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On the Munn–Silbey approach to nonlocal exciton–phonon coupling

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A canonical transformation method originally proposed by Munn and Silbey is used to partially diagonalize a model Hamiltonian which incorporates both local and nonlocal exciton–phonon coupling. At the heart of the method is a secular elimination principle which poses a difficult self-consistency problem. A limited form of this self-consistency problem was solved in an approximate fashion by primarily analytical methods in the original work of Munn and Silbey. We take a numerical approach, solving the general self-consistency problem to desired accuracy. Among the differences between our findings and those of the original work are polaron binding energies much larger and Debye–Waller factors much smaller than originally anticipated.

I. INTRODUCTION

In this paper we are concerned with that part of polaron theory focused on the problem of “nonlocal” exciton–phonon (or electron–phonon) interactions; local coupling being defined as a nontrivial dependence of diagonal Hamiltonian matrix elements $\langle n|H|n\rangle$ upon phonon states, and nonlocal coupling as a nontrivial dependence of nondiagonal Hamiltonian matrix elements $\langle m|H|n\rangle$ upon phonon states, where $|m\rangle$ and $|n\rangle$ are the rigid-lattice Wannier states of the exciton. The body of polaron theory identified with local coupling is quite large, including the “optical” polaron of Fröhlich,^{1–4} small and large polaron of Holstein,^{5,6} and the many-electron problem of traditional BCS theory,⁷ to name only a few examples. The body of polaron theory identified with nonlocal coupling is smaller, but includes the generic contribution of nonlocal coupling to the phonon-assisted transport of excitons and charge carriers,^{8–15} the many-electron problem of Su–Schrieffer–Heeger type models,^{16–18} and applications more chemical in nature, such as the problem of excimer formation.^{19–24}

We should emphasize at the outset that the common appellation “phonon assisted” embraces a larger suite of behaviors than is addressed by nonlocal coupling alone. For example, even in the absence of nonlocal coupling the nearest-neighbor transfer of small polarons can be assisted by the transient modulation of the effective energy difference between the self-trapped level and neighboring bare levels. This effect is present in ordered materials, but is of even greater importance in disordered materials where polarons preferentially occupy states in the band tail, relative to which most neighboring bare levels are found at higher energies.^{25–35}

Canonical transformations, of great importance in polaron theory, further blur the distinctions between local and nonlocal coupling. The displaced oscillator transformation, when applied to a local coupling Hamiltonian, imposes a phonon modulation upon the transfer term that

could be characterized as a pseudononlocal component. This pseudononlocal character represents one and the same phenomenon as the phonon-assisted transport noted above; the “phonon-diagonal” part of this term represents tunneling between self-trapped levels, while the “phonon-nondiagonal” part represents more complex phonon-assisted transfers.

In this paper, we examine the influence of simultaneous local and nonlocal exciton–phonon coupling on the correlations which define polaron structure. We do not address transport, but we do employ canonical transformations. Thus, while we do not address the competition or cooperation of local and nonlocal coupling in phonon-assisted transport, we do face the blurring of local and nonlocal effects in the polaron basis.

The central problem of polaron theory is the determination of the best possible polaron state, which, depending on one’s particular approach, may involve identifying collective coordinates, minimizing the size of a remainder term in perturbation theory, optimizing some trial state by variational methods, etc.^{4–6,36–44} In this paper we address a method introduced by Munn and Silbey which is essentially a perturbation method, but which contains an element of optimization. Munn and Silbey generalized the displaced oscillator transformation common in local-coupling polaron theory³⁶ to the case of combined local and nonlocal coupling, observing that one perturbative term in particular had the potential to grow arbitrarily large with increasing temperature. Such a secular growth would be inconsistent with a convergent perturbation theory, and so they chose their transformation coefficients to eliminate this secular growth with the temperature.

This secular elimination principle produced a set of self-consistency equations that could be solved only approximately. Here, we follow Munn and Silbey and pose the same general self-consistency problem; however, we solve this problem numerically and examine the solution

with a generality and quantitative accuracy previously unavailable.

We note in advance a shortcoming of this approach. The self-consistency equations which result from this secular elimination scheme are independent of the rigid-lattice tunneling matrix elements " J " which determine the rigid-lattice band structure, including such essential quantities as the rigid-lattice effective mass and density of states. This implies that the validity of this approach is limited to the narrow (rigid) band regime where traditional small polaron theory is understood to hold. Wide (rigid) band scenarios are generally beyond the scope of these methods.

We begin with the general Hamiltonian, describing so-called linear local and nonlocal exciton-phonon coupling in a translationally invariant system

$$H = \sum_n E a_n^+ a_n + \sum_{mn} J_{mn} a_m^+ a_n + \sum_n \left[\frac{P_n^2}{2M} + \frac{1}{2} M \omega^2 Q_n^2 \right] + \sum_{lmn} \gamma_{mn}^l Q_l a_m^+ a_n, \quad (1)$$

where a_n^+ creates an exciton in the rigid-lattice Wannier state n , and Q_n and P_n are the coordinate and momentum describing the Einstein oscillator identified with the site n . Owing to the hermiticity of the Hamiltonian and translational invariance, the coefficients satisfy the symmetries

$$J_{mn} = J_{nm}^* = J_{m+r, n+r}, \quad (2)$$

$$\gamma_{mn}^l = \gamma_{nm}^{l*} = \gamma_{m+r, n+r}^{l*}. \quad (3)$$

We choose the coefficients to be real. For definiteness, in specific computations we choose

$$J_{mn} = J(\delta_{mn+1} + \delta_{mn-1}), \quad (4)$$

$$\gamma_{mn}^l = \gamma_0 \delta_{ml} \delta_{nl} + \frac{1}{2} (\gamma_1^l + \gamma_1^a) (\delta_{ml} \delta_{nl-1} + \delta_{nl} \delta_{ml-1}) + \frac{1}{2} (\gamma_1^l - \gamma_1^a) (\delta_{nl} \delta_{ml+1} + \delta_{ml} \delta_{nl+1}). \quad (5)$$

In writing the Hamiltonian in this way, we are including only the simplest exciton tunneling geometry and the most minimal possibilities for both local and nonlocal coupling to Einstein phonons. The two nonlocal coupling constants account for the two symmetries which may be involved. In this paper we follow closely the development and results presented by Munn and Silbey; thus, the majority of our specific results are presented for the antisymmetric case studied by them ($\gamma_1^l = 0$, $\gamma_1^a = \gamma_1$). At the close of this paper we present illustrative results for the symmetric coupling case.

It will prove advantageous to implement our analysis in k space, for which we adopt the transformation conventions

$$Q_l = \sqrt{\frac{\hbar}{2NM\omega}} \sum_q e^{-iql} (b_{-q}^+ + b_q), \quad (6)$$

$$a_n = \frac{1}{\sqrt{N}} \sum_k e^{-ikn} a_k. \quad (7)$$

In order to define a momentum space form for the force triadic γ_{mn}^l we make use of translational invariance to define coordinates relative to the site associated with the exciton creation operator [cf. Eq. (1)]; thus, with $\mu \equiv n - m$ and $\nu \equiv l - m$,

$$\gamma_k^q = \sum_{\mu\nu} e^{-iq\nu} e^{ik\mu} \gamma_{0\mu}^\nu. \quad (8)$$

This implies that the triple Fourier transform involved in going from Eq. (1) to Eq. (12) below yields

$$\sum_{lmn} e^{-iql} e^{ik'm} e^{-ikn} \gamma_{mn}^l \equiv N \delta_{k'k+q} \gamma_{-k}^q. \quad (9)$$

For the coupling geometry considered in this paper,

$$\gamma_k^q = \gamma_0 + \gamma_1^l [\cos(k) + \cos(k-q)] - i\gamma_1^a [\sin(k) - \sin(k-q)]. \quad (10)$$

We further define dimensionless coupling constants f_k^q , etc., such that any f is related to the corresponding γ through the relation

$$f = \frac{1}{\sqrt{2M\hbar\omega^3}} \gamma. \quad (11)$$

With these conventions, the momentum-space form of the Hamiltonian is

$$H = \sum_k (\epsilon + J_k) a_k^+ a_k + \sum_q \hbar \omega_q (b_q^+ b_q + 1/2) + N^{-1/2} \sum_{kq} f_{-k}^q \hbar \omega_q (b_q + b_{-q}^+) a_{k+q}^+ a_k. \quad (12)$$

Transformation of the Hamiltonian is carried out as

$$H \rightarrow \tilde{H} = e^L H e^{-L}, \quad (13)$$

with

$$L = N^{-1/2} \sum_{kq} A_{-k}^q (b_{-q}^+ - b_q) a_{k+q}^+ a_k, \quad (14)$$

where the transformation coefficients A_k^q have the symmetry property

$$A_k^q = (A_{-k-q}^q)^*. \quad (15)$$

This dressing transformation yields polaron and dressed phonon operators

$$\tilde{a}_n \equiv e^L a_n e^{-L} = \sum_m \theta_{nm} a_m, \quad (16)$$

$$\tilde{b}_q \equiv e^L b_q e^{-L} = b_q - N^{-1/2} \sum_{mn} A_{mn}^{-q} a_m^+ a_n. \quad (17)$$

(The general definition of θ_{nm} is given below.) When restricted to the small-polaron regime of local-coupling theory, $A_k^q \rightarrow f_k^q$ and the "thunder operators" θ_{nm} take the form

$$\theta_{nm} = \delta_{mn} e^{N^{-1/2}} \sum_q f_m^q (b_q^+ - b_{-q}). \quad (18)$$

In the presence of nonlocal coupling, however, θ_{nm} is non-

diagonal, implying that the polaron created by $\tilde{a}_n^+$ represents a superposition of bare exciton states which, though centered on the site n , is at least somewhat delocalized.

After the transformation, the Hamiltonian $\tilde{H}$ can be separated into a zeroth-order band Hamiltonian $\tilde{H}_0$ and a scattering interaction $\Delta\tilde{H}$:

$$\tilde{H} = \tilde{H}_0 + \Delta\tilde{H}, \quad (19)$$

$$\tilde{H}_0 = \sum_k \left(\epsilon + \tilde{J}_k - N^{-1/2} \sum_q |A_k^q|^2 \hbar\omega_q \right) a_k^+ a_k + \sum_q \hbar\omega_q (b_q^+ b_q + 1/2), \quad (20)$$

$$\Delta\tilde{H} = \sum_{kk'} \left[\sum_p J_p T_{pk, pk'} - 2N^{-1} \sum_{pq} \hbar\omega_q f_{-p}^q A_{-k'}^{-q} T_{p-q, k; p, k'+q} + N^{-1/2} \sum_{pq} \hbar\omega_q f_{-p}^q [T_{p+q, k; p, k'} (b_q + b_{-q}^+) - \langle T_{p+q, k; p, k'} (b_q + b_{-q}^+) \rangle] \right] a_k^+ a_{k'} + N^{-1/2} \sum_{kq} \hbar\omega_q \left[A_{-k}^q - \sum_{k'} f_{-k'}^q \langle \theta_{k'+q, k+q}^+ \theta_{k'k} \rangle \right] (b_q + b_{-q}^+) a_{k+q}^+ a_k, \quad (21)$$

where

$$\tilde{J}_k = \sum_{k'} J_{k'} \langle \theta_{k'}^+ \theta_{k'k} \rangle, \quad (22)$$

$$\theta_{kk'} = [\exp(-S)]_{kk'}, \quad (23)$$

$$\theta_{kk'}^+ = [\exp(S)]_{k'k}, \quad (24)$$

$$S_{kk'} = N^{-1/2} A_{-k'}^{k-k'} (b_{k'-k}^+ - b_{k-k'}), \quad (25)$$

$$T_{kk'; pp'} = \theta_{kk'}^+ \theta_{pp'} - \langle \theta_{kk'}^+ \theta_{pp'} \rangle, \quad (26)$$

where $\langle \dots \rangle$ denotes the thermal average in the free-phonon basis at the temperature T .

This separation has the appeal that the thermal average of the perturbation $\Delta\tilde{H}$ vanishes, and every term of $\Delta\tilde{H}$ containing a T operator remains bounded in a mean-square sense. The one formal difficulty is the last term of $\Delta\tilde{H}$ which contains phonon displacement operators uncompensated by a T operator. This last term has the potential to grow with increasing temperature, motivating Munn and Silbey's choice of A_k^q to eliminate this potential secular growth

$$A_{-k}^q = \sum_{k'} f_{-k'}^q \langle \theta_{k'+q, k+q}^+ \theta_{k'k} \rangle. \quad (27)$$

The problem of optimizing the zeroth-order Hamiltonian is now reduced to determining the transformation coefficients A_k^q for given exciton-phonon coupling parameters f_k^q . Using Eqs. (23)–(27), one may show that the transformation coefficients must satisfy the self-consistency equations

$$E_{kk'}^q = N^{-1} (2n_{k-k'} + 1) (A_{k-k'}^{k-k'})^* A_k^{k-k'}, \quad (28)$$

$$\langle \theta_k \rangle = \exp \left[-\frac{1}{2} \sum_{k'} E_{kk'}^0 \right], \quad (29)$$

$$A_k^q = \langle \theta_{k-q} \rangle \langle \theta_k \rangle \sum_{k'} f_{k'}^q [\exp(E^q)]_{kk'}, \quad (30)$$

in which n_q is the Bose distribution (since we compute only for the Einstein phonon model, $2n_q + 1 = \coth \frac{1}{2} \beta \hbar \omega$) and

the triadic $E_{kk'}^q$ is an auxiliary intermediate quantity introduced for convenience. We emphasize that these self-consistency equations are the exact consequence of the Munn–Silbey secular elimination scheme. We note that the temperature enters explicitly only in Eq. (28), the exciton-phonon coupling constants enter explicitly only in Eq. (30), and the tunneling matrix element does not enter at all. All the computations to follow were performed for the nominally moderate temperature $k_B T = \hbar\omega$.

II. METHOD OF SOLUTION

In the small polaron limit of local coupling polaron theory, the optimal transformation coefficients are given by $A_k^q = f_k^q$. Munn and Silbey assumed a similar form for A_k^q in which the local and nonlocal coupling constants were scaled by variational parameters ξ and η

$$A_k^q = f_0 \xi - i f_1 \eta [\sin(k) - \sin(k-q)]. \quad (31)$$

One can show, however, that $A_k^0 = f_0$ exactly, implying that $\xi = 1$. This leaves η as the single parameter to be varied, and leads to a single nonlinear equation to be solved.

Our aim is to solve Eqs. (28)–(30) numerically, avoiding any restriction on the form of the transformation coefficients. As a practical matter, however, computation is facilitated by generalizing Munn and Silbey's variational parameters ξ and η to real matrices such that

$$A_k^q = f_0 \xi_k^q - i f_1 \eta_k^q [\sin(k) - \sin(k-q)]. \quad (32)$$

The reader may observe that this form is not completely general since the explicit sin functions force the imaginary part to vanish along the lines $q=0$, $2k \pm \pi$. The $q=0$ line constitutes no restriction, however, since the symmetry relation (15) requires A_k^0 to be real. Similarly, although it is not clear from the known symmetries that the $q=2k \pm \pi$ lines do not constitute a restriction, sample calculations using completely general A_k^q 's consistently show that A_k^q is real along these lines. In our calculations we treat the $q=0$ and $q=2k \pm \pi$ lines as lines of removable singularities and

FIG. 1. Momentum-space components of A_k^q [cf. Eq. (32)]. Nonlocal coupling is the antisymmetric type. ξ_k^q, η_k^q for $\gamma_0 = \gamma_1 = 1.0$.

choose the values of η_k^q along these lines to be continuous with neighboring values; this convention has no effect on the value of A_k^q .

The ξ and η matrices introduced in this way inherit the symmetry properties of the transformation coefficients such that

$$\xi_k^q = \xi_{k-q}^{-q}, \quad \eta_k^q = \eta_{k-q}^{-q}. \quad (33)$$

At the start of each iterative process, some initial guess for ξ and η is made, often a uniform matrix of order unity (consistent with Munn and Silbey's approximation), or the

FIG. 2. Momentum-space components of A_k^q [cf. Eq. (32)]. Nonlocal coupling is the antisymmetric type. ξ_k^q, η_k^q for $\gamma_0=0.03, \gamma_1=1.0$.

output from a previous run. The output of one iteration is fed back into the self-consistency equations in a controlled way to generate the next ξ and η . Computation ends when the output set is within precision requirements of the last input set.

Iteration is stable when exciton-phonon coupling is

not too large. In this situation iteration converges upon unique solutions rapidly and to machine precision for any initial guess for ξ and η . As f_0 and/or f_1 are increased beyond unity, computation becomes increasingly sensitive to the details of the iteration, though convergence to unique solutions remains possible. When exciton-phonon

FIG. 3. Upper panel: Logarithm of the Debye-Waller factor, based on Eq. (35). Center panel: Wave vector dependent binding energy, based on Eq. (36). Lower panel: Total polaron energy band, based on Eq. (34), using a rigid-lattice bandwidth $J=1$ and $\epsilon=0$. Chain-dotted ($\cdots$), $\gamma_0=1.0$, $\gamma_1=0.3$. Solid ($-$), $\gamma_0=1.0$, $\gamma_1=1.0$. For comparison, also plotted are corresponding quantities from Ref. 14 Dashed ($---$), $\gamma_0=1.0$, $\gamma_1=0.3$. Dotted ($\cdots$), $\gamma_0=1.0$, $\gamma_1=1.0$.

coupling is large, however, convergence tends to fail either by failing to minimize errors to desired precision, or by converging to multiple solutions sensitive to the initialization set. It is possible that convergence fails in the strong-coupling regime for purely numerical reasons. For example, certain intermediate results involve exponentiated

matrices having large positive and negative eigenvalues which must be resolved to obtain final results of order unity;⁴⁵ this problem increases greatly with increasing exciton-phonon coupling and could generate purely numerical instabilities. On the other hand, there is precedent for the existence of multiple solutions in strong-coupling polaron theory (e.g., in the context of the self-trapping transition); however, we were unable to refine our study sufficiently to make reliable statements on this possibility. Thus, for definiteness, we limit our discussion to weak and moderate coupling where our solutions are reliable by all available criteria.

III. NUMERICAL RESULTS

Our results share a few common characteristics.

(1) When nonlocal coupling is weak relative to local coupling, the wave vector dependences of ξ_k^q and η_k^q are also weak; e.g., when $f_0=1$ and $f_1=0.03$, the maximum relative wave vector variation is less than approximately 0.15%, and when $f_0=1$ and $f_1=0.3$ (a case studied by Munn and Silbey) the maximum relative wave vector variation is less than approximately 15%. When these circumstances hold, our numerical values for the average ξ and η are in reasonable agreement with the approximate results of Munn and Silbey, though there exist systematic deviations.

(2) Significant wave vector dependence emerges in ξ_k^q and η_k^q when both local and nonlocal coupling are order unity or greater (cf. Fig. 1), and wave vector dependence is strong when nonlocal coupling is significantly greater than local coupling (cf. Fig. 2).

(3) When wave vector dependence is significant, the maximum relative wave vector variation appears to scale roughly with the ratio f_1/f_0 ; e.g., when $f_0=1.0$ and $f_1=0.03$, the maximum relative wave vector variation is approximately 0.15%; however, when $f_0=0.03$ and $f_1=1.0$, the maximum relative wave vector variation is approximately 3000%.

(4) ξ_k^q is weakly structured in the neighborhood $q=0$, regardless of coupling strength, and $\xi_k^0=1$ for all parameter values. η_k^q generally has a more significant wave vector dependence in the small q regime; however, the impact of this variability on the value of A_k^q is muted by the structure factors which accompany η_k^q .

(5) Regardless of coupling strength, the wave vector dependence of ξ_k^q and η_k^q has a characteristic "manta ray" shape. The detail of this shape can be understood through an examination of the real-space structure of the exciton-phonon coupling, which is deferred to Sec. V.

This handful of characteristics helps to sort out the piecemeal agreement between our results and those of our predecessors. While the explanation is clearly bound up in the nonuniform wave vector dependence of ξ_k^q and η_k^q , it is significant that the *average* ξ and η which follow from our calculations differ systematically from the ξ and η of Munn and Silbey. We have found that the η of Munn and Silbey is more representative of an approximate lower bound to η_k^q than its average; our average η is consistently of order unity, while that of Munn and Silbey is consistently

FIG. 4. Real-space representation of the transformation coefficients for $\gamma_0=0.03$, $\gamma_1=1.0$; translational invariance is used to display $A_{0\mu}^v$. Nonlocal coupling is the antisymmetric type.

smaller, and tends to zero with increasing local coupling. We have also found that the $\xi=1$ assumption of Munn and Silbey represents a lower bound for ξ_k^0 rather than an average; our average ξ is typically significantly greater than unity, and scales roughly with the ratio f_1/f_0 . These systematic deviations explain the basic trends in the magnitudes of other quantities as well.

The consistency test Munn and Silbey performed was limited to comparing the computed A_k^0 with the known value f_0 . Our results show that the $q \approx 0$ region of $\text{Re}\{A_k^q\}$ is nearly structureless even when overall wave vector variation is strong, so that *a posteriori* this test does not provide good information on the momentum-space variability of the transformation coefficients.

IV. POLARON ENERGY BAND

Polaron bands are computed using $\tilde{H}_0$ only [cf. Eq. (20)]

$$\epsilon_k = \epsilon + J_k e^{-\sigma_k} - E_k^b \quad (34)$$

in which we have written $\tilde{J}_k$ as $J_k e^{-\sigma_k}$ so as to make the Debye-Waller factor explicit. In addition to the usual wave vector dependence due to the rigid lattice energy band J_k , this energy band derives its structure from the wave vector dependence of the Debye-Waller factor and the binding energy

$$e^{-\sigma_k} = \langle \theta_k \rangle^2 \sum_{k'} [\exp(E^0)]_{kk'} J_{k'}/J_k, \quad (35)$$

$$E_k^b = N^{-1} \sum_q |A_k^q|^2 \hbar \omega_q. \quad (36)$$

These two quantities are closely related. Indeed, in the Munn-Silbey approximate results, the binding energy and the logarithm of the Debye-Waller factor are proportional by factors independent of the exciton-phonon coupling constants

$$e^{-\sigma_k} = \exp \left(-(2n+1) \left\{ f_0^2 + \frac{1}{2} \eta^2 f_1^2 [1 + 2 \sin^2(k)] \right\} \right), \quad (37)$$

$$E_k^b = \hbar \omega \left\{ f_0^2 + \frac{1}{2} \eta^2 f_1^2 [1 + 2 \sin^2(k)] \right\}. \quad (38)$$

The k dependence of these quantities takes the form of a modulation which peaks in the intermediate zone at $k = \pm \pi/2$. Correspondence between our numerical results and this approximate analytical form is limited. While we always find a bimodal variation of σ_k and E_k^b symmetric about $k=0, \pi$, and $\pm \pi/2$, the amplitude of this wave vector variation is strongly suppressed relative to Eqs. (37) and (38); on the other hand, the average binding energy is significantly larger and the average Debye-Waller factor significantly smaller than predicted by Eqs. (37) and (38).

One of the more interesting results to emerge from this and prior analyses of nonlocal coupling is the possibility that polaron energy bands may become sufficiently distorted to allow new energy minima to emerge which would introduce new peaks in densities of states and correspond-

FIG. 5. Exciton-phonon correlation functions for antisymmetric nonlocal coupling. Upper panel: Site-centered exciton-phonon correlation function C_l [see Eq. (39)] for $\gamma_0=0.03$, $\gamma_1=1.0$. The polaron is taken to be fully localized at the origin; C_l reflects the organization of the lattice in the neighborhood of the polaron. Center panel: Bond-centered exciton-phonon correlation function $\bar{C}_l$ [see Eq. (40)] for $\gamma_0=0.03$, $\gamma_1=1.0$. The polaron is taken to occupy sites 0 and 1 equally, in a coherent symmetric superposition of probability amplitudes. Lower panel: Bond-centered exciton-phonon correlation function $\bar{C}_l$ [see Eq. (40)] for $\gamma_0=0.03$, $\gamma_1=1.0$. The polaron is taken to occupy sites 0 and 1 equally, in a coherent antisymmetric superposition of probability amplitudes.

ing optical spectra. In order for this bimodal variation to be resolved, the amplitude of the variation in the binding energy must be comparable to the average renormalized energy band width. For a typical cosine band, Eqs. (37) and (38) suggests this should be possible in the nominally moderate regime $J=f_0=f_1=1$ (cf. Fig. 3). However, owing to the strong suppression of structure in the Debye-Waller factor and the binding energy which we find rela-

tive to Eqs. (37) and (38), it would appear that such band distortions should be significantly more difficult to observe in practice. For example, of the two energy bands in Fig. 3 that we computed by our methods, the result for stronger nonlocal coupling ($f_1=f_0=1.0$) actually *does* contain a coupling-induced minimum; however, the modulation is too small to be resolved in the figure.

It is somewhat counterintuitive to see that the *greater* momentum-space variability we find for the transformation coefficients A_k^q should translate into *weaker* distortions of the energy band. The explanation can be found, however, in the interplay of the real and imaginary parts of A_k^q in producing physical quantities such as the binding energy. The binding energy is proportional to the average of $|A_k^q|^2$ over the phonon quasimomenta q ; this is, in turn, the sum of the mean square values of the real and imaginary parts of A_k^q .

$$|A_k^q|^2 = f_0^2(\xi_k^q)^2 + f_1^2(\eta_k^q)^2 \{[\sin(k) - \sin(k-q)]\}^2. \quad (39)$$

It is clear from Figs. 1 and 2 that separately the mean square values of ξ_k^q and η_k^q exhibit strong variations as functions of the exciton quasimomentum k ; however, when combined as in Eq. (39) using the required structure factors, these variations are found to be nearly complementary, such that the aggregate quantity has only a weak dependence on k .

V. SITE-SPACE INTERPRETATION

Using translational invariance and defining $A_{mn}^l = A_{0\mu}^l$ as in Eq. (8), we may invert the double Fourier transformation of A_k^l as in Eq. (8) to examine the real-space structure of the transformation coefficients. This is a natural way to compare the transformation coefficients, which directly determine the structure of the polaron state, with the (nearest-neighbor) coupling coefficients which appear in the Hamiltonian.

First let us note that the ansatz (31) on which the previous analysis was based implies that the transformation coefficients A connect exactly the same lattice sites as do the coupling coefficients f [cf. Eq. (10)]. This assumption is reasonable when nonlocal coupling is weak relative to local coupling; however, it breaks down as nonlocal coupling gains prominence because nonlocal coupling is itself a transport mechanism capable of spreading the effects of exciton-phonon correlations in space.

Figure 4 displays the result for the strong nonlocal coupling case $f_0=0.03$, $f_1=1.0$. Apart from a modest renormalization of their magnitudes (e.g., $f_{00}^1=0.5 \rightarrow A_{00}^1 \approx 0.36$), the four dominant positive/negative peaks correspond to the nonlocal coupling components of the exciton-phonon interaction. Similarly, apart from a more substantial renormalization ($f_{00}^0=0.03 \rightarrow A_{00}^0 \approx 0.18$), the positive central peak corresponds to the local coupling component. The balance of the structure visible in this figure out to fifth neighbors and beyond must be attributed to an extended exciton

FIG. 6. Momentum-space representation of the transformation coefficients for $\gamma_0=0.03$, $\gamma_1=1.0$. Nonlocal coupling is the symmetric type; thus, A_k^q is real. Note that the graphic has been rotated relative to Figs. 1 and 2 in order to optimally display the squaring off of the wave vector dependence which grows in with strong nonlocal coupling, as in Fig. 2.

structure supported by nonlocal exciton-phonon coupling. The width of this broad component is controlled by the ratio of nonlocal to local coupling.

It is the spreading of exciton-phonon correlations in space which is responsible for the characteristic manta ray shape of the momentum-space structure noted above. The symmetries are such that the even- μ components of $A_{0\mu}^q$ contribute to ξ_k^q and that the odd- μ components contribute to η_k^q . If $A_{0\mu}^q$ is truncated to include only the $\mu=0, \pm 1$ components, the resulting ξ_k^q and η_k^q are independent of wave vector. If this truncation is expanded to include $\mu=0, \pm 1, \pm 2, \pm 3$, the dominant bimodal structure seen in Fig. 1 is recovered. Including higher space components of $A_{0\mu}^q$ does not alter the fundamental modulation frequency, but refines the shape of the fundamental. When nonlocal coupling is weak or moderate relative to local coupling (as in Fig. 1), $A_{0\mu}^q$ is fairly compact so that including components up to $\mu=\pm 3$ is sufficient to recover the basic shape of ξ_k^q and η_k^q . The modulation in this regime is smooth and nearly sinusoidal. When nonlocal coupling is large relative to local coupling (as in Figs. 2, 4, and 6), $A_{0\mu}^q$ is more broad so that components well beyond $\mu=\pm 3$ make significant contributions. The modulation of ξ_k^q and η_k^q in this regime is quite anharmonic.

Exciton-phonon correlation functions are useful means for analyzing the structure of polaron states. We define a site-centered correlation function C_l

$$C_l = \left(\frac{\hbar}{2M\omega} \right)^{-1/2} \langle \tilde{\psi} | \sum_m Q_{m+l} a_m^+ a_m | \tilde{\psi} \rangle, \quad (40)$$

and a bond-centered correlation function $\bar{C}_l$

$$\bar{C}_l = \left(\frac{\hbar}{2M\omega} \right)^{-1/2} \langle \tilde{\psi} | \sum_m Q_{m+l} (a_{m+1}^+ a_m + a_m^+ a_{m+1}) | \tilde{\psi} \rangle, \quad (41)$$

in which the state used to compute the expectation value is a polaron state containing no excited dressed phonons

$$|\tilde{\psi}\rangle = \sum_m \tilde{\psi}_m \tilde{a}_m^+ |0\rangle. \quad (42)$$

These correlation functions are similar to diagnostics computed by Wang *et al.*^{46,47} for local coupling only, and by Song³⁹ and Umehara⁴² for combined local and nonlocal coupling.

C_l is sensitive to exciton density, while $\bar{C}_l$ probes spatial coherence due to quantum tunneling. The natural polaron state to use in computing C_l is a site-localized state in which $\tilde{\psi}_m = \delta_{m0}$. The natural polaron state to use in computing $\bar{C}_l$ is a bond-localized state in which $\tilde{\psi}_m = (1/\sqrt{2})(\delta_{m0} \pm \delta_{m1})$. Computation of the site-centered correlation function was made using the formula

FIG. 7. Exciton-phonon correlation functions for symmetric nonlocal coupling. Upper panel: Site-centered exciton-phonon correlation function C_l [see Eq. (39)] for $\gamma_0=0.03$, $\gamma_1=1.0$. The polaron is taken to be fully localized at the origin; C_l reflects the organization of the lattice in the neighborhood of the polaron. Center panel: Bond-centered exciton-phonon correlation function $\bar{C}_l$ [see Eq. (40)] for $\gamma_0=0.03$, $\gamma_1=1.0$. The polaron is taken to occupy sites 0 and 1 equally, in a coherent symmetric superposition of probability amplitudes. Lower panel: Bond-centered exciton-phonon correlation function $\bar{C}_l$ [see Eq. (40)] for $\gamma_0=0.03$, $\gamma_1=1.0$. The polaron is taken to occupy sites 0 and 1 equally, in a coherent antisymmetric superposition of probability amplitudes.

$$C_l = \frac{1}{N^2} \sum_{kk'q} 2A_{-k',-q}^{-q} e^{-iq|l|} [\exp(E^q)]_{-k',-k} \langle \theta_{-k'-q} \rangle \times \langle \theta_{-k'} \rangle. \quad (43)$$

Computation of the bond-centered correlation function was made using the same formula; however, modified such that the structure factor

$$S_{kk'}^q = \left[1 \pm \cos\left(k' + \frac{1}{2}q\right) \cos\left(k' - \frac{1}{2}q\right) \right] [e^{-ik} + e^{i(k+q)}] \quad (44)$$

is included in the summation, with the $+$ ($-$) sign being chosen to correspond to the symmetric (antisymmetric) superposition implicit in $\tilde{\psi}_m$. Results for the strong nonlocal coupling case are displayed in Fig. 5. Appropriately, the strongest exciton-phonon correlations are found for the states most compatible with the type of the exciton-phonon coupling present.

VI. SYMMETRIC COUPLING

All numerical results presented so far have been for the case of antisymmetric exciton-phonon coupling. We now present a few illustrative results for the case of symmetric coupling. The central formulas of this paper are valid for either case; however, since the coupling function is real in the symmetric coupling case, it follows from Eqs. (28)–(30) that it is sufficient to restrict computation to real A_k^q .

Numerical results for the strong coupling case $f_0^s=0.03$, $f_1^s=1.0$ are displayed in Figs. 6 and 7. The matrix of transformation coefficients A_k^q shown in Fig. 6 should be compared with Fig. 2. The primary difference between the results for symmetric and antisymmetric coupling is the change in the fundamental symmetry of the A matrix. The absence of a prominent bimodal modulation leads to energy band structures lacking the intermediate-zone minima which can emerge with strong antisymmetric nonlocal coupling. This qualitative distinction is compounded by differences in less prominent features of the transformation coefficients.

VII. CONCLUSION

We have followed the approach of Munn and Silbey for determining appropriate zeroth-order polaron states in the presence of simultaneous local and nonlocal exciton-phonon coupling. Rather than deriving approximate analytical expressions for the quantities of interest, we have solved the self-consistency equations numerically. Owing to practical limitations on our computation, we have been limited to values of local and nonlocal coupling coefficients which are not large by absolute measures; however, in the regime of small and moderate coupling coefficients we experience no limitation on the relative magnitudes of local and nonlocal coupling, and have exploited this freedom to examine the full range of possible relative magnitudes.

The transformation coefficients which define the structure of polaron states and energy band structure in this approach respond to increasing nonlocal exciton-phonon coupling by developing dramatic momentum-space modulations. These distortions can be related to a spreading of exciton-phonon correlations in real space, suggesting a polaron state based on an extended exciton structure supported by coherent phonon-assisted exciton transfers. The width of this extended structure is in rough empirical proportion to the ratio of the nonlocal to local exciton-phonon coupling constants (f_1/f_0); as a trend in the ratio of a

tunneling parameter to a local coupling parameter, this resembles behavior found in the nonlinear theory of large polarons where the width of the self-consistent localized state is related to similar ratios.⁴⁸⁻⁵²

Debye-Waller factors and polaron binding energies familiar from local-coupling polaron theory acquire weak wave vector dependences which display a characteristic modulation centered around $|k| = \pi/2$. These modulations have the potential to distort the polaron energy band, and for resonance integrals J small enough, introduce new extrema in the energy band, and new peaks into the density of states. The main consequences of nonlocal coupling, however, are found to be a strong enhancement of band narrowing and of the binding energy.

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