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Small-polaron theory of phonon-assisted defect tunneling with quadratic defect-lattice coupling

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The usual polaronlike treatment of phonon-assisted tunneling of lattice defects is a linear-coupling theory in which the defect-lattice interaction is linear in lattice displacements. We extend the treatment to include coupling terms quadratic in lattice displacements and momenta. Both the linear and the quadratic coupling are treated to all orders in the interaction so that the resulting theory is a union of small-polaron theory with Lifshitz perturbed phonon theory. Our formal results are presented in diagramatic series form and in terms of integral equations. Approximations suitable for high- and low-temperature ranges are discussed.

I. INTRODUCTION

In a recent paper[1] one of us discussed a heuristic model of the effects of in-band defect-induced phonon resonant modes on phonon-assisted defect tunneling. The reader is referred to that paper and the references therein for a general discussion of this problem. It is the purpose of the present paper to develop a proper theory of these effects: i.e., those effects arising from the inclusion of terms quadratic in lattice coordinates and momenta in the defect-lattice Hamiltonian. These quadratic defect-lattice coupling terms are terms additional to the usual linear-coupling terms which are responsible for the well-known polaron aspects of defect tunneling.[2] The theory we develop here is not a perturbation treatment of either the linear (polaron) or the quadratic (perturbed phonon) terms in the defect-lattice interaction. It is known that low-order perturbation treatment of these effects is typically inadequate.[2,3] Both terms are treated, in effect, to all orders in the interactions; and the resulting theory may be regarded as a sort of wedding between small-polaron theory and Lifshitz perturbed-phonon theory, neither one a perturbation theory. O'Rourke[4] and Kubo and Toyozawa[5] have also investigated closely related problems. We will mention the relation to our work at appropriate places below.

In the following paper[6] we apply the theoretical developments of this paper to a specific defect system, RbCl:Ag^+. The present paper is devoted to the formal development of the theory. Section II presents the Hamiltonian we will use. In Sec. III an expression for the transition rate of interest is developed and in Sec. IV this transition rate is developed in terms of diagrammatic series. These series are formally summed in terms of integral equations in Sec. V. Sections VI–VIII discuss approximate forms of the theory which should be valid at sufficiently high and low temperatures. Two appendices discuss certain limiting forms of the diagrammatic series sums which are useful in developing the low-temperature approximation of Sec. VII

II. HAMILTONIAN

The Hamiltonian of the defect-lattice system is written[1]

$$H = H_D + H_L + H_{DL}(1) + H_{DL}(2) + H_E + H_S \,. \tag{1}$$

Here H_D is the Hamiltonian of a single defect in a rigid lattice,

$$H_D = \sum_{i,j} \Delta_{ij} |i\rangle\langle j| \,, \tag{2}$$

where the $|i\rangle$ are directed or pocket states for the defect and Δ_{ij} is a tunneling Hamiltonian matrix element between directed states.

H_L is the Hamiltonian of the ideal host lattice:

$$H_L = \frac{1}{2} \sum_{L\alpha} \left(\frac{P_{L\alpha}^2}{M_L} + V_{L\alpha;L'\alpha'} X_{L\alpha} X_{L'\alpha'} \right) = \sum_f \hbar\omega_f a_f^\dagger a_f \tag{3}$$

in terms, alternatively, of lattice displacements and momenta or phonon creation and annihilation operators. L is a site index, α a Cartesian component label, and f is a phonon normal mode index.

$H_{DL}(1)$ and $H_{DL}(2)$ are defect-lattice interaction terms linear and quadratic, respectively, in $X_{L\alpha}$ and $X_{L\alpha}$, $P_{L\alpha}$. The Condon approximation is assumed so that $H_{DL}(1)$ and $H_{DL}(2)$ are diagonal in the directed-state representation, that is,

$$H_{DL}(1) = \sum_i H_{DL}(1)_i |i\rangle\langle i| \tag{4}$$

and

$$H_{DL}(2)=\sum_i H_{DL}(2)_i|i\rangle\langle i|, \tag{5}$$

where

$$H_{DL}(1)_i=\sum_{L\alpha} L^i_{L\alpha}X_{L\alpha}$$
$$=\sum_\beta L^i_\beta X_\beta \equiv \underline{\tilde{L}}^i\cdot\underline{X}. \tag{6}$$

Here the $L^i_{L\alpha}$ are linear-coupling coefficients for the defect-lattice interaction when the defect is in directed state $|i\rangle$. In practice we will assume that the defect couples only to nearest-neighbor displacements. This is indicated in the β sum in (6). β will be used as a convenient abbreviation for those $L\alpha$ in the defect space, that is, those $L\alpha$ which correspond to the defect and its nearest neighbors. (For a defect with six nearest neighbors the defect space has dimension 21).

We will frequently write vectors with components corresponding to $L\alpha$ in the notation appearing in the last equality in (6). $\underline{\tilde{L}}^i$ is the transpose (row vector) of $\underline{L}^i$ and $\underline{\tilde{L}}^i\cdot\underline{X}$ is a vector inner product. Note that $\underline{L}^i$ has nonzero components only in the defect space.

Similarly, again limiting interaction to the nearest-neighbor defect space,

$$H_{DL}(2)_i=\frac{1}{2}\sum_{\beta\beta'}\left[P^2_\beta\left(\frac{1}{M_\beta+\delta M_\beta}-\frac{1}{M_\beta}\right)\delta_{\beta\beta'}+\delta V^i_{\beta\beta'}X_\beta X_{\beta'}\right], \tag{7}$$

where δM_β is the mass increment of the defect which is nonzero when β corresponds to the defect itself and $\delta V^i_{\beta\beta'}$ is the potential energy matrix increment introduced by the defect in directed state $|i\rangle$.

Phonon-assisted tunneling (and polaron) theory is usually studied in the approximation in which $H_{DL}(2)$ is assumed to be zero, an approximation which we will refer to as the linear-coupling theory. Inclusion of both $H_{DL}(1)$ and $H_{DL}(2)$ will be called the quadratic-coupling theory.

H_E and H_S are interactions of the defect with electric or stress bias fields and are given by

$$H_E=-\sum_i \vec{P}_i\cdot\vec{E}_i|i\rangle\langle i|, \tag{8}$$

$$H_S=\sum_i S_i|i\rangle\langle i|, \tag{9}$$

in notation given in Ref. 1.

It will be convenient to introduce the following notation

$$H_i\equiv H_L+H_{DL}(2)_i \tag{10}$$

and

$$\mathcal{H}\equiv\sum_i \mathcal{H}_i|i\rangle\langle i|, \tag{11}$$

where

$$\mathcal{H}_i\equiv H_L+H_{DL}(1)_i+H_{DL}(2)_i. \tag{12}$$

H_i is the lattice Hamiltonian without linear-coupling terms and is thus a harmonic-lattice Hamiltonian, the phonons of which can be calculated from those of H_L by standard Lifshitz theory. Note that the total Hamiltonian (1) can be written as $H=\mathcal{H}+H_D+H_E+H_S$.

III. TRANSITION RATES

As discussed in Ref. 1 a quantity of interest in describing phonon-assisted defect tunneling is the temperature-dependent transition rate for defect reorientation among directed states. The development of a theoretical expression for this quantity is the goal of this paper.

We consider transitions produced between eigenstates of $\mathcal{H}+H_E$ by the perturbation H_D, H_S being zero. Suppose the applied electric bias field is so oriented as to remove all tunneling degeneracy and make the directed states $|i\rangle$ eigenstates of H_E with eigenvalues E_i. We then have

$$(\mathcal{H}+H_E)|in_i\rangle=\left(\sum_f \hbar\omega_f n_{fi}+E_i\right)|in_i\rangle, \tag{13}$$

where

$$|in_i\rangle\equiv|i\rangle\prod_f|n_{fi}\rangle \tag{14}$$

the $|n_{fi}\rangle$ being f-mode eigenstates of H_i. As is well known, the effect of $H_{DL}(1)_i$ in H_i is to relax the equilibrium positions of the lattice atoms about the defect and that of $H_{DL}(2)_i$ to produce perturbed phonons. Thus the $|n_{fi}\rangle$ involve lattice relaxations and perturbed phonons suitable to defect orientation i.

Suppose that at $t=0$ the lattice-defect system is in state $|in_i\rangle$. The probability that the system will be in state $|jn'_j\rangle$ after time t, due to the perturbing action of the tunneling term H_D is given by

$$P(in_i\rightarrow jn'_j)=|\langle jn'_j|U(t,0)|in_i\rangle|^2, \tag{15}$$

where, to first order in H_D,

$$U(t,0)=1+\frac{1}{i\hbar}\int_0^t dt'H_D(t') \tag{16}$$

and

$$H_D(t') = \exp[i(\mathcal{H}+H_E)t'/\hbar] \times H_D \exp[-i(\mathcal{H}+H_E)t'/\hbar]. \quad (17)$$

Summing (15) over final phonon states and thermally averaging over initial phonon states, taking its time derivative and letting t go to infinity so as to get a temperature-dependent transition rate w_{ij}, one gets

$$w_{ij} = \left(\frac{\Delta ij}{\hbar}\right)^2 \int_{-\infty}^{\infty} ds \exp(ie_{ij}s) \times \langle\langle \exp(i\mathcal{H}_i s/\hbar)\exp(-i\mathcal{H}_j s/\hbar)\rangle\rangle . \quad (18)$$

In (18) we have introduced the notation

$$e_{ij} = (E_i - E_j)/\hbar \quad (19)$$

so that $\hbar e_{ij}$ is the bias-produced energy difference between states $|i\rangle$ and $|j\rangle$. Further $\langle\langle\ \rangle\rangle_i$ indicates a thermal average using the nonharmonic Hamiltonian in the ensemble weighting factor $\exp(-\mathcal{H}_i/kT)$. Equation (18) can be written in a more convenient form by use of the operator identity

$$\exp[s(P+Q)] = \exp(sP)T_\lambda \exp\left(\int_0^s Q(\lambda)\,d\lambda\right), \quad (20)$$

where $Q(\lambda) = \exp(-\lambda P)Q\exp(\lambda P)$ and T_λ is the time ordering operator (later left) to be applied on the λ parameter in the terms in the expansion of the second exponential on the right-hand side of (20). Using (20), (18) becomes

$$w_{ij} = \left(\frac{\Delta_{ij}}{\hbar}\right)^2 \int_{-\infty}^{\infty} ds \exp(ie_{ij}s) \left\langle\left\langle T_u \exp\left(\frac{i}{\hbar}\int_0^s du\, \Delta\mathcal{H}^{ij}((u))_i\right)\right\rangle\right\rangle_i , \quad (21)$$

where

$$\Delta\mathcal{H}^{ij} \equiv \mathcal{H}_i - \mathcal{H}_j \quad (22)$$

and

$$\Delta\mathcal{H}^{ij}((u))_i \equiv \exp(iu\mathcal{H}_i/\hbar)\Delta\mathcal{H}^{ij}\exp(-iu\mathcal{H}_i/\hbar). \quad (23)$$

Here, as in the double-bracket notation for the thermal average, the double parenthesis notation for Heisenberg-picture time dependence is used to emphasize that the Hamiltonian $\mathcal{H}_i$ producing this time dependence includes the linear term $H_{DL}(1)_i$ and so is not harmonic.

Notice that in $\Delta\mathcal{H}^{ij}$ the kinetic energy part of $H_{DL}(2)$, which is orientation independent, drops out leaving

$$\Delta\mathcal{H}^{ij} \equiv \sum_\beta L_\beta^{ij} X_\beta + \frac{1}{2}\sum_{\beta\beta'} \Delta V_{\beta\beta'}^{ij} X_\beta X_{\beta'} = \Delta\underline{\tilde{L}}\cdot\underline{X} + \tfrac{1}{2}\underline{\tilde{X}}\cdot\Delta\underline{V}\cdot\underline{X}. \quad (24)$$

Here $\Delta L_\beta^{ij} \equiv L_\beta^i - L_\beta^j$ and $\Delta V_{\beta\beta'}^{ij} \equiv V_{\beta\beta'}^i - V_{\beta\beta'}^j$. We will frequency drop the ij subscript or superscript, as in the last equation of (24), when no confusion can arise.

In what follows we will need to use phonon creation and annihilation operators as well as Cartesian components of lattice displacements. The connection between them is given for i phonons by[7]

$$X_{L\alpha} = \sum_f \chi_{L\alpha}^i(f) i(\hbar/2\omega_f)^{1/2}(a_f^i - a_f^{i\dagger}), \quad (25)$$

where the eigenvector $\chi^i(f)$ is defined by

$$[\underline{V}^i - \omega_f^2(\underline{M}+\delta\underline{M}^i)]\cdot\underline{\chi}^i(f) = 0, \quad (26)$$

where it is to be recalled that $\underline{V}^i$ is the full H_i potential energy $\underline{V}+\delta\underline{V}^i$. In this case the vector notation is not confined to the defect space but includes Cartesian component elements for all ions in the crystal. The $\underline{\chi}(f)$ are orthonormal with respect to $\underline{M}+\delta\underline{M}^i$

$$\underline{\tilde{\chi}}^i(f)\cdot(\underline{M}+\delta\underline{M}^i)\cdot\underline{\chi}^i(f') = \delta_{ff'} . \quad (27)$$

It will later be useful to have the harmonic Lifshitz–Green's-function matrix which is defined as

$$\underline{G}^i(\omega^2) = [\underline{V}^i - (\omega^2 + i\epsilon)(\underline{M}+\delta\underline{M}^i)]^{-1} = \lim_{\epsilon\to 0}\sum_f \underline{\chi}^i(f)\underline{\tilde{\chi}}^i(f)[\omega_f^2 - (\omega^2+i\epsilon)]^{-1}. \quad (28)$$

We note two useful facts which follow from (28):

$$\underline{G}^i(0) = \sum_f \underline{\chi}^i(f)\underline{\tilde{\chi}}^i(f)/\omega_f^2 = (\underline{V}^i)^{-1} \quad (29)$$

and

$$\operatorname{Im}\underline{G}^i(\omega^2) = \pi\sum_f \underline{\chi}^i(f)\underline{\tilde{\chi}}^i(f)\delta(\omega^2 - \omega_f^2). \quad (30)$$

Using (25), Eq. (6) becomes

$$H_{DL}(1)_i = \sum D_f^i(a_f^i - a_f^{i\dagger}), \quad (31)$$

where

$$D_f^i = \sum_\beta L_\beta^i \chi_\beta^i(f) i(\hbar/2\omega_f)^{1/2}. \quad (32)$$

To make progress in evaluating the thermal average in (21) and the Heisenberg-picture operator in (23) it is useful to eliminate $H_{DL}(1)_i$ from $\mathcal{H}_i$ by a unitary transformation. The thermal average of (21) being a trace is, of course, unaltered by this transformation. This is the polaron transformation which introduces i-dependent static relaxations into the lattice. The required unitary transformation is generated by $\exp(U_i)$ where

$$U_i = \sum_f D_f^i(a_f^i + a_f^{i\dagger})/\hbar\omega_f \tag{33}$$

which has the effects

$$e^{-U_i} X_\beta e^{U_i} = X_\beta + \delta_i X_\beta , \tag{34}$$

the static displacement of lattice coordinates just mentioned, and

$$e^{-U_i}\mathcal{H}_i e^{U_i} = H_i - E_r \tag{35}$$

in which the linear term is absent and an orientation-independent relaxation or self-trapping energy appears. Here

$$\delta_i X_\beta \equiv \left(\frac{2}{\hbar}\right)^{1/2} \sum_f \chi_\beta^i(f) i D_f^i \omega_f^{-3/2} \tag{36}$$

and the i-independent

$$E_r = \sum_f |D_f^i|^2/\hbar\omega_f . \tag{37}$$

Note that by use of (29) and (32) we can write a useful alternative form for (36):

$$\delta_i \underline{X} = -(\underline{V}^i)^{-1}\underline{L}^i . \tag{38}$$

Applying the polaron unitary transformation to the thermal average in (21) does several things: It removes the $H_{DL}(1)_i$ term from $\mathcal{H}_i$ according to (35) allowing standard methods to be used on the thermal average trace. The relaxation energy (37) drops out of the thermal average since such an average is independent of energy zero choice. Further the time-ordered exponential in (21) becomes

$$T_u \exp\left(\frac{i}{\hbar}\int_0^s du \exp(iuH_i/\hbar)[\Delta\underline{\tilde{L}}\cdot(\underline{X}+\delta_i\underline{X}) + \tfrac{1}{2}(\underline{\tilde{X}}+\delta_i\underline{\tilde{X}})\cdot\Delta\underline{V}\cdot(\underline{X}+\delta_i\underline{X})]\exp(-iuH_i/\hbar)\right) \tag{39}$$

in which we see the harmonic H_i generating the Heisenberg-picture time dependence and the appearance of static relaxations $\delta_i \underline{X}$ in $\Delta\mathcal{H}^{ij}$. Define the notation

$$\Delta D_\beta^{ij} = \Delta L_\beta^{ij} + \sum_{\beta'} \Delta V_{\beta\beta'}^{ij}\delta_i X_{\beta'} \tag{40}$$

or

$$\Delta\underline{D} = \Delta\underline{L} + \Delta\underline{V}\cdot\delta\underline{X} , \tag{40'}$$

and

$$\hbar c_{ij} \equiv \frac{1}{2}\sum_{\beta\beta'} \Delta V_{\beta\beta'}^{ij}\delta_i X_\beta \delta_i X_{\beta'} + \sum_\beta \Delta L_\beta^{ij}\delta_i X_\beta \tag{41}$$

or

$$\hbar c = \tfrac{1}{2}\delta_i\underline{\tilde{X}}\cdot\Delta\underline{V}\cdot\delta_i\underline{X} + \Delta\underline{\tilde{L}}\cdot\delta_i\underline{X} . \tag{41'}$$

In terms of these quantities the thermal average in (21) can be written

$$\left\langle\left\langle T_u \exp\left(\frac{i}{\hbar}\int_0^s du\,\Delta\mathcal{H}^{ij}((u))\right)\right\rangle\right\rangle_i = \exp(isc_{ij})\left\langle T_u \exp\left(\frac{i}{\hbar}\int_0^s du\,\Delta H^{ij}(u)\right)\right\rangle_i , \tag{42}$$

where

$$\Delta H^{ij} = \tfrac{1}{2}\underline{\tilde{X}}\cdot\Delta\underline{V}\cdot\underline{X} + \Delta\underline{D}\cdot\underline{X} , \tag{43}$$

$$\Delta H^{ij}(u)_i \equiv \exp(iH_i u/\hbar)\Delta H^{ij}\exp(-iH_i u/\hbar) \tag{44}$$

and $\langle\ \rangle_i$ indicates a thermal average using the harmonic but quadratically perturbed Hamiltonian H_i.

Note one of the effects of the polaron transformation: the ΔL of (24) has been replaced by the ΔD, given by (40), in (43). There has been, so to speak, a renormalization of the linear-coupling constant due to the presence of $H_{DL}(2)$ and linear terms in lattice displacements that come from it in the process of the lattice relaxation produced by the polaron transformation.

Thus by use of identity (20) and the polaron transformation (33)–(35), we can write the transition rate (18) in the form

$$w_{ij} = \left(\frac{\Delta_{ij}}{\hbar}\right)^2 \int_{-\infty}^{\infty} ds \exp[i(e_{ij}+c_{ij})s] \times\left\langle T_u \exp\left(\frac{i}{\hbar}\int_0^s du\,\Delta H^{ij}(u)_i\right)\right\rangle_i . \tag{45}$$

IV. DIAGRAMS

In this section we shall produce a way of handling the thermal average in (45). For this purpose it is easier to work in terms of phonon creation and annihilation operators than in terms of Cartesian components of lattice displacements. Accordingly we rewrite (43) with the help of (25) as

$$\Delta H^{ij} = \frac{1}{2}\sum_{ff'} \Delta V_{ff'}^{ij} A_f A_{f'} + \sum_f \Delta D_f^{ij} A_f \tag{46}$$

where

$$\Delta V_{ff'}^{ij} \equiv \sum_{\beta\beta'} \Delta V_{\beta\beta'}^{ij}\chi_\beta^i(f)\chi_{\beta'}^i(f')\hbar/2(\omega_f\omega_{f'})^{1/2} , \tag{47}$$

$$\Delta D_f^{ij} \equiv \sum_\beta \Delta D_\beta^{ij}\chi_\beta^i(f)(\hbar/2\omega_f)^{1/2} , \tag{48}$$

and

$$A_f \equiv i\,(a_f^i - a_f^{i\dagger})\,. \tag{49}$$

We employ a cumulant expansion to simplify the thermal average in (45) which can be written, dropping the ij superscripts, as

$$\exp\left[\ln\left\langle T_u \exp\left(\frac{i}{\hbar}\int_0^s du\,\Delta H(u)_i\right)\right\rangle\right] = \exp\left(iM_1 + \frac{i^2}{2!}M_2 + \frac{i^3}{3!}M_3 \cdots\right), \tag{50}$$

where[8]

$$M_1 = \frac{1}{\hbar}\left\langle \int_0^s du\,\Delta H(u)\right\rangle,$$

$$M_2 = \frac{1}{\hbar^2}\left(\left\langle T_u \int_0^s du_1 \int_0^s du_2\,\Delta H(u_1)\Delta H(u_2)\right\rangle - \left\langle \int_0^s du\,\Delta H(u)\right\rangle^2\right),$$

$$M_3 = \frac{1}{\hbar^3}\left(\left\langle T_u \int_0^s du_1 \int_0^s du_2 \int_0^s du_3\,\Delta H(u_1)\Delta H(u_2)\Delta H(u_3)\right\rangle\right.$$
$$\left. -3\left\langle T_u \int_0^s du_1 \int_0^s du_2\,\Delta H(u_1)\Delta H(u_2)\right\rangle\left\langle \int_0^s du\,\Delta H(u)\right\rangle + 2\left\langle \int_0^s du\,\Delta H(u)\right\rangle^3\right), \tag{51}$$

$$\vdots$$

In working out the expressions in (51) the general term arising is $\langle T_u A_{f1}(u_1)A_{f2}(u_2)\cdots A_{fn}(u_n)\rangle_i$ which can be written in terms of "pairings" with the help of Wick's theorem[9] in a way that involves only products of harmonic Green's functions,

$$\begin{aligned}\langle T_u A_f(u_1)A_{f'}(u_2)\rangle_i &= \delta_{ff'}[(n_f+1)\exp(-i\omega_f|u_1-u_2|)\\ &\quad + n_f\exp(i\omega_f|u_1-u_2|)]\\ &\equiv \delta_{ff'}\,g_f(u_1-u_2)\,,\end{aligned} \tag{52}$$

where n_f is the thermal equilibrium occupation number of the phonon state f and it is to be emphasized that these are phonons associated with the initial-state perturbed-phonon Hamiltonian H_i.

Consider one example of the application of Wick's theorem and the effect of the cumulant expansion, that of M_2. Using (46) in M_2 from (51), noting that thermal averages of products of odd numbers of A_f operators vanish, and using Wick's theorem and (52) one gets

$$\begin{aligned}M_2 = \frac{1}{\hbar^2}\int_0^s du_1\int_0^s du_2 \Bigg(\frac{1}{4}\sum_{f_1,\ldots,f_4} \Delta V_{f1f2}\,\Delta V_{f3f4}\\ \times[\delta_{f1f2}g_{f1}(0)\delta_{f3f4}g_{f3}(0) + \delta_{f1f3}g_{f1}(u_1-u_2)\delta_{f2f4}g_{f2}(u_1-u_2)\\ + \delta_{f1f4}g_{f1}(u_1-u_2)\delta_{f2f3}g_{f3}(u_1-u_2)] + \sum_{f1f2}\Delta D_{f1}\,\Delta D_{f2}\delta_{f1f2}g_{f1}(u_1-u_2)\Bigg)\\ -\frac{1}{\hbar^2}\left(\int_0^s du_1\sum_{f1f2}\Delta V_{f1f2}\delta_{f1f2}g_{f1}(0)\right)^2.\end{aligned} \tag{53}$$

We associate a diagram with the integrand of each term in (53). This is shown in Fig. 1 where a circle with two points of attachment corresponds to a ΔV_{f1f2} factor, a line to a harmonic Green's function (52), and a dot with only a single point of attachment to a factor ΔD_f. One notices that the fifth term in (53) cancels the term corresponding to the first unconnected diagram, Fig. 1(a). This is a general feature of the diagrams coming from the cumulant expansion (50), (51); only the linked diagrams survive.

The nonzero linked nth-order diagrams are of two types, called circle and dot diagrams, shown in Fig. 2. Each must be given a combinatorial

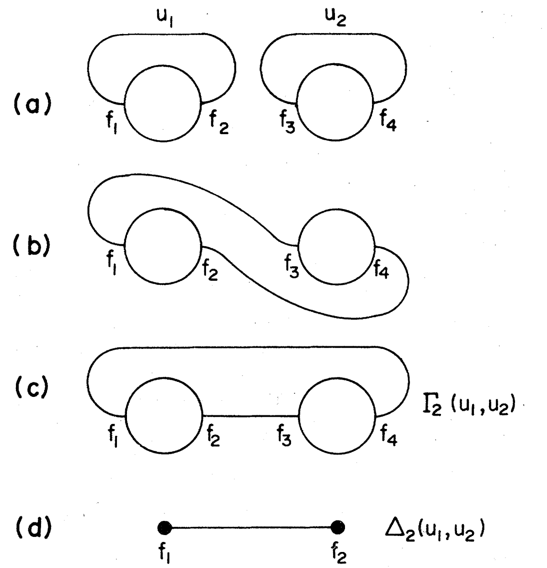

FIG. 1. Second-order diagrams associated with M_2, Eq. (53). (a)–(c) are diagrams associated with terms in the same sequence as those appearing in Eq. (53).

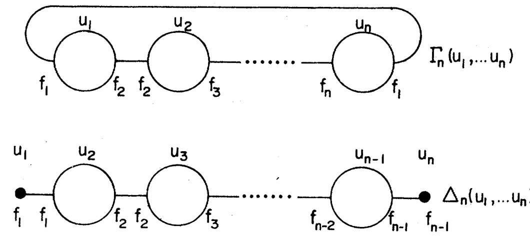

FIG. 2. Nonzero linked nth-order circle and dot diagrams.

weighting factor according to the number of times it or a permutation of it with the same integral occurs in M_n. For the circle diagrams this weighting factor is $(n-1)!2^{n-1}$ and for the dot diagrams it is $n!2^{n-3}$.

We introduce the following notation for dot-diagram integrands including combinatorial factors and the cumulant expansion factors of (50):

$$\Delta_n(u_1,\ldots,u_n)\equiv\left(\frac{i}{\hbar}\right)^n\sum_{f1\cdots f(n-1)}\Delta D_{f1}g_{f1}(u_1-u_2)\Delta V_{f1f2}g_{f2}(u_2-u_3)\cdots\Delta V_{f(n-2)f(n-1)}g_{f(n-1)}(u_{n-1}-u_n)\Delta D_{fn} \tag{54}$$

and similarly for the circle-diagram integrands

$$\Gamma_n(u_1,\ldots,u_n)=\left(\frac{i}{\hbar}\right)^n\sum_{f1\cdots fn}\Delta V_{f1f2}g_{f2}(u_1-u_2)\cdots\times\Delta V_{fnf1}g_{f1}(u_n-u_1)\,. \tag{55}$$

We can, using (54) and (55) in (50) substituted into (45), write

$$w_{ij}=\left(\frac{\Delta_{ij}}{\hbar}\right)^2\int_{-\infty}^{\infty}ds\,\exp[i(e_{ij}+c_{ij})s]\times\exp[F_d(s)+F_c(s)]\,, \tag{56}$$

where the dot-diagram series is

$$F_d(s)=\frac{1}{2}\left(\int_0^s du_1\int_0^s du_2\,\Delta_2(u_1,u_2)+\int_0^s du_1\int_0^s du_2\int_0^s du_3\,\Delta_3(u_1,u_2,u_3)+\cdots\right) \tag{57}$$

and the circle-diagram series is

$$F_c(s)=\frac{1}{2}\left(\int_0^s du_1\,\Gamma_1+\frac{1}{2}\int_0^s du_1\int_0^s du_2\,\Gamma_2(u_1,u_2)+\frac{1}{3}\int_0^s du_1\int_0^s du_2\int_0^s du_3\,\Gamma_3(u_1,u_2,u_3)+\cdots\right). \tag{58}$$

Thus we have changed the thermal average of the time-ordered exponential of (45) into the diagrammatic expansion of (56)–(58), and (56) is the main result of this paper. Figure 3 shows a pictorial representation of $F_d(s)$ and $F_c(s)$. Notice that if $H_{DL}(2)=0$, all the circle diagrams disappear and the only surviving term is the first one of $F_d(s)$ in (57), the term corresponding to the diagram Fig. 1(d). In this case $F_c(s)=0$. Thus the linear-theory is recovered by suppressing all circle diagrams.

V. INTEGRAL EQUATIONS

Because the defect space has a low dimensionality (21 for defect plus 6 nearest neighbors) compared with the very large dimensionality of the f space ($\approx 10^{23}$), it is more convenient in actual cal-

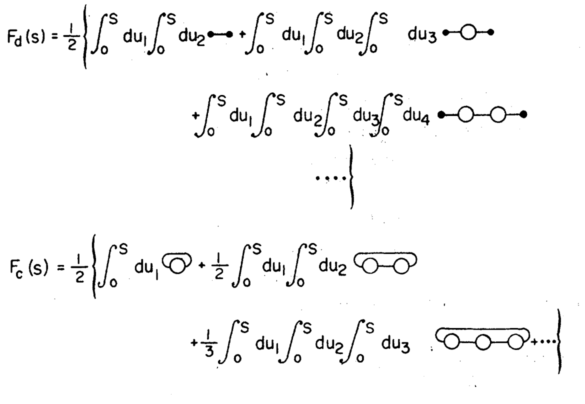

FIG. 3. Pictorial representations of the diagrammatic expansions of $F_d(s)$, Eq. (57): and $F_c(s)$, Eq. (58).

culations to work in terms of the Cartesian components β rather than in the normal-mode space. We define

$$h_{\beta\beta'}(u_1-u_2)\equiv\hbar\sum_f\chi_\beta(f)\chi_{\beta'}(f)\,g_f(u_1-u_2)/2\omega_f\,. \quad (59)$$

This function $h_{\beta\beta'}$ can be expressed in terms of the imaginary part of a Lifshitz–Green's-function matrix element. Using (30) we see that

$$h_{\beta\beta'}(u_1-u_2)=\frac{\hbar}{\pi}\int d\omega^2\,\mathrm{Im}\,\frac{G^i_{\beta\beta'}(\omega^2)}{2\omega}\,g_\omega(u_1-u_2)\,. \quad (60)$$

This form of $h_{\beta\beta'}$ is useful since $G^i_{\beta\beta'}(\omega^2)$ for perturbed phonons is a readily calculated quantity and the h matrix is only needed in the defect space.

Using (59) we can express Δ_n Eq. (54) and Γ_n Eq. (55) in alternative form

$$\Delta_n(u_1,\ldots,u_n)=\left(\frac{i}{\hbar}\right)^n\sum_{\beta1\ldots\beta(2n-2)}\Delta D_{\beta1}h_{\beta1\beta2}(u_1-u_2)\times\Delta V_{\beta2\beta3}h_{\beta3\beta4}(u_3-u_2)\times\Delta V_{\beta4\beta5}\cdots\Delta D_{\beta(2n-2)} \quad (61)$$

and

$$\Gamma_n(u_1,\ldots,u_n)=\left(\frac{i}{\hbar}\right)^n\sum_{\beta1\ldots\beta n}\Delta V_{\beta1\beta2}h_{\beta1\beta2}(u_1-u_2)\times\Delta V_{\beta3\beta4}h_{\beta3\beta4}(u_2-u_3)\cdots\times h_{\beta(n-1)\beta1}(u_{n-1}-u_1)\,. \quad (62)$$

In this β-Cartesian-component representation we gain the advantage of having sums restricted to the relatively small defect space but pay the price of having nondiagonal $h_{\beta\beta'}$ in place of the diagonal $g_{ff'}$ functions.

The sum $F_d(s)$ Eq. (57) can be expressed in terms of the solution of an integral equation using (61) for Δ_n and defining the generalized matrix

$$M^{u1u2}_{\beta1\beta2}\equiv\frac{i}{\hbar}\sum_{\beta3}\Delta V_{\beta1\beta3}h_{\beta3\beta2}(u_1-u_2) \quad (63)$$

and the generalized matrix product,

$$(M^2)^{u1u2}_{\beta1\beta2}=\sum_{\beta3}\int_0^s du_3\,M^{u1u3}_{\beta1\beta3}M^{u3u2}_{\beta3\beta2}\,. \quad (64)$$

We note that we can write

$$F_d(s)=\frac{1}{2}\left(\frac{i}{\hbar}\right)^2\int_0^s du_1\int_0^s du_2\int_0^s du_3\sum_{\beta1\beta2\beta3}\Delta D_{\beta1}h_{\beta1\beta2}(u_1-u_2)(1+M+M^2+\cdots)^{u2u3}_{\beta2\beta3}\Delta D_{\beta3}\,, \quad (65)$$

where

$$1^{u1u2}_{\beta2\beta3}=\delta_{\beta2\beta3}\delta_s(u_1-u_2)\,, \quad (66)$$

δ_s being a Dirac delta function over the finite interval 0 to s.

The generalized matrix $1+M+M^2+\cdots$ in (65) is formally the same as $R\equiv(1-M)^{-1}$. The generalized matrix is thus defined by the requirement $R(1-M)=1$ or

$$\sum_{\beta3}\int_0^s du_3(1^{u1u3}_{\beta1\beta3}-M^{u1u3}_{\beta1\beta3})R^{u3u2}_{\beta3\beta2}=1^{u1u2}_{\beta1\beta2}\,. \quad (67)$$

The quantity we actually need in (65) is

$$\theta^{u1}_{\beta1}(s)\equiv\sum_{\beta2}\int_0^s du_2\,R^{u1u2}_{\beta1\beta2}\Delta D_{\beta2}\,. \quad (68)$$

Multiplying (67) by $\Delta D_{\beta2}$, summing over β_2, integrating over u_2, and using (63) we get an integral equation for the θ of (68):

$$\underline{\theta}^{u_1}(s)=\frac{i}{\hbar}\int_0^s du_2\,\Delta\underline{V}\cdot\underline{h}(u_1-u_2)\cdot\underline{\theta}^{u_2}(s)+\Delta\underline{D} \quad (69)$$

which is confined to the defect space. In terms of the solution of (69),

$$F_d(s)=\frac{1}{2}\left(\frac{i}{\hbar}\right)^2\int_0^s du_1\int_0^s du_2\,\Delta\underline{\tilde{D}}\cdot\underline{h}(u_1-u_2)\cdot\underline{\theta}^{u_2}(s)\,. \quad (70)$$

The u_2 integration can be done by use of (69) to give

$$F_d(s)=\frac{i}{2\hbar}\int_0^s du_1\,\Delta\tilde{\underline{D}}\cdot\Delta\underline{V}^{-1}\cdot[\underline{\theta}^{u_1}(s)-\Delta\underline{D}]. \quad (71)$$

Thus solution of the integral equation (69) and performance of the integral (71) would be equivalent to summation of the series (57).

$F_c(s)$ can be found in a similar way with the complication of the $1/n$ factors in the series (58). Using the generalized matrix M, Eq. (63), one finds

$$F_c(s)=\frac{1}{2}\sum_{\beta}\int_0^s du\,(M+\tfrac{1}{2}M^2+\tfrac{1}{3}M^3+\cdots)^{uu}_{\beta\beta}. \quad (72)$$

Put a factor ξ into $\Delta\underline{V}$ so that M has a factor of ξ in it. Then

$$F_c(s)=\frac{1}{2}\sum_{\beta}\int_0^s du\int_0^1\frac{d\xi}{\xi}K^{uu}_{\beta\beta}(\xi,s), \quad (73)$$

where

$$K^{uu}_{\beta\beta}(\xi,s)\equiv(\xi M+\xi^2M^2+\ldots)^{uu}_{\beta\beta} \quad (74)$$

which is given by the integral equation

$$K^{u1u2}_{\beta1\beta2}(\xi,s)=\xi\sum_{\beta3}\int_0^s du_3 K^{u1u3}_{\beta1\beta3}(\xi,s)M^{u3u2}_{\beta3\beta2}+\xi M^{u1u2}_{\beta1\beta2}. \quad (75)$$

The summation (58) is thus equivalent to the solution of (75) and the use of (73).

The matrix-integral equations (69) and (75) are confined to the defect space and it is conceivable that they could be solved numerically, used in (71) and (73) and eventually in the numerical evaluation of the Fourier integral of (56). If such a program could be carried out it would constitute a solution of the quadratic-coupling phonon-assisted tunneling problem; it has not, however, been undertaken as yet in the general case. For the special case in which $\Delta V_{ff'}$ is diagonal in f and f' a solution of the integral equations is possible and the results achieved are those of O'Rouke.[4] Kubo and Toyazawa's[5] solution of the general quadratic-coupling problem requires taking the square root of the complete perturbed-lattice potential energy matrix, an object that does not appear to be readily calculable.

In the next sections we discuss approximations for $F_d(s)$ and $F_c(s)$ which are useful at appropriately high and low temperatures.

VI. HIGH-TEMPERATURE APPROXIMATION

We will use the Holstein method of steepest descents[10] to get an approximation of Eq. (56) which is suitable at sufficiently high temperatures. For the linear-coupling theory in the long-wave Debye approximation[1] this approximation turns out to be a good one for temperatures above about $\frac{1}{2}$ of the Debye temperature. The steepest descents approximation replaces $F_d(s)+F_c(s)$ by its Taylor's expansion about $s=0$ up to second order. The Fourier integral in (56) can then be performed analytically leading to an Arrhenius-like form for the dependence of w_{ij} on T.

Using (54), (55), (56), and (57) one finds that $F_d(0)$ and $F_d'(0)$ are zero and

$$\begin{aligned}F_d''(0)&=-\frac{1}{\hbar^2}\sum_f\Delta\bar{D}_f(2\bar{n}_f+1)\Delta\bar{D}_f\\&=-\frac{1}{2\pi\hbar}\int d\omega^2\,\Delta\tilde{\underline{D}}\cdot\mathrm{Im}\underline{G}^i(\omega^2)\cdot\Delta\underline{D}(2n_\omega+1)/\omega\,.\\&\equiv-2b_d\,.\end{aligned} \quad (76)$$

Similarly, using (58), $F_c(0)=0$ and

$$\begin{aligned}F_c'(0)&=\frac{i}{2\hbar}\sum_f\Delta V_{ff}(2\bar{n}_f+1)\\&=\frac{i}{4\pi}\int d\omega^2\,\mathrm{Tr}\,\Delta\underline{V}\,\mathrm{Im}\,\underline{G}^i(\omega^2)(2\bar{n}_\omega+1)/\omega\\&\equiv ia_c\end{aligned} \quad (77)$$

and

$$\begin{aligned}F_c''(0)&=-\frac{1}{2\hbar^2}\sum_{ff'}\Delta V_{ff'}\Delta V_{f'f}(2n_f+1)(2n_{f'}+1)\\&=-\frac{1}{8\pi^2}\int d\omega^2\int d\omega'^2\,\mathrm{Tr}\Delta\underline{V}\,\mathrm{Im}\,\underline{G}^i(\omega^2)\Delta\underline{V}\,\mathrm{Im}\,\underline{G}^i(\omega'^2)\\&\qquad\times(2n_\omega+1)(2n_{\omega'}+1)/(\omega\omega')\\&\equiv-2b_c\,.\end{aligned} \quad (78)$$

Using these quantities we have the high-temperature approximation

$$\begin{aligned}w_{ij}&=(\Delta/\hbar)^2\int_{-\infty}^{\infty}ds\,\exp[i(e+c)s]\\&\qquad\times\exp[F(0)+F'(0)s+\tfrac{1}{2}F''(0)s^2]\\&=(\Delta/\hbar)^2\int_{-\infty}^{\infty}ds\,e^{ias}e^{-bs^2}\\&=(\Delta/\hbar)^2(\pi/b)^{1/2}\exp(-a^2/4b)\,,\end{aligned} \quad (79)$$

where $F=F_d+F_c$, c is given by (41′), e by (19), and

$$a\equiv e+c+a_c\,, \quad (80)$$

$$b\equiv\bar{b}_d+b_c\,. \quad (81)$$

Although ij subscripts have been omitted from the quantities in (79) for brevity we must remember that they do depend on the initial and final defect states and will differ for nonequivalent defect orientation transitions.

Note how the high-temperature approximate w_{ij} (79) differs in the quadratic-coupling case from the linear-coupling case. If $H_{DL}(2)$ is set equal to zero, a number of things occur: first, the temperature-dependent circle-diagram terms a_c and b_c drop out of a and b. This leaves the temperature-independent $a=e+c$ which is characteristic of the linear-coupling theory. Second, the constant c is altered by the loss of the first term in (41′). Third, the term b_d in (81), defined in (76), becomes altered by the fact that ΔD loses its second term in (40′) and the Liftshitz-Green's-function matrix $G^i(\omega^2)$ loses its i dependence, that is, becomes that of the ideal host lattice rather than the defect-perturbed lattice.

For this linear-coupling case it is known that for sufficiently high T the exponent $a^2/4b$ in (79) becomes proportional to T^{-1} and the rate w_{ij} in this hopping regime shows Arrhenius or activated T behavior. Due to the presence of the temperature-dependent terms a_c and b_c in the quadratic-coupling case it is not immediately obvious that the Arrhenius behavior will survive when $H_{DL}(2)$ is introduced into the problem. We will investigate this question in connection with a specific system in the following paper.[6]

VII. ONE-PHONON F APPROXIMATION

It is not as easy to find a low-temperature approximation to (56) as it is to find a high-temperature approximation. In Sec. VI the process of making a Taylor's expansion of $F(s)$ to $O(s^2)$ automatically truncated the infinite series (57) and (58). At low temperatures the steepest-descents approximation ceases to be valid and this truncation does not occur. We have seen in Sec. IV how the presence of the circle vertices coming from $H_{DL}(2)$ produce very considerable complications of the form of the exponent $F=F_d+F_c$. In the absence of $H_{DL}(2)$ F comes from the single dot diagram of Fig. 1(d), a diagram which involves a single harmonic Green's-function factor g_f. Higher-order diagrams, which occur in the quadratic-coupling theory involve more and more g_f factors indicating the participation of more and more phonons. At sufficiently low temperatures we shall suppose that the "one phonon part" of $F(s)$ is most important part. We now explain what we mean by this.

Consider successively the terms in the series (57) for F_d. The first terms involve the integrals

$$I_2(s)=\int_0^s du_1\int_0^s du_2\, g_f(u_1-u_2)\,, \tag{82}$$

$$I_3(s)=\int_0^s du_1\int_0^s du_2\int_0^s du_3\, g_f(u_1-u_2)\, g_{f'}(u_2-u_3)\,. \tag{83}$$

In evaluating these integrals we define the notation

$$j_f(u)\equiv-(n_f+1)e^{-i\omega_f u}+n_f e^{i\omega_f u}\,, \tag{84}$$

$$\begin{aligned} h_f(s)&\equiv\int_0^s du\, j_f(u)\\ &=(i/\omega_f)[(2n_f+1)-(n_f+1)e^{-i\omega_f s}-n_f e^{i\omega_f s}]\,, \end{aligned} \tag{85}$$

and note that

$$\int_0^s du_1\, g_f(u_1-u_2)=(1/i\omega_f)[2+j_f(u_2)+j_f(s-u_2)]\,. \tag{86}$$

It then follows that

$$I_2(s)=(2/i\omega_f)[s+h_f(s)]\,, \tag{87}$$

$$\begin{aligned} I_3(s)=&\left(\frac{2}{i\omega_f}\right)\left(\frac{2}{i\omega_{f'}}\right)\\ &\times\left(s+h_f(s)+h_{f'}(s)+\frac{1}{2}\int_0^s du\, j_f(u)j_{f'}(u)\right.\\ &\left.+\frac{1}{2}\int_0^s du\, j_f(u)j_{f'}(s-u)\right)\,. \end{aligned} \tag{88}$$

We note from (84) that the last two terms of (88) involve products of one-phonon functions j_f and $j_{f'}$. We eliminate such contributions in our one-phonon selection process and write

$$I_3'(s)=\left(\frac{2}{i\omega_f}\right)\left(\frac{2}{i\omega_{f'}}\right)[s+h_f(s)+h_{f'}(s)]\,, \tag{89}$$

where the prime indicates that we have eliminated all except the one-phonon terms. By eliminating terms which involve products of n's and $(n+1)$'s we are eliminating all terms corresponding to omission and or absorption of more than one phonon. Note that $I_2'=I_2$. Continuing this process, one finds

$$\begin{aligned} I_4'(s)=&\left(\frac{2}{i\omega_f}\right)\left(\frac{2}{i\omega_{f'}}\right)\left(\frac{2}{i\omega_{f''}}\right)\\ &\times[s+h_f(s)+h_{f'}(s)+h_{f''}(s)]\,. \end{aligned} \tag{90}$$

The emerging pattern is clear from inspection of (87), (89), and (90). Keeping just one-phonon parts of the terms we have as $F_d'(s)$, the one-phonon version of $F_d(s)$,

$$F_d'(s)=\frac{i}{2\hbar}\left[\sum_f \Delta D_f \Delta D_f \frac{2}{\hbar\omega_f}[s+h_f(s)]+\sum_{ff'} \Delta D_f \Delta V_{ff'} \Delta D_{f'}\left(\frac{2}{\hbar\omega_f}\right)\left(\frac{2}{\hbar\omega_{f'}}\right)[s+h_f(s)+h_{f'}(s)]\right.$$
$$\left.+\sum_{ff'f''} \Delta D_f \Delta V_{ff'} \Delta V_{f'f''} \Delta D_{f''}\left(\frac{2}{\hbar\omega_f}\right)\left(\frac{2}{\hbar\omega_{f'}}\right)\left(\frac{2}{\hbar\omega_{f''}}\right)[s+h_f(s)+h_{f'}(s)+h_{f''}(s)]+\cdots\right]$$
$$\equiv ic_d's-2R_d'+G_d'(s)\,, \tag{91}$$

where c_d', R_d', and $G_d'(s)$ will be defined presently.

Consider first the sum coming from the terms s which occur at the beginning of the square brackets in (91) and call this part of the sum $ic_d's$. It turns out that this sum exactly cancels the prefactor $\exp(ic_{ij}s)$ in (56). This can be seen as follows. First collect the terms in (91) which come from the s in the square brackets, reexpress the ΔD_f and $\Delta V_{ff'}$ using (47) and (48), eliminate the χ's by use of (29) and one finds

$$\hbar c_d'=\tfrac{1}{2}\Delta\underline{\tilde{D}}\cdot\underline{V}_i^{-1}[1+\underline{V}_i^{-1}\Delta\underline{V}+(\underline{V}_i^{-1}\Delta\underline{V})^2+\cdots]\cdot\Delta\underline{D}. \tag{92}$$

The sum in (92)is recognized to be

$$(\underline{1}-\Delta\underline{V}\underline{V}_i^{-1})^{-1}=\underline{V}_i\underline{V}_j^{-1} \tag{93}$$

so that

$$\hbar c_d'=\tfrac{1}{2}\Delta\underline{\tilde{D}}\cdot\underline{V}_j^{-1}\cdot\Delta\underline{D}. \tag{94}$$

We have changed the superscript on V^i to a subscript to simplify the notation. Now, use (38) in (41′). Using (40′) and (38) in (94) one finds that $c_d'=-c_{ij}$ which accomplishes the cancellation mentioned.

The next part of $F_d'(s)$ to be considered is that part $-2R_d'$, independent of s. The notation is dictated by the fact that R_d' becomes a dressing exponent analogous to the exponent R of Ref. 1, Eq. (23). This s-independent part of $F_d'(s)$ comes from the $2n_f+1$ terms of the $h_f(s)$ functions. Collecting these parts of (91), using (47), (48), and (29) and summing the series as in (92) one finds

$$R_d'=\frac{1}{4\pi\hbar}\int d\omega^2\,\frac{2n_\omega+1}{\omega^3}\,\Delta\underline{\tilde{D}}\cdot\underline{V}_j^{-1}\underline{V}_i$$
$$\times\operatorname{Im}\underline{G}^i(\omega^2)\underline{V}_i\,\underline{V}_j^{-1}\cdot\Delta\underline{D}. \tag{95}$$

It remains to collect and sum those parts of $F_d'(s)$ which come from the s-dependent parts of the h_f functions, the parts proportional to

$$\gamma_f(s)\equiv(n_f+1)e^{-i\omega_f s}+n_f e^{i\omega_f s}. \tag{96}$$

Denoting this part as $G_d'(s)$ and proceeding as before one finds

$$G_d'(s)=\frac{1}{2\pi\hbar}\int d\omega^2\frac{\gamma_\omega(s)}{\omega^3}\,\Delta\underline{\tilde{D}}\cdot\underline{V}_j^{-1}\underline{V}_i$$
$$\times\operatorname{Im}\underline{G}^i(\omega^2)\,\underline{V}_i\,\underline{V}_j^{-1}\cdot\Delta\underline{D}. \tag{97}$$

If $H_{DL}(2)=0$, V_i becomes equal to V_j and the potential energy matrices drop out of (95). Also the ΔD revert to their linear-coupling form and $G^i(\omega^2)$ becomes the unperturbed $G(\omega^2)$ leaving exactly the linear-coupling case result which is presented in Ref. 1.

Some insight into the meaning of the i and j potential energy matrices in (95) and (97) can be gained by using (40′) for ΔD and remembering (38) for $\delta_i X$ along with the analogous expression for $\delta_j X$ to write

$$\Delta\underline{\tilde{D}}\cdot\underline{V}_j^{-1}\underline{V}_i\operatorname{Im}\underline{G}^i(\omega^2)\underline{V}_i\,\underline{V}_j^{-1}\cdot\Delta\underline{D}$$
$$=(\delta_i\underline{\tilde{X}}-\delta_j\underline{\tilde{X}})\cdot\underline{V}_i\operatorname{Im}\underline{G}^i(\omega^2)\,\underline{V}_i\cdot(\delta_i\underline{X}-\delta_j\underline{X}). \tag{98}$$

Thus, one can see that the role of the $V_j^{-1}V_i$ and $V_i V_j^{-1}$ factors is to introduce the difference of i-relaxed initial and j-relaxed final lattice configurations into the displaced-harmonic-oscillator overlap integral, which is responsible[10] for the dressing factor $\exp(-R)$. It is interesting to see the formalism producing a statically relaxed final j state. This result, though certainly plausible, is not entirely obvious in our treatment since the final phonon states drop out of the formalism in the summation which produces Eq. (18).

We still have to extract the one-phonon part from the circle diagrams. Using the same procedure as we did in getting $F_d'(s)$ we did find that only the first term in the series (58) contributes with the result

$$F_c'(s)=\frac{is}{2\hbar}\sum_f V_{ff}(2n_f+1)$$
$$=\frac{is}{4\pi}\int d\omega^2\operatorname{Tr}\Delta\underline{V}\operatorname{Im}\underline{G}^i(\omega^2)(2n_\omega+1)/\omega$$
$$=ia_c s\,, \tag{99}$$

where in the last line we note that the coefficient a_c is the same as the quantity a_c arising in the high-temperature approximation in (77).

By using (91) and (99) one finds that the transition rate w'_{ij} in the one-phonon F approximation is

$$w'_{ij}=\left(\frac{\Delta}{\hbar}\exp(-R'_d)\right)^2\int_{-\infty}^{\infty}ds\,\exp[i(e+a_c)s]\times\exp[G'_d(s)] \qquad (100)$$

with a_c given by (99), R'_d by (95), and $G'_d(s)$ by (97). We will now argue that the term a_c in this expression should be omitted.

The term a_c in (100) plays the role of a temperature-dependent biaslike term added to the true bias term e. Its presence would imply that the energy difference between the initial and final defect states would be $\hbar(e+a_c)$ rather than the bias $\hbar e$. The term $\hbar a_c$ would thus be an additional initial-final state transition energy difference beyond that produced by the applied bias. Since a_c depends on $H_{DL}(2)$ but not on $H_{DL}(1)$ its presence cannot indicate some nonadiabatic time dependence of the dressing relaxations since these are determined by $H_{DL}(1)$ and not $H_{DL}(2)$. In any case the form of (98) suggests that the final j state is indeed a j-relaxed state. These observations arouse suspicion concerning the circle-diagram contribution to the one-phonon F approximation. We will, in fact, reject the ia_cs term in (100) on the ground that ia_cs does not correctly represent the large-s behavior of $F_c(s)$. This is discussed in Appendix A. The long-time nonoscillatory behavior of $F_d(s)$, on the other hand, is correctly given by ic'_ds as in (91) and we retain it. This is discussed in Appendix B.

VIII. FIRST-ORDER APPROXIMATION

In the usual linear-coupling theory with $H_{DL}(2)=0$ it is customary to expand the analog of $\exp[G'_d(s)]$ in powers of $G'_D(s)$ at low temperatures thereby getting a series which describes phonon-assisted tunneling processes which involve zero, one, two, . . . phonons to conserve energy. This approximation, which is of questionable validity[1] when $H_{DL}(2)\neq 0$, would be yet another stage of approximation beyond that of the one-phonon version of F_d+F_c. We will list the first-order term $w'^{(1)}_{ij}$ in the $\exp[G'_d(s)]$ expansion here for completeness.

$$w'^{(1)}_{ij}=\left(\frac{\Delta}{\hbar}\exp(-R'_d)\right)^2\left(\frac{2}{\hbar e^2}\right)(n_e+1)\times\Delta\underline{\tilde{D}}\cdot\underline{V}_j^{-1}\underline{V}_i\,\mathrm{Im}\,\underline{G}^i(e^2)\underline{V}_i\,\underline{V}_j^{-1}\cdot\Delta\underline{D}. \qquad (101)$$

If we set $H_{DL}(2)=0$ and use Debye phonons to calculate $\mathrm{Im}\,G^i(e^2)$ we can recover from (101) the linear-coupled Debye one-phonon rate Eq. (30) of Ref. 1.

APPENDIX A: ASYMPTOTIC BEHAVIOR OF $F_c(s)$

There is a subset of terms in (58), the circle-diagram series for $F_c(s)$, which can be summed. The one-phonon term $F'_c(s)$ given by (99) is among these terms. We will show in this Appendix that the sum of the subset of terms vanishes as $s\to\infty$.

Consider a Taylor's expansion of $F_c(s)$ about $s=0$. The nth-order term in this series will have a contribution which comes from the n derivatives with respect to the upper integration limits of the nth term in series (58). These n derivatives can be taken in $n!$ sequences so the $n!$ Taylor's-series denominator will be cancelled by this factor. Many other terms, i.e., those involving derivatives of the integrands, contribute to the nth Taylor coefficient. We limit ourselves to the subset which excludes these other terms and call this partial summation of the terms of the $F_c(s)$ series $F_{cp}(s)$:

$$F_{cp}(s)\equiv\frac{1}{2}\left[\frac{i}{\hbar}\sum_f\Delta V_{ff}(2n_f+1)s+\frac{1}{2}\left(\frac{i}{\hbar}\right)^2\sum_{ff'}\Delta V_{ff'}(2n_f+1)\times\Delta V_{f'f}(2n_{f'}+1)s^2+\cdots\right] \qquad (A1)$$

or, symbolically in an obvious notation,

$$F_{cp}(s)=\tfrac{1}{2}\,\mathrm{Tr}[s(i\,\Delta\underline{V}\underline{N}/\hbar)+\tfrac{1}{2}s^2(i\Delta\underline{V}\underline{N}/\hbar)^2+\cdots] \qquad (A2)$$

where the $\underline{N}$ matrix has elements

$$N_{ff'}=\delta_{ff'}(2n_f+1)\,. \qquad (A3)$$

In the defect space one finds, using (47) and (30),

$$\Delta\underline{V}\underline{N}=\Delta\underline{V}\int d\omega^2\,\mathrm{Im}\,\underline{G}^i(\omega^2)\,\frac{2n_\omega+1}{2\pi\omega}\equiv\hbar\,\Delta\underline{V}\,\underline{F} \qquad (A4)$$

which is a matrix of small dimension. In these terms

$$F_{cp}(S)=\tfrac{1}{2}\,\mathrm{Tr}[is\,\Delta\underline{V}\,\underline{F}+(\tfrac{1}{2}is)^2(\Delta\underline{V}\,\underline{F})^2+\cdots]=-\tfrac{1}{2}\,\mathrm{Tr}\ln(1-is\,\Delta\underline{V}\,\underline{F})\,. \qquad (A5)$$

Suppose the eigenvalues of the matrix $\Delta\underline{V}\,\underline{F}$ are $\lambda_j=\alpha_j+i\beta_j$. Then the argument of the logarithm, in the representation which diagonalizes $\Delta\underline{V}\,\underline{F}$ is diagonal and the trace becomes a sum:

$$F_{cp}(S) = -\tfrac{1}{2}\sum_j \ln[1 - is(\alpha_j + i\beta_j)]$$
$$= -\tfrac{1}{2}\left(\sum_j \tfrac{1}{2}\ln[(1+\beta_j s)^2 + (\alpha_j s)^2] - i\sum_j \tan^{-1}[\alpha_j s/(1+\beta_j s)]\right). \tag{A6}$$

As $s \to \infty$ the real part of F_{cp} goes to $-\infty$. The imaginary part becomes a finite constant unlike $F_c'(s)$ of Eq. (99) which is $ia_c s$, imaginary and proportional to s. Since $F_{cp}(s)$ is a more complete partial summation of $F_c(s)$ than is $F_c'(s)$ we have rejected the a_c term in (100).

APPENDIX B: ASYMPTOTIC BEHAVIOR OF $F_d(s)$

We start from (71) for $F_d(s)$ and notice that if $\underline{\theta}^u(s)$ had a part which was independent of u and s then this would contribute a term in $F_d(s)$ which would be proportional to s. With this in mind, write

$$\underline{\theta}^u(s) = \underline{c} + \underline{f}^u(s) \tag{B1}$$

and substitute this trial solution into (69) to get

$$\underline{c} + f^u(s) = \Delta\underline{D} + \int_0^s du_1 \underline{K}(u-u_1)[\underline{c} + \underline{f}^{u1}(s)], \tag{B2}$$

where we have used the notation

$$\underline{K}(u-u_1) \equiv i\Delta\underline{V}\underline{h}(u-u_1)/\hbar. \tag{B3}$$

The first term in the integration in (B2) can be evaluated using (86) to give

$$\underline{c} + \underline{f}^u(s) = \Delta\underline{D} + \Delta\underline{V}\,\underline{V}_i^{-1}\underline{c} + \underline{E}^u(s) + \int_0^s du_1 \underline{K}(u-u_1)\underline{f}^{u1}(s), \tag{B4}$$

where we have used (29) and $\underline{E}^u(s)$ is given by

$$\underline{E}^u(s) \equiv \Delta\underline{V}\int d\omega^2\, \mathrm{Im}\,\underline{G}^i(\omega^2)[j_\omega(u) + j_\omega(s-u)]\,\frac{c}{2\pi\omega^2}. \tag{B5}$$

The j functions are defined by (84).

The constant parts of (B4) cancel if we set

$$\underline{c} = \underline{V}_i\,\underline{V}_j^{-1}\Delta\underline{D}. \tag{B6}$$

This leaves as the equation for $\underline{f}^u(s)$:

$$\underline{f}^u(s) = \underline{E}^u(s) + \int_0^s du_1 \underline{K}(u-u_1)\underline{f}^{u1}(s) \tag{B7}$$
$$\equiv \underline{E}^u(s) + \underline{\mathcal{K}}\,\underline{f}^u(s), \tag{B7$'$}$$

where $\underline{\mathcal{K}}$ is a matrix integral operator.

Notice that (B1) in (71) using (B6) gives

$$F_d(s) = ic_d's + \frac{i}{2\hbar}\int_0^s du\, \Delta\underline{\tilde{D}}\cdot\Delta\underline{V}^{-1}\cdot f^u(s), \tag{B8}$$

where c_d' is that given in (94). We have seen that this term in $F_d(s)$ cancels with the prefactor $\exp(ic_{ij}s)$ in (56).

We need to examine the second term in (B8). We will show that it becomes negligible compared with $ic_d's$ as s becomes large.

By iteration of (B7) we can write

$$\underline{f}^u(s) + (\underline{1} + \underline{K} + \underline{K}^2 + \cdots)\underline{E}^u(s). \tag{B9}$$

The quantity of interest for use in (B8) is the integral of (B9):

$$\int_0^s du\,\underline{f}^u(s) = \int_0^s du\,\underline{E}^u(s) + \int_0^s du\int_0^s du_1 \underline{K}(u-u_1)\underline{E}^{u_1}(s) + \int_0^s du\int_0^s du_1\int_0^s du_2 \underline{K}(u-u_1)\underline{K}(u_1-u_2)\underline{E}^{u_2}(s) + \cdots. \tag{B10}$$

Consider, as an example of a general term, the absolute value of the third term on the right-hand side of (B10). Using (60) and (86) the u integration can be performed to give

$$A_3 \equiv \left|\int_0^s du\int_0^s du_1\int_0^s du_2\, \underline{K}(u-u_1)\underline{K}(u_1-u_2)\cdot\underline{E}^{u_2}(s)\right|$$

$$= \left|\int_0^s du_1\int_0^s du_2\,\frac{1}{\pi}\,\Delta\underline{V}\int d\omega^2[\mathrm{Im}\,\underline{G}^i(\omega^2)/2\omega^2]\,[2 + j_\omega(u_1) + j_\omega(s-u_1)]\,\underline{K}(u_1-u_2)\cdot\underline{E}^{u_2}(s)\right|. \tag{B11}$$

Using the fact that $|j_\omega(u)| \le 2n_\omega + 1$ we have

$$A_3 \le \left| \underline{B} \int_0^s du_1 \int_0^s du_2 \underline{K}(u_1 - u_2) \cdot \underline{E}^{u_2}(s) \right| , \tag{B12}$$

where

$$\underline{B} \equiv \frac{2}{\pi} \int d\omega^2 [\mathrm{Im}\, \underline{G}^i(\omega^2)/\omega^2](n_\omega + 1) \tag{B13}$$

is an upper bound on $\int_0^s du\, \underline{K}(u - u_1)$. Treating the u_1 integration as we did the u integration in (B11) we have

$$A_3 \le \underline{B}^2 \cdot \left| \int_0^s du_2 \underline{E}^{u_2}(s) \right| . \tag{B14}$$

Using a similar result for the general term in (B10) we have

$$\left| \int_0^s du \underline{f}^u(s) \right| \le (\underline{1} + \underline{B} + \underline{B}^2 + \cdots) \left| \int_0^s du\, \underline{E}^u(s) \right| = (\underline{1} - \underline{B})^{-1} \left| \int_0^s du \underline{E}^u(s) \right| \tag{B15}$$

which an s-independent upper bound since

$$\left| \int_0^s du\, \underline{E}^u(s) \right| = \left| \frac{\Delta V}{\pi} \int d\omega^2\, \mathrm{Im}\, \underline{G}^i(\omega^2) \underline{c} \int_0^s du [j_\omega(u) + j_\omega(s-u)]/(2\omega^2) \right|$$
$$\le \frac{\Delta V}{\pi} \int d\omega^2\, \mathrm{Im}\, \underline{G}^i(\omega^2) [(2n_\omega + 1)/\omega^3] \underline{c} \, . \tag{B16}$$

As a consequence (B15) and (B16), the second term on the right-hand side of (B8) is seen to have an s-independent upper bound so that for large s

$$F_d(s) \sim i c_d' s \, , \tag{B17}$$

a general result and not one limited in validity to the one-phonon F approximation where it first arose in (91).

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