Theory of electronic transport in molecular crystals. II. Zeroth order states incorporating nonlocal linear electron–phonon coupling

R. W. Munn and R. Silbey

Citation: J. Chem. Phys. **83**, 1843 (1985); doi: 10.1063/1.449372
View online: http://dx.doi.org/10.1063/1.449372
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v83/i4
Published by the American Institute of Physics.

Theory of electronic transport in molecular crystals. II. Zeroth order states incorporating nonlocal linear electron–phonon coupling

R. W. Munn
Department of Chemistry, UMIST, Manchester M60 IQD, England

R. Silbey
Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 3 January 1985; accepted 28 February 1985)

A generalized transformation is applied to a model Hamiltonian incorporating both local and nonlocal exciton–phonon coupling. For the application of the usual transport theory, the difference between the transformed coupling and its thermal average over the free phonon ensemble must be small. This is achieved by a temperature-dependent set of transformation coefficients defined by a transcendental equation which is soluble numerically after some approximation. Nonlocal coupling increases both the exciton binding energy and the usual band narrowing, but it also changes the band shape in a way which may introduce new minima and band broadening. The exciton velocities are then no longer related to the exciton hopping and scattering rates in the same way as in local coupling.

I. INTRODUCTION

In a previous paper,[1] we presented a theory of exciton transport[2,3] in a system with *local linear* phonon–exciton scattering, valid in both the limit of weak coupling (where it reduces to standard band theories)[4] and in the limit of strong coupling (where it reduces to the small polaron theory).[5] In addition, because this theory used density matrix methods and retained the thermally averaged exciton bandwidth in the zeroth order Hamiltonian (in contrast to most treatments), the results interpolate smoothly from the weak to the strong coupling limits. Thus this theory provides an excellent *first* order description of exciton transport in all regimes.

The measurement of the transport of electrons and holes in aromatic hydrocarbon crystals in recent years[6] has indicated that *nonlocal* linear phonon coupling may play a significant role in the scattering of the transporting species. Although some aspects of the theory of nonlocal scattering have been treated by Sumi,[7] Metiu *et al.*,[8] Duke *et al.*,[9] Friedman,[10] and Vilfan,[11] there is no theory which attempts to interpolate between the two limits of band and hopping transport which includes both local and nonlocal scattering. In this paper, we begin this task by formulating zeroth order states for this problem; transport is considered in a later paper.

Local electron–phonon coupling changes the vibrations at a site where an excitation is created; for linear coupling, the equilibrium position of the vibration changes but the frequency does not. For molecular modes, this coupling corresponds to the usual vibronic coupling leading to molecular distortion in the excited state or molecular ion. For lattice modes involving the relative displacement of molecules (optic modes or the shorter-wavelength acoustic modes), this coupling corresponds to fluctuations in the exciton site shift or in the charge-carrier polarization energy. The importance of polarization energy fluctuations has been stressed several times.[12–14]

Nonlocal electron–phonon coupling changes the vibrations when an excitation is transferred between sites. It is usually considered conversely as a vibrational variation of the excitation transfer integral between molecules, which gives rise to the "phonon-assisted current."[11,12,15] This coupling should arise mainly from lattice modes, both translational and librational.

Since lattice modes may produce simultaneous local and nonlocal coupling, in this paper we treat both types together. Our methods of deducing transport properties are outlined elsewhere.[15] They require the Hamiltonian to be transformed to yield a weak residual coupling. For local coupling, the conventional polaron transformation is local in excitation operators,[16] but on including nonlocal coupling we have to use a more general nonlocal transformation.[17] This transformation is not only new, so far as we are aware, but it is also more complicated. The coupling term can be eliminated only in the thermal average, which means that the transformation parameters are determined only implicitly and are temperature dependent. The present paper is therefore confined to an analysis of the nonlocal polaron transformation and the polaron states it produces.

In Sec. II we describe the Hamiltonian and the transformation, evaluating certain thermal averages which determine the transformation parameters and the polaron energies. In Sec. III and the appendices we evaluate the transformation parameters algebraically by assuming that they are scalar multiples of the corresponding coupling parameters. This yields a nonlinear equation which is solved numerically in Sec. IV for a simple model distribution of nonlocal coupling parameters. The solutions are then used to calculate the polaron band structure for a simple model.

II. HAMILTONIAN

We consider simultaneous local and nonlocal coupling to a single phonon band. The results can be extended fairly

 0021-9606/85/161843-11$02.10

readily to other bands which produce only local or only nonlocal coupling. With $\hbar$ taken as 1, the Hamiltonian is

$$H = \sum_n \epsilon a_n^+ a_n + \sum_{n,m} J_{nm} a_n^+ a_m + \sum_q \omega_q (b_q^+ b_q + 1/2) + N^{-1/2} \sum_{nmq} \omega_q f_{nm}^q a_n^+ a_m (b_q + b_{-q}^+). \quad (2.1)$$

Here the operators a_n^+ and a_n create and destroy an excitation (exciton or charge carrier) of energy ϵ at site n, while the operators b_q^+ and b_q create and destroy a phonon of frequency ω_q and wave vector q. The quantity J_{nm} is the transfer integral between sites n and m. The last term is the electron–phonon coupling, from which a factor ω_q has been separated for convenience. To make H Hermitian, the coupling parameter must satisfy

$$f_{nm^*}^q = f_{mn}^{-q} \quad (2.2)$$

and because of translational symmetry we require also

$$f_{nm}^q = e^{-iq\cdot R_n} f_{n-m}^q, \quad (2.3)$$

where R_n is the position vector of site n. Combining Eqs. (2.2) and (2.3) shows that the new coupling parameters f_{n-m}^q in Eq. (2.3) must satisfy

$$f_{n-m^*}^q = e^{-i\mathbf{q}\cdot(\mathbf{R}_n - \mathbf{R}_m)} f_{m-n}^{-q}. \quad (2.4)$$

When $n = m$, f_{nm}^q and f_{n-m}^q reduce to the usual local coupling parameters[1] $f_{nn}^q = g_q^n$ and $f_0^q = g_q$. A general expression for the nonlocal coupling parameters for translational modes has been given[12] and can be extended to librational or mixed modes.

A. Transformation

The Hamiltonian is transformed according to

$$H \to \tilde{H} = e^{\mathcal{S}} H e^{-\mathcal{S}}, \quad (2.5)$$

with

$$\mathcal{S} = N^{-1/2} \sum_{nmq} A_{nm}^q (b_{-q}^+ - b_q) a_n^+ a_m \quad (2.6)$$

and the A_{nm}^q to be determined. For a proper unitary transformation we require $\mathcal{S}^+ = -\mathcal{S}$ which means that A_{nm}^q must satisfy the same condition (2.2) as f_{nm}^q. Under the transformation (2.5), the phonon operators change according to

$$b_q \to b_q - N^{-1/2} \sum_{nm} A_{nm}^{-q} a_n^+ a_m, \quad (2.7)$$

$$b_q^+ \to b_q^+ - N^{-1/2} \sum_{nm} A_{nm}^q a_n^+ a_m, \quad (2.8)$$

$$(b_q + b_{-q}^+) \to (b_q + b_{-q}^+) - 2N^{-1/2} \sum_{nm} A_{nm}^q a_n^+ a_m, \quad (2.9)$$

much as for local coupling.[16] The excitation operators change in a more complicated way which can, however, be deduced using techniques for handling exponential quadratic operators.[18] The results are

$$a_n \to \sum_m \theta_{nm} a_m, \quad (2.10)$$

$$a_n^+ \to \sum_m \theta_{nm}^+ a_m^+, \quad (2.11)$$

where

$$\theta_{nm} = \left\{ \exp\left[-N^{-1/2} \sum_q \mathsf{A}^q (b_{-q}^+ - b_q) \right] \right\}_{nm}, \quad (2.12)$$

$$\theta_{nm}^+ = \left\{ \exp\left[N^{-1/2} \sum_q \mathsf{A}^q (b_{-q}^+ - b_q) \right] \right\}_{nm}, \quad (2.13)$$

so that

$$\sum_m \theta_{mn}^+ \theta_{pm} = \delta_{np} = \sum_m \theta_{nm} \theta_{mp}^+. \quad (2.14)$$

Here A^q is the matrix of the A_{nm}^q and the derivation of Eq. (2.13) from Eq. (2.12) uses the symmetry property (2.2) and the result $f(\mathsf{A}^T) = [f(\mathsf{A})]^T$, where T denotes the transpose.

Translational symmetry makes it natural to consider using the exciton wave vector representation instead of the site representation. For local coupling, the advantages of the wave vector representation are outweighed by the disadvantages of having to use a nonlocal transformation instead of the local transformation in the site representation. However, for nonlocal coupling the transformation is nonlocal in either representation and use of the wave vector representation becomes preferable. The untransformed Hamiltonian can be written as

$$\mathrm{H} = \sum_k \epsilon_k a_k^+ a_k + \sum_q \omega_q (b_q^+ b_q + 1/2) + N^{-1/2} \sum_{kq} \omega_q f_{-k}^q (b_q + b_{-q}^+) a_{k+q}^+ a_k, \quad (2.15)$$

where $\epsilon_k = \epsilon + J_k$, with

$$J_k = \sum_m e^{i\mathbf{k}\cdot(\mathbf{R}_n - \mathbf{R}_m)} J_{nm} \quad (2.16)$$

and similarly,

$$f_k^q = \sum_m e^{-i\mathbf{k}\cdot(\mathbf{R}_n - \mathbf{R}_m)} f_{n-m}^q. \quad (2.17)$$

The transformation exponent becomes

$$\mathcal{S} = N^{-1/2} \sum_{kq} A_{-k}^q (b_{-q}^+ - b_q) a_{k+q}^+ a_k, \quad (2.18)$$

where

$$A_k^q = \sum_m e^{-i(\mathbf{k}-\mathbf{g})\cdot\mathbf{R}_n} e^{i\mathbf{k}\cdot\mathbf{R}_m} A_{nm}^q = (A_{k-q}^{-q})^* \quad (2.19)$$

with corresponding changes in the transformations (2.7)–(2.9). If Eq. (2.18) is written in the form

$$\mathcal{S} = \sum_{kk'} a_k^+ S_{kk'} a_{k'}, \quad (2.20)$$

where now

$$S_{kk'} = N^{-1/2} A_{-k}^{k-k'} (b_{-k+k'}^+ - b_{k-k'}^+), \quad (2.21)$$

then the transformations (2.10) and (2.11) becomes

$$a_k \rightarrow \sum_{k'} \theta_{kk'} a_{k'}, \tag{2.22}$$

$$a_k^+ \rightarrow \sum_{k'} \theta^+_{kk'} a^+_{k'}, \tag{2.23}$$

with

$$\theta_{kk'} = [\exp(-S)]_{kk'}, \tag{2.24}$$

$$\theta^+_{kk'} = [\exp(S)]_{k'k}, \tag{2.25}$$

S being the matrix $\{S_{kk'}\}$. The operator $S_{kk'}$ creates a net phonon momentum of $k'-k$, and it is readily shown that the same momentum is created by $[S^n]_{kk'}$ for any power $n>0$ and hence by all terms in the series expansion of $\theta_{kk'}$ except the first, which creates zero momentum (i.e., the first term is $\delta_{kk'}$).

The transformed Hamiltonian can now be written

$$\begin{aligned}\tilde{H} = &\sum_{k'k''}\left(\sum_k \epsilon_k \theta^+_{kk'}\theta_{kk''}\right)a^+_{k'}a_{k''} + \sum_q \omega_q (b^+_q b_q + 1/2) \\ &+ N^{-1/2}\sum_{qk'k''}\omega_q\left(\sum_k f^q_{-k}\theta^+_{k+q,k'}\theta_{kk''} - A^q_{-k''}\delta_{k',k''+q}\right) \\ &\times (b_q + b^+_{-q})a^+_{k'}a_{k''} + N^{-1}\sum_{qk}\omega_q |A^{-q}_{-k}|^2 a^+_k a_k \\ &- 2N^{-1}\sum_{qkk'k''}\omega_q f^q_{-k} A^{-q}_{-k''-q}\theta^+_{k'+q,k'}\theta_{kk''}a^+_{k'}a_{k''+q},\end{aligned} \tag{2.26}$$

where states with more than one excitation are ignored as usual. As in previous work, we partition $\tilde{H}$ into a zeroth-order part H_0 and a perturabtion V. The correct thermal equilibrium behavior is ensured by taking H_0 as the pure excitation and phonon terms plus the thermal average of the interaction terms over the free phonon ensemble. In the thermal average, nonzero contributions entail the creation and annihilation of equal numbers of phonons for each momentum, and hence entail creation of zero net momentum. It follows that

$$\langle \theta^+_{k,k+q}\theta_{k',k'+q'}\rangle = \langle \theta^+_{k,k+q}\theta_{k',k'+q}\rangle \delta_{qq'}, \tag{2.27}$$

where the angle brackets denote the thermal phonon average. This and similar results ensure that H_0 is diagonal in excitation wave vector:

$$\begin{aligned}H_0 = &\sum_q \omega q (b^+_q b_q + 1/2) + \sum_k \{(\epsilon + \tilde{J}_k) \\ &+ N^{-1}\sum_q \omega_q |A^{-q}_{-k}|^2 - 2N^{-1} \\ &\times \sum_{qk'}\omega_q f^q_{-k'} A^{-q}_{-k}\langle \theta^+_{k'+q,k}\theta_{k',k-q}\rangle + N^{-1/2} \\ &\times \sum_{qk'}\omega_q f^q_{-k'}\langle \theta^+_{k'+q,k}\theta_{k'k}(b_q + b^+_{-q})\rangle\} a^+_k a_k,\end{aligned} \tag{2.28}$$

where the renormalized transfer integral is

$$\tilde{J}_k = \sum_{k'} J_{k'}\langle \theta^+_{k'k}\theta_{k'k}\rangle \tag{2.29}$$

and Eq. (2.19) has been used to write $A^{-q}_{-k-q} = (A^q_{-k})^*$. The perturbation is then

$$\begin{aligned}V = &\sum_{kk'k''}\{J_k \mathsf{T}_{kk';kk''} - 2N^{-1}\sum_q \omega_q f^{-q}_{-k}(A^q_{-k''})\mathsf{T}_{k+q,k';k,k''-q} \\ &+ N^{-1/2}\sum_q \omega_q f^q_{-k}[\mathsf{T}_{k+q,k';kk''}(b_q + b^+_{-q}) - \langle \mathsf{T}_{k+q,k';kk''}(b_q + b^+_{-q})\rangle]\}a^+_{k'}a_{k''} \\ &+ N^{-1/2}\sum_{qk}\omega_q\left[A^q_{-k} - \sum_{k'} f^q_{-k'}\langle \theta^+_{k'+q,k+q}\theta_{k'k}\rangle\right](b_q + b^+_{-q})a^+_{k+q}a_k,\end{aligned} \tag{2.30}$$

where

$$\mathsf{T}_{kk';uu'} = \theta^+_{kk'}\theta_{uu'} - \langle \theta^+_{kk'}\theta_{uu'}\rangle. \tag{2.31}$$

We now choose the transformation coefficients A^q_k. Strictly speaking, this should be done variationally as in previous work on local coupling,[19,20] but we expect to retain most qualitative features of such a procedure by a more direct approach like that adopted for linear coupling.[1] In that work, combinations of exponential operators similar to $\mathsf{T}_{kk';uu'}$ ensured that matrix elements of V^2 remained small for any electron–phonon coupling strength. For weak coupling the operators differ little from the unit operator and hence from their thermal average, while for strong coupling the exponentials of negative argument keep the terms small in magnitude. Similar considerations should apply to all the terms in Eq. (2.30) except the last, where the phonon displacement operator could give large contributions. This possibility is eliminated by the choice

$$A^q_{-k} = \sum_{k'} f^q_{-k'}\langle \theta^+_{k'+q,k+q}\theta_{k'k}\rangle, \tag{2.32}$$

which makes the last term zero. This defines the transformation coefficients only implicitly, since the exponential operators $\theta_{kk'}$ depend on A^q_k.

With the choice of Eq. (2.32), H_0 becomes

$$\begin{aligned}H_0 = &\sum_k (\epsilon + \tilde{J}_k - N^{-1}\sum_q |A^{-q}_{-k}|^2)a^+_k a_k + \sum_q \omega_q (b^+_q b_q + \tfrac{1}{2}) \\ &+ N^{-1/2}\sum_{qkk'}\omega_q f^q_{-k'}\langle \theta^+_{k'+q,k}\theta_{k'k}(b_q + b^+_{-q})\rangle a^+_k a_k.\end{aligned} \tag{2.33}$$

The form resembles that for local coupling, with a renormalized transfer integral and a polaron-like energy lowering or binding from the term in $|A^{-q}_{-k}|^2$. However, in contrast to the earlier case, the dependence on **k** in this latter term affects the band shape as well as its absolute energy. The last

term in Eq. (2.33) has no counterpart for local coupling, but is found below to vanish identically. The form of V becomes

$$V=\sum_{kk'k''}\{J_k \mathsf{T}_{kk';kk''}-2N^{-1}\sum_q \omega_q f^q_{-k} A^{-q}_{-k''}\mathsf{T}_{k+q,k';k,k''-q}$$
$$+N^{-1}\sum_q \omega_q f^q_{-k}[\mathsf{T}_{k+q,k';kk''}(b_q+b^+_{-q})$$
$$-\langle \mathsf{T}_{k+q,k';kk''}(b_q+b^+_{-q})\rangle]\}a^+_{k'}a_{k''}, \tag{2.34}$$

where the last term in square brackets will also be found to vanish. By construction, $\langle V\rangle = 0$.

Now, we collect all the term of H_0 and V, using the definitions and calculations of thermal averages of Appendix A. The zeroth-order Hamiltonian becomes

$$H_0=\sum_k \tilde{\epsilon}_k a_k a_k+\sum_q \omega_q(b^+_q b_q+\tfrac{1}{2}), \tag{2.35}$$

where

$$\tilde{\epsilon}_k=\epsilon+\tilde{J}_k-N^{-1}\sum_q |A^q_k|^2\omega_q. \tag{2.36}$$

From Eqs. (2.29), (A18), and (A24) the renormalized transfer integral is found after some manipulation to be given by

$$\tilde{J}_k=\sum_{k'}\langle\theta_k\rangle^2(\exp \mathsf{E}^0)_{kk'}J_{k'}. \tag{2.37}$$

The perturbation becomes

$$V=\sum_{kk'k''}\{J_k \mathsf{T}_{kk';kk''}-2N^{-1}\sum_q \omega_q f^q_{-k}A^{-q}_{-k''}\mathsf{T}_{k+q,k';k,k''-q}$$
$$+N^{-1/2}\sum_q \omega_q f^q_{-k}\mathsf{T}_{k+q,k';kk''}(b_q+b^+_{-q})\}a^+_{k'}a''_k, \tag{2.38}$$

where the second term can be regarded as modifying the transfer integral.[21,22]

III. TRANSFORMATION PARAMETERS AND APPROXIMATIONS

Since Eq. (A25) gives the transformation parameters A^Q_q implicitly in terms of an exponential matrix function, an exact algebraic solution seems unlikely to be easily obtained. In this section, we examine the properties of the coupling parameters f^Q_q and reasonable approximations for them. We then argue that the A^Q_q must behave similarly and proceed with the calculation. In Appendix B, a test of the approximations is made.

The local and nonlocal parts of the coupling parameters f^Q_{n-m} can be separated according to[12]

$$f^Q_{n-m}=g_Q\delta_{nm}+[1-e^{i\mathbf{Q}\cdot(\mathbf{R}_n-\mathbf{R}_m)}]\phi^Q_{n-m}. \tag{3.1}$$

Here ϕ^Q_{n-m} is related to the derivative of J_{nm} with respect to the relative displacements (translational, rotational, or mixed) at sites n and m in mode Q of the phonon branch in question. From Eq. (2.4) it follows that

$$g^*_Q=g_{-Q}, \tag{3.2}$$
$$\phi^{Q*}_{n-m}=-\phi^{-Q}_{m-n}. \tag{3.3}$$

With these results we find

$$f^{q-q'}_q=g_{q-q'}+\sum_r(e^{-i\mathbf{q}\cdot\mathbf{R}_r}-e^{-i\mathbf{q}'\cdot\mathbf{R}_r})\phi^{q-q'}_r \tag{3.4}$$
$$\equiv g_{q-q'}-i(\phi^{q-q'}_q-\phi^{q-q'}_{q'}), \tag{3.5}$$

where $g_{q-q'}$ and $\phi^{q-q'}_q$ are real if g_q and ϕ^q_r are symmetric in q.

At least for optic modes, the dispersion in g_q and ϕ^q_r should be small and these quantities can be replaced by suitable averages over q. For example, the Hamiltonian used by Sumi[7] has coupling parameters independent of phonon wave vector. Then we obtain

$$f^{q-q'}_q\approx g-i(\phi_q-\phi_{q'}), \tag{3.6}$$

where now ϕ_q is odd in q. This expression yields g as either f^0_q or the average of f^q_λ over q. From Eqs. (2.32) and (3.6), we find that $A^0_\lambda = g$ for all λ. We then assume that A^q_λ can be written by analogy with Eq. (3.6) as

$$A^q_\lambda=g-i\eta(\phi_\lambda-\phi_{\lambda-q}); \tag{3.7}$$

this proves to be a self-consistent assumption to within a weakly q dependent factor.

With these assumptions, the matrix E^Q of Eq. (A24) has elements

$$E^Q_{\lambda q}=N^{-1}(2n+1)[g-i\eta(\phi_{q-Q}-\phi_{\lambda-Q})]$$
$$\times[g+i\eta(\phi_q-\phi_\lambda)], \tag{3.8}$$

where we have also assumed that the weak dispersion allows $n_{q-\lambda}$ to be replaced by an average n. For $Q=0$, E^Q is real, with elements

$$E^0_{\lambda q}=N^{-1}(2n+1)[g^2+\eta^2(\phi_q-\phi_\lambda)^2]. \tag{3.9}$$

For later use it is convenient to expand Eq. (3.8) and collect together factors dependent on λ and $\mathbf{q}$ together.

$$E^Q_{\lambda q}=N^{-1}(2n+1)[g^2+V^Q_\lambda$$
$$+V^{Q*}_q-\eta^2(\phi_\lambda\phi_{q-Q}+\phi_q\phi_{\lambda-Q})], \tag{3.10}$$

where

$$V^Q_\lambda=\eta^2\phi_\lambda\phi_{\lambda-Q}-ig\eta(\phi_\lambda-\phi_{\lambda-Q}). \tag{3.11}$$

In order to test the approximation of Eq. (3.7) we compute A^0_λ in Appendix B, and in Sec. IV compare the values of A^0_λ with g for various values of the parameters. It is seen there that our assumption of Eq. (3.7) yields self-consistent results for all parameters.

In order to determine H_0 explicitly, we must still compute $\tilde{J}_\lambda$ and A^q_k which require an evaluation of η. Because the expressions for all these quantities are quite complicated, the dependence of these terms on the bandwidth, phonon frequencies, and coupling parameters are best displayed as numerically computed figures, rather than mathematical expressions. We therefore relegate the algebra to the appendices and proceed to the numerical evaluations of Sec. IV. In Appendix C, a self-consistent expression is derived for η which is numerically evaluated in Sec. IV. Finally in Appendix D, we evaluate $\tilde{J}_\lambda$, completing our evaluation of the terms in H_0.

IV. NUMERICAL CALCULATIONS

A. Coupling parameters

For numerical calculations it is necessary to specify a distribution for the nonlocal coupling parameters. In Ref. 1 we used Gaussian distributions of energy for analytical convenience. However, since the ϕ_λ are antisymmetric in λ, a pair of Gaussians would be required to represent the distribution, with maximum densities of states intermediate between the zone center and the zone boundary in opposite directions. For the present purposes it is therefore simpler to take

$$\phi_\lambda = \phi \sin \lambda. \tag{4.1}$$

It follows that

$$N^{-1} \sum_\lambda \phi_\lambda^2 = \tfrac{1}{2}\phi^2, \tag{4.2}$$

$$N^{-1} \sum_\lambda \phi_\lambda^4 = \tfrac{3}{8}\phi^4, \tag{4.3}$$

and hence

$$V^0 = \tfrac{1}{2}\eta^2\phi^2, \tag{4.4}$$

$$F^0 = g^2 + \eta^2\phi^2, \tag{4.5}$$

$$G^0 = \tfrac{1}{8}\eta^4\phi^4 = \tfrac{1}{2}(V^0)^2, \tag{4.6}$$

and so on.

The scaling parameter η is obtained as the solution of Eq. (C33). In the limit of very weak local coupling $g \ll \phi$, $F^0 \approx 2V^0$ so that $X \approx 0$ but $g^2 c_\pm \approx 0$ also. Then Eq. (C33) reduces to

$$\eta = \exp[-(n+\tfrac{1}{2})\phi^2(2-\eta^2)\eta^2], \tag{4.7}$$

the solutions of which are plotted in Fig. 1 as a function of $(n+\frac{1}{2})\phi^2$; solutions for $\eta^2 \geqslant 2$ are excluded by continuity. It is seen that η falls farther and farther below unity as n and ϕ increase. However, for n fixed, η decreases slightly less rapidly than ϕ increases, so that the product $\eta\phi$ determining the transformation parameters increases steadily with ϕ (roughly like $\ln \phi$).

The solutions for η as a function of g for different values of ϕ are plotted for different temperatures in Figs. 2–4. The parameter η shows varied by systematic behavior, decreasing from the initial value given in Fig. 1 for $g = 0$ as g increases. As ϕ increases, η decreases for a given value of g, and as T increases, η decreases more rapidly with g for a given value of ϕ. In all cases, the product $\eta\phi$ determining the transformation parameters increases with increasing ϕ, though less rapidly than ϕ itself.

Although in the present treatment the transformation parameters are not optimized in any variational sense, they can be regarded as effecting a compromise between the conflicting aspects of nonlocal coupling. On the one hand, electron–phonon coupling tends to produce localization, but on the other hand, nonlocal coupling tends to increase the kinetic energy and so produce delocalization.[23] Because of this equivocal nature of nonlocal coupling, η must be less than unity.

Figures 2–4 also show the calculated values of the test parameter ξ introduced in Appendix B. It is essentially unity for all values of ϕ and T when $g \geqslant 1$, and deviates by no more than 15% for smaller values of g. The deviation from unity is larger for larger values of ϕ; hence the approximate form assumed for A_λ^q appears to be largely justified as far as this test goes.

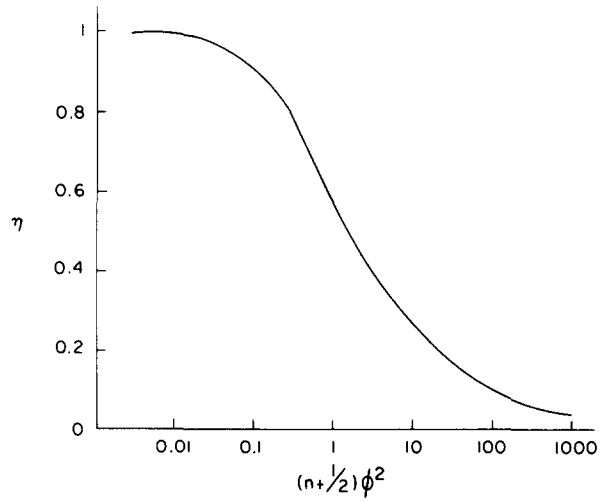

FIG. 1. Scaling parameter η as a function of $(n + 1/2)\phi^2$ for zero local coupling ($g = 0$).

B. Polaron band

The states in the transformed zeroth-order Hamiltonian H_0 have energies ϵ_λ given by Eq. (2.36), which with the present assumptions for A_λ^q reduces to

$$\epsilon_\lambda = \epsilon + \tilde{J}_\lambda - N^{-1} \sum_q \omega_q [g^2 + \eta^2(\phi_\lambda - \phi_{\lambda-q})^2]. \tag{4.8}$$

Using Eq. (4.1) for ϕ_λ and ignoring the dispersion in ω_q leads to

$$\epsilon_\lambda = \epsilon + \tilde{J}_\lambda - \omega(g^2 + \tfrac{1}{2}\eta^2\phi^2 + \eta^2\phi^2 \sin^2 \lambda). \tag{4.9}$$

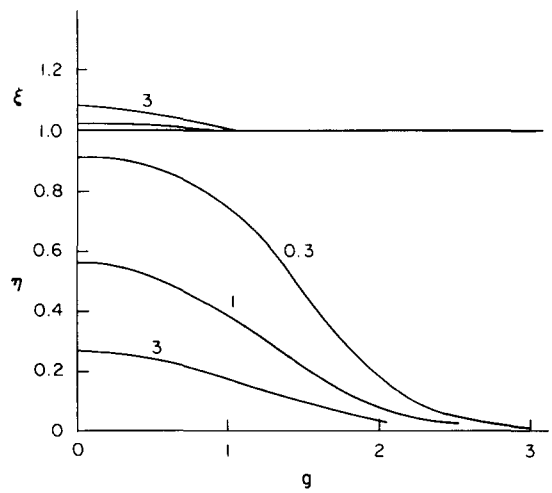

FIG. 2. Test and scaling parameters ξ and η as functions of local coupling parameter g for different nonlocal coupling parameters ϕ at $T/\omega = 1$. The curves are marked with the value of ϕ. The upper three curves show ξ, the second and third down corresponding to $\phi = 1$ and $\phi = 0.3$, respectively. The lower three curves show η.

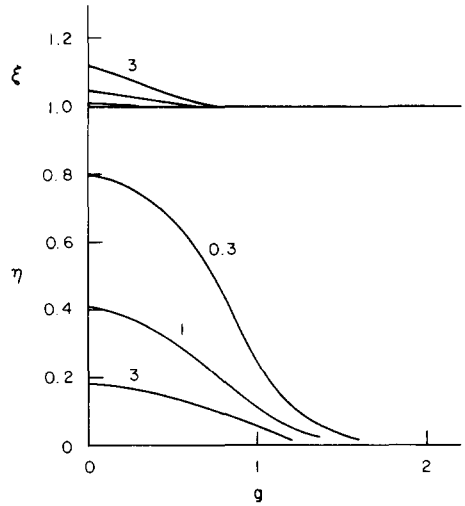

FIG. 3. Same as Fig. 2 but at $T/\omega = 3$.

The polaron transfer integral $\tilde{J}_\lambda$ is given by Eq. (D5). For simplicity we assume

$$J_\lambda = J\cos\lambda, \tag{4.10}$$

where J is the bare transfer integral, in which case the parameter M defined by Eq. (D4) is zero. Substitution for quantities determining E^0_λ in Eq. (B6) then yields

$$\tilde{J}_\lambda = J\exp[\,-(2n+1)(g^2+\tfrac{1}{2}\eta^2\phi^2+\eta^2\phi^2\sin^2\lambda\,]\cos\lambda. \tag{4.11}$$

Equations (4.9) and (4.11) together can be written as

$$\epsilon_\lambda = \epsilon' + J'\exp[\,-(2n+1)\eta^2\phi^2\sin^2\lambda\,] \times\cos\lambda - \omega\eta^2\phi^2\sin^2\lambda, \tag{4.12}$$

where

$$\epsilon' = \epsilon - \omega(g^2+\tfrac{1}{2}\eta^2\phi^2), \tag{4.13}$$

$$J' = J\exp[\,-(2n+1)(g^2+\tfrac{1}{2}\eta^2\phi^2)]. \tag{4.14}$$

These expressions illustrate the conclusions reached at the end of Sec. III. The nonlocal coupling produces an additional polaron binding energy through the additional term in $\eta^2\phi^2$ in ϵ'. The last term in Eq. (4.12) can also be regarded as an additional binding energy which is largest midway between the Brillouin zone center and the zone boundary. Similarly, the same factors produce an additional and nonuniform polaron band narrrowing.

The wave vector dependent binding energy may change the band structure qualitatively as well as quantitatively.[17] Differentiation of ϵ_λ with respect to λ shows that the band has extrema at the zone center and the zone boundary, as usual, and also at wave vectors satisfying

$$J'\exp[\,-(2n+1)\eta^2\phi^2\sin^2\lambda\,] \times[1+(2n+1)2\eta^2\phi^2\cos^2\lambda\,]+2\omega\eta^2\phi^2\cos\lambda = 0. \tag{4.15}$$

The first term here takes the signs of J' and hence of J (which determines whether the bottom of the bare band is at the zone center or the zone boundary), while the second terms takes both positive and negative signs as λ varies. The equation therefore has a real solution provided J' is not too large compared with $\omega\eta^2\phi^2$, a situation favored by small J, large ω, and large ϕ. The additional extremum is the new band minimum, which moves in from the zone boundary or out from the zone center (according as J is positive or negative), leaving these as local maxima. As J becomes smaller, the minimum moves closer to the point $\lambda = \pi/2$, midway between the center and the boundary.

The changes can also be understood directly from Eq. (4.12) for ϵ_λ. The last term on the right-hand side lowers the energy, and produces a new minimum provided it increases in magnitude faster than the second term on the right-hand side—which is the condition expressed by Eq. (4.15). One consequence of these changes is an additional peak in the density of polaron states at the new minimum, together with a widening of the band. This contrasts with the local polaron transformation which always narrows the band.

The band structure is illustrated in Figs. 5–7. Figure 5 shows how the band structure changes with ϕ for fixed values of J, g, and T. The quantity plotted is $\epsilon'_\lambda = (\epsilon_\lambda - \epsilon')/\omega$, which equals J'/ω for $\lambda = 0$ and $-J'/\omega$ for $\lambda = \pi$. The val-

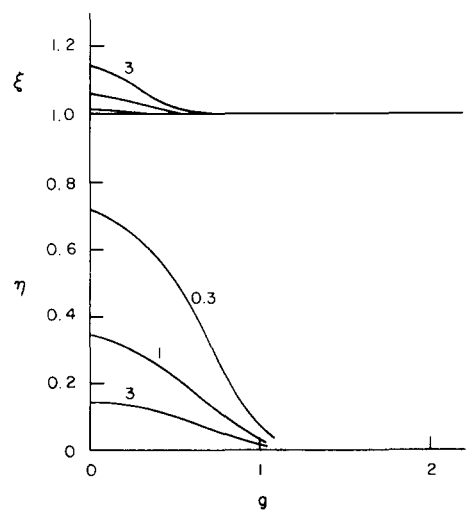

FIG. 4. Same as Fig. 2 but at $T/\omega = 5$.

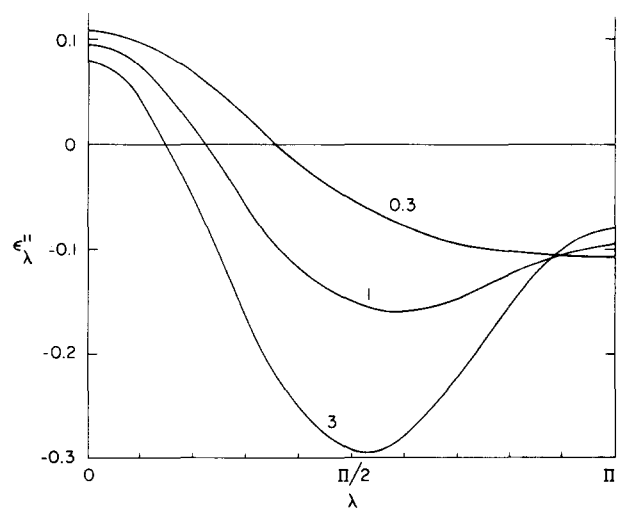

FIG. 5. Polaron band structure and nonlocal coupling. Reduced energy $\epsilon' = [\epsilon_\lambda - \epsilon']/\omega$ as function of wave vector λ for different nonlocal coupling parameters ϕ, marked on the curves; $J/\omega/1$, $g = 1$, $T/\omega = 1$.

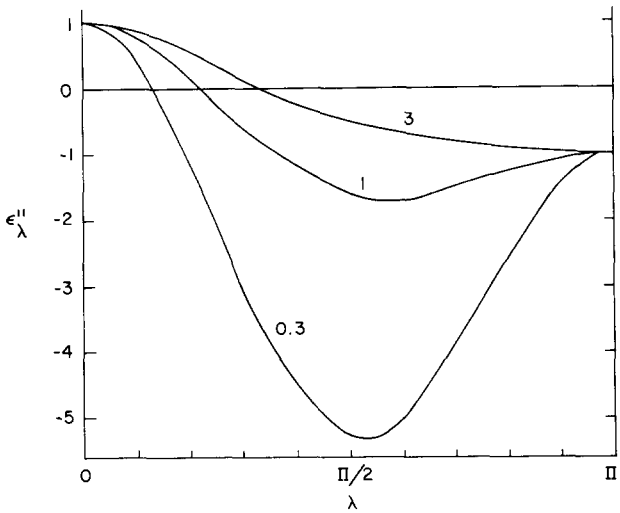

FIG. 6. Polaron band shape and transfer integral. Relative energy $\epsilon''_\lambda = (\epsilon_\lambda - \epsilon')/J'$ as a function of wave vector λ for different transfer integrals J, marked on the curves; $g = 1$, $\phi = 1$, $T/\omega = 1$.

ue of J' decreases slightly as ϕ increases, through the increase in the product $\eta\phi$, and the condition for a new band minimum is satisfied before ϕ reaches 1. For $\phi = 3$ the minimum is deeper and close to $\lambda = \pi/2$, making the bandwidth nearly double its value for $\phi = 0$. This effect is particularly marked because $J' \approx 0.1\ \omega$ whereas the extra binding energy varies like ω; for smaller g and lower T, J' is larger and the band shape changes less markedly, acquiring a new minimum only for a very large ϕ, while for larger g and higher T, J' is smaller and the band has a new minimum for all but the smallest ϕ.

Figure 6 shows how the band shape changes with J for fixed values of g, ϕ, and T. The quantity plotted is $\epsilon''_\lambda = (\epsilon_\lambda - \epsilon')/J'$ in order to make the changes more readily comparable than if an absolute energy scale were used. As J decreases, a new band minimum develops, deepens, and moves towards $\lambda = \pi/2$. The changes are more marked than when ϕ changes because there is no offsetting change in ϕ.

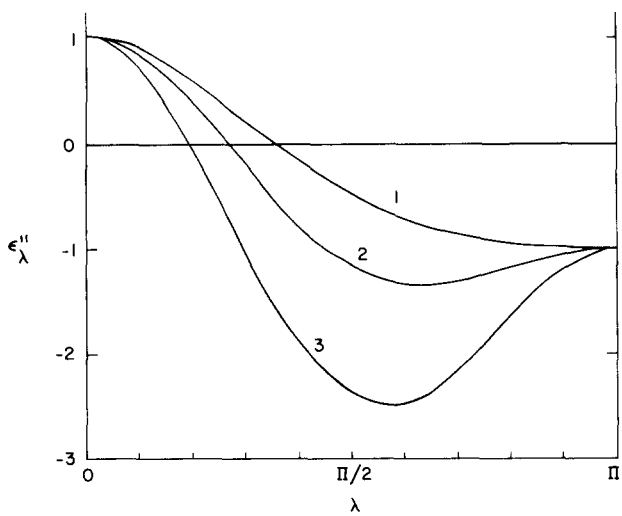

FIG. 7. Polaron band shape and temperature. Relative energy $\epsilon'' = (\epsilon_\lambda - \epsilon')/J'$ as a function of wave vector λ for different temperatures T/ω, marked on the curves; $J/\omega = 1$, $g = 1$, $\phi = 0.3$.

Figure 7 shows how the band shape, again plotted as ϵ''_λ, changes with T for fixed values of J, g, and ϕ. As T increases, J' decreases faster than η does, and a new band minimum develops as before. The effects in Figs. 6 and 7, like those in Fig. 5, are less marked for other parameter sets, which tend to produce a new minimum for practically all values or for practically none. It is to be expected that the main qualitative changes should occur for parameters all of the same magnitude. ($J/\omega \approx 1$, $T/\omega \approx 1$, $g \approx 1$, $\phi \approx 1$) as in the figures.

V. DISCUSSION

We have shown here the consequences of applying a nonlocal polaron transformation to a model Hamiltonian incorporating both local and nonlocal coupling. With a view to applications in transport theory, the transformed Hamiltonian has been partitioned according to our previous prescription.[1] Various differences from pure local coupling are seen, all in the direction of greater complexity. To ensure a perturbation which can reasonably be treated as small in transport theory, a temperature-dependent transformation is required, more like the variationally optimized local transformation than the simple explicit clothing with constant transformation parameters used before.[1] Even to evaluate the transformation parameters for nonlocal coupling has required approximations, though it is hoped that these are of only minor and quantitative significance, as suggested by the test parameter ξ.

The rest of this paper has concentrated on the nature of the polaron states. Nonlocal coupling displays ambivalence between binding and transfer effects. Even for a simple bare band structure and a simple distribution of coupling parameters, the band structure may change significantly in width, shape, and density of states. This has consequences for transport theorys, where obtaining tractable results has often depended on using simple model densities of polaron states which may be qualitatively unsuitable with nonlocal coupling.

Transport depends also on correlation functions of the form $\langle V_{kk'}(t) V_{qq'} \rangle$. The perturbation V has not been discussed here in detail. For weak nonlocal coupling, the polaron transformation becomes purely local, and the first two terms in V can be interpreted as involving a modified transfer integral which may be bigger or smaller than J itself, depending on the relative signs of local and nonlocal coupling. This agrees with previous work in this limit,[21,24] which in turn agrees with other results on transport.[12] One consequence of the form of V is that the polaron hopping and scattering rates are no longer governed by the same parameter as the polaron velocities once there is nonlocal coupling for local coupling J governs all these quantities. The detailed application of the present results to transport is in hand.

ACKNOWLEDGMENTS

This work was supported by NATO Grant 1054 and by the National Science Foundation.

APPENDIX A: EVALUATION OF THERMAL AVERAGES

It is necessary to evaluate the thermal averages not only to complete the specification of H_0 and V but also to obtain a

useful equation determining the A^{q}_{λ}. This is complicated by the need to take matrix elements of two exponential functions separately while taking their thermal average simultaneously. We require averages like

$$\langle \theta^{+}_{kk'} \theta_{qq'} \rangle = \langle (\exp \mathsf{S})_{k'k} (\exp -\mathsf{S})_{qq'} \rangle . \tag{A1}$$

The two exponents differ only in signs, and hence commute, so that they can be combined into a single exponent as

$$\langle \theta^{+}_{kk'} \theta_{qq'} \rangle = \langle \exp(\mathsf{S} - \mathsf{S}') \rangle_{k'k;\, qq'}, \tag{A2}$$

where the $k'k$ matrix element of all functions of S is implied and the qq' matrix element of all functions of S'. Now $\mathsf{S} = \mathsf{T} - \mathsf{U}$, where

$$T_{kk'} = N^{-1/2} A^{k-k'}_{-k'} b^{+}_{-k+k'}, \tag{A3}$$

$$U_{kk'} = N^{-1/2} A^{k-k'}_{-k'} b_{k-k'}, \tag{A4}$$

so that with similar definitions for T' and U' from S' we find

$$\langle \theta^{+}_{kk'} \theta_{qq'} \rangle = \langle \exp[(\mathsf{T} - \mathsf{T}') - (\mathsf{U} - \mathsf{U}')] \rangle_{k'k;\, qq'} . \tag{A5}$$

Here $\mathsf{T} - \mathsf{T}'$ involves only creation operators and $(\mathsf{U} - \mathsf{U}')$ only annihilation operators; these two matrix operators are Hermitian conjugates which commute with their commutator and hence satisfy the relation for operators L of this type

$$\langle \exp(L^{+} - L) \rangle = \exp -\tfrac{1}{2} \langle (L^{+}L + LL^{+}) \rangle, \tag{A6}$$

where the exponent now conserves the number of phonons.

The exponent in Eq. (A5) can then be written as a sum of exponents which with Eq. (A6) can be factorized to yield

$$\begin{aligned} \langle \theta^{+}_{kk'} \theta_{qq'} \rangle = {} & [\exp \langle \mathsf{TU} + \mathsf{TU} \rangle]_{k'k'} \\ & \times [\exp \tfrac{1}{2} \langle \mathsf{TU}' + \mathsf{UU}' + \mathsf{T} + \mathsf{T}'\mathsf{U} + \mathsf{UT}' \rangle]_{k'k;\, qq'} \\ & \times [\exp \tfrac{1}{2} \langle \mathsf{T}'\mathsf{U}' + \mathsf{U}'\mathsf{T}' \rangle]_{q'q'}, \end{aligned} \tag{A7}$$

where momentum conservation makes the first and last factors diagonal. These factors can be seen to be the thermal averages of $\theta^{+}_{k'k'}$ and $\theta_{q'q'}$ separately, and are evaluated as

$$\langle \theta^{+}_{-k} \rangle \equiv [\exp -\tfrac{1}{2} \langle \mathsf{TU} + \mathsf{UT} \rangle]_{kk} = \langle \theta_{-k} \rangle \tag{A8}$$

$$= \exp\left[-N^{-1} \sum_{q} (n_q + \tfrac{1}{2}) |A^{-q}_{-k}|^2 \right] \tag{A9}$$

with $n_q = [\exp(\beta\omega_q] - 1]^{-1}$ and $\beta = 1/k_B T$. This expression resembles the Franck–Condon factor obtained for local coupling, apart from the dependence on k.

In the middle factor of Eq. (A7) the order of primed and unprimed matrix operators affects the thermal average, with terms like TU' giving contributions proportional to n and terms like U'T giving contributions proportional to $n + 1$. Their sum gives contributions proportional to $2n + 1$, so that it suffices to study $\langle \exp \mathsf{TU}' \rangle$ and then replace n by $2n + 1$ everywhere. The zeroth-order term is

$$\delta_{k'k} \delta_{qq'} = \delta_{kk'} \delta_{k-k',\, q-q'}, \tag{A10}$$

where the factor $\delta_{k-k',\, q-q'}$ expected from Eq. (2.27) has been extracted. The first-order term is

$$\langle TU' \rangle_{k'k;\, qq'} = \langle T_{k'k} U_{qq'} \rangle \tag{A11}$$

$$= N^{-1} n_{k-k'} A^{k'-k} A^{q-q'}_{-q} \delta_{k-k',\, q-q'}, \tag{A12}$$

where relabeling using the symmetry of the A^{q}_{k} gives

$$\langle TU' \rangle_{k'k;\, qq'} = N^{-1} n_{k-k'} (A^{k-k'}_{-k'})^{*} A^{k-k'}_{-k'+k-q} \delta_{k-k',\, q-q'} . \tag{A13}$$

The total contribution is therefore $D^{k-q}_{kk'} \delta_{k-k',\, q-q'}$; where the matrix D^{Q} has elements

$$D^{Q}_{kk'} = N^{-1} (2n_{k-k'} + 1) (A^{k-k'}_{-k'})^{*} A^{k-k'}_{-k'+Q} . \tag{A14}$$

The second-order term depends on

$$[\langle TU' \rangle^2]_{k'k;\, qq'} = \sum_{KQ} \langle T_{k'K} \langle T_{Kk} U_{qQ} \rangle u_{Qq'} \rangle \tag{A15}$$

$$\begin{aligned} = {} & \sum_{k} [N^{-1} n_{k-K} (A^{k-K}_{-K})^{*} A^{k-K}_{-K+k-q}] \\ & \times [N^{-1} n_{K-k'} (A^{K-k'}_{-k'})^{*} A^{K-k'}_{-k'+k-q}] \delta_{k-k',\, q-q'}, \end{aligned} \tag{A16}$$

leading to a total contribution depending on

$$\sum_{K} D^{k-q}_{kK} D^{k-q}_{Kk'} \delta_{k-k',\, q-q'} = (\mathsf{D}^{k-q})^2_{kk'} \delta_{k-k',\, q-q'} . \tag{A17}$$

By induction the nth-order term follows similarly from $(\mathsf{D}^{k-q})^n$, so that Eq. (2.41) can be written as

$$\langle \theta^{+}_{kk'} \theta_{qq'} \rangle = \langle \theta_{-k'} \rangle (\exp D^{k-q})_{kk'} \langle \theta_{-q'} \rangle \delta_{k-k',\, q-q'} . \tag{A18}$$

Extensions of these methods show how the remaining thermal averages in H_0 and V give zero contribution as already asserted. From Eq. (A6) and results in Ref. 16 we deduce that

$$\begin{aligned} & \langle \exp[(T - T') - (U - U')](b + b^{+}) \rangle \\ & \quad = [\langle Tb \rangle - \langle Ub^{+} \rangle] \langle \exp[(T - T') - (U - U')] \rangle \\ & \qquad - \langle \exp[(T - T') - (U - U')\ ] \rangle [\langle T'b \rangle - \langle U'b^{+} \rangle] \end{aligned} \tag{A19}$$

and hence that

$$\begin{aligned} & \langle \theta^{+}_{k'+q,k} \theta_{k'k} (b_q + b^{+}_{-q}) \rangle \\ & \quad = \sum_{K} \{ [\langle T_{kK} b_q \rangle - \langle U_{kK} b^{+}_{-q} \rangle] \langle \theta^{+}_{k'+qK} \theta_{k'k} \rangle \\ & \qquad - \langle \theta^{+}_{k'+q,k} \theta_{k'K} \rangle [\langle T_{Kk} b_q \rangle - \langle U_{Kk} b^{+}_{-q} \rangle] \} \end{aligned} \tag{A20}$$

$$= N^{-1/2} [A^{-q}_{-k} \langle \theta_{k'+q,k} \theta_{k',k-q} \rangle$$

$$- A^{-q}_{-k-q} \langle \theta_{k'+q,k+q} \theta_{k'k} \rangle] . \tag{A21}$$

When Eq. (A21 is substituted in Eq. (2.33), Eq. (2.32) can be used to evaluate the sum over k', yielding a term proportional to

$$\sum_{q} \omega_q (A^{-q}_{-k} A^{q}_{-k+q} - A^{-q}_{-k-q} A^{q}_{-k}) . \tag{A22}$$

Since ω_q is even in q, the second sum is made equal and opposite to the first by changing the summation variable to $-q$, and so the term vanishes. The last term in Eq. (2.34) for V vanishes similarly, consisting from Eq. (2.31) of two parts, one like that just discussed and the other proportional to $\langle b_q + b^{+}_{-q} \rangle$.

We now collect the foregoing results. The choice of Eq. (2.32) for the transformation coefficients can be written as

$$A^q_k = \sum_{k'} f^q_{k'} \langle \theta_{k-q} \rangle (\exp \mathsf{D}^q)_{q-k',q-k} \langle \theta_k \rangle. \quad \text{(A23)}$$

By introducing the matrix E^q with elements

$$E^q_{kk'} = D^q_{q-k',q-k} = N^{-1}(2n_{k-k'}+1)(A^{k-k'}_{k-q})^*(A^{k-k'}_k), \quad \text{(A24)}$$

we obtain alternatively

$$A^q_k = \sum_{k'} f^q_{k'} \langle \theta_{k-q} \rangle (\exp \mathsf{E}^q)_{kk'} \langle \theta_k \rangle. \quad \text{(A25)}$$

The new matrix also enables Eq. (A9) to be written as

$$\langle \theta_k \rangle = \exp\Big[-\tfrac{1}{2} \sum_{k'} E^0_{kk'} \Big]. \quad \text{(A26)}$$

APPENDIX B: TEST OF APROXIMATIONS

One simple test of the approximations is to use them in Eq. (A25) to calculate A^0_λ and compare with the exact value g. From Eq. (A25),

$$A^0_\lambda = \langle \theta^2_\lambda \rangle \sum_q (\exp \mathsf{E}^0)_{\lambda q} f^0_q, \quad \text{(B1)}$$

where, since $f^0_q = g$, we find

$$\xi = A^0_\lambda g^{-1} = \langle \theta_\lambda \rangle^2 \sum_q (\exp \mathsf{E}^0)_{\lambda q}. \quad \text{(B2)}$$

From Eqs. (A9) and (3.7) we have at once

$$\langle \theta_\lambda \rangle^2 = \exp[-(2n+1)(g^2 + V^0 + \eta^2 \phi^2_\lambda)], \quad \text{(B3)}$$

where

$$V^0 \equiv \eta^2 N^{-1} \sum_q \phi^2_q = N^{-1} \sum_\lambda V^0_\lambda. \quad \text{(B4)}$$

We therefore require

$$\sum_q (\exp \mathsf{E}^0)_{\lambda q} = \sum_q (\delta_{\lambda q} + E_{\lambda q} + \tfrac{1}{2} \sum_{q'} E^0_{\lambda q'} E^0_{q' q} + \cdots). \quad \text{(B5)}$$

Here $\Sigma_q \delta_{\lambda q} = 1$ and

$$\sum_q E^0_{\lambda q} = (2n+1)(g^2 + V^0 + \eta^2 \phi^2_\lambda) \equiv (2n+1) E^0_\lambda. \quad \text{(B6)}$$

The next term involves

$$\sum_{qq'} E^0_{\lambda q'} E^0_{q' q} = (2n+1) \sum_{q'} E^0_{\lambda q'} E^0_{q'} \quad \text{(B7)}$$

$$= (2n+1)^2 (F^0 E^0_\lambda + G^0), \quad \text{(B8)}$$

where

$$F^0 = g^2 + 2V^0, \quad \text{(B9)}$$

$$G^0 = W^0 - (V^0)^2, \quad \text{(B10)}$$

$$W^0 = \eta^4 N^{-1} \sum_q \phi^4_q \quad \text{(B11)}$$

are all positive quantities. It follows from these results that a factor E^0_λ in one order gives rise to a factor $(2n+1)(F^0 E^0_\lambda + G)$ in the next order, while a constant factor G^0 gives rise to a factor $(2n+1) G^0 E^0_\lambda$. We can therefore write

$$\sum_q (E^0)^r_{\lambda q} = (2n+1)^r (u_r E^0_\lambda + v_r), \quad \text{(B12)}$$

where the coefficients u_r and v_r satisfy

$$u_{r+1} = F^0 u_r + v_r, \quad \text{(B13)}$$

$$v_{r+1} = G^0 u_r, \quad \text{(B14)}$$

subject to $u_0 = 0$, $v_0 = 1$; $u_1 = 1$, $v_1 = 0$; $u_2 = F^0$, $v_2 = G^0$.

The difference equations (B13) and (B14) are solved by assuming $u_r \propto x^r$, which is valid provided

$$x_\pm = \tfrac{1}{2}\{F^0 \pm [(F^0)^2 + 4G^0]^{1/2}\} \equiv \tfrac{1}{2}(F^0 \pm H^0), \quad \text{(B15)}$$

where, since $G^0 \geqslant 0$, $H^0 \geqslant F^0$. The general solution is then the linear combination $u_r = u_+ x^r_+ + u_- x^r_-$. The boundary conditions yield $u_+ = 1/H = -u_-$, with the solutions for $n \geqslant 0$;

$$u_r = (H^0)^{-1}\{ [\tfrac{1}{2}(F^0 + H^0)]^r - [\tfrac{1}{2}(F^0 - H^0)]^r \}, \quad \text{(B16)}$$

$$v_r = G^0 (H^0)^{-1}\{ [\tfrac{1}{2}(F^0 + H^0)]^{r-1} - [\tfrac{1}{2}(F^0 - H^0)]^{r-1} \}. \quad \text{(B17)}$$

The solutions enable the series for $\Sigma_q (\exp E^0)_{\lambda q}$ to be summed, with the result

$$\sum_q (\exp E^0)_{\lambda q} = (H^0)^{-1}\{ e^{(n+1/2)(F^0+H^0)} [E^0_\lambda - \tfrac{1}{2}(F^0 - H^0)] - e^{(n+1/2)(F^0+H^0)} [E^0_\lambda - \tfrac{1}{2}(F^0 - H^0)] \}, \quad \text{(B18)}$$

where G^0 has been replaced by $[(H^0)^2 - (F^0)^2]/4$. The factor ξ is obtained by multiplying this exponential by $\langle \theta_\lambda \rangle^2$, which from Eqs. (B3) and (B4) is $\exp[-(2n+1)E^0_\lambda]$.

We therefore obtain an expression for ξ, which should be independent of λ, but in fact depends on E^0_λ. We eliminate this dependence by replacing E^0_λ by its average over λ, which is F^0. Then

$$\xi = (1/2H^0)[(F^0 + H^0) e^{-(n+1/2)(F^0 - H^0)} - (F^0 - H^0) e^{-(n+1/2)(F^0 + H^0)}]. \quad \text{(B19)}$$

In the limit of diagonal coupling, $G^0 \to 0$ and $H^0 \to F^0$, so that $\xi \to 1$ as required to obtain previous results. In general, Eq. (B19) gives ξ in terms of η and averages over the distribution of coupling parameters. Values of ξ calculated as a test of the assumption Eq. (3.7) are presented in Sec. IV A, Figs. 2–4, which show that the deviations from unity are small, and thus the approximations are reasonable.

APPENDIX C: EVALUATION OF η

We obtain the scaling parameter η from Eq. (3.7) which implies

$$\eta(\phi_\lambda - \phi_{\lambda - Q}) = \mathrm{Re}(iA^Q_\lambda). \quad \text{(C1)}$$

From Eqs. (A25) and (3.6), this means

$$\eta(\phi_\lambda - \phi_{\lambda-Q}) = \langle \theta_{\lambda-Q} \rangle \langle \theta_\lambda \rangle \{ -g\, \mathrm{Im}\Big[\sum_q (\exp \mathsf{E}^Q)_{\lambda q} \Big] + \mathrm{Re}\Big[\sum_q (\exp \mathsf{E}^Q)_{\lambda q} \Big] (\phi_{q-} \phi_{q-Q}) \}. \quad \text{(C2)}$$

The evaluation of $\Sigma_q (\exp \mathsf{E}^Q)_{\lambda q}$ proceeds much as for $Q = 0$. In particular,

$$\sum_q \mathsf{E}^Q_{\lambda q} = (2n+1)(g^2 + V^Q + V^Q_\lambda) \equiv (2n+1) E^Q_\lambda, \quad \text{(C3)}$$

where V^Q is a generalization of V^0:

$$V^Q = \eta^2 N^{-1} \sum_q \phi_q \phi_{q-Q} = N^{-1} \sum_\lambda V^Q_\lambda. \tag{C4}$$

Note that V^Q is real, while V^Q_λ has an imaginary part which contributes to Eq. (C2). the next order term yields

$$\sum_{qq'} E^Q_{\lambda q'} E^Q_{q'q} = (2n+1)^2 (F^Q E^Q_\lambda + G^Q + I\eta^2 \phi_\lambda \phi_{\lambda - Q}), \tag{C5}$$

where

$$F^Q = g^2 + V^0 + V^Q, \tag{C6}$$

$$G^Q = W^Q - V^0 V^Q + Ig^2, \tag{C7}$$

$$W^Q = \eta^4 N^{-1} \sum_q \phi_q^2 \phi_{q-Q}^2, \tag{C8}$$

$$I = V^Q - V^0. \tag{C9}$$

As $Q \to 0$, $I \to 0$, and these equations reduce to Eqs. (B10)–(B13). However, the additional factor in $\phi_\lambda \phi_{\lambda - Q}$ for nonzero Q means that the third-order term is needed to complete the recursive specification of higher terms. The result is

$$\sum_q (E^Q)^3_{\lambda q} = (2n+1)^3 (KE^0_\lambda + L + F^Q I \eta^2 \phi_\lambda \phi_{\lambda - Q}), \tag{C10}$$

where

$$K = (F^Q)^2 + G^Q + IV^Q, \tag{C11}$$

$$L = F^Q G^Q + I[W^Q - (V^Q)^2]. \tag{C12}$$

We can therefore write

$$\sum_q (E^Q)^r_{\lambda q} = (2n+1)^r (u_r E^Q_\lambda + v_r + w_r \eta^2 \phi_\lambda \phi_{\lambda - Q}), \tag{C13}$$

where the coefficients satisfy

$$u_{r+1} = F^Q u_r + v_r + V^Q w_r, \tag{C14}$$

$$v_{r+1} = G^Q u_r + [W^Q - (V^Q)^2] w_r, \tag{C15}$$

$$w_{r+1} = I u_r. \tag{C16}$$

These equations have the solution

$$u_r = c_1 x_1^r + c_2 x_2^r + c_3 x_3^r, \tag{C17}$$

where the x_i are the roots of

$$x^3 - F^Q x^2 - (G^Q + IV^Q)x - [W^Q - (V^Q)^2] I = 0, \tag{C18}$$

and the boundary conditions determining the c_i are $u_0 = 0$, $u_1 = 1$, $u_2 = F^Q$. Algebraic solution of cubic equations is complicated, so for the time being we leave the x_i and c_i undetermined. For Eq. (C2) we require the imaginary part of $\Sigma_q (\exp \mathsf{E}^Q)_{\lambda q}$, from which Eq. (C13) comes from that of E^Q_λ. Through Eqs. (C3) and (3.11) we obtain

$$-\mathrm{Im}\left[\sum_q (\exp \mathsf{E}^Q)_{\lambda q}\right] = g\eta (\phi_\lambda \phi_{\lambda - Q}) \times \sum_{i=1} c_i \exp(2n+1) x_i. \tag{C19}$$

In the evaluation of the final term in Eq. (C3), we first obtain simply $\phi_\lambda - \phi_{\lambda - Q}$. The next term is

$$\sum_z E^Q_{\lambda q} (\phi_q - \phi_{q-Q}) = -(2n+1)\eta I [2ig + \eta(\phi_\lambda - \phi_{\lambda - Q})], \tag{C20}$$

so that in the rth-order term the coefficient of $(\phi_\lambda - \phi_{\lambda - Q})$ is $[-(2n+1)\eta^2 I]^r$. The term independent of $\boldsymbol{\lambda}$ on the right-hand side of Eq. (C20) gives rise to a series of terms like those in Eq. (C13), but the constant contributed in each order by the $(\phi_\lambda - \phi_{\lambda - Q})$ in the preceding order means that the coefficients now obey the inhomogeneous equation

$$u_{r+3} - F^Q u_{r+2} - (G^Q + IV^Q) u_{r+1} - [W^Q - (V^Q)^2] I u_r = iY(-\eta^2 I)^{r+2}, \tag{C21}$$

where $y = 2g/\eta$. This has solutions

$$u_r = d_1 x_1^r + d_2 x_2^r + d_3 x_3^r + iZ(-\eta^2 I)^r, \tag{C22}$$

where the x_i solve the previous homogeneous equation and the new coefficients d_i are fixed by the boundary conditions $u_0 = 0$, $u_1 = 0$, $u_2 = -iY\eta^2 I$. The term $Z(-y^2 I)^r$ in Eq. (C22) is a particular solution of Eq. (C21),

$$Z = Y(-Y^2 I^2 \{(-\eta^2 I)^3 - F^Q (-\eta^2 I)^2 - (G^Q + IV^Q)(-\eta^2 I) - ([W^Q - (V^Q)^2] I\}^{-1}. \tag{C23}$$

Since the initial nonzero value u_2 is imaginary, so are the coefficients d_i, which we rewrite as ie_i. Then real contributions to Eq. (C2) come from the imaginary part of E^Q_λ and directly from the terms in $(\phi_\lambda - \phi_{\lambda - Q})$, giving

$$(\phi_\lambda - \phi_{\lambda - Q})\{g\eta \sum_{i=1}^{3} e_i e^{(2n+1)x_i} + (1 + g\lambda Z) \times \exp[-(2n+1)\eta^2 I]\}. \tag{C24}$$

Combining this result with Eq. (C19) in Eq. (C2), we obtain

$$\eta = \langle \theta_{\lambda - Q} \rangle \langle \theta_\lambda \rangle \{g\eta \sum_{i=1}^{3} (gc_i + e_i) e^{(2n+1)x_i} + (1 + g\eta Z) \exp[-(2n+1)\eta^2 I]\}. \tag{C25}$$

Although the factors $(\phi_\lambda - \phi_{\lambda - Q})$ cancel, this expression for η still contains a dependence on $\boldsymbol{\lambda}$ and $\mathbf{Q}$. As with ξ, we eliminate this dependence by replacing the various quantities in Eq. (C25) by their averages over $\boldsymbol{\lambda}$ and $\mathbf{Q}$. Thus in $\langle \theta_{\lambda - Q} \rangle$ and $\langle \theta_\lambda \rangle$, $E^0_{\lambda - Q}$ and E^0_λ are both replaced by F^0; V^Q is replaced by zero, so that F^Q is replaced by $F^0 - V^0$ and I by $-V^0$; and W^0 is replaced by $(V^0)^2$, so that G^Q is replaced by $V^0(F^0 - V^0)$. These replacements not only make η a constant as originally postulated, but also simplify the averages over the ϕ_q required in the treatment by eliminating power of $\phi_q \phi_{q'}$, for $q' \neq q$. Furthermore, the replacements allow a factorization of Eq. (C18), which reduces to

$$(x + V^0)[x^2 - F^0 x + (V^0)^2] = 0. \tag{C26}$$

It follows that $x_1 = -V^0$ and

$$x_{2,3} = \tfrac{1}{2}\{F^0 \pm [(F^0)^2 - 4(V^0)^2]^{1/2}\} = \tfrac{1}{2}(F^0 \pm X), \tag{C27}$$

where X is real because from Eq. (B9) $F^0 \geq 2V^0$. The coefficients c_i are then obtained as

$$c_1 = (F^0 + 2V^0)^{-1}, \tag{C28}$$

$$C_{2,3} = [(F^0 + 2V^0)^{-1} \pm X^{-1}]/2. \tag{C29}$$

The quantity Z in Eq. (C24) reduces to

$$Z = Y\eta^4/(\eta^2+1)[(\eta^4+1)V^0 - \eta^2 F^0], \tag{C30}$$

$$e_1 = Y\eta^2/(\eta^2+1)(F^0+2V^0), \tag{C31}$$

$$e_{2,3} = -YV^0\eta^2\frac{[(\eta^2+1)(F^0+2V^0)^{-1} \pm (\eta^2-1)X^{-1}]}{2[(\eta^4+1)V^0 - \eta^2 F^0]}. \tag{C32}$$

With these results we find

$$\eta = (1+g\eta Z)\exp[-(2n+1)(F^0-\eta^2 V^0)] + g^2\eta\{(F^0+2V^0)^{-1}[2\eta(\eta^2+1)^{-1}]\} \times\exp\{-(2n+1)(F^0+V)\} + \frac{1}{2}\sum_{\pm} c_{\pm}\exp[-(n+1/2)(F^0 \mp X)], \tag{C33}$$

where

$$c_{\pm} = \left[1 - \frac{2\eta V^0(\eta^2+1)}{(\eta^4+1)V^0 - \eta^2 F^0}\right](F^0+2V^0)^{-1} \pm \left[1 - \frac{2\eta V^0(\eta^2-1)}{(\eta^4+1)V^0 - \eta^2 F^0}\right]X^{-1} \tag{C34}$$

and it must be remembered that F^0, V^0, X, and Z depend on η. This equation is solved numerically for η in Sec. IV.

APPENDIX D: EVALUATION OF $\tilde{J}_\lambda$

The expression for $\tilde{J}_\lambda$ given in Eq. (2.37) can be evaluated by techniques similar to those used for A^Q_λ. We make use of the fact that J_λ is even in λ and that

$$\sum_\lambda J_\lambda = 0, \tag{D1}$$

because J_{rs} is purely nonlocal ($J_{rr}=0$). Then in evaluating $\Sigma_\mu(\exp E^0)_{\lambda\mu}J_\mu$, the first term in J_λ and the second is, from Eq. (3.9),

$$\sum_\mu E^0_{\lambda\mu}J_\mu = N^{-1}(2n+1)\sum_\mu [g^2 + \eta^2(\phi_\lambda - \phi_\mu)^2]J_\mu. \tag{D2}$$

The terms in g^2 and ϕ^2_λ vanish by Eq. (D1) and that in $\phi_\lambda\phi_\mu$ by symmetry, leaving

$$N^{-1}(2n+1)\sum_\mu \eta^2\phi^2_\mu J_\mu \equiv (2n+1)\eta^2 M. \tag{D3}$$

We note that in the simple case where $\phi_\mu = \phi\sin\mu$ and $J_\mu = J\cos\mu$, M is zero, so that presumably M is often small.

By arguments analogous to those used previously, it follows that

$$\sum_\mu (\mathsf{E}^0)^{r+1}_{\lambda\mu}J_\mu = (2n+1)^{r+1}(u_r E^0_\lambda + v_r)\eta^2 M \tag{D4}$$

with boundary conditions $u_0=0$, $v_0=1$, $u_1=1$, $v_1=0$. These yield the previous solutions (B16) and (B17). With $\langle\phi_\lambda\rangle^2$ from Eqs. (B3) and (B6) we finally obtain

$$\tilde{J}_\lambda = [\exp -(2n+1)E^0_\lambda]\Big(J_\lambda - (E^0_\lambda - F^0)\eta^2 M/G^0 + (\eta^2 M/2G^0H^0)\{e^{(n+1/2)(F^0+H^0)} \times(H^0-F^0)(E^0_\lambda - \tfrac{1}{2}F^0 - H^0)e^{(n+1/2)(F^0-H^0)} \times(H^0+F^0)[E^0_\lambda - \tfrac{1}{2}(F^0+H^0)]\}\Big). \tag{D5}$$

Even when M is zero, $\tilde{J}_\lambda$ can differ from J_λ in a complicated way. From Eq. (B6) it can be seen that there is a uniform band narowing caused by both local and nonlocal coupling plus further narrowing and distortion caused by nonlocal coupling which is greatest in regions intermediate between the Brillouin zone center and the zone boundary.

[1] R. Silbey and R. W. Munn, J. Chem. Phys. **72**, 2763 (1980).
[2] Exciton transport has been reviewed recently by P. Reineker and V. Kenkre, in *Exciton Dynamics in Molecular Crystals and Aggregates* (Springer, New York, 1982).
[3] C. B. Harris and D. Zwemer, Annu. Rev. Phys. Chem. **29**, 473 (1978).
[4] V. Agranovitch and Y. Konobeev, Opt. Spectrosc. (USSR) **6**, 241 (2959); Sov. Phys. Solid State **5**, 999 (1963); Phys. Status Solidi **27**, 435 (1968).
[5] T. Holstein, Ann. Phys. (NY) **8**, 325, 343 (1959); D. Emin and T. Holstein, Ann. Phys. (NY) **53**, 439 (1969); Y. Toyozawa, in *Relaxation of Elementary Excitations*, edited by R. Kubo (Springer, New York, 1980).
[6] Reviewed by G. G. Roberts, N. Apsley, and R. W. Munn, Phys. Rep. (Phys. Lett. C) **60**, 59 (1980).
[7] H. Sumi, Solid State Commun. **28**, 309 (1978); J. Chem. Phys. **70**, 3775 (1979).
[8] S. Efrima and H. Metiu, Chem. Phys. Lett. **60**, 226 (1979).
[9] C. Duke, L. Schein, and A. McGhie, Phys. Rev. Lett. **40**, 197 (1978); C. B. Duke, Ann. NY Acad. Sci. **313**, 166 (1978); C. B. Duke and L. B. Schein, Phys. Today **33**, 42 (1980).
[10] L. Friedman, Phys. Rev. **140**, A 1649 (1965).
[11] I. Vilfan, in *Lecture Notes in Physics* (Springer, Heidelberg, 1977), Vol. 65, p. 629.
[12] P. Gosar and S. -I. Choi, Phys. Rev. **150**, 529 (1966).
[13] I. Vilfan, Phys. Status Solidi B **59**, 351 (1973); **78**, K131 (1976).
[14] P. Gosar and I. Vilfan, Mol. Phys. **18**, 49 (1970).
[15] R. W. Munn and R. Silbey, Mol. Cryst. Liq. Cryst. **57**, 131 (1980).
[16] M. Grover and R. Silbey, J. Chem. Phys. **52**, 2099 (1970); **54**, 4843 (1971).
[17] R. W. Munn and R. Silbey, Ninth Molecular Crystal Symposium, Mittelberg, Austria (1980); R. W. Munn, Inst. Phys. Conf. Ser. **58**, 98 (1980).
[18] R. Balian and E. Brezin, Nuovo Cimento. B **64**, 37 (1969); R. W. Munn and R. Silbey, J. Phys. A: Math. Nucl. Gen. **11**, 939 (1978).
[19] D. R. Yarkony and R. Silbey, J. Chem. Phys. **65**, 1042 (1976).
[20] D. R. Yarkony and R. Silbey, J. Chem. Phys. **67**, 5818 (1977).
[21] V. Capek and R. W. Munn, Phys. Status Solidi **108**, 521 (1981); **109**, 245 (1982).
[22] M. I. Klinger, Phys. Status Solidi **2**, 1062 (1962); *Problems of Linear Electron (Polaron) Transport Theory in Semiconductors* (Pergamon, Oxford, 1979).
[23] M. Umehara, J. Phys. Soc. Jpn. **47**, 852 (1979).
[24] M. D. Clarke, D. P. Craig, and L. A. Dissado, Mol. Cryst. Liq. Cryst. **44**, 309 (1978).