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Studies of Polaron Motion

Part II. The "Small" Polaron

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The one-dimensional molecular-crystal model of polaron motion, described in the preceding paper, is here analyzed for the case in which the electronic-overlap term of the total Hamiltonian is a small perturbation. In zeroth order —i.e., in the absence of this term—the electron is localized at a given site, p. The vibrational state of the system is specified by a set of quantum-numbers, N_k, giving the degree of excitation of each vibration-mode; the latter differ from the conventional modes in that in each of them, the equilibrium displacement, about which the system oscillates, depends upon the location of the electron.

The presence of a nonvanishing electronic-overlap term gives rise to transitions in which the electron jumps to a neighboring site ($p \rightarrow p \pm 1$), and in which either all of the N_k remain unaltered ("diagonal" transitions) or in which some of them change by ± 1 ("nondiagonal" transitions). The two types of transitions play fundamentally different roles. At sufficiently low temperatures, the diagonal transitions are dominant. They give rise to the formation of Bloch-type bands whose widths (see Eq. 37) are each given by the product of the electronic-overlap integral, and a vibrational overlap-integral, the latter being an *exponentially falling* function of the N_k (and, hence, of temperature). In this low-temperature domain, the role of the nondiagonal transitions is essentially one of scattering. In the absence of other scattering mechanisms, such as impurity scattering, they determine the lifetimes of the polaron-band states and, hence, the mean free path for typical transport quantities, such as electron diffusivity.

With rising temperature, the probability of the off-diagonal transitions goes up exponentially. This feature, together with the above-mentioned drop in bandwidth, results, e.g., in an exponentially diminishing diffusivity. Eventually, a temperature, $T_t \sim \frac{1}{2}$ the Debye Θ, is reached at which the energy uncertainty, $\hbar/\tau$, associated with the finite lifetime of the states, is equal to the bandwidth. At this point, the Bloch states lose their individual characteristics (in particular, those which depend upon electronic wave number); the bands may then be considered as "washed out." For temperatures $> T_t$, electron motion is predominantly a diffusion process. The elementary steps of this process consist of the random-jumps between neighboring sites associated with the nondiagonal transitions. In conformance with this picture, the electron diffusivity is, apart from a numerical factor, the product of the square of the lattice

distance and the total non-diagonal transition probability, and is therefore an *exponentially rising* function of temperature.

The limit, $J_{\max}$, of the magnitude of the electronic overlap term, beyond which the perturbation treatment of the present paper becomes inapplicable, is investigated. For representative values of the parameters entering into the theory, $J_{\max} \sim 0.12$ ev and 0.035 ev for the extreme cases of (a) width of the ground-state polaron-band and (b) high-temperature site-jump probabilities (these numbers correspond to *electronic* bandwidths of 0.24 ev and 0.07 ev, respectively). For electronic bandwidths in excess of these limits, a treatment based on the adiabatic approach is required; preliminary results of such a treatment are given for the above two cases.

I. INTRODUCTION

In this paper, the one-dimensional molecular-crystal model, developed in the preceding paper (*1*),[1] will be applied to the study of the *small* polaron. The basic features of the molecular-crystal model are contained in Eq. (9) of I, which may be written as

$$i\hbar \frac{\partial a_n(x_1, \cdots, x_N)}{\partial t} = \left[\sum_{m=1}^{N} \left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_m^2} + \frac{1}{2}M\omega_0^2 x_m^2\right) - Ax_n\right] a_n - J[a_{n+1} + a_{n-1}]. \tag{1}$$

Here, the "wave function," $a_n(x_1, \cdots, x_N)$, is a function of the "lattice-vibration" coordinates, $x_1, \cdots, x_N$ (each of which describes the internuclear vibration of a single (diatomic) molecular site of the linear chain), and of a discrete "electronic" coordinate, n. The latter is to be understood in terms of the tight-binding approximation, according to which the actual wave function of the system has the form

$$\psi(\mathbf{r}, x_1, \cdots, x_N) = \sum_n a_n(x_1, \cdots, x_N)\phi(\mathbf{r} - n\mathbf{a}, x_n) \tag{2}$$

(where $\phi(\mathbf{r} - n\mathbf{a}, x_n)$ is a one-electron wave-function, localized about the nth molecular site, its precise definition being given by Eq. (I 3) in the appendix of I).

The sum over m in the square-bracket of (1) represents the "lattice" Hamiltonian, consisting of the vibratory kinetic and potential energies of the molecules in the absence of the electron; it is expressed in terms of the reduced mass, M, and vibration frequency, ω_0, of the individual molecules. The remaining term in the square bracket, $-Ax_n$, gives the "electron-lattice" interaction as a linear function of the vibration coordinate of the occupied site. Finally, the term pro-

[1] To be referred to hereafter as I. Here, as in I, the term "small polaron" designates the case in which the linear dimension of the polaron is of the order of a lattice spacing.

portional to the electronic "overlap" integral,[2] $-J$, describes the motion of the electron through the lattice. As discussed in I, this feature of the model is strictly analogous to the conventional atomic tight-binding approach; in particular, if all the x_n's are fixed at one and the same value (thereby suppressing vibrational motion), Eq. (1) reduces to the standard tight-binding approximation of the Bloch one-electron equation, as illustrated by Eqs. (4)–(7) of I.

As pointed out in I (Eqs. 43–46, and accompanying text), the case of the small-polaron is realized when the electronic bandwidth, $2J$, is small compared to a characteristic energy, $A^2/2M\omega_0^2$, which (see I, Eq. 46) is, in essence, the binding energy of the small polaron. This circumstance suggests that Eq. (1) be solved by a perturbation approach in which the zeroth order Hamiltonian consists of the square-bracket of (1), whereas the J-proportional term is the perturbation. Such a procedure has, in fact, been applied by Tjablikov (*2*) and by Yamashita and Kurosawa (*3*)[3] to the continuum-polarization model, and will form the basis of the present work. In anticipation of results to be obtained below, it may be remarked that the domain of validity of the treatment will not be sufficient to cover the whole range of interest for the small polaron. Namely, as will be shown in Section 6, the small-polaron condition (see Eq. 43 of I)

$$2J < A^2/2M\omega_0^2 \tag{3}$$

is not sufficient for the applicability of the perturbation approach; in particular, the more restrictive conditions

$$\begin{aligned} 2J &< (A^2/2M\omega_0^2)^{1/2}\,(\hbar\omega_0)^{1/2} \\ J &< (A^2/4M\omega_0^2)^{1/4}\,(2\kappa T/\pi)^{1/4}\,(\hbar\,\omega_0/\pi)^{1/2} \end{aligned} \tag{4}$$

will be shown to be necessary.

[2] Strictly speaking, (see I, Eq. 3), this term has the form, $J(x_n\,,\,x_{n+1})a_{n+1} + J(x_n\,,\,x_{n-1})a_{n-1}$ where the overlap integrals, $J(x_n\,,\,x_{n\pm1})$ are defined by Eq. (I-15) in the appendix of I. As discussed in I, the x_n dependence of the J's is to be ignored for the time being, so that all the J's are assumed equal to a single constant, $-J$.

[3] Referred to hereafter as Y and K. It should be stated at the outset that the treatment of the present paper overlaps, in considerable measure, the earlier work of Y and K. However, there are a number of features of the problem, which constitute important elements of the present paper, and which are absent from Y and K's treatment. Examples are (a) the roles of the diagonal and off-diagonal transitions at temperatures above and below the "transition" temperature, T_t [as given by Eq. (88) and subsequent text], (b) the classical activation approach in the high-temperature region ($\kappa T \gg \hbar\omega_k$), and (c) the estimation of the limits of validity of the perturbation treatment (together with the question of the alternate applicability of the adiabatic approach). Moreover, in the opinion of the present author, the specific results obtained by Y and K are not correct in detail. A discussion of these results is presented at the end of the paper.

Before entering upon detailed calculation, let us generalize Eq. (1) by adding to the lattice Hamiltonian coupling terms of the form mentioned in footnote 3 of I. The augmented equation reads

$$i\hbar \frac{\partial a_n(x_1, \cdots, x_n)}{\partial t} = \sum_{m=1}^{N} \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_m^2} + \frac{1}{2} M\omega_0^2 x_m^2 + \frac{1}{2} M\omega_1^2 x_m x_{m+1} \right) + A x_n \Big] a_n - J[a_{n+1} + a_{n-1}]. \tag{5}$$

As is known, the presence of coupling terms gives rise to dispersion of the lattice vibration frequencies. It will later be seen that this dispersion has to be taken into account in the calculation of probabilities of transitions in which a change of electron-site variable is accompanied by the simultaneous absorption and emission of vibrational quanta. In particular, it will turn out that the standard approximation of replacing the vibration frequencies by a single frequency (Einstein model) yields meaningless results for these probabilities.

For the treatment of (5) it is desirable to express the vibrational coordinates, x_n, in terms of the normal-mode coordinates of the host crystal. This is done by means of the one-dimensional analog of Eq. (50) of I [the transformation is also given by Eq. (II-2) of Appendix II]; one then has

$$i\hbar \frac{\partial a_n(\cdots q_k \cdots)}{\partial t} = \sum_k \left[\left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_k} + \frac{1}{2} M\omega_k^2 q_k^2 \right) - \left(\frac{2}{N} \right)^{1/2} A q_k \sin(kn + \pi/4) \right] \times a_n(\cdots q_k \cdots) - J(a_{n+1} + a_{n-1}) \tag{6}$$

where ω_k is given by the dispersion relation

$$\omega_k^2 = \omega_0^2 + \omega_1^2 \cos k \tag{7}$$

and where $k = 2\pi\kappa/N$, the integer κ lying in the range $-\frac{1}{2}(N-1) \leqq \kappa \leqq \frac{1}{2}(N-1)$ (N being assumed odd for the sake of convenience).

The zeroth-order wave equation is obtained by setting J equal to zero in (6). The zeroth-order eigenstates are then seen to have the form

$$a_n^{(p)}(\cdots q_k \cdots) = \delta_{np} \chi^{(p)}(\cdots q_k \cdots) \tag{8}$$

where δ_{np} is the Krönecker delta—unity for $n = p$ and zero otherwise—and where $\chi^{(p)}$ satisfies the equation

$$E\chi^{(p)} = \sum_k \left[-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial q_k^2} + \frac{1}{2} M\omega_k^2 q_k^2 - \left(\frac{2}{N} \right)^{1/2} A q_k \sin(kp + \pi/4) \right] \chi^{(p)}. \tag{9}$$

Noting that the square-bracket of (9) represents a system of independent harmonic oscillators, with equilibrium points

$$q_k^{(p)} = \frac{A}{M\omega_k^2}\left(\frac{2}{N}\right)^{1/2} \sin(kp + \pi/4) \tag{10}$$

one readily obtains for the eigenfunctions and eigenvalues of (8)

$$\chi^{(p)}_{\cdots N_k \cdots}(\cdots q_k \cdots) = \pi_k \Phi_{N_k}[(M\omega_k/\hbar)^{1/2}(q_k - q_k^{(p)})] \tag{11}$$

$$E_{\cdots N_k \cdots} = \sum_k \hbar\omega_k(N_k + \tfrac{1}{2}) + E_b \tag{12}$$

where

$$\Phi_N(z) \equiv (2^N N!\pi^{1/2})^{-1/2} e^{-z^2/2} H_N(z)$$

are normalized harmonic oscillator eigenfunctions [the $H_N(z)$ being Hermite polynomials] and where

$$Eb = -\sum_k \frac{A^2}{2M\omega_k^2}\left(\frac{2}{N}\right)\sin^2(kp + \pi/4)\,. \tag{13}$$

Finally, from (8) and (11), one has for the zeroth order eigenstates of the total system

$$a_{p,\cdots N_k \cdots}(n, \cdots q_k \cdots) = \delta_{np}\pi_k \Phi_{N_k}[(M\omega_k/\hbar)^{1/2}(q_k - q_k^{(p)})]. \tag{14}$$

In the representation of these zeroth order eigenstates, the wave function of the system takes the form

$$a_n(\cdots q_k \cdots) = \sum_{p', \cdots N_k' \cdots} C(p', \cdots N_k' \cdots) a_{p', \cdots N_k' \cdots}(n, \cdots q_k \cdots) \times \exp[-(it/\hbar)E_{\cdots N_k' \cdots}]. \tag{15}$$

Inserting this expression into (6), multiplying on the left by $a_{p \cdots N_k \cdots}(n, \cdots q_k \cdots)$, and integrating with respect to the vibration coordinates, q_k, one obtains, with the aid of (8)–(13)

$$i\hbar \frac{\partial C(p, \cdots N_k \cdots)}{\partial t} = \sum_{p', N_k'} (p, \cdots N_k \cdots | V | p', \cdots N_k' \cdots) \times C(p', \cdots N_k' \cdots) \exp[(it/\hbar)(E_{\cdots N_k \cdots} - E_{\cdots N_k' \cdots})] \tag{16}$$

where

$$(p, \cdots N_k \cdots | V | p', \cdots N_k' \cdots) = -J \sum_{\epsilon = \pm 1} \delta_{p, p'+\epsilon} \times \pi_k \left[\int_{-\infty}^{+\infty} \Phi_{N_k}[(M\omega_k/\hbar)^{1/2}(q_k - q_k^{(p)})]\phi_{N_k'}[(M\omega_k/\hbar)^{1/2}(q_k - q_k^{(p')})] \cdot (M\omega_k/\hbar)\, dq_k\right] \tag{17}$$

the product, π_k, going over all vibration modes. Taking advantage of the circumstance that the $q_k^{(p)}$ are actually infinitesimal (i.e., $\sim 1/N$), one may evaluate the multiplicands of π_k simply by developing, say, $\phi_{N_k}[(M\omega_k/\hbar)^{1/2}(q_k - q_k^{(p)})]$ as a Taylor series in $q_k^{(p)} - q_k^{(p')}$, and by making use of the standard formula

$$\frac{\partial \phi_N(z)}{\partial z} = \left(\frac{N}{2}\right)^{1/2} \Phi_{N-1}(z) - \left(\frac{N+1}{2}\right)^{1/2} \Phi_{N+1}(z).$$

The result is, to the second order in $q_k^{(p)} - q_k^{(p')}$,

$$\begin{aligned}(p', \cdots N_k' \cdots | V | p \cdots N_k \cdots) = -J \sum_{\epsilon=\pm 1} \delta_{p', p+\epsilon} \\ \times \pi_k \left\{ \left[1 - \frac{4}{N}(N_k + 1/2)\gamma_k \cos^2(k(p + \epsilon/2) + \pi/4) \right] \delta_{N_k', N_k} \right. \\ - \left[\left(\frac{8}{N}\right)^{1/2} \epsilon \mu_k \gamma_k^{1/2} \left(\frac{N_k + 1/2 \pm 1/2}{2} \right) \cos(k(p + \epsilon/2) + \pi/4) \right] \\ \left. \cdot \delta_{N_k', N_k \pm 1} + \frac{\alpha_k^{(\pm)}}{N} \gamma_k \delta_{N_k', N_k \pm 2} \right\}\end{aligned} \tag{18}$$

where

$$\gamma_k \equiv \frac{A^2}{2M\omega_k^2 \hbar \omega_k}(1 - \cos k), \tag{19}$$

μ_k being equal to ± 1, depending on whether k is positive or negative, and where the $\alpha_k^{(\pm)}$ are dimensionless quantities of the order of unity or $\langle N_k \rangle_{\text{Av}}$, whichever is larger. They are not given explicitly since, as will be seen later, the two-quantum jumps to which they pertain turn out to be unimportant. In obtaining (18), the expansion parameter, $q_k^{(p)} - q_k^{(p')}$, was eliminated by use of (8). It may be remarked here that the γ_k are important parameters of the theory. Apart from the trigonometric factor, $1 - \cos k$, they represent, in essence, the ratio of the poleron binding energy, $(\sim A^2/2M\omega_0^2)$, to the quantum of vibrational energy. In order of magnitude, this ratio is to be assumed large compared to unity, e.g., ~ 10 (see footnote 17).

II. DIAGONAL AND NONDIAGONAL TRANSITIONS: COMPLEMENTARITY OF BAND AND LOCAL SITE-JUMP APPROACHES

The transitions arising from the matrix elements (18) may be grouped into two different categories: one in which the vibration quantum numbers remain unaltered ($N_k = N_{k'}$), the other in which some of these numbers change by one (or two) units. These two types will be designated as "diagonal" and "nondiagonal," respectively.

In order to exhibit the role played by the diagonal transitions, let us consider

the simplest case—prevalent at the absolute zero of temperature—in which the vibration quantum numbers, N_k, are all zero. In this case, by virtue of energy conservation, transitions of substantial amplitude are all of the diagonal type. It is now to be noted that such transitions connect states, $a_{p,\cdots 0_k \cdots}(n, \cdots q_k \cdots)$, whose unperturbed energies all coincide at one and the same value, $E_{\cdots 0_k \cdots} = E_b + \sum_k \hbar\omega_k/2$. Hence, to the first order in the perturbation parameter, J, the stationary states of the system are of the form[4]

$$a_n(x_1, \cdots, x_N) = \sum_p C_p a_{p,\cdots 0_k \cdots}(n, \cdots q_k \cdots) \exp\{-i[E_b + \sum_k \hbar\omega_k/2]t/\hbar\} \tag{20}$$

where the C_p constitute the stationary solution of the equations

$$ih \frac{\partial C_p}{\partial t} = \sum_p (p, \cdots 0_k \cdots | V | p', \cdots 0_k \cdots) C_{p'} \tag{21}$$

[obtained from (16) by dropping all terms for which $N_k \neq 0$]. From (18) one has

$$(p, \cdots 0_k \cdots | V | p', \cdots 0_k \cdots) = -J \sum_{\epsilon=\pm 1} \delta_{p,p'+\epsilon\pi k} \cdot \left\{1 - \frac{2}{N} \gamma_k \cos^2\left[k\left(p' + \frac{\epsilon}{2}\right) + \frac{\pi}{4}\right]\right\}$$

which may be written as[5]

$$(p, \cdots 0_k \cdots | V | p', \cdots 0_k \cdots) = -J \sum_{\epsilon=\pm 1} \delta_{p,p'+\epsilon} \cdot \exp\left\{-\frac{2}{N} \sum_k \gamma_k \cos^2\left[k\left(p' + \frac{\epsilon}{2}\right) + \frac{\pi}{4}\right]\right\} = -J \sum_{\epsilon=\pm 1} \delta_{p,p'+\epsilon} \exp\{\sum_k \gamma_k/N\}. \tag{22}$$

Inserting (22) into (21), and assuming the time dependence of the C_p to be of the form $e^{-iEt/\hbar}$, one has

$$EC_p = -J \exp\{-\sum_k \gamma_k/N\}(C_{p+1} + C_{p-1})$$

the solution of which is

$$C_p^{(\sigma)} = e^{ip\sigma} \tag{23}$$

[4] The notation C_p is used as an abbreviation of $C_{p,\cdots 0_k \cdots}$.

[5] The second equality results from the circumstance that $\gamma_k = \gamma_{-k}$, so that, when terms of plus and minus k are combined, one has

$$\sum_{(\pm)} \cos^2\left[\pm k\left(p' + \frac{\epsilon}{2}\right) + \frac{\pi}{4}\right] = \frac{1}{2} \sum_{(\pm)} \left(1 - \cos\left[\pm k(2p' + \epsilon) + \frac{\pi}{2}\right]\right) = \frac{1}{2}$$

with

$$E = E_\sigma = -2J \cos \sigma \exp \{-\sum_k \gamma_k/N\} \tag{24}$$

where σ ranges over the same values as k.

Referring back to (20) and (14), one observes that the $N_k = 0$ eigenstates of the system are

$$a_{\sigma,\cdots 0,\cdots}(n, \cdots q_k \cdots) = e^{in\sigma} \pi_k \Phi_0[(M\omega_k/\hbar)^{1/2}(q_k - q_k^{(p)})] \tag{25}$$

with eigenvalues

$$E_{\sigma,\cdots 0\cdots} = E_b + \sum_k \hbar\omega_k/2 - 2J \cos \sigma \, e^{-S} \tag{26}$$

where

$$S \equiv \sum_k \gamma_k/N = \frac{1}{\pi}\int_0^\pi \gamma_k \, dk = \frac{1}{\pi}\int_0^\pi (A^2/2M\omega_k{}^2\hbar\omega_k)(1 - \cos k) \, dk. \tag{27}$$

The eigenstates (25) may be considered as constituting the groundstate *polaron-band*. This band is characterized by a half-width

$$\Delta E_{\sigma,\cdots 0_k\cdots} = 2J \, e^{-S}. \tag{28}$$

In practical cases, S may be expected to be of the order of 5–10, so that the factor e^{-S}, which gives the ratio of the polaron-bandwidth to the original *electronic* bandwidth, $2J$, will be quite small ($\sim 10^{-2}$–10^{-4}).

Turning now to the excited states, in which some of the N_k differ from zero, and continuing for the moment to neglect the nondiagonal matrix elements, one may approximate (16) by[6]

$$i\hbar \frac{\partial C(p, \cdots N_k \cdots)}{\partial t} = \sum_{p'} (p, \cdots N_k \cdots | \, V \, | p', \cdots N_k \cdots) \cdot C(p', \cdots N_k \cdots) \tag{29}$$

where, in analogy with (21) and (22), one has

$$(p, \cdots N_k \cdots | \, V \, | p, \cdots N_k' \cdots) = -J \sum_{\epsilon=\pm 1} \delta_{p,p'+\epsilon} \cdot \exp\left\{-\sum_k \frac{2(1 + 2N_k)}{N} \gamma_k \cos^2\left[k\left(p + \frac{\epsilon}{2}\right) + \frac{\pi}{4}\right]\right\}. \tag{30}$$

For the further simplification of (30) it will be assumed[7] that

[6] Of special significance is the fact that, due to the coincidence of initial and final unperturbed energies, the time dependent exponential factor in (16) is here unity.

[7] Actually, this assumption would not have been necessary had "running-wave" vibration coordinates been used instead of the "standing-wave" coordinates, q_k. This deficiency,

$$N_k = N_{-k}\,. \tag{31}$$

The step analogous to the last equality of (22) may then be carried out, and one has

$$(p, \cdots N_k \cdots \mid V \mid p, \cdots N_k' \cdots) = -J \sum_{\epsilon=\pm 1} \delta_{p,p'+\epsilon} e^{-S(\cdots N_k \cdots)} \tag{32}$$

where

$$S(\cdots N_k \cdots) = \sum_k (1 + 2N_k)\gamma_k/N = \frac{1}{\pi}\int_0^\pi (A^2/2M\omega_k{}^2\hbar\omega_k) \cdot (1 - \cos k)(1 + 2N_k)\, dk. \tag{33}$$

Proceeding as before, one then obtains for the stationary solution of (29)

$$C(p, \cdots N_k \cdots) = e^{ip\sigma} \exp[+(it/\hbar)(2J \cos \sigma\, e^{-S(\cdots N_k \cdots)})]. \tag{34}$$

The wave functions corresponding to (34) are

$$a_{\sigma,\cdots N_k \cdots}(n, \cdots q_k \cdots) = e^{in\sigma}\pi_k \Phi_{N_k}[(M\omega_k/\hbar)^{1/2}(q_k - q_k^{(p)})] \tag{35}$$

with eigenvalues

$$E_{\sigma,\cdots N_k \cdots} = E_b + \sum_k (N_k + \tfrac{1}{2})\hbar\omega_k - 2J \cos \sigma\, e^{-S(\cdots N_k \cdots)}. \tag{36}$$

Attention is called to the rather novel feature that the bandwidth

$$\Delta E_{\sigma,\cdots N_k \cdots} = 2J\, e^{-S(\cdots N_k \cdots)} \tag{37}$$

is [by virtue of (33)] a function of the vibrational quantum numbers, and, in fact, an exponentially *decreasing* function of these variables.[8] *The bandwidth is thus maximal at absolute zero and diminishes rapidly with rising temperature.*

The above discussion has been predicated on the assumption that the non-diagonal transitions play a subordinate, higher-order role. This assumption will now be investigated. One may begin by expressing the equations of motion (16) in the representation of the polaron-band states $a_{\sigma,\cdots N_k \cdots}(n_1 \cdots q_k \cdots)$. In this representation, the total wave function takes the form

$$a_n(\cdots q_k \cdots) = \sum_{\sigma,\cdots N_k \cdots} C(\sigma, \cdots N_k \cdots) a_{\sigma,\cdots N_k \cdots}(n, \cdots q_k \cdots) \times \exp[-(it/\hbar)E_{\sigma,\cdots N_k \cdots}] \tag{38}$$

however, is not serious (since, in practice, N_{-k} and N_k are always, in effect, equal (see footnote 9); the formal advantages of running-wave coordinates are to some extent offset by an increased conceptual complexity of the zeroth order wave functions.

[8] This feature appears to have first been noted by Yamashita and Kurosawa (*3*).

where $E_{\sigma,\cdots N_k\cdots}$ is given by (36); i.e., it is the original unperturbed energy (taken with reference to localized wave-functions) augmented by the polaron-band energy. The $C(\sigma, \cdots N_k \cdots)$ satisfy the equations

$$i\hbar \frac{\partial C(\sigma, \cdots N_k \cdots)}{\partial t} = \sum_{\sigma', \cdots N_{k'} \cdots} (\sigma, \cdots N_k \cdots | V | \sigma', \cdots N_{k'} \cdots) \times \exp[(it/\hbar)(E_{\sigma, \cdots N_k \cdots} - E_{\sigma', \cdots N'_k \cdots})] \tag{39}$$

where

$$(\sigma, \cdots N_k \cdots | V | \sigma', \cdots N_{k'} \cdots) = \sum_{p p'} e^{-i[\sigma p - \sigma' p']} (p, \cdots N_k \cdots | V | p', \cdots N_{k'} \cdots) \tag{40}$$

and where the sum in (39) excludes the term for which $\sigma = \sigma'$ and $N_k = N_{k'}$ [this term being automatically subtracted out by the inclusion of the polaron-band energy in the time-dependent exponential of (39)].

It is readily verified that the σ dependence of the diagonal matrix elements is of the form[9] $\delta_{\sigma,\sigma'}$, so that, in effect, (39) represents only nondiagonal transitions.

The actual computation of the nondiagonal transitions (in the polaron-band representation) is carried out below (see Section 5). Some of the principal features of these transitions may however be noted here. First of all, the initial and final unperturbed energies no longer coincide exactly. However, primarily because of the dispersion of vibrational frequencies, as represented by (7), the unperturbed energy spectrum is continuous, so that energy conservation (in the sense of time-dependent perturbation theory) is possible for a wide variety of multiphonon processes. It then follows that transitions of the type $\sigma, \cdots N_k \cdots \rightarrow \sigma', \cdots N_{k'} \cdots$ develop uniformly in time, and are therefore describable in terms of the conventional (time-independent) transition probabilities

$$W(\sigma, \cdots N_k \cdots \rightarrow \sigma', \cdots N_{k'} \cdots) = \frac{2\pi}{\hbar} | (\sigma, \cdots N_k \cdots \cdot | V | \sigma', \cdots N_k \cdots) |^2 \delta(E_{\sigma, \cdots N_k \cdots} - E_{\sigma', \cdots N_{k'} \cdots}) \tag{41}$$

[9] As in the case of footnote 7, this statement is strictly true only when $N_k = N_{-k}$. Here, also, the need for this qualification arises from the use of standing-wave vibration coordinates, and could have been avoided by the use of running-wave coordinates. Actually, however, it is only required that the *average* quantum number (the average being taken over a range Δk small compared to unity but large compared to the spacings of the individual modes) be the same for plus and minus k. Since this condition is always obeyed in practice, the equality $N_k = N_{-k}$ may be applied to (30). It then follows that

$$(p, \cdots N_k \cdots | V | p', \cdots N'_k \cdots)$$

depends only of the difference, $p - p'$, in site variable; this feature, in turn, leads straightforwardly to the above-mentioned factor, $\delta_{\sigma,\sigma'}$.

where $\delta(E)$ is the Dirac delta function, and where, from (40) and (18),

$$(\sigma', \cdots N_k \cdots | V | \sigma, \cdots N_k \cdots) = -J \sum_{pp'} \delta_{p',p+\epsilon} e^{i[\sigma p - \sigma p']} \times \pi_k \left\{ \left[1 - \frac{4}{N} (N_k + 1/2)\gamma_k \cos^2 \left[k\left(p + \frac{\epsilon}{2}\right) + \frac{\pi}{4} \right] \right] \delta_{N_k', N_k} - \left(\frac{8}{N}\right)^{1/2} \left(\frac{N_k + \frac{1}{2} \pm \frac{1}{2}}{2} \right)^{1/2} \mu_k \epsilon \gamma_k^{1/2} \cos \left[k\left(p + \frac{\epsilon}{2}\right) + \frac{\pi}{4} \right] \cdot \delta_{N_k', N_k \pm 1} + \frac{\alpha_k^{(\pm)}}{N} \gamma_k \delta_{N_k', N_k \pm 2} \right\}. \tag{42}$$

Due to the requirements of energy conservation, the number of phonon absorptions will be comparable to that of phonon emissions. It is to be noticed (from Eq. 42) that each absorption process gives rise to a factor, $N_k^{1/2}$, in the matrix, and hence a factor, N_k, in the transition probability. Thus, for example, the probability of the process $\sigma, \cdots N_{k_1}, N_{k_2}, N_{k_3}, N_{k_4} \rightarrow \sigma' \cdots N_{k_1} - 1, N_{k_2} - 1, N_{k_3} + 1, N_{k_4} + 1, \cdots$ is proportional to the factor $N_{k_1}, N_{k_2}(1 + N_{k_3})(1 + N_{k_4})$. It is therefore to be concluded that, at sufficiently low temperatures (such that $\langle \gamma_k N_k \rangle_{\text{Av}} \ll 1$), those transitions which are of lowest order in the number of photon absorptions will dominate.

In discussing these lowest-order transitions, let us assume that all vibrational frequencies, ω_k, differ from zero,[10] i.e., $\omega_1 < \omega_0$ in (7). It then follows, by virtue of energy conservation, that a one-phonon (emissive) transition is forbidden; the lowest-order transition is a two-phonon process of the type $\sigma, \cdots N_{k_1}, N_{k_2} \rightarrow \sigma', \cdots N_{k_1} - 1, N_{k_2} + 1, \cdots$; in conformity with the above remarks, its probability is proportional to N_{k_1}. Hence, although this type of transition is the dominant one at low temperatures, its probability also vanishes as the temperature approaches absolute zero.

From this discussion, it is apparent that, in the limit of very low temperatures, the nondiagonal transitions play a role subordinate to that of the diagonal transitions. In particular, in the domain of temperatures such that the mean life of a polaron-band state

$$\tau_{\sigma, \cdots N_k \cdots} = 1 / \sum_{\sigma', \cdots N_k' \cdots} W(\sigma, \cdots N_k \cdots \rightarrow \sigma', \cdots N_k' \cdots) \tag{43}$$

is large enough for the fulfillment of the inequality

$$\hbar / \tau_{\sigma, \cdots N_k \cdots} \ll \Delta E_{\sigma, \cdots N_k \cdots} = 2J\, e^{-S(\cdots N_k \cdots)}, \tag{44}$$

[10] This assumption means simply that the vibrational spectrum is of optical, rather than acoustical, character, this being the relevant case for polaron theory.

a sufficiently accurate description of the physical situation is indeed provided by the polaron-band approach, according to which the principal characteristics of the states depend on the diagonal matrix elements, the role of the off-diagonal elements being limited to determining their lifetimes.

However, as the temperature increases from some low value, at which (44) is valid, the situation changes. First of all, $\tau_{\sigma,\cdots N_k\cdots}$ decreases by virtue of the fact that, the probability for a given transition, $\sigma, \cdots N_k \cdots \rightarrow \sigma', \cdots N_k' \cdots$ is proportional to the product of those N_k which are involved in absorption, and these all increase rapidly with temperature. Secondarily, as shown by Eqs. (33) and (37), the bandwidth, $\Delta E_{\sigma,\cdots N_k\cdots}$ diminishes with increasing temperature. Thus a temperature is eventually reached[11] at which (44) breaks down, i.e., at which the polaron-bandwidth becomes smaller than the energy uncertainty of the individual band states. Regarded from another point of view, the lifetime is less than the time ($\sim h/\Delta E_{\sigma,\cdots N_k\cdots}$) required for the polaron to move a distance equal to a lattice spacing. Under such circumstances, the band approach is clearly inapplicable. The fact is that, at this point, the relative importance of the diagonal and nondiagonal transitions has been reversed. The appropriate zeroth-order states, to be used in a perturbation treatment, are the original localized polaron states, $a_{p,\cdots N_k\cdots}(n, \cdots q_k \cdots)$, given by (14), rather than their plane wave combinations, $a_{\sigma,\cdots N_k\cdots}(n, \cdots q_k \cdots)$. The nondiagonal matrix elements, $(p, \cdots N_k \cdots \mid V \mid p', \cdots N_k' \cdots)$, between these localized states (which have now to be taken into account *before* the diagonal elements) give rise to transitions of the type $p, \cdots N_k \cdots \rightarrow p \pm 1, \cdots N_k' \cdots$ in which a jump to a neighboring site is accompanied by the emission and absorption of a number of phonons. The computation of the probabilities of these transitions, $W(p, \cdots N_k \rightarrow p', \cdots N_k' \cdots)$, by conventional time-dependent perturbation theory is presented below.

The subsequent inclusion of the diagonal matrix elements in the perturbation treatment leads to a state of affairs which, although somewhat novel, is actually not unexpected. Namely, it is found that, by virtue of the *exact* conservation of energy which characterized the diagonal transitions, the resultant transition probabilities are not time-independent—as is the case for the nondiagonal variety—but increase linearly with time. From this it follows that, if the time interval, over which perturbation theory is valid, were arbitrarily large, the diagonal transitions would ultimately dominate. Actually, however, perturbation theory breaks down when the time intervals (over which it is applied) get to be of the order of the mean lives of the individual (localized) states

$$\tau_{p,\cdots N_k\cdots} = 1/\sum_{N_k' p'} W(p, \cdots N_k \cdots \rightarrow p', \cdots N_k' \cdots). \tag{45}$$

[11] An estimate given below (see Eq. 88 and subsequent text) shows that, for representative values of the parameters of the theory, this temperature is of the order of $(0.5 - 1)$ times the Debye Θ.

A proper treatment of the diagonal transitions would then require the introduction of collision-damping into the theory. A criterion for the diagonal transitions to be of subsidiary importance may, however, be stated on simple physical grounds, without recourse to a formal damping theory. It is namely that the probability for a diagonal transition to occur in a time $\sim\tau_{p,\cdots N_k\cdots}$ (as computed by perturbation theory) must be small compared to unity. Using (29) and (32), the reader may readily establish[12] that this criterion is equivalent to

$$\hbar/\tau_{p,\cdots N_k\cdots} \gg 2J\, e^{-S(\cdots N_k\cdots)}. \tag{46}$$

If, now, it be assumed (as will be verified in Section 5) that $\tau_{p,\cdots N_k\cdots}$ has a magnitude comparable to that of the mean life, $\tau_{\sigma,\cdots N_k\cdots}$, of the polaron-band states, (46) is seen to be simply the converse of (44) and may thus be considered as defining a regime complementary to that in which (44) obtains.

III. NONDIAGONAL TRANSITIONS BETWEEN LOCALIZED STATES: SITE-JUMP PROBABILITIES

After these general orienting remarks, let us proceed to the perturbation calculation of the probabilities of nondiagonal transition between localized states. Two quantities will be of specific interest. The first of these is the probability

$$W_{\cdots N_k\cdots}(p \to p') = \sum_{\cdots N_k'\cdots} W(p, \cdots N_k \cdots \to p', \cdots N_k' \cdots) \tag{47}$$

for a site-jump with arbitrary final vibrational quantum numbers. The second is the thermal average of (47), namely,

$$W_T(p \to p') = Z^{-1} \sum_{\cdots N_k\cdots} W_{\cdots N_k\cdots}(p \to p') \exp[-\sum_k \beta\hbar\omega_k(N_k + \tfrac{1}{2})] \tag{48}$$

where $\beta \equiv 1/\kappa T$ (κ and T are Boltzmann's constant and absolute temperature, respectively) and

$$Z \equiv \sum_{\cdots N_k\cdots} \exp[-\sum_k \beta\hbar\omega_k(N_k + \tfrac{1}{2})]$$

is the vibrational partition function.

Standard perturbation theory (4)[13] yields for the elementary transition probabilities the expression

$$W(p, \cdots N_k \cdots \to p', \cdots N_k' \cdots) = 2\hbar^{-2}|(p', \cdots N_k' \cdots | V | p, \cdots N_k)|^2 \cdot \frac{\partial}{\partial t}\Omega[\sum_k \hbar\omega_k(N_k' - N_k)] \tag{49}$$

[12] An explicit expression for the diagonal transition probability, given by Eq. (63), may be used here.

[13] As will be seen later, some care is required in going to the limit of infinite "interaction" time, t.

where

$$\Omega(x) \equiv \frac{1-\cos(xt/\hbar)}{x^2/\hbar^2} = \frac{2\sin^2(xt/2\hbar)}{x^2/\hbar^2} \tag{50}$$

is the characteristic energy-resonance function of perturbation theory; it has the property

$$\lim_{t\to\infty} \Omega(x) = \pi\hbar t\delta(x)$$

and may be expressed in the integral form

$$\Omega(x) = \frac{1}{2}\int_0^t dt' \int_{-t'}^{+t'} e^{\frac{ixt''}{\hbar}} dt''$$

so that

$$\frac{\partial}{\partial t}\Omega(x) = \frac{1}{2}\int_{-t}^{+t} e^{\frac{ixt'}{\hbar}} dt' . \tag{51}$$

Upon substituting (51) and (18) into (49), one observes that the sum over the final occupation numbers, N_k', required by (47), splits into a product of sums over the individual multiplicands of π_k. These are easily evaluated; the result is

$$\begin{aligned} W_{\cdots N_k \cdots}(p \to p') &= \frac{J^2}{\hbar^2}\sum_{\epsilon=\pm 1}\delta_{p',p+\epsilon}\int_{-t}^{+t}\pi_k\left\{\left[1-\frac{4}{N}(N_k+\tfrac{1}{2})\right.\right. \\ &\qquad \left.\times\gamma_k\cos^2\left[k\left(p+\frac{\epsilon}{2}\right)+\frac{\pi}{4}\right]\right]^2 \\ &\quad +\frac{4\gamma_k}{N}\left(N_k e^{-\omega_k t'}+(N_k+1)e^{i\omega_k t'}\right)\cos^2\left[k\left(p+\frac{\epsilon}{2}\right)+\frac{\pi}{4}\right]\Bigg\}dt' \\ &= \frac{J^2}{\hbar^2}\sum_{\epsilon=\pm 1}\delta_{p,p+\epsilon}\int_{-t}^{+t}\exp\left\{\sum_k\frac{8\gamma_k}{N}\cos^2\left[k\left(p+\frac{\epsilon}{2}\right)+\frac{\pi}{4}\right]\right. \\ &\qquad \left.\times\left[-(N_k+\tfrac{1}{2})+(N_k+\tfrac{1}{2})\cos\omega_k t'+\frac{i}{2}\sin\omega_k t'\right]\right\}dt' \end{aligned} \tag{52}$$

wherein the contributions of the transitions $N_k \to N_k \pm 2$ have been neglected; this neglect is clearly justified in view of the fact that the terms in question are $\sim 1/N^2$ (in contrast to the retained terms, which are $\sim 1/N$).[14]

As before (see footnotes 7 and 9), one takes $N_k = N_{-k}$, and is thereby free to replace $\cos^2[k(p+\tfrac{1}{2}\epsilon)+\tfrac{1}{4}\pi]$ by $\tfrac{1}{2}$. Thus,

[14] For the same reason, the terms in γ_k^2 coming from the first square-bracket in the first equality of (52) have also been discarded.

$$W_{\ldots N_k \ldots}(p \to p') = \frac{J^2}{\hbar^2} \sum_{\epsilon=\pm 1} \delta_{p',p+\epsilon} \int_{-t}^{+t} \exp\left\{ \sum_k \frac{4\gamma_k}{N} \left[-(N_k + \tfrac{1}{2}) + (N_k + \tfrac{1}{2}) \cos \omega_k t' + \frac{i}{2} \sin \omega_k t' \right] \right\} dt' . \tag{53}$$

Further progress in the evaluation of (53) is possible for an arbitrary variation of N_k with k, as long as this variation is well-behaved. However, in practice, the distribution in N_k is always thermal, so that we may as well proceed immediately to the thermal average defined by (48). In the evaluation of this average, it is expedient to employ the product form of the exponential integrand in (53), which reads

$$\pi_k \left\{ 1 + \frac{4\gamma_k}{N} \left[-(N_k + \tfrac{1}{2}) + (N_k + \tfrac{1}{2}) \cos \omega_k t' + \frac{i}{2} \sin \omega_k t' \right] \right\},$$

It is then apparent that the thermal average over the N_k results in the replacement of each N_k by its equilibrium value, $(e^{\beta\hbar\omega_k} - 1)^{-1}$; this replacement (together with the summation over ϵ) yields

$$W_\tau(p \to p \pm 1) = \frac{J^2}{\hbar^2} \int_{-t}^{+t} \exp\left\{ -\sum_k \frac{2\gamma_k}{N} \left[\coth \frac{\beta\hbar\omega_k}{2} (1 - \cos \omega_k t') - i \sin \omega_k t' \right] \right\} dt' . \tag{54}$$

For the further simplification of (54), it is desirable to introduce the transformation

$$t' = \frac{i\beta\hbar}{2} + \tau \tag{55}$$

which transforms the integrand to

$$\exp\left\{ -\sum_k \frac{2\gamma_k}{N} \left[\coth \frac{\beta\hbar\omega_k}{2} - \operatorname{csch} \frac{\beta\hbar\omega_k}{2} \cos \omega_k \tau \right] \right\}.$$

The τ-integration, which goes from $-t - i\beta\hbar/2$ to $+t - i\beta\hbar/2$ is now deformed into a component along the real axis (from $-t$ to $+t$) and two components perpendicular to this axis (from $-t - i\beta\hbar/2$ to $-t$, and from t to $t - i\beta\hbar/2$). Combining the latter two into a single integral, one obtains

$$W_\tau(p \to p \pm 1) = \frac{J^2}{\hbar^2} [g_1(t) + g_2(t)] \tag{56}$$

where

$$g_1(t) = \int_{-t}^{+t} \exp\left\{ -\sum_k \frac{2\gamma_k}{N} \left[\coth \frac{\beta\hbar\omega_k}{2} - \operatorname{csch} \frac{\beta\hbar\omega_k}{2} \cos \omega_k \tau \right] \right\} d\tau \tag{57}$$

and

$$\vartheta_2(t) \equiv \sum_{(\pm)} \mp \int_0^{\beta\hbar/2} \exp\left\{-\frac{2\gamma_k}{N}\left[\coth\frac{\beta\hbar\omega_k}{2} - \operatorname{csch}\frac{\beta\hbar\omega_k}{2} \times \cos\left[\omega_k(t \pm i\sigma)\right]\right]\right\} d\sigma. \tag{58}$$

In proceeding further, let us focus attention on the case for which the "interaction" time, t, is large compared to the vibrational periods, i.e.,

$$t \gg 1/\omega_k\,. \tag{59}$$

It is of specific interest to determine whether $W_\tau(p \to p \pm 1)$ becomes independent of t in this limit (as would be required in order that $W_\tau(p \to p \pm 1)$ be interpretable as a conventional transition probability).

One may begin by considering the behavior of the integrands of $\vartheta_1(t)$ and $\vartheta_2(t)$ for large τ. Inspection of (57) and (58) indicates that this behavior is conditioned by that of

$$G(\tau) \equiv \sum_k \frac{2\gamma_k}{N} \operatorname{csch}\frac{\beta\hbar\omega_k}{2} \cos\omega_k\tau\,. \tag{60}$$

Asymptotic (large τ) expressions for $G(\tau)$ may be obtained by the method of steepest descents. The details of the computation will not be given; the result is

$$G(\tau) \cong 4\gamma_{k=\pi} \frac{(\omega_0^2 - \omega_1^2)^{1/4}}{\omega_1\tau^{1/2}} \operatorname{csch}\frac{\beta\hbar(\omega_0^2 - \omega_1^2)}{2} \cos\left[(\omega_0^2 - \omega_1^2)^{1/2}\tau + \frac{\pi}{4}\right], \tag{61}$$

i.e., $G(\tau)$ is an oscillatory function whose amplitude diminishes with increasing τ. It will be noticed that the parameter, ω_1, which is a measure of the vibrational dispersion (see Eq. 7), occurs in the denominator of (61). This feature testifies to the fact that, in order for (61) to be valid, dispersion of vibrational frequencies is necessary. In the absence of this dispersion ($\omega_k = \omega_0$, Einstein spectrum), the expressions on the right-hand side of (60) obviously reduce to simple trigonometric functions of τ, and do not go to zero with increasing τ, as indicated by (61). The presence of vibrational frequency dispersion is thus a vital ingredient of the theory.

From (61) it is clear that, in the limit specified by (59), $\vartheta_2(t)$ approaches zero as $t^{-1/2}$, and may hence be discarded. On the other hand

$$\lim_{t\to\infty} \vartheta_1(t) = \int_{-t}^{+t} \exp\left\{-\sum_k \frac{2\gamma_k}{N}\left[\coth\frac{\beta\hbar\omega_k}{2} - \mathcal{O}(\tau^{-1/2})\right]\right\} d\tau \tag{62}$$

(the notation $\mathcal{O}(\tau^{-1/2})$, denoting a term $\sim\tau^{-1/2}$ for large τ), which does not

approach a finite limit at all, but simply becomes proportional to t. Thus (56) is itself linear in t, and hence cannot represent a transition-probability in the conventional sense.

Actually, (56) is not the correct expression for the thermal average of the total nondiagonal transition probability. Referring back to (52), one may observe that this expression represents the sum of (49) over all final vibrational quantum numbers, N_k', and thus includes the diagonal transitions, $N_k = N_k'$, as well. These have now to be subtracted from (56).

A simple way of evaluating the diagonal contribution to (56) is to note that the nondiagonal contributions [see the first equality of (52)] always involve the time-dependent exponentials, $e^{\pm i\omega_k t'}$; the elimination of quantities containing these factors is then equivalent to restricting the $N_{k'}$ sum to $N_{k'} = N_k$. Applying this recipe to (56) and (57), one immediately finds for the diagonal contribution,[15]

$$W_T^{(d)}(p \to p \pm 1) = \frac{J^2}{\hbar^2}\int_{-t}^{+t} \exp\left\{-\sum_k \frac{2\gamma_k}{N}\coth\frac{\beta\hbar\omega_k}{2}\right\} d\tau = \frac{2tJ^2}{\hbar^2}\, e^{-2S_T} \tag{63}$$

where

$$S_T = \sum_k \frac{\gamma_k}{N}\coth\frac{\beta\hbar\omega_k}{2} \tag{64}$$

is clearly the thermal average of $S(\cdots N_k \cdots)$, as defined by (33).

Subtracting the first equality of (63) from (56), one obtains the correct expression for $W_T(p \to p \pm 1)$, namely,

$$W_T(p \to p \pm 1) = \frac{J^2}{\hbar^2}\, e^{-2S_T}\int_{-\infty}^{+\infty}\left\{\exp\left[\sum_k \frac{2\gamma_k}{N}\operatorname{csch}\frac{\beta\hbar\omega_k}{2}\cos\omega_k\tau\right] - 1\right\} d\tau \tag{65}$$

wherein the interaction time, t, has finally been permitted to go to infinity; the fact that no convergence difficulties are thereby occasioned may be seen from the form of the integrand at large τ, which, by (61), is

$$\sim(1/\omega_1\tau^{1/2})\cos[(\omega_0^2 - \omega_1^2)^{1/2}\tau + \pi/4]$$

and hence clearly integrable over the infinite domain.

It is of interest to evaluate (65) in the two limits in which the argument of the exponential term in the integrand is small or large compared to unity. For fixed values of the parameters, A, M, ω_0, and ω_1, which determine the γ_k, these cases occur at low and high temperatures, respectively.

[15] The proportionality of (63) to t was discussed earlier (in the text surrounding Eq. 45) and needs no further comment.

Considering first the low-temperature case, one expands the second exponent as a power-series in the argument, obtaining

$$W_T(p \to p \pm 1) = \frac{J^2}{\hbar^2} e^{-2S_T} \Bigg[\int_{-\infty}^{+\infty} \frac{1}{\pi} \int_0^\pi F(k) \cos \omega_k \tau \, dk + \frac{1}{2\pi^2} \times \int_0^\pi \int_0^\pi F(k)F(k') \cos \omega_k \tau \cos w_{k'} \, dk \, dk' + \frac{1}{6\pi^3} \int_0^\pi F(k)F(k')F(k'') \cos \omega_k \tau \cos \omega_{k'} \tau \cos \omega_{k''} \tau \, dk \, dk' \, dk'' + \cdots \Bigg]$$

where

$$F(k) = 2\gamma_k \operatorname{csch} \frac{\beta\hbar\omega_k}{2}.$$

The integrations over τ are readily carried out, leading to the replacement of the cosines by delta functions; thus

$$\begin{aligned} W_T(p \to p \pm 1) = \frac{J^2}{\hbar^2} e^{-2S_T} \Bigg\{ & \int_0^\pi F(k)\delta(\omega_k) \, dk + \frac{1}{2\pi} \int_0^\pi \int_0^\pi F(k)F(k') \\ & \cdot \left[\frac{1}{2} \delta(\omega_k + \omega_{k'}) + \frac{1}{2} \delta(\omega_k - \omega_{k'}) \right] dk \, dk' \\ + \frac{1}{6\pi^3} \int_0^\pi \int_0^\pi \int_0^\pi & F(k)F(k')F(k'') \left(\frac{1}{4}\right) [\delta(\omega_k + \omega_{k'} + \omega_{k''}) + \delta(\omega_k + \omega_{k'} - \omega_{k''}) \\ & + \delta(\omega_k - \omega_{k'} + \omega_{k''}) + \delta(\omega_k - \omega_{k'} - \omega_{k''})] \, dk \, dk' \, dk'' \Bigg\} + \cdots . \end{aligned} \tag{66}$$

From the form of (66) (as exhibited in particular by the curly bracket of the right-hand side), it is seen that $W_T(p \to p \pm 1)$ may be broken down into a series of processes in which one, two, three, etc. phonons are either emitted or absorbed; for each such process, the delta functions of the individual terms incorporate the requirement of conservation of energy. For example, the first term of the second curly bracket, representing a one-phonon process, is actually zero (since $\omega_k \neq 0$, in accordance with footnote [12]); i.e., a single-phonon process cannot conserve energy. Similarly, the second term represents two-phonon processes; the delta function, $\delta(\omega_k + \omega_{k'})$ and $\delta(\omega_k - \omega_{k'})$ occurring in the integrand correspond, respectively, to processes in which both phonons are emitted (or absorbed) and to those in which one phonon is emitted and the other absorbed. Since the condition $\omega_k + \omega_{k'} = 0$ cannot be realized, only the

latter process actually occurs. Finally, the third term represents three-phonon processes in which one has

$$\omega_k \pm \omega_{k'} \pm \omega_{k''} = 0,$$

i.e., one phonon is emitted (absorbed) and two absorbed (emitted).

The above interpretation also accounts for the temperature dependence of the curly-bracket of (66). For example, in the case of two-phonon processes, which are subject to the restriction, $\omega_k = \omega_{k'}$, it is readily verified that the temperature-dependent factor, csch $(\beta\hbar\omega_k/2)$ csch $(\beta\hbar\omega_{k'}/2)$, may be replaced by $\frac{1}{8}[N_k(N_{k'} + 1) + N_{k'}(N_k + 1)]$ (where N_k here represents the equilibrium Planck distribution). The first term of the square bracket is clearly the appropriate Bose–Einstein population factor for the transition $N_k \rightarrow N_k - 1$, $N_{k'} \rightarrow N_{k'} + 1$; the second term plays an analogous role for the reverse transition. Similarly, for three-phonon processes obeying, e.g., the condition, $\omega_k = \omega_{k'} + \omega_{k''}$, the temperature-dependent factor

$$\operatorname{csch} \frac{\beta\hbar\omega_k}{2} \operatorname{csch} \frac{\beta\hbar\omega_{k'}}{2} \operatorname{csch} \frac{\beta\hbar\omega_{k''}}{2}$$

may be shown to be equivalent to

$$\tfrac{1}{16}[N_k(N_{k'} + 1)(N_{k''} + 1) + (N_k + 1)N_{k'}N_{k''}].$$

The individual terms of the square bracket are clearly the correct Bose–Einstein population factors for the transitions $N_k \rightarrow N_k \pm 1$, $N_{k'} \rightarrow N_{k'} \mp 1$, $N_{k''} \rightarrow N_{k''} \mp 1$.

Let us now consider the behavior of (65) in the high-temperature limit, in which

$$\frac{1}{\pi}\int_0^\pi F(k)\, dk = \frac{1}{\pi}\int_0^\pi 2\gamma_k \operatorname{csch} \frac{\beta\hbar\omega_k}{2}\, dk \gg 1. \tag{67}$$

In this case the integral in (65) may be evaluated by the method of steepest descents.

We may begin by considering the contributions to the integral from the neighborhood of the point $\tau = 0$, for which the exponential factor attains an absolute maximum. One then has for the argument of the exponential

$$\frac{1}{\pi}\int_0^\pi F(k) \cos \omega_k\tau\, dk = \frac{1}{\pi}\int_0^\pi F(k)\, dk - \frac{\tau^2}{2\pi}\int_0^\pi F(k)\omega_k{}^2\, dk. \tag{68}$$

It is now to be observed that the second term of (68) will cause the exponential to drop off sharply from its maximum value. In particular, it is seen that the principal contribution to the integral will come from the region in which

$$\tau \lesssim \left(\frac{1}{2\pi}\int_0^\pi F(k)\omega_k{}^2\, dk\right)^{-1/2}. \tag{69}$$

Noting that, according to (7),

$$\omega_0^2 + \omega_1^2 \geqslant \omega_k^2 \geqslant \omega_0^2 - \omega_1^2$$

so that

$$\frac{1}{2\pi}\int_0^\pi F(k)\omega_k^2\, dk > \frac{\omega_0^2 - \omega_1^2}{2\pi}\int_0^\pi F(k)\, dk,$$

one may conclude that, in the domain specified by (69),

$$\omega_k\tau \lesssim \left(\frac{\omega_0^2 + \omega_1^2}{\omega_0^2 - \omega_1^2}\right)^{1/2} \Big/ \left(\frac{1}{2\pi}\right)\int_0^\pi F(k)\, dk \ll 1 \tag{70}$$

the last inequality holding by virtue of (67). It then follows that the higher order terms of (68), resulting from the expansion of cos $\omega_k\tau$, may be ignored, so that the substitution of (68) into (65) yields

$$W_T^{(0)}(p \to p \pm 1) = \frac{J^2}{\hbar^2} e^{-2S_T}\left[\frac{2\pi}{\frac{1}{\pi}\int_0^\pi 2\gamma_k\omega_k^2 \operatorname{csch}\frac{\beta\hbar\omega_k}{2}\, dk}\right]^{1/2} \cdot \exp\left[\frac{1}{\pi}\int_0^\pi 2\gamma_k \operatorname{csch}\frac{\beta\hbar\omega_k}{2}\, dk\right], \tag{71}$$

where the superscript "(0)" on the left-hand side indicates that (71) represents only the contribution in the neighborhood of $\tau = 0$.

Let us now consider the contributions to $W_T(p \to p \pm 1)$ from the other points, $\tau_i \neq 0$, which minimize the integrand of (65). It is expedient to write the argument of the exponential term of that integrand in the form

$$2\gamma \operatorname{csch}\frac{\beta\hbar\omega_0}{2}\frac{1}{\pi}\int_0^\pi H(k)\cos\omega_k\tau\, dk$$

where

$$\gamma \equiv \frac{A^2}{2M\omega_0^3\hbar} \tag{72}$$

and where

$$H(k) \equiv \frac{\omega_0^3}{\omega_k^3}\frac{\operatorname{csch}\frac{\beta\hbar\omega_k}{2}}{\operatorname{csch}\frac{\beta\hbar\omega_0}{2}}(1 - \cos k) \tag{73}$$

is a function of the order of unity (as long as ω_k is not too small compared to ω_0

and $\beta\hbar\omega_0/2 = \hbar\omega_0/2\kappa T$ not too large). The condition (67) is then essentially equivalent to

$$2\gamma \operatorname{csch} \frac{\beta\hbar\omega_0}{2} \gg 1. \tag{74}$$

It is now physically reasonable that, if the vibration spectrum (as given by Eq. 7) exhibits sufficient dispersion (e.g., if $\omega_1 \sim \omega_0$), the numerical values of the quantity

$$\frac{1}{\pi}\int_0^\pi H(k) \cos \omega_k \tau_i \, dk$$

at the maximal points, τ_i, will be smaller than the absolute maximum

$$\frac{1}{\pi}\int_0^\pi H(k) \, dk$$

attained at $\tau = 0$, by amounts of the order of unity. If this be granted, it then follows, by virtue of (74), that the values of the maxima of the integrand of (65) at the points τ_i are negligibly small compared to the principal one at $\tau = 0$. The contributions from the neighborhoods of $\tau_i \neq 0$ may thus forthwith be neglected, with the result that the right-hand side of (71) is a sufficiently good approximation to the total $W_T(p \to p \pm 1)$.

As a check of the above qualitative argument, a calculation has been carried out in Appendix I for the case of a narrow frequency band ($\omega_1 \ll \omega_0$). It is found that the contributions associated with the subsidiary maxima at $\tau_i \neq 0$ are negligible provided that (see Eq. I-15)

$$2\gamma \frac{\pi^2\omega_1^4}{8\omega_0^4} \operatorname{csch} \frac{\beta\hbar\omega_0}{2} \gg 1. \tag{75}$$

If, now, for the purpose of order-of-magnitude comparison (75) be extrapolated to the region of $\omega_1 \sim \omega_0$, it clearly becomes equivalent to (74). This equivalence, in the opinion of the present author, constitutes adequate confirmation of the above qualitative argument for the neglect of the contributions of the subsidiary maxima, and for the consequent applicability of (71) to the *total* $W_T(p \to p \pm 1)$.

Of course, in the case that the frequency spectrum is actually of narrow-band character, the more stringent condition (75) should be used in place of (74). A significant consequence is that in the limiting case of an Einstein spectrum ($\omega_1 = 0$, $\omega_k = \omega_0$), in which (75) cannot be fulfilled, the approximation represented by (71) breaks down altogether. This breakdown can be seen more directly by setting $\omega_k = \omega_0$ in (65), whence one obtains upon integrating over k,

$$W_T(p \to p \pm 1) = \frac{J^2}{\hbar^2} \exp[-2S_T] \int_{-\infty}^{+\infty} \left\{ \exp\left[2\gamma \operatorname{csch} \frac{\beta\hbar\omega_0}{2} \cos \omega_0 \tau \right] - 1 \right\} dt \tag{76}$$

which clearly diverges, since the integrand is now a positive periodic function of τ [with a period of $(2\pi/\omega_0)$].

In proceeding further, it is convenient to write (71) in the alternate form

$$W_T(p \to p \pm 1) = \frac{J^2}{\hbar^2}\left[\frac{2\pi}{\pi^{-1}\int_0^\pi 2\gamma_k\omega_k{}^2 \operatorname{csch}\frac{\beta\hbar\omega_k}{2}\,dk}\right]^{1/2} \times \exp\left\{\pi^{-1}\int_0^\pi 2\gamma_k \tanh(\beta\hbar\omega_k/4)\,dk\right\} \tag{77}$$

where the superscript (0) has now been dropped, in accordance with the above discussion.

Considerable insight into the physical significance of the various factors in (77) is gained by considering the "classical" limit, for which

$$\beta\hbar\omega_k \equiv \hbar\omega_k/\kappa T \ll 1. \tag{78}$$

In this limit the hyperbolic tangent gets replaced by its argument; then, upon eliminating γ_k by use of its definition (19), one has

$$W_T^{(\mathrm{cl})}(p \to p \pm 1) = \frac{J^2}{\hbar^2}\left[\frac{\pi}{4\kappa T E_a}\right]^{1/2} e^{-E_a/\kappa T} \tag{79}$$

where

$$E_a \equiv \pi^{-1}\int_0^\pi (\gamma_k\hbar\omega_k/2)\,dk = \pi^{-1}\int_0^\pi (A^2/4M\omega_k{}^2)(1-\cos k)\,dk. \tag{80}$$

It will be observed that the temperature dependence of (79) is of the type characteristic of an activation process, with E_a playing the role of an activation energy. It turns out, in fact, that, in the approximation in which the vibrational motion is treated classically, (79) may be obtained by a simple "occurrence-probability" approach. This approach is presented in Appendix II. It is shown therein that site jumps between neighboring sites (say, p and $p \pm 1$) occur principally when the values of the unperturbed "electronic" energies, $-Ax_p$ and $-Ax_{p+1}$, coincide. Specifically, it is found that (79) may be written in the form

$$W_T^{(\mathrm{cl})}(p \to p \pm 1) = \int_{-\infty}^{+\infty} P_T^{(c)}(v_r) W_c(p \to p+1)\,dv_r \tag{81}$$

where (see II 18)

$$P_T^{(c)}(v_r)\,dv_r = \left(\frac{M}{4\pi\kappa T}\right)^{1/2} e^{-Mv_r{}^2/4\kappa T} \mid v_r \mid \frac{A}{2\pi}\left(\frac{\pi}{4\kappa T E_a}\right)^{1/2} e^{-E_a/\kappa T} \tag{82}$$

is the probability per unit time for the occurrence of a coincidence event, $x_p =$

x_{p+1}, in which the "relative" velocity, $v_r = v_p - v_{p+1} = (d/dt)(x_p - x_{p+1})$ lies in a specified differential range, and where (see II 9),

$$W_c(p \to p + 1) = \frac{2\pi J^2}{\hbar} \frac{1}{A \mid v_r \mid} \tag{83}$$

is the probability that, in such an event, a site-jump takes place.[16]

One may, in addition, show that the activation energy, E_a, is the minimum potential energy (in excess of the absolute minimum, $-E_b$) of a configuration for which $x_p = x_{p+1}$. It should, in particular, be emphasized that E_a is substantially smaller than the binding energy of the polaron,

$$E_b = \frac{1}{\pi} \int_0^\pi \frac{A^2}{2M\omega_k^2}\, dk \tag{84}$$

(see Eq. 13). This inequality means simply that the energy necessary to establish a "neighbor" coincidence must always be less than that required for the thermal dissociation of the polaron.

Having discussed the behavior of $W_T(p \to p \pm 1)$ in the classical limit, let us utilize the general quantal expression (77) to estimate the "transition" temperature, T_t, at which the mean life of the localized state,

$$\frac{1}{\tau_{p,T}} \equiv W_T(p \to p + 1) + W_T(p \to p - 1) = 2W_T(p \to p + 1) \tag{85}$$

is equal to $1/\hbar$ times the mean polaron bandwidth

$$\Delta E_T = 2J\, e^{-S_T}. \tag{86}$$

From the discussion of Eqs. (44)–(46), T_t is to be considered as defining the boundary between the two regions of high and low temperature, in which the random site-jump and band descriptions of polaron motion are respectively valid. Equating (85) to $1/\hbar$ times (86), and employing (71) and (64), one obtains

$$\frac{\hbar}{J}\left[\frac{1}{2\pi^2}\int_0^\pi 2\gamma_k\omega_k^2 \operatorname{csch}\frac{\beta\hbar\omega_k}{2}\, dk\right]^{1/2} = \exp\left\{\frac{1}{\pi}\int_0^\pi \gamma_k\left[2\operatorname{csch}\frac{\beta\hbar\omega_k}{2} - \coth\frac{\beta\hbar\omega_k}{2}\right] dk\right\}. \tag{87}$$

For an order of magnitude estimate of T_t, it will be sufficient to consider the case of a narrow-band vibrational spectrum (in which $\omega_k \cong \omega_0$). Then, upon taking logarithms on both sides, one has

$$2\operatorname{csch}\frac{\beta_t\hbar\omega_0}{2} - \coth\frac{\beta_t\hbar\omega_0}{2} = \frac{1}{\gamma}\log\left[\frac{\hbar\omega_0}{J}\left(\frac{\gamma \operatorname{csch} \beta_t\hbar\omega_0/2}{\pi}\right)^{1/2}\right] \tag{88}$$

[16] The fact that, when (82) and (83) are inserted into (81), the resultant expression reduces to (79) may readily be verified.

which constitutes a transcendental equation for $\beta_t \equiv 1/\kappa T_t$. Choosing for γ a representative value[17] of 10, one finds that, for $\hbar\omega_0/J$ contained between the extremes of units and 100, T_t lies in the range 0.4–0.55 times the Debye Θ.

It may be remarked that, in view of the exponential temperature dependence of both ΔE_T and $\hbar/\tau_{p,T}$, the transition region, within which neither the site-jump or band approaches are valid, is quite small, and may in practice be ignored.

It may also be pointed out here, that, in the neighborhood of the transition temperature, and with γ large compared to unity, as is the case at hand, inequality (67) (or (74)) holds; it then follows that (77), rather than (66), is the appropriate formula to use for $W_T(p \to p \pm 1)$ in the high-temperature domain in which the site-jump approach applies.

IV. NONDIAGONAL TRANSITIONS BETWEEN POLARON-BAND STATES: MEAN LIFETIMES

In order to round out the theory, it is desirable to obtain an expression for the mean probability per unit time, $W_T(\sigma \to \sigma')$, that a nondiagonal transition between polaron-band states σ and σ' takes place. Due to limitations of space, the derivation of this expression will not be given in detail; a brief outline follows.

One starts with (41), which, with the aid of (36), (40) and the Fourier integral expression for the delta function, may be written as

$$W(\sigma, \cdots N_k \cdots \to \sigma', \cdots N_{k'} \cdots) = \frac{1}{N^2} \sum_{\substack{p p' \\ q q'}} e^{i[\sigma(p-q)-\sigma'(p'-q')]} \times W(p, q, \cdots N_k \cdots \to p', q', \cdots N_{k'} \cdots) \tag{89}$$

where

$$\begin{aligned} W(p, q, \cdots N_k \cdots \to p', q', \cdots N_{k'} \cdots) &= \frac{1}{\hbar^2} \int_{-t}^{+t} e^{i(\Delta\epsilon_{\sigma\sigma'})t'/\hbar} \exp\left\{\sum_k i\omega t'(N_{k'} - N_k)\right\} \\ &\quad \times (p', \cdots N_{k'} \cdots \mid V \mid p, \cdots N_k \cdots) \\ &\quad \cdot (q', \cdots N_{k'} \cdots \mid V \mid q, \cdots N_k \cdots)\, dt' \end{aligned} \tag{90}$$

and

$$\Delta\epsilon_{\sigma\sigma'} = -2J[\cos\sigma' e^{-S(\cdots N_{k'} \cdots)} - \cos\sigma\, e^{-S(\cdots N_k \cdots)}]. \tag{91}$$

Substituting (18) into (90), one carries out the sum over $N_{k'}$ and the thermal average over N_k in essentially[18] the same way as was done for the computation

[17] With this value, the activation energy $E_a \sim \gamma(\hbar\omega_0/2)$ is five times the Debye energy, $\hbar\omega_0$; taking the latter to be, e.g., 0.04 ev, one has $E_a = 0.2$ ev. The corresponding value of the polaron binding energy, E_b, is = 0.4 ev. These estimates are suggested by experiments on hole conduction in transition metal oxides [see Heikes and Johnston (*5*)] to which the present theory may find application.

[18] Some difficulties arise in principal because of the dependence of the $N_{k'}$ (via the fac-

of $W_T(p \to p')$. The result is

$$W_T(\sigma \to \sigma') = \sum_{M=-\frac{N}{2}}^{+M_2} \sum_{\epsilon=\pm 1} \frac{2J^2}{N\hbar^2} \cos[(\sigma - \sigma')M] \cos\left[\frac{(1-\epsilon)(\sigma+\sigma')}{2}\right] e^{-2S_T} \times \int_{-\infty}^{+\infty} e^{i(\Delta\epsilon_{\sigma\sigma'})t'/\hbar} \exp\left\{\sum_k 2\epsilon\gamma_k \operatorname{csch}\frac{\beta\hbar\omega_k}{2} \cos\omega_k t' \cos kM\right\} dt', \tag{92}$$

where, in accordance with footnote 18, the N_k' in (91) are to be replaced[19] by the N_k.

One may now treat (92) in a manner analogous to (65) to obtain formulae for the two cases in which $\sum_k (2\gamma_k/N) \operatorname{csch}(\beta\hbar\omega_k/2)$ is small or large compared to unity. In the first case, one obtains an expression analogous to (66), which incorporates the added feature of wave-vector conservation, via the occurrence of Krönecker-delta factors of the form $\delta_{\sigma-\sigma'\pm k\pm k'\pm k''\cdots}$. This case will not be discussed further, since it is most likely that, in the domain in which it is valid, other scattering mechanisms, such as impurity scattering, would be dominant.

In the alternate case, defined by inequality (67), the method of steepest descents is applicable. One finds here that the term in (92) for which $M = 0$ and $\epsilon = 1$ gives by far the largest contribution. Ignoring the other terms, and replacing $\exp[i(\Delta\epsilon_{\sigma\sigma'})t'/\hbar]$ by unity, in accordance with footnote 19, one then sees that, apart from the factor, $2/N$, the expression for $W_T(\sigma \to \sigma')$ is identical with that for $W_T(p \to p')$, i.e.,[20]

$$W_T(\sigma \to \sigma') = \frac{2J^2}{N\hbar^2} e^{-2S_T} \left[\frac{2\pi}{\pi^{-1}\int_0^\pi 2\gamma\omega_k{}^2 \operatorname{csch}\frac{\beta\hbar\omega_k}{2}\, dk}\right]^{1/2} \times \exp\left\{\pi^{-1}\int_0^\pi 2\gamma_k \operatorname{csch}\frac{\beta\hbar\omega_k}{2}\, dk\right\}. \tag{93}$$

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tor $\exp[-S(\cdots N_{k'} \cdots)]$). However, as can be inferred by examination of the higher order terms in (66), or in fact verified by a computation of

$$\langle\textstyle\sum_k(\Delta N_k)^2\rangle_{\mathrm{Av}} \equiv \sum_k\langle\sum_{N_{k'}} (N_k - N_k)^2 W(\sigma, \cdots N_k \cdots \to \sigma', \cdots N_{k'} \cdots)\rangle_T / \langle\textstyle\sum_{N_{k'}} W(\sigma, \cdots N_k \cdots \to \sigma', \cdots N_{k'} \cdots)\rangle_T$$

the average number of phonon emissions and absorptions accompanying a transition is finite [in fact, of the order of $\gamma \operatorname{csch}(\beta\hbar\omega_0/2)$] rather than, say, $\sim N$. For such transitions, the difference between $S(\cdots N_{k'} \cdots)$ and $S(\cdots N_k \cdots)$ is $\sim 1/N$, and hence to be ignored.

[19] Actually, in view of the smallness ($\sim 10^{-3}$) of $\Delta\epsilon_{\sigma\sigma'}$ in comparison with $\hbar\omega_k$, one may, for all practical purposes, ignore the factor $\exp\{i\Delta\epsilon_{\sigma\sigma'}t/\hbar\}$ in (92) altogether.

[20] It is of interest to note, in passing, that (93) does not depend on either the initial or final electron wave vectors, σ and σ'. This feature is analogous to the lack of occurrence in (93) (or 77) of energy delta functions, both features being characteristic of multi-phonon processes.

The mean lifetime of a polaron-band state, $\tau_{\sigma,T}$, is given by summing (93) over all σ', i.e.,

$$\frac{1}{\tau_{\sigma,T}} = \sum_{\sigma'} W_T(\sigma \to \sigma') = 2W_T(p \to p') = 1/\tau_{p,T} \tag{94}$$

where $1/\tau_{p,T}$ is the total site-jump probability, given by (85). Equation (94) exhibits the fact that the lifetimes of the localized states and the polaron-band states are equal.

V. TRANSPORT PHENOMENA: POLARON DIFFUSIVITY

The stage has now been reached where applications to transport properties may be considered. In what follows, attention will be focussed on the diffusivity, D, which, for the case of a nondegenerate polaron gas, is related to the mobility, b, through the Einstein relation

$$b = \frac{eD}{\kappa T} . \tag{95}$$

Two cases have to be considered:

Case I. $T > T_t$ *:* Here, as discussed above, polaron motion takes place via a succession of random site-jumps, in each of which the electron hops to a neighbor site with probability, $W_T(p \to p \pm 1)$. For the one-dimensional model under consideration, the diffusivity is easily seen to be

$$D = a^2 W_T(p \to p \pm 1) \tag{96}$$

where a is the lattice spacing. For illustrative purposes, let us consider the narrow-band approximation of $\omega_k = \omega_0$. One then has, from (77) and (96)

$$D = \omega_0 a^2 \frac{J^2}{\hbar^2 \omega_0^2} \left[\frac{2\pi}{2\gamma \operatorname{csch} \frac{\beta\hbar\omega_0}{2}} \right]^{1/2} \exp\left\{ -2\gamma \tanh \frac{\beta\hbar\omega_0}{4} \right\} . \tag{97}$$

The "relative" diffusivity

$$\mathfrak{D} \equiv D/\omega_0 a^2 \tag{98}$$

is plotted in Fig. 1 as a function of $\beta\hbar\omega_0 \equiv \kappa T$ for representative values of the model parameters [$J = \hbar\omega_0$, $\gamma = 10$ (see footnote 17)]. Also, shown (as the dotted curve) is the classical approximation, obtained by using (79) in place of (77).

Case II. $T < T_t$ *:* Here, the band approach applies, and one has the conventional formula[21] (adapted to a one-dimensional model)

$$D = \langle v^2_{\sigma,T} \tau_{\sigma,T} \rangle_{\mathrm{AV}}$$

[21] In the case at hand, the independence of $W_T(\sigma \to \sigma')$ with respect to σ', permits identification of the momentum-transfer rate with the total collision probability.

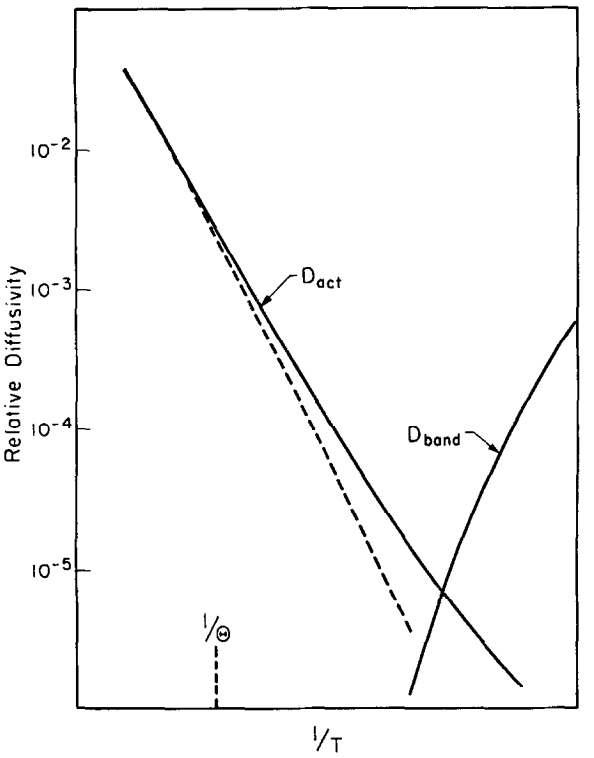

FIG. 1. Polaron diffusivity versus temperature. The solid curves labelled "D_{act}" and "D_{band}" represent the contribution arising from random site jumps and polaron-band motion, respectively. The dashed curve gives the classical approximation to D_{act}.

where, from (36),

$$v_{\sigma,T} \equiv \frac{a}{\hbar}\frac{\partial}{\partial k}E_{\sigma,T} = \frac{2J}{\hbar}\sin\sigma\, e^{-s_T} \tag{99}$$

is the expectation velocity in a state of wave-number σ, and where the average in (98) is to be taken over the distribution in σ. In view of the extreme smallness of the bandwidth ($\sim 10^{-3}\ \hbar\omega_0 \ll \kappa T$), one may assume the σ's to be equally populated, so that

$$D = \pi^{-1}\int_0^{\pi} v_{\sigma,T}^2 \tau_{\sigma,T}\, d\sigma$$

which, with (99) and (94), becomes

$$D = \frac{2J^2}{\hbar}a^2\tau_{p,T}\, e^{-2s_T}. \tag{100}$$

Using (85), (71), and (64) (in the narrow-band approximation), one then has for the relative diffusivity

$$\mathfrak{D} = \frac{D}{\omega_0 a^2} = \frac{2J^2}{\hbar^2\omega_0^2}\,\omega_0\tau_{p,T}\,e^{-2S_T}$$
$$= 2\left[\frac{\gamma\ \mathrm{csch}\ \dfrac{\beta\hbar\omega_0}{2}}{\pi}\right]^{1/2} \exp\left\{-2\gamma\ \mathrm{csch}\ \frac{\beta\hbar\omega_0}{2}\right\}. \tag{101}$$

This expression is also plotted in Fig. 1 for the same numerical values of the model-parameters as (97) (i.e., $J = \hbar\omega_0$, $\gamma = 10$). As is to be expected, (101) and (97) attain comparable numerical values in the neighborhood of the transition temperature, T_t.

VI. LIMITS OF APPLICABILITY OF THE PERTURBATION TREATMENT

It is now of interest to discuss the limitations of the perturbation approach, upon which the treatment of the present paper is based. Specifically, one wants an estimate of the upper limit of the electronic bandwidth parameter, $J_{\max}$, for which perturbation theory is valid. Two extreme cases will here be considered: (a) random site-jumps in the classical limit, $\kappa T \gg \hbar\omega_0$, and (b) the polaron-band at the absolute zero of temperature.

Case (a): For this case, the limitations of the perturbation approach are treated in Appendix III. It is found [see (III 7) and subsequent discussion], that

$$J_{\max} \sim (A\hbar\,|\,v_{p+1} - v_p\,|/2\pi)^{1/2} \tag{102}$$

where $v_{p+1} - v_p = (d/dt)(x_{p+1} - x_p)$ is the velocity with which a crossing point $x_{p+1} = x_p$ is approached; in line with the discussion of Eqs. (81)–(83) (as well as with Appendix II), such crossing (or coincidence) events are crucially significant for the occurrence of site-jumps. Taking $|\,v_{p+1} - v_p\,| \sim (2\kappa T/\pi M)^{1/2}$, one finds

$$J_{\max} \sim \left(\frac{A\hbar}{2\pi}\right)^{1/2}\left(\frac{2\kappa T}{\pi M}\right)^{1/4}$$

which, in the narrow-band case of $\omega_k \cong \omega_0$, may be transformed via (80) to read

$$J_{\max} \sim E_a^{1/4}\left(\frac{2\kappa T}{\pi}\right)^{1/4}\left(\frac{\hbar\omega_0}{\pi}\right)^{1/2}. \tag{103}$$

When J is larger than (103), the adiabatic approach (also discussed in Appendix III) becomes valid. In particular, $W_T(p \to p + 1)$ is obtained by integrating the coincidence probability (82), over all positive values of $v_r = v_{p+1} -$

v_p. The result of such an integration is

$$W_T(p \to p + 1) = \left(\frac{\kappa T}{\pi M}\right)^{1/2} \frac{A}{2\pi} \left(\frac{\pi}{4\kappa T E_a}\right)^{1/2} e^{-E_a/\kappa T}$$

which, again in the narrow-band limit, becomes

$$W_T(p \to p + 1) = \frac{\omega_0}{2\pi} e^{-E_a/\kappa T}. \tag{104}$$

Case (b): For the polaron-band at absolute zero, the discussion will be based upon preliminary computations which have been carried out for the simplest possible case, namely, a linear chain consisting of only two molecular sites. While this case represents a considerable oversimplification of the multi-site chain, it is, in the opinion of the present author, still relevant.[22] The basic equations are (with neglect of intermolecular coupling, i.e., $\omega_1 = 0$)

$$\begin{aligned}
&\left[E + \frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) - \frac{1}{2} M\omega_0^2(x_1^2 + x_2^2) + Ax_1\right] a_1(x_1, x_2) \\
&\qquad = -Ja_2(x_1, x_2), \\
&\left[E + \frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}\right) - \frac{1}{2} M\omega_0^2(x_1^2 + x_2^2) + Ax_2\right] a_2(x_1, x_2) \\
&\qquad = -Ja_2(x_1, x_2).
\end{aligned} \tag{105}$$

Two limiting methods are available for the treatment of (105); the perturbation and the adiabatic approaches, valid in the extremes of small and large J, respectively. These will now be developed; comparison of the results will then provide an estimate for $J_{\max}$.

In the perturbation approach, one takes odd and even combinations of the zeroth order "wave functions"

$$\begin{aligned}
a_1^{(1)} &= \exp\left\{-\frac{1}{2}\frac{M\omega_0}{\hbar}[(x_1 - A/M\omega_0^2)^2 + x_2^2]\right\}; \qquad a_2^{(1)} = 0, \\
a_1^{(2)} &= 0; \qquad a_2^{(2)} = \exp\left\{-\frac{1}{2}\frac{M\omega_0}{\hbar}[x_1^2 + (x_2 - A/M\omega_0^2)^2]\right\}.
\end{aligned}$$

These combinations are

$$\begin{aligned}
a_1^{(\pm)} &= \exp\left\{-\frac{1}{2}\frac{M\omega_0}{\hbar}[(x_1 - A/M\omega_0^2)^2 + x_2^2]\right\}, \\
a_2^{(\pm)} &= \pm \exp\left\{-\frac{1}{2}\frac{M\omega_0}{\hbar}[(x_2 - A/M\omega_0^2)^2 + x_1^2]\right\},
\end{aligned} \tag{106}$$

[22] In particular, preliminary calculations indicate the existence of a rather good possibility that the adiabatic treatment of the two-site case, given below, will be capable of generalization to the multi-site case of physical interest.

where the superscript $(\pm)$ designates the even and odd combinations, respectively. The corresponding eigenvalues, $E^{(\pm)}$, of (105) are obtained by the standard secular calculations, and are

$$E^{(\pm)} = -\frac{A^2}{M\omega_0^2} + \hbar\omega_0 \mp \Delta E \tag{107}$$

where[23]

$$\Delta E = J \exp\{-A^2/2M\omega_0^2\hbar\omega_0\}. \tag{108}$$

In the adiabatic approach, one assumes a wave function of the form

$$\begin{aligned} a_1(x_1,x_2) &= \chi(x_1,x_2)c_1(x_1,x_2), \\ a_2(x_1,x_2) &= \chi(x_1,x_2)c_2(x_1,x_2), \end{aligned} \tag{109}$$

where the c's are solutions of the "electronic" equations

$$\begin{aligned} (\mathcal{E} + Ax_1)c_1 &= -Jc_2, \\ (\mathcal{E} + Ax_2)c_2 &= -Jc_1, \end{aligned} \tag{110}$$

the eigenvalue $\mathcal{E}(x_1,x_2)$ constituting the "electronic" energy. As is known, $\mathcal{E}(x_1,x_2)$ also plays the role of a potential energy term in the equation for the "vibrational" wave function, $\chi(x_1,x_2)$, which reads

$$\left[E + \frac{\hbar^2}{2M}\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} - \frac{1}{2}M\omega_0^2(x_1^2 + x_2^2) - \mathcal{E}(x_1,x_2)\right]\chi(x_1,x_2) = 0. \tag{111}$$

The eigenvalues of (110) have already been obtained in the latter part of Appendix II; of these, only the lowest

$$\mathcal{E}_{(-)}(x_1,x_2) = -\frac{A(x_1 + x_2)}{2} - \left[\frac{A^2(x_1 - x_2)^2}{4} + J^2\right]^{1/2} \tag{112}$$

is of interest in the adiabatic approximation.

Upon substituting (112) into (111), one observes that the transformation

$$\begin{aligned} X &= \frac{x_1 + x_2}{2}, \\ x &= x_2 - x_1 \end{aligned} \tag{113}$$

leads to a product solution of the form $\chi(x_1,x_2) = \phi(X)\psi(x)$. The equation for $\phi(X)$ is that of a simple harmonic oscillator in the presence of a constant force,

[23] Apart from a numerical factor of 2, (108) is just what would be obtained from (28) and (27) in the narrow-band limit of $\omega_k = \omega_0$. The absence of the factor of 2 in (108) is due to the special feature of a two-site system, in which the number of nearest neighbors is one, rather than two.

A; apart from the fact that its lowest eigenvalue is $-(A^2/4M\omega_0^2) + (\hbar\omega_0/2)$, it is of no further interest.

The equation for $\psi(x)$ is

$$\left[E + \frac{A^2}{8\mu\omega_0^2} - \frac{\hbar\omega_0}{2} + \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial x^2} - \frac{\mu}{2}\omega_0^2 x^2 + \left\{\left(\frac{Ax}{2}\right)^2 + J^2\right\}^{1/2}\right]\psi(x) = 0 \quad (114)$$

where

$$\mu \equiv M/2. \quad (115)$$

The potential energy for this problem, namely

$$V(x) = \frac{\mu}{2}\omega_0^2 x^2 - \left\{\left(\frac{Ax}{2}\right)^2 + J^2\right\}^{1/2}$$

possesses two minima, which, for J small compared to $A^2/2M\omega_0^2$ (small-polaron condition), are approximately located at $x = \pm A/2\mu\omega_0^2$, and have the common value

$$V_{\min} \cong -\frac{A^2}{8\mu\omega_0^2}.$$

These two minima are separated by a barrier whose height (relative to the minima) is $A^2/8\mu\omega_0^2 - J \cong A^2/8\mu\omega_0^2$. The potential is thus quite similar to that encountered in the theory of the inversion spectrum of the ammonia molecule. As in that case, the condition, $\hbar\omega_0 \ll$ barrier height, ($\gamma \gg 1$) permits solving for the energy splitting of the two lowest states by WKB tunnelling techniques. Omitting the detailed computations, one finds

$$\Delta E = J\left[\frac{1}{\pi}\frac{A^2}{2M\omega_0^2}\frac{\hbar\omega_0}{J^2}\right]^{1/2}\exp\left\{-\frac{A^2}{2M\omega_0^2\hbar\omega_0}\right\} \cdot \exp\left\{\frac{J^2}{2\hbar\omega_0(A^2/2M\omega_0^2)} + \frac{J^2}{\hbar\omega_0(A^2/2M\omega_0^2)}\log\frac{A^2}{M\omega_0^2 J}\right\}. \quad (116)$$

It will now be noticed that, apart from the logarithmic term, (116) and (108) are of comparable magnitude when

$$J \sim J_{\max} \equiv (A^2/2M\omega_0^2)^{1/2}(\hbar\omega_0)^{1/2}. \quad (117)$$

From this comparison it may be inferred that $J_{\max}$, as defined by (117), gives the upper limit of applicability of perturbation theory.

Considering, now, the logarithmic term, one sees that, since, for $J \sim J_{\max}$,

$$\frac{A^2}{M\omega_0^2 J} \sim \left(\frac{A^2}{M\omega_0^2\hbar\omega_0}\right)^{1/2} \gg 1$$

deviations between (112) and (108) occur at J values somewhat smaller than

the right-hand side of (117). Strictly speaking, then, $J_{\max}$ should be redefined as

$$J_{\max} = (A^2/2M\omega_0^2)^{1/2}(\hbar\omega_0)^{1/2}/\log(A^2/M\omega_0^2\hbar\omega_0)^{1/2}.$$

However, in view of the circumstance that the logarithm is numerically comparable to unity, this last expression is essentially equivalent to (117).

Let us note, in passing, that (117) may be written in a form analogous to the high-temperature limit, namely,

$$J_{\max} = (Ahv_r^{(\text{eff})}/2\pi)^{1/2} \tag{118}$$

where

$$v_r^{(\text{eff})} = (\pi A/M\omega_0) = (\pi A/2\mu\omega_0). \tag{119}$$

It may now be noted, from (114) and subsequent text, that (119) is of the same order as the "imaginary" velocity

$$\left(\frac{2}{\mu}\frac{A^2}{8\mu\omega_0^2}\right)^{1/2} = \frac{A}{2\mu\omega_0},$$

which the system possesses in the neighborhood of the barrier maximum at $x = 0$, i.e., in the neighborhood of the crossing point of the unperturbed ($J = 0$) potential energy curves. In the high-temperature case, this point is classically accessible, so that, in the general formula, $v_r = (2E_{\text{kin}}/\mu)$, the actual kinetic energy $\sim\kappa T$ is to be used. In the case of the ground state, the crossing point is classically inaccessible; from the analogy to conventional barrier problems, one takes $E_{\text{kin}} \sim A^2/8\mu\omega_0^2$.

It is now of interest to obtain numerical estimates for $J_{\max}$. In terms of the numbers given in footnote 9, these estimates are

$$J_{\max}^{(T)} \cong 0.67\hbar\omega_0(T/\Theta)^{1/4} = 0.027(T/\Theta)^{1/4}\ \text{ev}$$

and

$$J_{\max}^{(0)} \cong 3\hbar\omega_0 = 0.12\ \text{ev}$$

for the cases of high-temperature site-jumps and ground-state bandwidths, respectively. Selecting for T/Θ a representative value of 3 (while this choice pushes (108) to the limit of its domain of applicability, the formula should still be serviceable for order-of-magnitude considerations), one has $J_{\max}^{(T)} \sim 0.035$ ev; both this value and that of 0.12 ev, cited for the ground-state limit, $J_{\max}^{(0)}$, represent rather small electronic bandwidths, indeed. It is thus apparent that the perturbation approach covers only part of the total region ($J < A^2/2M\omega_0^2 \sim 0.4$ ev) of significance for the small polaron; for the remainder of this region, the adiabatic, rather than the perturbation, approach is to be employed.

Some orienting calculations, based on the adiabatic approach, have been performed for the energy levels of the ground-state polaron band. On the basis of these calculations, it appears likely that the levels in question are given by an expression of the form of (26), in which the coefficient, $2Je^{-S}$, gets replaced by twice the right-hand side of (116).

In the other extreme of high-temperature site-jumps, it appears that the adiabatic expression (104) will hold, subject to the stipulation that formula (80) for the activation energy will have to be modified to take account of the progressive lowering of the potential barrier[24] with increasing J.

VII. COMPARISON WITH OTHER SMALL POLARON TREATMENTS

The discussion given here will deal exclusively[25] with the paper of Y and K (*3*). These authors were primarily concerned with computing the probabilities of thermally activated site-jumps. Using a method originally developed for the treatment of optical transitions in F-centers (which is substantially equivalent to that of the present paper), but also restricting themselves to the Einstein approximation ($\omega_k = \omega_0$), they obtain an expression for the site-jump probability, which reads (see their Eq. 43)

$$W = \frac{2\pi}{\hbar} |M|^2 \exp\{-S(2n+1)\} \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \exp\{2S[n(n+1)]^{1/2} \cdot \cos \omega t\}\, dt \tag{120}$$

where $n \equiv [e^{\beta\hbar\omega_0/2} - 1]^{-1}$, M is the electronic-overlap parameter ($\equiv J$), and where S apparently[26] corresponds to twice the vibrational overlap parameter, $\gamma = A^2/2M\omega_0^2$, employed in the present paper. Noting that $2n + 1 = \coth(\beta\hbar\omega_0/2)$, and $[n(n+1)]^{1/2} = \frac{1}{2}\operatorname{csch}(\beta\hbar\omega_0/2)$, one sees that, apart from the term, -1, in the integrand of (76) (this term being absent from Y and K's formula, because of their neglect to subtract the diagonal transitions from the total transition probability expression), (120) is completely equivalent[27] to (76), and is hence also infinite. The finite result given by Y and K, namely

$$W = \frac{2\pi}{\hbar} |M|^2 \exp\{-S(2n+1)\} \frac{1}{\hbar\omega} I_0\{2S[n(n+1)]^{1/2}\} \tag{121}$$

[24] It may be remarked that barrier lowering also results in an enhancement of quantal barrier penetration; this feature is responsible for the appearance of the positive terms, proportional to J^2, in the exponent of (116).

[25] The treatment of Tjablikov, cited in Ref. *2* (as well as that of a recent paper by Sewell) is limited to the consideration of the polaron-band states (Tjablikov, in particular, to the ground state band at absolute zero). In neither of these papers, is any attempt made to include the non-diagonal transitions within the framework of the theory.

[26] The reason for this uncertainty will become evident shortly.

[27] Note that, in (76), S_T is to be equated to $\gamma \coth(\beta\hbar\omega_0/2)$.

[where $I_0(x)$ is the modified Bessel function of the first kind] was apparently obtained by replacing the infinite integral of (120) by one going from zero to 2π.

It should here be remarked that, despite the above-discussed error in its derivation, Y and K's formula (121) is still applicable to the case of a narrow-band vibrational spectrum in the region defined by inequality (75). As discussed above, in connection with the derivation of (77), a consequence of this inequality is that the maximum of the integrand of (65) at $t = 0$ is so large, relative to the other maxima, that in effect the integration may be restricted to the interval $-\pi \leqq t \leqq +\pi$, thereby coinciding with Y and K's procedure. [The actual equivalence of (121) to (77) is readily demonstrated by inserting for $I_0(x)$ the standard asymptotic expression, $e^x/(2\pi x)^{1/2}$.]

On the other hand, in the domain in which the converse of (75) holds (either at low temperatures or for small values of γ), (121) is clearly incorrect. In this region, as shown by equation (66) and subsequent discussion, the site-jump probability is expressed as a sum of terms each representing site-jumps in which two, three, etc., phonons are emitted or absorbed, and hence possessing both the temperature variation and dependence on vibrational frequency spectrum[28] characteristic of such processes. These features are not exhibited by (121).

Y and K have also obtained an expression analogous to (36) for the energy bands of the polaron-bands (see their Eq. 26 and its generalization, stated in the subsequent paragraph)

$$E = E_0 + 2M\{\cos(k_x a) + \cos(k_y a) + \cos(k_z a)\}e^{-(2n+1)S} \tag{122}$$

where M and S have the same significance as in (120). (Also, the band energy is here a function of three wave numbers, since Y and K's treatment is three-dimensional.) If, now, one introduces Y and K's symbols into Eq. (36) of the present paper and goes over to the narrow-band approximation in which $\omega_k \to \omega_0$ and $N_k \to n$, one has

$$E_{\sigma,\ldots N_k \ldots} = E_b + \sum_k (n + \tfrac{1}{2})\hbar\omega_0 - 2J \cos\sigma\, e^{-(n+1/2)S} \tag{123}$$

which differs from (122) by a factor of $\frac{1}{2}$ in the exponent of the last term.

This numerical difference is far from trivial; in particular, from (122) Y and K apparently concluded that band-type motion of the polaron could never be of any practical significance (irrespective of temperature), and that thermally-induced, site-jump transport would always be dominant.

Due to the circumstance that Y and K gave only a brief outline of their cal-

[28] The dependence of (66) in the vibrational frequency spectrum is contained implicitly in the frequency delta functions. Integration over any one of the k's contained in a given delta function results in its replacement by a typical "frequency-density" factor, of the form, $\partial k/\partial\omega_k$.

culation, the present author has not succeeded in tracking down the discrepancy. However, the fact that the exponent of (122) is too large by a factor of two may be established by the following considerations.

If one takes the special case of absolute zero, at which the vibrational quantum numbers are all zero, one may establish a simple correspondence between the exponents occurring in (122) and the site-jump-probability expression, (120). Disregarding the question of the actual divergence of (120), which was discussed earlier, one sees that, for $n = 0$, the exponents are apparently identical. It is now to be realized that, in both cases, the exponential factor enters in as part of the matrix element for the transition $p \rightarrow p + 1$. This matrix element, given by the product of the right-hand-side of Y and K's Eq. (27) and the vibrational overlap integral immediately following [or, in the present paper by (17), enters *linearly* into the band-energy (123)], but *quadratically* into the random-jump probability (120) (as is evidenced by the M dependence of these two expressions). It therefore follows that the exponent occurring in (122) should actually be half that contained in (120).

APPENDIX I

In this appendix, the maxima of the integrand of the text Eq. (65) will be computed for the "narrow-band" case, in which

$$\omega_1 \ll \omega_0 . \tag{I-1}$$

In this case, (7) may be approximated by

$$\omega_k = \omega_0 + \omega_b \cos k \tag{I-2}$$

where

$$\omega_b = \omega_1^2/2\omega_0 \tag{I-3}$$

is the half-width of the band.

Subject to (I-1), one may also introduce the approximations

$$\omega_0^3/\omega_k^3 \cong 1 - 3(\omega_b/\omega_0) \cos k, \tag{I-4a}$$

$$\operatorname{csch} \frac{\hbar\omega_k}{2\kappa T} = \frac{\hbar\omega_0}{2\kappa T}\left(1 - (\beta\hbar\omega_0)\left(\frac{\omega_b}{\omega_0}\right)(\cos k) \coth \frac{\beta\hbar\omega_0}{2}\right) \tag{I-4b}$$

so that the quantity $H(k)$, defined by the text equation (73), becomes

$$H(k) \cong \left(1 - \frac{3\omega_b}{\omega_0} \cos k\right)(1 - \cos k)\left(1 - (\beta\hbar\omega_0)\left(\frac{\omega_b}{\omega_0}\right) \cos k \coth \frac{\beta\hbar\omega_0}{2}\right). \tag{I-5}$$

Neglecting terms of quadratic or higher order in ω_b/ω_0, one may further approximate $H(k)$ by

$$H(k) \cong 1 - (1 + a) \cos k + a \cos^2 k \tag{I-6}$$

where

$$a \equiv \left(3 + \frac{\beta\hbar\omega_0}{2} \coth \frac{\beta\hbar\omega_0}{2}\right) \frac{\omega_b}{\omega_0}. \tag{I-7}$$

Using (I-6), one then has for the argument of the exponential term in the integrand of (65)

$$\begin{aligned}
\mathcal{K}(\tau) &\equiv 2\gamma \operatorname{csch} \frac{\beta\hbar\omega_0}{2} \frac{1}{\pi} \int_0^\pi H(k) \cos \omega_k \tau \, dk \\
&= 2\gamma \operatorname{csch} \frac{\beta\hbar\omega_0}{2} \frac{1}{\pi} \int_0^\pi [1 - (1 + a) \cos k + a \cos^2 k] \\
&\qquad \cdot [\cos \omega_0\tau \cos(\omega_0\tau \cos k) - \sin \omega_0\tau \sin (\omega_0\tau \cos k)] \, dk \qquad \text{(I-8)} \\
&= 2\gamma \operatorname{csch} \frac{\beta\hbar\omega_0}{2} \left\{ \cos \omega_0\tau \left[\left(1 + \frac{a}{2}\right) J_0(\omega_b\tau) - \frac{a}{2} J_2(\omega_b\tau) \right] \right. \\
&\qquad \left. + \sin \omega_0\tau [(1 + a) J_1(\omega_b\tau)] \right\}
\end{aligned}$$

where the J's are Bessel functions.

The absolute maximum of $\mathcal{K}(\tau)$ is attained at $\tau = 0$, and is

$$\mathcal{K}(0) = 2\gamma \operatorname{csch} \frac{\beta\hbar\omega_0}{2} \left(1 + \frac{a}{2}\right).$$

For the computation of the other maxima, it is expedient to rewrite (I-8) in the form

$$\begin{aligned}
\mathcal{K}(\tau) = \mathcal{K}(0) \left\{ \left[J_0\left(\frac{\omega_b}{\omega_0} x\right) - \frac{a}{2 + a} J_2\left(\frac{\omega_0}{\omega_0} x\right) \right]^2 \right. \\
\left. + \left(\frac{(1 + a)}{1 + a/2}\right)^2 J_1^{\,2}\left(\frac{\omega_b}{\omega_0} x\right) \right\}^{1/2} \cos[x - \varphi(\tau)]
\end{aligned} \tag{I-9}$$

where

$$\varphi(\tau) \equiv \arctan \frac{(1 + a) J_1(\omega_b\tau)}{\left(1 + \frac{a}{2}\right) J_0(\omega_b\tau) - \frac{a}{2} J_2(\omega_b\tau)} \tag{I-10}$$

and

$$x = \omega_0\tau \tag{I-11}$$

In the case of those maximal points for which $(\omega_b/\omega_0)x_i < 1$, the Bessel functions

may be expanded, yielding, to the lowest order in ω_b/ω_0,

$$\mathcal{K}(\tau) \cong \mathcal{K}(0)\left(1 - \frac{\omega_b^2 x^2}{8\omega_0^2}\right)\cos\left[x - \varphi(\tau)\right], \tag{I-12}$$

$$\varphi(\tau) \cong \omega_b x/2\omega_0. \tag{I-13}$$

It is now to be noted, that, since $\varphi(\tau)$ is small, the maximal points, x_i, may to a sufficiently good approximation, be set equal to $2\pi n_i$. One then has

$$\mathcal{K}_i(\tau) = \mathcal{K}(0)\left[1 - \left(\frac{\pi^2\omega_b^2}{2\omega_0^2}\right)n_i\right]. \tag{I-14}$$

From (I-14), it is then seen that, in order for the contributions of these maxima to (65) to be negligible, it is required that

$$\mathcal{K}(0)\,\frac{\pi^2\omega_b^2}{2\omega_0^2} \gg 1$$

or, in view of (I-3), and of the definition of $\mathcal{K}(0)$ [given between (I-8) and (I-9)]

$$2\gamma\,\operatorname{csch}\frac{\beta\hbar\omega_0}{2}\,\frac{\pi^2\omega_1^4}{8\omega_0^4} \gg 1. \tag{I-15}$$

Turning now briefly to the other maxima, for which $(\omega_b/\omega_0)x_i > 1$, one sees that their magnitudes are essentially given by the curly bracket of (I-9). In particular, if this bracket does not approach unity in the domain $(\omega_b/\omega_0)x_i > 1$, the contributions to (65) will be negligible. The fact that this is actually the case may be established by numerical analysis of the curly bracket. However, in view of the above results, and of the arguments already presented in the text subsequent to Eq. (74), this analysis will not be carried out here.

APPENDIX II

In this appendix, the classical occurrence-probability derivation of the text Eq. (79) for $W_T(p \to p \pm 1)$ will be presented. The basis of the treatment is the set of equations

$$i\hbar\,\frac{\partial a_n}{\partial t} = -Ax_n(t)a_n - J(a_{n+1} + a_{n-1}) \tag{II-1}$$

which is obtained from the text set (5) by omitting the vibrational Hamiltonian. The $x_n(t)$ are to be considered as given functions of time, determined by classical trajectories.[29] It is assumed that, at some initial time, t_i, the electron

[29] In the zeroth approximation, in which the electron remains localized on a given pth side, the time dependence of $x_n(t)$ is determined by the Hamiltonian, $H^{(p)} = H_L - Ax_p$ (H_L representing the purely vibrational Hamiltonian of the host crystal). When, in the

is in a definite (pth) site, so that

$$a_n(t_i) = \delta_{np} . \tag{II-2}$$

The application of first-order perturbation theory then gives, say, for $a_{p+1}(t)$, at a time $t > t_i$

$$\dot{a}_{p+1}(t) = -\frac{J}{i\hbar} \exp\left\{\left(\frac{iA}{\hbar}\right)\int^t x_{p+1}(t')\,dt'\right\} \int_{t_i}^t \exp\left\{\frac{iA}{\hbar}\int^{t'} [x_p(t'') - x_{p+1}(t'')]\,dt''\right\} dt' \tag{II-3}$$

where the lower limit of the "phase integrals," occurring in the exponents of (II-3), is to be specified later.

The procedure to be used in the evaluation of the integral on the right-hand side of (II-3) is based on the fact that, over the region of interest for the present classical treatment, in which the inequalities

$$A^2/M\omega_0^2 \gg \hbar\omega, \tag{II-4}$$

$$\kappa T \gg \hbar\omega \tag{II-5}$$

obtain, the relative variation of $x_p - x_{p+1}$ in a time of the order of an instantaneous "period," $\hbar/A(x_p - x_{p+1})$, [i.e., the quantity $(\hbar/A \mid x_p - x_{p+1} \mid)(\partial/\partial t) \log(x_p - x_{p+1})$], is small, except at a "coincidence" point, t_c [at which $x_{p+1}(t_c) = x_p(t_c)$].[30] It then follows that the oscillations in the exponential integrand will interfere destructively, except at the coincidence points, t_c, at which the phase of the exponential is momentarily stationary.

Let us assume that such a point of stationary phase, t_c, occurs in the interval between t_i and t. Let us further introduce the assumption[31] that, in the neighborhood of t_c, the time variation of $x_p(t) - x_{p+1}(t)$ may be considered linear, so that

$$x_p(t) - x_{p+1}(t) = (v_p - v_{p+1})(t - t_c) \tag{II-6}$$

where the velocities v_{p+1} and v_p are evaluated at t_c.

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next approximation, site jumps of the type $p \to p + 1$ are computed, the question arises as to whether $H^{(p)}$ or $H^{(p+1)}$ (or some mixture thereof) should be used in determining the $x_n(t)$. It turns out, however, that, as will be seen below, within the domain of validity of the classical calculation, this ambiguity does not cause any trouble.

[30] That such a situation prevails when (II-4) and (II-5) are satisfied, can be seen by noting that $\mid x_p - x_{p+1} \mid \gtrsim (\kappa T/M\omega_0^2)^{1/2}$ and $\mid (d/dt) \log(x_p - x_{p+1}) \mid \sim \omega_0$ so that

$$[\hbar/(A \mid x_p - x_{p+1} \mid)] \mid (\partial/\partial t) \log(x_p - x_{p+1}) \mid \ll 1.$$

[31] The domain of validity of this assumption will be discussed later.

Inserting (II-6) into (II-3), and choosing the lower limit of the phase integrals to be t_c, one has

$$a_{p+1}(t) = -\frac{J}{i\hbar} \exp\left\{iA \int_{t_c}^{t} x_{p+1}(t')\, dt'\right\} \int_{t_i}^{t} \exp\left\{\frac{i}{2}[A(v_p - v_{p+1})/\hbar](t' - t_c)^2\right\} dt. \tag{II-7}$$

It will now be noticed that important contributions to the integral occur over a time interval,

$$\Delta t \sim [\hbar/A(v_p - v_{p+1})]^{1/2} \sim [\hbar/A(\kappa T/M)^{1/2}]^{1/2} = \frac{1}{\omega_0}\left[\frac{\hbar\omega_0}{(A/M\omega_0^2)^{1/2}(\kappa T)^{1/2}}\right]^{1/2}.$$

If the spacing in time between successive coincidence points be assumed large compared to Δt (this assumption also will be examined later), the contributions of different coincidence points will not overlap. One may then replace the integration limits, t and t_i, by plus and minus infinity, respectively, so that

$$\begin{aligned} a_{p+1}(t) &= -\frac{J}{i\hbar} \exp\left\{iA \int_{t_c}^{t} x_{p+1}(t')\, dt'\right\} \int_{-\infty}^{+\infty} \exp\left\{\frac{i}{2}[A(v_p - v_{p+1})/\hbar]\,(t' - t_c)^2\right\} dt' \\ &= -\frac{J}{i\hbar} \exp\left\{iA \int_{t_c}^{t} x_{p+1}(t')\, dt'\right\} e^{-i\pi/4} \left(\frac{2\pi\hbar}{A\,|\,v_p - v_{p+1}\,|}\right)^{1/2}. \end{aligned} \tag{II-8}$$

In going from occupation amplitudes to occupation probabilities, it will be assumed that there is no phase correlation between successive coincidence points (or, alternatively, that any such correlation for a given classical trajectory averages to zero when all possible trajectories are taken into account).[32] Then, upon taking the absolute square of both sides of (II-8), one has

$$W_c(p \to p + 1) = \frac{2\pi J^2}{\hbar} \frac{1}{A\,|\,v_p - v_{p+1}\,|} \tag{II-9}$$

where $W_c(p \to p + 1) = |\, a_{p+1}(\infty)\,|^2$ represents the probability of a site jump, $p \to p + 1$, occurring in a single coincidence event.

In order to obtain the transition probability, $W_T(p \to p + 1)$, giving the average site-jump probability per second, one multiplies (II-9) by the proba-

[32] In view of the generally large number of oscillations between successive coincidence points (this number can be estimated from the material given in footnote 30), such correlations would occur only if the motion were perfectly periodic. This possibility, however, is specifically ruled out by the frequency dispersion of the vibrational frequencies.

bility per second, $P_T^{(c)}(v_r)\,dv_r$, for a coincidence in which the relative velocity, $v_r = v_p - v_{p+1}$, lies within a given differential range, and integrates over all values of v_r.

To compute $P_T^{(c)}(v_r)\,dv_r$, one notes that, in a time dt, all configurations for which $x_p - x_{p+1} \leqq v_r\,dt$ will give rise to the coincidence, $x_p = x_{p+1}$, in time dt. The classical occurrence-probability of such a configuration, in which v_r is also specified to lie within a given differential range, is

$$Z^{-1}\int\cdots\int e^{-(H_L - Ax_p)/\kappa T}\,[S(x_p - x_{p+1}) - S(x_p - x_{p+1} - v_r\,dt)]$$
$$\times\,[S(v_p - v_{p+1} - v_r) - S(v_p - V_{p+1} - v_r - dv_r)]$$
$$\cdot dx_1\cdots dx_N\,dv_1\cdots dv_N$$

where

$$Z \equiv \int\cdots\int e^{-(H_L - Ax_p)/\kappa T}\,dx_1\cdots dx_N\,dv_1\cdots dv_N$$

and where

$$S(x) \equiv \int_{-\infty}^{x}\delta(x')\,dx'$$

is the conventional step function. It will be noticed that both of the square brackets are equal to zero, except for the differential intervals, $x_{p+1} \leqq x_p \leqq x_{p+1} + v_r\,dt$ and $v_{p+1} + v_r \ll v_p \leqq v_{p+1} + v_r + dv_r$, respectively, within which they are unity. These differential impulse functions may more conveniently be represented by the expressions $\delta(x_p - x_{p+1})v_r\,dt$ and $\delta(v_p - v_{p+1} - v_r)\,dv_r$. Then, upon carrying out the velocity integrations, and dividing by dt to obtain the occurrence-probability per unit time, one has

$$P_T^{(c)} = \left(\frac{M}{4\pi\kappa T}\right)^{1/2} dv_r\,e^{-Mv_r^2/4\kappa T}\,|\,v_r\,|\,\mathfrak{F} \tag{II-10}$$

where

$$\mathfrak{F} \equiv \frac{\int\cdots\int e^{-(V_L - Ax_p)/\kappa T}\,\delta(x_p - x_{p+1})\,dx_1\cdots dx_N}{\int\cdots\int e^{-(V_L - Ax_p)/\kappa T}\,dx_1\cdots dx_N} \tag{II-11}$$

V_L representing the vibrational potential energy of the host crystal.

At this point it is expedient to introduce the Fourier-integral formula for the delta function:

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{ix\alpha}\,d\alpha$$

and to transform to the normal coordinates, q_k, via the relations

$$x_n = \sum_k \left(\frac{2}{N}\right)^{1/2} q_k \sin(kn + \pi/4) \tag{II-12}$$

The numerator and denominator of the resulting expression for $\mathfrak{F}$ are each reduced, therewith, to a product of integrals over the q_k. The individual integrations are readily carried out, the result being

$$\mathfrak{F} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp\left\{\sum_k \frac{\beta_k^2(\alpha) - \beta_k^2(0)}{NM\omega_k^2 \kappa T}\right\} d\alpha \tag{II-13}$$

where

$$\beta_k(\alpha) = (-A + i\alpha\kappa T) \sin[kp + \pi/4] - i\alpha\kappa T \sin[k(p+1) + \pi/4]. \tag{II-14}$$

One now introduces a new integration variable

$$\gamma \equiv \alpha + \frac{iA}{2\kappa T}. \tag{II-15}$$

Then, upon pairing terms of plus and minus k, one may write the exponent of the integrand of (II-13) as

$$\sum_k -\frac{A^2}{4NM\omega_k^2 \kappa T}(1 - \cos k) - \sum \frac{\kappa T}{NM\omega_k^2}(1 - \cos k)\gamma^2. \tag{II-16}$$

From the form of this exponent, it is clear that the γ-integration limits $(-\infty + iA/2\kappa T, +\infty + iA/2\kappa T)$ may be replaced by $(-\infty, +\infty)$, so that, upon introducing the "activation energy"

$$\begin{aligned} E_a &= \frac{1}{N} \sum_k A^2 (1 - \cos k)/4M\omega_k^2 \\ &= \frac{1}{\pi} \int_0^\infty \frac{A^2(1 - \cos k)\, dk}{4M\omega_k^2}, \end{aligned} \tag{II-17}$$

one obtains

$$\mathfrak{F} = \frac{A}{2\pi} \left(\frac{\pi}{4\kappa T E_a}\right)^{1/2} e^{-E_a/\kappa T}$$

which, when inserted into (10), yields

$$P_T^{(c)}(v_r)\, dv_r = \left(\frac{M}{4\pi\kappa T}\right)^{1/2} dv_r\, e^{-Mv_r^2/4\kappa T} \mid v_r \mid \frac{A}{2\pi} \left(\frac{\pi}{4\kappa T E_a}\right)^{1/2} e^{-E_a/\kappa T} \tag{II-18}$$

Multiplying (II-18) by (II-9), and integrating over all $v_r \equiv v_p - v_{p+1}$ one obtains the text relation (79), q.e.d.

The assumptions introduced in the derivation of (II-9) will now be examined.

Of these, the most delicate is embodied in (II-6). The significance of the approximation implied by this expression is that the relative velocity, $v_p - v_{p+1}$, does not change appreciably in a time

$$\Delta t \sim [\hbar/A(v_p - v_{p+1})]^{1/2} \sim \omega_0^{-1}[\hbar\omega_0/(A^2/M\omega_0^2)^{1/2}(\kappa T)^{1/2}]^{1/2};$$

as pointed out in the discussion subsequent to (II-7), Δt defines the neighborhood of a coincidence-point within which the principal contribution to the right-hand side of (II-7) is contained.

In order to assess the validity of this assumption, an estimate of the relative acceleration, $(d/dt)(v_p - v_{p+1})$, is required. In obtaining this estimate, the vibrational coupling between the individual molecules will be neglected ($\omega_1 = 0$); this procedure should be quantitatively accurate for a narrow-band vibrational spectrum ($\omega_1 \ll \omega_0$), and should be suitable for at least order-of-magnitude considerations in the more general case of $\omega_1 \sim \omega_0$.

Neglecting, then, the intermolecular vibrational coupling term in the lattice Hamiltonian, one has for the relative acceleration at a coincidence point ($x_p = x_{p+1}$)

$$\frac{d}{dt}(v_p - v_{p+1}) = -\omega_0^2(x_p - x_{p+1}) + \frac{A}{M} \tag{II-19}$$

wherein it has been assumed that the effective Hamiltonian is[33] $H^{(p)} \equiv H_L - Ax_p$. On the other hand, the order of magnitude of the relative velocity is

$$|v_p - v_{p+1}| \sim \left(\frac{2\kappa T}{M}\right)^{1/2} \tag{II-20}$$

From (II-19), (II-20), and the estimate for Δt, it follows that, in order for (II-6) to be applicable, it is necessary that

$$\frac{A}{M\omega_0}\left[\frac{\hbar\omega_0}{(A^2/M\omega_0^2)^{1/2}(\kappa T)^{1/2}}\right]^{1/2} \ll \left(\frac{2\kappa T}{M}\right)^{1/2}$$

or

$$\left(\frac{A^2}{M\omega_0^2}\right)^{1/2}\frac{\hbar\omega_0}{(\kappa T)^{3/2}} \ll 1,$$

i.e.,

$$\kappa T \gg \left[\left(\frac{A^2}{M\omega_0^2}\right)(\hbar\omega_0)^2\right]^{1/3}. \tag{II-21}$$

[33] If, instead, one assumed the effective Hamiltonian to be $H^{(p+1)}$, the sign of the right-hand side of (II-9) would be changed but the magnitude would remain unaltered; if one took some average of $H^{(p)}$ and $H^{(p+1)}$, the relative acceleration would still be $\sim A$, times a numerical factor $\leqq 1$.

It is of interest to point out that (II-21), rather than $\kappa T \gg \hbar\omega$, is the appropriate condition for the approximation of the quantal relation (77) by (79). Namely, if in the Taylor expansion of the hyperbolic tangent occurring in the exponential factor of (77), one retains two terms, i.e.,

$$\tanh\frac{\beta\hbar\omega_k}{4} \to \frac{\hbar\omega_k}{4\kappa T} - \frac{1}{3}\left(\frac{\hbar\omega_k}{4\kappa T}\right)^3$$

one obtains (79) multiplied by the factor

$$\exp\left[-\frac{1}{\pi}\int_0^\pi \frac{A^2}{M\omega_k{}^2}\,\frac{(1-\cos k)(\hbar\omega_k)^2}{3(4\kappa T)^3}\,dk\right]$$

which, for order of magnitude considerations, may be approximated by

$$\exp\left[-\left(\frac{A^2}{M\omega_0{}^3}\right)\frac{(\hbar\omega_0)^2}{3(4\kappa T)^3}\right].$$

In order for this quantity to be replaceable by unity, it is necessary that

$$\kappa T \gg \frac{1}{4}\left[3\,\frac{A^2}{M\omega_0{}^2}\,(\hbar\omega_0)^2\right]^{1/3}$$

which, apart from numerical factors, is identical with (II-21).

It remains to discuss the assumption, introduced in the paragraph preceding (II-8), that the time between successive coincidence points is large compared to $\Delta t \sim \omega_0^{-1}[\hbar\omega_0/(A^2/M\omega_0{}^2)^{1/2}(\kappa T)^{1/2}]^{1/2}$. Apart from one special feature, said time is of the order of $1/\omega_0$, and hence larger than Δt by a factor

$$(A^2/M\omega_0{}^2/\hbar\omega_0)^{1/2}(\kappa T/\hbar\omega_0)^{1/4} \gg 1.$$

The special feature in question arises from the fact that, when $A^2/M\omega_0{}^2$ is large compared to κT, the coincidences tend to occur in closely-spaced pairs. For example, using the same narrow-band limit of $\omega_1 = 0$, as in the previous discussion, one sees that every coincidence in which $v_p - v_{p+1}$ is positive is preceded by one in which it is numerically equal, but negative, and that the time interval between them is of the order of twice the mean relative velocity divided by the mean relative acceleration [given by (II-20) and (II-19), respectively], i.e., $\Delta t_c \sim (2\kappa T/A^2/M\omega_0{}^2)^{1/2}(1/\omega_0)$. It is then immediately clear that the requirement that Δt_c be large compared to Δt is equivalent to (II-21).

It may finally be remarked that the uncertainty, discussed in footnote 29, as to the proper choice of vibrational Hamiltonian to be used in computing classical orbits, would affect only the relative acceleration; hence, in the approximation represented by (II-6), in which acceleration effects are neglected altogether, this uncertainty is of no consequence.

APPENDIX III

In this appendix, the classical treatment of site-jump probabilities, given in Appendix II, is further developed to cover the case in which the electronic bandwidth parameter, J, is too large for perturbation theory to be applicable. The problem has actually been discussed rather extensively in the literature, principally from standpoint of the theory of nonadiabatic transitions between molecular potential energy curves. In the case at hand, these potential energy curves are the eigenvalues $E(x_1, \cdots, x_N)$ of the equations

$$E(x_1, \cdots, x_N)a_n(x_1, \cdots, x_N) = [V_L(x_1, \cdots, x_N) - Ax_n]a_n - J(a_{n+1} + a_{n-1}) \quad \text{(III-1)}$$

obtained from the text Eq. (5) by discarding the vibrational kinetic energies; as in Appendix II, $V_L(x_1, \cdots, x_N)$ is the vibrational potential energy

$$V_L(x_1, \cdots, x_N) = \sum_n \left(\frac{M\omega_0^2}{2} x_m^2 + \frac{M\omega_1^2}{2} x_m x_{m+1} \right). \quad \text{(III-2)}$$

If one attempts a development of the solution of (III-1) as a power series in J, via perturbation theory, one obtains

$$E^{(p)}(x_1, \cdots, x_N) = V_L(x_1, \cdots, x_N) - Ax_p - \frac{J^2}{A}\left[\frac{1}{x_p - x_{p+1}} + \frac{1}{x_p - x_{p-1}}\right] + \cdots, a_n^{(p)} \quad \text{(III-3)}$$

$$= \delta_{np} - \frac{J}{A(x_n - x_p)}[\delta_{n+1,p} + \delta_{n-1,p}] + \cdots.$$

Generally,[34] $x_p - x_{p+1} \sim A/M\omega_0^2$, so that in the case of the small polaron for which $J \ll A^2/M\omega_0^2$ (see I, Eq. 43), (III-2) and (III-3) are accurate. Within the domain of applicability of these relationships, the electronic state corresponding to a given potential-energy curve, $E^{(p)}(x_1, \cdots, x_N)$, is strongly localized about a single site, p.

However, in the neighborhood of the "crossing-points" of two potential energy curves, say, $E^{(p)}$ and $E^{(p+1)}$, (in particular, when $|x_p - x_{p+1}| < J/A$), the perturbation expansion must be modified to take account of the fact that a_p and a_{p+1} are both appreciable. One is thus led to the consideration of the two equations

$$E(x_1, \cdots, x_N)a_p = (V_L - Ax_p)a_p - Ja_{p+1}, \quad \text{(III-4)}$$

$$E(x_1, \cdots, x_N)a_{p+1} = (V_L - Ax_{p+1})a_{p+1} - Ja_p,$$

[34] In the limiting case of $\omega_1 = 0$, for example, the equilibrium x_n's are (for the small polaron), $x_p = A/M\omega_0^2$, $x_{n\neq p} = 0$.

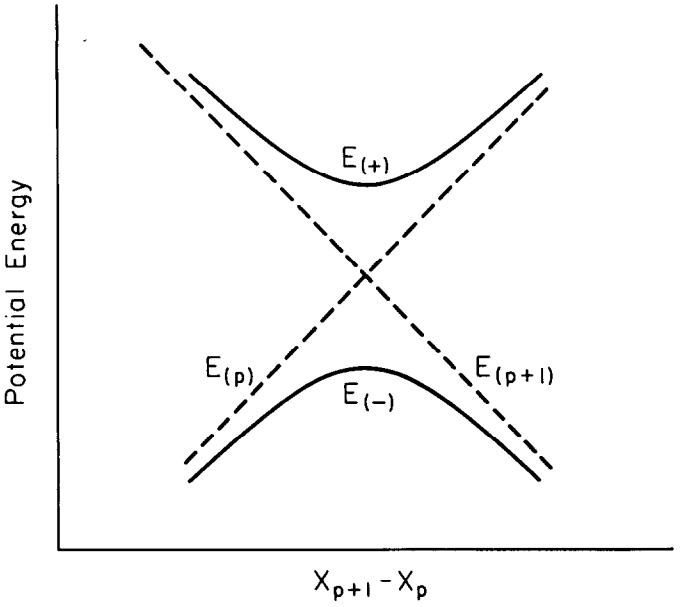

FIG. 2. Potential energy curves for the two-site system

the eigenvalues of which are

$$E_{(\pm)}(x_1, \cdots, x_N) = V_L(x_1, \cdots, x_N) - A\left(\frac{x_p + x_{p+1}}{2}\right) \pm \left\{\left[\frac{A^2(x_p - x_{p+1})^2}{4} + J^2\right]\right\}^{1/2}. \quad \text{(III-5)}$$

These two solutions are shown in Fig. 2 as the solid curves. The dashed lines, denoted by $E^{(p)}$ and $E^{(p+1)}$, give the unperturbed ($J = 0$) potential curves; they are also the asymptotic limits of the actual curves for sufficiently large $|x_{p+1} - x_p|$.

In a site jump of the type $p \rightarrow p + 1$, the system is initially in a configuration in which $x_p \gg x_{p+1}$; since the associated electronic state is localized about the p'th site, its limiting potential energy curve is $E^{(p)}$. It may thus be represented in Fig. 2 by a point which moves along the lower solid curve, $E_{(-)}$, approaching the crossing point from the left. In the neighborhood of the crossing point a variety of possibilities is available.

Firstly, the system may remain on the lower potential curve, $E_{(-)}$, continuing its motion to the right,[35] and thereby eventually attaining the region of

[35] In this discussion, as in the perturbation treatment of Appendix II, the relative velocity, $v_{p+1} - v_p$, in the vicinity of the crossing point is assumed sufficiently large so as to be considered essentially constant in this vicinity.

$x_{p+1} \gg x_p$ on the curve $E^{(p+1)}$. The net result of this process is the realization of a site-jump event.

The alternate possibility, in which the system jumps from the $E_{(-)}$ to the $E_{(+)}$ curve, on going to the right, results in a situation in which the system is moving "uphill"; it must then eventually "turn around" and reapproach the crossing point from the right. If in the latter trajectory, it jumps to the lower curve, it moves "downhill" towards the initial configuration, with the net result that no site jump takes place. On the other hand, if the system remains on the $E_{(+)}$ curve, it gets another chance to traverse the crossing region from left to right; if, in this traversal, it jumps to the $E_{(-)}$ curve, the site-jump event is realized.

By summing over all possibilities of this type, one may compute the site-jump probability, $W_c(p \to p + 1)$, in terms of the probability, P_t, of (nonadiabatic) transitions between the potential energy curves.[36] Specifically, one obtains for $W_c(p \to p + 1)$ the series

$$W_c(p \to p + 1) = 1 - P_t + P_t(1 - P_t)P_t + P_t(1 - P_t)P_t + \cdots,$$

which is readily summed, the result being

$$W_c(p \to p + 1) = 2\frac{1 - P_t}{2 - P_t}. \tag{III-6}$$

As stated above, the problem of computing P_t has been treated in the literature. In particular, an explicit solution has been given by Zener (7), which, in the notation of the present paper, reads

$$P_t = \exp\left\{-\frac{2\pi J^2}{\hbar A \mid v_p - v_{p+1} \mid}\right\}. \tag{III-7}$$

From (III-6) and (III-7) it is seen that, when $J^2 \ll \hbar A \mid v_{p+1} - v_p \mid/2\pi$, $W_c(p \to p + 1)$ reduces to

$$W_c = 2\frac{2\pi J^2}{\hbar A \mid v_{p+1} - v_p \mid} \tag{III-8}$$

which is twice the right-hand side of the perturbation result (II-9). In this limit, the system may be considered as moving up and down the zeroth order energy curve, $E^{(p)}$ (represented in Fig. 2 by the appropriately-labelled dashed line). At each of *two* transits through the crossing point (in which the relative velocity is first positive and then negative) a transfer to the $E^{(p+1)}$ curve may take place with a probability given by (II-9). The total probability (for the two transits) is then equal to the right-hand side of (III-8), as it should be.

[36] As will be seen immediately below, this probability is symmetrical in the direction of the transition ($E_\pm \to E_\mp$), and independent of the sign of the relative velocity.

In the alternate limit of $J^2 \gg \hbar A \mid v_{p+1} - v_p \mid /2\pi$, the site-jump probability, $W_c(p \rightarrow p + 1)$, is unity. In this limit the system simply stays on the lower potential curve, $E_{(-)}$, in its left-to-right motion, and thus effects an adiabatic site-jump transition, without further ado.[37]

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[37] In all of the above discussion, it has been tacitly assumed that once the system moves downhill from the crossing point (in the $E_{(-)}$ curve), in either direction, its energy gets sufficiently dissipated so that the likelihood of an immediate return (say within a time of the order of $1/\omega_0$) is negligible. Without going into this question in detail, it seems safe to say that a necessary and sufficient condition for its validity is the existence of adequate frequency dispersion. For the case in which the perturbation treatment, given in the text of this paper, applies, an estimate of the required amount of dispersion is in fact contained in the inequality (75).