\alpha..\xi)|^2 \, d\xi dQ_1..dQ_\alpha$$

$$= \int \left|1 + \frac{M}{M_p} \sum_\alpha S_\alpha Q_\alpha\right| |\psi(..Q_\alpha..\xi)|^2 \, ..dQ_\alpha..d\xi \quad . \tag{19}$$

The occurrence of the factor $\left|1 + \frac{M}{M_p} \sum_\alpha S_\alpha Q_\alpha\right|$ in the last equality is connected with the fact that this factor constitutes the Jacobian of the transformation from the u_n to the variables $..Q_\alpha..\xi$.

The time dependent Schrödinger equation for χ [replacing Eq. (4)] is written in the form

$$i\hbar \frac{\partial \chi}{\partial t} = H\chi = (H_0 + H_1)\chi \quad . \tag{20}$$

Here [cf. Section III of M],

$$H_0 = -\frac{\hbar^2}{2M} \sum_\alpha \frac{\partial^2}{\partial Q_\alpha^2} + \frac{M}{2} \sum_\alpha \omega_\alpha^2 Q_\alpha^2$$

$$- \frac{\hbar^2}{2M_p} \left(\frac{\partial}{\partial \xi} - \sum_{\alpha,\alpha'} G_{\alpha\alpha'} Q_\alpha \frac{\partial}{\partial Q_\alpha}\right)^2$$

$$= \sum_\alpha \hbar\omega_\alpha \left(b_\alpha^\dagger b_\alpha + \frac{1}{2}\right) - \frac{\hbar^2}{2M_p} \left(\frac{\partial}{\partial \xi} - \sum_{\alpha,\alpha'} b_\alpha'^\dagger b_\alpha\right)^2 \tag{21}$$

and

$$H_1 = -\frac{\hbar^2}{2M_p}\left\{\left[\frac{1/2}{1+\frac{M}{M_p}\sum_\alpha S_\alpha Q_\alpha}\left(\frac{\partial}{\partial\xi} - \sum_{\alpha,\alpha'} G_{\alpha\alpha'} Q_{\alpha'} \frac{\partial}{\partial Q_\alpha}\right)\right.\right.$$

$$\left.\left. + \left(\frac{\partial}{\partial\xi} - \sum_{\alpha,\alpha'} G_{\alpha\alpha'} Q_{\alpha'} \frac{\partial}{\partial Q_\alpha}\right)\left(\frac{1/2}{1+\frac{M}{M_p}\sum_\alpha S_\alpha Q_\alpha}\right)\right]^{1/2}\right.$$

$$\left. - \left(\frac{\partial}{\partial\xi} - \sum_{\alpha,\alpha'} G_{\alpha\alpha'} Q_{\alpha'} \frac{\partial}{\partial Q_\alpha}\right)^2\right\}$$

$$- \frac{\hbar^2}{2M_p}\sum_\alpha (M/M_p)^2 S_\alpha{}^2 \left[\frac{1}{\left(1+\frac{M}{M_p}\sum_\alpha S_\alpha Q_\alpha\right)^2} - 1\right] , \quad (22)$$

where the (antisymmetric) matrix elements $G_{\alpha\alpha'}$ are defined by the formula

$$G_{\alpha\alpha'} = -G_{\alpha'\alpha} = \sum_n u_\alpha(n-\xi/a)\frac{\partial u_{\alpha'}(n-\xi/a)}{\partial\xi} , \quad (23)$$

(in our work, we treat the n-sums as integrals), and where $b_\alpha{}^\dagger$ and b_α are boson creation and annihilation operators associated with the MSW-excitations. Their explicit form is given by inverting the standard relations

$$Q_\alpha = (\hbar/2M\omega_\alpha)^{1/2}(b_\alpha + b_\alpha{}^\dagger) \quad ;$$

$$\frac{\partial}{\partial Q_\alpha} = (M\omega_\alpha/2\hbar)^{1/2}(b_\alpha - b_\alpha{}^\dagger) \quad . \quad (24)$$

The decomposition of the total Hamiltonian into the two components, H_0 and H_1, corresponds to the circumstance that (as discussed exhaustively in Sec. III of M), for the case where the adiabatic approach is valid, H_1 may be treated as a perturbation relative to the zero'th order Hamiltonian. Here, we note that, when factors of the form $[1 + (M/M_p)\sum_\alpha S_\alpha Q_\alpha]^{-1}$ are replaced by unity, H_1 vanishes. The detailed considerations of M show that a binomial expansion of these

denominators in powers of the operator, $(M/M_p)\sum_\alpha S_\alpha Q_\alpha$, leads to a perturbation development in which the basic smallness parameter is the dimensionless ratio $(\hbar\omega_o/E_p)^{1/2}$. We now remark that a necessary condition for the applicability of the adiabatic approach is the inequality

$$\hbar\omega_o/E_p << 1 \quad , \tag{25}$$

i.e., the vibrational quantum energy should be small compared to characteristic electronic energies [a typical such quantity being the polaron binding energy, E_p, as given by Eq. (8)]. From this fact, we conclude that it is indeed quite appropriate to treat H_1 as a perturbation, as we have done in our treatment.

Turning now to H_0, we take note of the important property, exhibited most explicitly in the last equality of Eq. (21), namely, that H_0 conserves the total number of MSW-mode excitations (phonons). Concretely, due to the occurrence of equal powers of creation and annihilation operators, b_α and $b_\alpha^\dagger$ in all the terms, it is immediately apparent that, with neglect of H_1,

$$\sum_\alpha N_\alpha = \sum_\alpha b_\alpha^\dagger b_\alpha = \text{constant}.$$

The eigenstates of H_0 may thus be classified according to the total phonon population, viz., zero-phonon, one-phonon, etc.

Within this classification framework, it may now be remarked that the eventual inclusion of H_1 gives rise to transitions between the different classes of zero'th order eigenstates, in which one, two, three, etc., phonons are emitted or absorbed. The number of phonons shows up in the occurrence of successively higher powers of the smallness parameter $\hbar\omega_o/E_p$, as far as the probabilities of such transitions are concerned [for each phonon, two powers of the basic parameter $(\hbar\omega_o/E_p)^{1/2}$ are introduced].

Apart from this preliminary observation, we have not as yet carried out specific calculations on the probabilities of such "Cherenkov" processes. However, we do not anticipate any essential difficulties, and we propose to study them as part of our future program. Our work up to this time has been focused on the eigenstates of H_0, in particular the zero-phonon and one-phonon states. It will be seen that,

especially in the case of one-phonon states, the theoretical treatment is quite non-trivial. In particular, it permits us to elucidate the principal features of an important transport-relaxation mechanism, namely that due to polaron collisions with ambient phonons.

We begin with some brief remarks on the relatively simple zero-phonon case. Here, all the terms involving phonon creation and annihilation operators are effectively zero, so that the only surviving term on the right hand side of Eq. (21) is

$$H_0^{(0)} = -\frac{\hbar^2}{2M_p}\frac{\partial^2}{\partial\xi^2} \quad . \tag{26}$$

The zero phonon eigenstates are conveniently chosen as

$$\chi(..Q_\alpha..\xi) \sim \exp(ik_\xi\xi)\ |0\rangle \tag{27}$$

where the ket, $|0\rangle$, denotes the "vacuum" vibrational state in which all the N_α are zero. Its (unnormalized) configurational representation is simply

$$|0\rangle \sim \prod_\alpha \exp[-(M\omega_\alpha/2\hbar)Q_\alpha^2] \quad . \tag{28}$$

From the ξ-dependence of Eq. (27), we see immediately that the state is one of momentum $\hbar k_\xi$, and energy $E_{k_\xi} = \hbar^2 k_\xi^2/2M_p$. In this simple case, the isolated polaron behaves as a quasi-particle of mass M_p.

We now discuss the much more involved, and interesting, problem of the one-phonon case. This is discussed at length in Sec. IV of M. We present a very brief summary of its contents.

Consider the sub-class of one-phonon states which have the form

$$|\psi\rangle = \sum_\alpha A_\alpha(t)\ b_\alpha^\dagger |0\rangle \exp(ik_\xi\xi) \tag{29}$$

where the $A_\alpha(t)$ are complex numbers whose values at some initial time are arbitrary (apart from normalization), and where $|0\rangle$ denotes the already described vacuum vibrational state, alternatively defined as the state for which $b_\alpha|0\rangle = 0$.

We remark that Eq. (29) embraces the totality of one-phonon states which are characterized by a fixed value, $\hbar k_\xi$, of the canonical momentum operator, $p_\xi = (\hbar/i)\partial/\partial\xi$, associated with the centroid coordinate ξ. The fact that p_ξ is a "good" quantum number is seen from inspection of Eq. (21). Specifically, H_0 (and, indeed, H_1 as well) does

not contain an explicit ξ-dependence. It is a function only of $\partial/\partial\xi$, so that

$$[H_0, p_\xi] = 0 \quad .$$

However, in contrast to the situation in the zero-phonon case, discussed at the end of the previous section, p_ξ is not to be identified with the kinetic momentum associated with the motion of the centroid. This latter quantity, $M_p\dot{\xi}$, is easily seen to be given by

$$M_p\dot{\xi} = M_p \frac{i}{\hbar}[H_0,\xi] = \hbar k_\xi - \frac{\hbar}{i}\sum_{\alpha,\alpha'} G_{\alpha\alpha'} b_{\alpha'}^\dagger b_\alpha \quad .$$

Actually, we should not be surprised at the lack of correspondence of p_ξ with the kinetic momentum, $M_p\dot{\xi}$. Specifically, we do not expect $\dot{\xi}$, also, to be a constant of the motion. If it were, we would conclude that the zero'th order theory based on H_0 is incapable of describing polaron-phonon collisions. However, the fact that $M_p\dot{\xi}$ differs from p_ξ impels us to two conclusions:

1) The quantity p_ξ must correspond to the (crystal) momentum of the entire system--polaron plus phonon. Its constancy arises from the invariance of the H_0 (and H_1 as well) with respect to the translation of both phonon and polaron in the one-dimensional ξ-space. [Remember that our description of the vibrational subsystem is formulated in terms of the MSW-modes, which are "attached" to the centroid coordinate ξ via our initial transformation relationship, Eq. (15)]. It must follow then that

2) the quantity $P_{ph} \equiv (\hbar/i)\sum_{\alpha,\alpha'} G_{\alpha\alpha'} b_{\alpha'}^\dagger b_\alpha$ corresponds to the momentum associated with the phonon field. In the one-phonon case this is simply the momentum of a single phonon.

In order to elucidate this last conclusion, we develop an alternate expression for P_{ph}. We refer to M [Eqs. (4.4) - (4.7) and intervening text] for details. The result is

$$P_{ph} = \frac{\hbar}{ia}\sum_\eta b^\dagger(\eta)\frac{\partial b(\eta)}{\partial\eta} \quad , \tag{30}$$

where, with the introduction of a "local" site-variable,

$$\eta \equiv n - \xi/a \tag{31}$$

the objects

$$b^\dagger(\eta) \equiv \sum_{\alpha=1}^{\infty} u_\alpha(\eta)\, b_\alpha^\dagger \tag{32a}$$

$$b(\eta) \equiv \sum_{\alpha=1}^{\infty} u_\alpha(\eta)\, b_\alpha \qquad (32b)$$

may be regarded as operators which create or annihilate site-localized phonons.

We now note that, if the $b^\dagger(\eta)$ and $b(\eta)$ were true boson operators, the right hand side of Eq. (30) could obviously correspond to phonon momentum. [This correspondence could be made more obvious by transforming to plane wave operators

$$b_q^\dagger = (1/N^{1/2}) \sum_\eta e^{iq\eta}\, b^\dagger(\eta)$$

$$b_q = (1/N^{1/2}) \sum_\eta e^{-iq\eta}\, b(\eta) \quad ,$$

(N = number of sites in the sample), in terms of which Eq. (30) would assume the form

$$P_{ph} = \sum_q \hbar q\, b_q^\dagger\, b_q \quad ,$$

which is the standard expression for the total momentum of the phonon field.]

However, the situation is complicated by the fact that, since the sums in Eqs. (32a) and (32b) go over an incomplete set of mode-functions (the translational mode-function being omitted), the $b(\eta)$, $b^\dagger(\eta)$ do not obey boson commutation rules. Instead [cf. Eq. (4.9) of M],

$$[b(\eta),\, b^\dagger(\eta)] = \delta_{\eta,\eta'} - u_0(\eta)\, u_0(\eta') \quad . \qquad (33)$$

The implications of Eq. (33) are discussed in Section IV of M, wherein it is concluded that, for all practical purposes [in which the principal concern is the asymptotic behavior of a localized phonon "wave packet" at large distances from the polaron centroid ($|R| \gg 1/\gamma$)], the correction to boson commutation rules embodied in the last term on the right hand side of Eq. (33) may be ignored. For such wave packets, the interpretation of Eq. (30) as the momentum of a phonon is acceptable.

The next step is to establish a Schrödinger type equation for a one-phonon state function in the site-variable representation. To this end, one introduces an η-dependent one-phonon "wave function," characterized by a fixed value of the total momentum $p_\xi = \hbar k_\xi$, via the definition

$$\psi(\eta) \equiv \langle 0|b(\eta)|\psi\rangle \quad , \qquad (34)$$

where

$$|\psi> = \sum_\alpha A_\alpha(t)\ b_\alpha^\dagger |0> \quad , \tag{35}$$

is the general one-phonon state. [Equation (35) differs from Eq. (29) only in that the explicit ξ-dependent, $\exp(ik_\xi \xi)$, has been omitted, it being understood that $\partial/\partial\xi$ is to be replaced uniformly by $ik\xi$.] In conjunction with Eqs. (34) and (35), the action of an arbitrary operator, α, on the "wave function" $\psi(\eta)$, is defined by the formula

$$\alpha\psi(\eta) \equiv <0|b(\eta)\alpha|\psi> \quad . \tag{36}$$

After straightforward, albeit lengthy, manipulations, detailed in Sec. IV of M, together with approximations also discussed therein, one obtains for the zero'th order Hamiltonian, the operator equation

$$H_0\psi(\eta) = \hbar\omega_o\psi(\eta) - \frac{\hbar\omega_o}{2}\sum_{\eta'} G(\eta,\eta')\ \psi(\eta') +$$

$$+ \frac{\hbar^2}{2M_p a^2}\left(k_\xi + i\frac{\partial}{\partial\eta}\right)^2 \psi(\eta) + \frac{\hbar^2}{2M_p a^2} B(\eta)\ \psi(\eta) \quad , \tag{37}$$

where

$$B(\eta)\ \psi(\eta) \equiv u_0(\eta)\sum_{\eta'} u_0(\eta')\left(\frac{\partial^2\psi(\eta')}{\partial\eta'^2} - 2ik_\xi\frac{\partial\psi(\eta')}{\partial\eta'}\right) +$$

$$+ \frac{\partial u_0(\eta)}{\partial\eta}\sum_{\eta'} u_0(\eta')\frac{\partial\psi(\eta')}{\partial\eta'} \quad . \tag{38}$$

The physical significance of Eq. (37) may be understood as follows. In the absence of the polaron, an Einstein phonon, initially localized on a given site, remains localized at that site. The presence of the polaron produces two types of motion. One of these, associated with the nonlocal term containing $G(\eta,\eta')$, is intersite migration; said migration occurring principally in the neighborhood of the polaron ($|\eta|,\ |\eta'| \lesssim 1/\gamma$). The second, associated with the terms proportional to $\hbar^2/2M_p a^2$ is due simply to the continuous kinetic motion of the polaron. Its appearance in Eq. (37) arises solely from the circumstance that our wave function, $\psi(\eta)$, depends upon the "position" of the phonon relative to the polaron centroid. Finally, the term containing the factor $B(\eta)\psi(\eta)$ takes account of the exclusion of the

translational MSW-mode, $u_o(\eta)$, from the phonon dynamics. Its mathematical structure, as discussed in M, does not present any inherent obstacles. Taking it into account requires tiresome but otherwise straightforward corrections.

We now sketch our work concerning the application of Eq. (37) to the solution of the polaron-phonon scattering problem. As in standard stationary-state scattering, we seek stational spatially unbounded solutions of the Schrödinger equation,

$$E\psi = H_0\psi \quad .$$

Writing

$$E = \psi + \hbar\omega_o$$

we have

$$\varepsilon\psi(\eta) = -\frac{\hbar\omega_o}{2}\sum_{\eta'} G(\eta,\eta')\psi(\eta') + \\ + \frac{\hbar^2}{2M_p a^2}\left(k_\xi + i\frac{\partial}{\partial\varepsilon}\right)^2\psi(\eta) + \frac{\hbar^2}{2M_p a^2}B(\eta)\psi(\eta) \quad . \qquad (39)$$

We remark that, upon examining the asymptotic form of Eq. (39) (where the first and third terms on the right hand side may be ignored), one immediately sees that the requirement of spatial unboundedness is satisfied by taking ε to be positive. We remark that, physically, ε is just the polaron kinetic energy at large distances from the phonon.

Our problem is now to solve Eq. (39) subject to boundary conditions such that for η positive and large, $\psi(\eta)$ has the form of an outgoing wave, $\exp(ik_p\eta a)$ [where $\hbar^2 k_p^2/2M_p = \varepsilon$]. The solution for large negative η, then, immediately yields the amplitude of the reflected wave relative to the incident. The absolute square of the ratio, R, is just the reflection coefficient for one-dimensional polaron-phonon collisions. From a knowledge of the reflection coefficient, the transport relaxation time is readily obtained in terms of polaron velocity and ambient phonon density.

In our actual procedure, we utilize the two defining equations (11) and (23) for $G(\eta,\eta')$ and $G(\eta,\eta')$ to replace Eq. (39) by two coupled differential equations. Referring to Sec. IV of M for the details, we proceed to write down these equations in dimensionless form. We have

$$\left[\kappa_0^2 - \left(\kappa + i \frac{\partial}{\partial z} \right)^2 \right] \psi(z) = 2\kappa_c \, \mathrm{sech} z \, F(z) + B(z)\psi(z) \quad , \quad (40)$$

$$\frac{\partial^2 F}{\partial z^2} + (2\mathrm{sech}^2 z - 1)F(z) = 2\kappa_c \, \mathrm{sech} z \, \psi(z) - 2\kappa_c \, D(z)\psi(z), \quad (41)$$

where $z = \gamma\eta$ is a dimensionless variable, giving length in units of the polaron size, L. Here also

$$L = a/\gamma \quad , \quad (42a)$$

$$\kappa_0 \equiv (2M_p \varepsilon)^{1/2} L/\hbar \quad , \quad (42b)$$

$$\kappa_c \equiv (16E_p/5\hbar\omega_o)^{1/2} \quad , \quad (42c)$$

and

$$\kappa \equiv k_\xi L/a \quad . \quad (42d)$$

[We remark that κ_o, the dimensionless polaron momentum at infinity, and κ, the corresponding dimensionless total momentum, are specified by the initial conditions, In particular, κ_o is contained in the form of the "incident beam," $\exp(i\kappa_o z)$, whereas κ is just $\pm\kappa_o$ augmented by the (arbitrary) momentum of the initial phonon. We further remark that the absolute magnitudes $|\kappa|$ and $|\kappa_o|$ are limited only by the circumstance that, ultimately, we want to take account of the discreteness of the lattice. Thus, $|\kappa|, |\kappa_o| \leq L\pi/a >> 1$.]

Finally,

$$B(z)\,\psi(z) \equiv u_0(z) \int u_0(z') \left(\frac{d^2\psi}{dz'^2} + 2i\kappa \frac{d\psi}{dz'} \right) dz'$$

$$+ \frac{\partial u_0}{\partial z} \int u_0(z') \frac{d\psi}{dz'} \, dz'$$

and

$$D(z)\,\psi(z) \equiv \frac{1}{2} \, \mathrm{sech} z \int \mathrm{sech}^2 z' \, \psi(z') \, dz' \quad .$$

As pointed out in M [cf. text between Eqs. (4.29) and (4.30)], these last terms play the role of "driving" terms in the coupled system given by Eqs. (40) and (41), which are easily treated once we know the solutions of the correspond-

ing duo of "homogeneous" equations. We shall not discuss them further, except to point out that, for the specific cases which we have studied, their role is subordinate.

The calculations which we have carried out so far are focused on two cases:

1) $\kappa >> \kappa_c$. In this case, it turns out that Eq. (41) may be approximated by an algebraic relationship between the coupled amplitudes $F(z)$ and $\psi(z)$, viz.,

$$-\kappa^2 F(z) \cong 2\kappa_c \operatorname{sech} z \, \psi(z) \tag{41'}$$

which, when substituted into Eq. (40), yields

$$\left[\kappa_0^2 - \left(\kappa + i \frac{\partial}{\partial z} \right)^2 \right] \psi(z) + (4\kappa_c^2/\kappa^2) \operatorname{sech}^2 z \, \psi(z) = 0 \tag{40'}$$

where we have omitted the driving terms for simplicity of presentation. Introducing the transformation $\psi(z) = [\exp(i\kappa z)] \, \chi(z)$ then yields

$$\frac{d^2\chi}{dz^2} + [(4\kappa_c^2/\kappa^2) \operatorname{sech}^2 z + \kappa_0^2] \, \chi(z) = 0 \quad , \tag{43}$$

which is just the one-dimensional Schrödinger equation for a $\operatorname{sech}^2 z$ potential-well. The continuum solutions are well known. In particular [cf. Landau and Lifshitz, 3rd edition, page 80 (1963)], the reflection coefficient is given by the expression

$$R = \frac{\cos^2[(\pi/2)(1 + 16\kappa_c^2/\kappa^2)^{1/2}]}{\sinh^2 \pi\kappa_0 + \cos^2[(\pi/2)(1 + 16\kappa_c^2/\kappa^2)^{1/2}]} \quad . \tag{44}$$

Apart from special values of κ such that the square-root in the argument of the cosine is an odd integer (the ultimate significance of these values being of zero measure as far as physical applications are concerned), the essential behavior of Eq. (44) is conveniently given by the formula

$$R \cong \exp[-2\pi\kappa_0] \quad . \tag{45}$$

2) $\kappa_o >> 1$, $\kappa = 0$. In this case, we have developed WKB-type solutions of the coupled equations, (40) and (41). Due to limitations of space, we shall not discuss details, but content ourselves with citing the general result that, in the limit

$$\kappa_0 \equiv (2M_p\varepsilon)^{1/2} L/\hbar >> 1 \quad ,$$

the reflectivity coefficient becomes exponentially small; in fact

$$R \simeq \exp[-2\pi\kappa_0] \quad ,$$

(just as in case 1).

It appears that, to obtain a more complete solution of the problem, numerical methods are required. In our opinion, the above quoted results already contain the essential physics, as embodied in Eqs. (45) and (45').

In connection with the last remark, we note from Eq. (4.47) of M that the basic energy unit of the problem, namely $\hbar^2/2M_pL^2$, turns out to be just

$$\hbar^2/2M_pL^2 = \hbar\omega_o(5/32)(\hbar\omega_o/E_p) \quad .$$

This unit is clearly small compared to the phonon energy. It is then clear that, for a wide range of physically interesting thermally ambient polaron kinetic energies, Eqs. (45) and (45') predict that polaron-phonon collisions contribute rather weakly to transport relaxation rates. Alternatively stated, effective transport mean-free-paths may be quite large compared to the reciprocal of (one-dimensional) phonon densities. In view of this result, it is obviously of importance to study the contribution of Cherenkov processes to transport relaxation. Such processes would become especially important for $\varepsilon > \hbar\omega_o$. This problem, in fact, constitutes one facet of our proposed research program.

An added note: With respect to conventional transport properties (diffusivity and mobility), the long mean-free-path energy region below the Cherenkov threshold, $\varepsilon = \hbar\omega_o$, will still be of decisive importance, as long as kT is not exceptionally large compared to $\hbar\omega_o$.

REFERENCES

1. T. Holstein, Ann. Phys. 8, 325 (1959).
2. T. Holstein, Ann. Phys. 8, 343 (1959).
3. L. Friedman and T. Holstein, Ann. Phys. 21, 494 (1963).
4. D. Emin and T. Holstein, Ann. Phys. 53, 439 (1969).
5. V. I. Melnikov, Sov. Phys. JETP 45, 1233 (1977).
6. P. Shaw and G. Whitfield, Phys. Rev. B14, 3346 (1976).
7. Y. Wada, J. R. Schrieffer, Phys. Rev. B18, 3897 (1978).
8. E. Tomboulis, Phys. Rev. D12, 1678 (1975).
9. J. A. Krumhansl and J. R. Schrieffer, Phys. Rev. B11, 3535 (1975).
10. W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B22, 2099 (1980).