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1997

Brown, D. W., Lindenberg, K., & Zhao, Y. (1997). Variational energy band theory for polarons: Mapping polaron structure with the global-local method. *Journal of Chemical Physics*, 107(8), 3179-3195.

<https://hdl.handle.net/10356/92317>

<https://doi.org/10.1063/1.474668>

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Variational energy band theory for polarons: Mapping polaron structure with the global-local method

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(Received 11 February 1997; accepted 16 May 1997)

In this paper we revisit from a contemporary perspective a classic problem of polaron theory in one dimension using a new variational approach generalizing that of Toyozawa, based on delocalized trial states including mixed global and local exciton-phonon correlations. Polaron structure is represented by variational surfaces giving the optimal values of the complete set of exciton and phonon amplitudes for every value of the joint exciton-phonon crystal momentum κ . Characteristic small polaron, large polaron, and nearly free phonon structures are identified, and the manner in which these compete and/or coexist is examined in detail. Through such examination, the parameter space of the problem is mapped, with particular attention given to problematic areas such as the highly quantum mechanical weak-coupling regime, the highly nonlinear intermediate-coupling regime, and to the self-trapping transition that may be said to mark the onset of the strong-coupling regime. Complete energy bands are presented in illustrative cases, and the principal trends in the ground-state energy, polaron bandwidth, and effective mass are identified. The internal structure of our variational Bloch states is examined for qualities that might reflect the typical characteristics of solitons, finding some intriguing qualitative comparisons, but little that bears close scrutiny.

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I. INTRODUCTION

In this paper we conclude a sequence of three increasingly refined variational attacks on a classic problem of polaron theory in one space dimension.¹⁻³ The first in this sequence applied the method of Merrifield⁴ in an exhaustive manner, characterizing polaron structure as rendered by that method over the entire parameter space of the underlying model; in the following we refer to this particular work as Paper I.² The second applied the method of Toyozawa,⁴⁻¹⁹ again exhaustively characterizing the range of polaron structure, and giving careful attention to the properties revealed with substantially improved clarity and quality relative to the Merrifield calculation; we refer to this work as Paper II.³ Here, we apply our own method generalizing that of Toyozawa, combining both global and local exciton-phonon correlations in a manner motivated by prior work²⁰⁻²² in the context of the theory of solitons.²⁰⁻⁴² The global-local method thus encompasses a wide range of polaron and soliton theoretic constructs within a framework that is rigorously consistent with the symmetry requirements of quantum mechanical energy-momentum eigenfunctions in discrete, translationally invariant lattices.

Our purpose is several-fold:

(1) Corroboration. It is clear from the preceding calcula-

tion that the Toyozawa method greatly improves upon that of Merrifield; even so, there are indications internal to the Toyozawa method that reflect its own limitations. A meaningful generalization of the Toyozawa method would serve as a check against distortions these limitations might cause.

(2) Improvement. Of course, we expect to improve at least quantitatively on the results of the Toyozawa method, and by extending the Toyozawa method in a manner that is nontrivially distinct and not merely increasing the number of qualitatively similar variational parameters, perhaps achieve qualitative as well as quantitative improvement.

(3) Refinement of polaron structure. It is well known that although the variational principle provides rigorous inequalities that discriminate between trial energies, it is not assured that improvement in the energy bound should be accompanied by meaningful improvement in the structure of the trial state. Counter examples include rough energy surfaces for which improvement in the energy bound may be accompanied by essentially random changes in the trial state. Less extreme and more pertinent to the present problem are situations where a class of trial states ill-suited to some essential feature of the target state may be forced into compensating distortions that may be more reflective of the insufficiencies of the trial class than of the structure of the underlying ground state. It is a central aim of our work not only to achieve high-quality variational estimates (bounds) of polaron bands, but to achieve a high-quality resolution of the structure of the underlying polaron states. It is with this in-

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tention that we have given great care to the assessment of diverse features of polaron structure over wide ranges of parameters within a sequence of mutually corroborating computations. Though rigorous measures of accuracy are not available, it is evident from the whole suite of our present and preceding results that the polaron structure contained in the present work constitutes such a high-quality resolution.

This paper is organized as follows: In the next section we sketch our approach, set down the model Hamiltonian, and define key parameters and conventions. In Sec. III we present a careful discussion of both the trial state used in our present calculations and the theoretical context of other trial states to which ours is closely related. In Sec. IV the variational energy is minimized using our trial state of choice, and the self-consistency equations defining the variational solution are set down. In Sec. V we present several complete variational solutions intended to reflect the range of typical polaron structures. In Sec. VI we take a broader view, presenting a phase diagram that in one illustration conveys qualitative information about the entire range of polaron structures at all parameter values, a central feature of which is the self-trapping transition. In Sec. VII we present specific polaron energy bands and consider closely several quantifiable characteristics of these energy bands, comparing and contrasting these with corresponding results obtained by the Toyozawa method. In Sec. VIII we examine the internal structure of our polaron Bloch states, with particular attention given to the possibility that this internal structure might bear some relation to similar constructs from the theory of solitons. Conclusions are summarized in Sec. IX.

II. APPROACH AND MODEL

Our central interest in this paper is in the polaron energy band, computed as

$$E^\kappa = \langle \Psi(\kappa) | \hat{H} | \Psi(\kappa) \rangle, \quad (1)$$

wherein κ is the total crystal momentum label, $|\Psi(\kappa)\rangle$ is a normalized delocalized trial state, and $\hat{H}$ is the system Hamiltonian. The set of E^κ so produced constitute an estimate (upper bound) for the polaron energy band.^{5,43} The trial states we use are eigenfunctions of the total momentum operator and are orthogonal for distinct κ . Overlaps of $\hat{H}$ between trial states of distinct κ vanish, implying the absence of $\kappa - \kappa'$ scattering among the self-consistent states. This independence of distinct momentum sectors allows variations to be performed independently for each κ . It is thus that our overall approach differs crucially from some that focus only on the global ($\kappa=0$) ground state; our goal is to obtain high-quality variational estimates of the lowest polaron energy band and its associated Bloch states at every κ .

Since our sights are set on the polaron energy band as a whole, our criteria for the “goodness” of our results extend well beyond the comparison of global ground state energies ($E^0 = E^{\kappa=0}$) from competing calculations. Indeed, in our whole-band approach E^0 proves to be one of the least informative quantities to consider when judging the quality of our results. Moreover, while the absolute value of E^0 is of con-

siderable formal interest, its precise value beyond a certain level of accuracy is of little practical importance.

As our model Hamiltonian we choose the traditional molecular crystal model of Holstein in one space dimension^{44,45}

$$\hat{H} = \hat{H}^{\text{ex}} + \hat{H}^{\text{ph}} + \hat{H}^{\text{ex-ph}}, \quad (2)$$

$$\hat{H}^{\text{ex}} = -J \sum_n a_n^\dagger (a_{n+1} + a_{n-1}), \quad (3)$$

$$\hat{H}^{\text{ph}} = \hbar \omega \sum_n b_n^\dagger b_n, \quad (4)$$

$$\hat{H}^{\text{ex-ph}} = -g \hbar \omega \sum_n a_n^\dagger a_n (b_n^\dagger + b_n), \quad (5)$$

in which $a_n^\dagger$ creates an electronic excitation in the rigid-lattice Wannier state at site n , and $b_n^\dagger$ creates a quantum of vibrational energy in the Einstein oscillator at site n . The Holstein Hamiltonian has been used to model a variety of electronic excitations, including electrons, holes, and excitons. In the single-particle case that concerns us, the statistics of the electronic excitation are immaterial, so we refer to the electronic excitation as an “exciton” and regard both excitons and phonons as bosons. The Einstein frequency is given by ω , J is the exciton transfer integral between nearest-neighbor sites, and g is the local coupling strength. Throughout this paper, $\hbar = \omega = 1$; consequently, J and g are understood to be measured in units of the optical phonon energy.

All of the methods used in this paper can be applied as well to common generalizations of this Hamiltonian, involving, for example, phonon dispersion, differing phonon types, exciton transfers beyond nearest neighbors, different exciton-phonon coupling geometries, and higher space dimensions. Nonlocal coupling in particular has been treated elsewhere,^{46,47} and other generalizations are the subject of work in progress.⁶⁵

We have posed our Hamiltonian in the site representation; however, we shall make heavy use of momentum representations as well as mixed representations. Throughout this paper we use the Fourier conventions

$$\zeta_n = N^{-1} \sum_p e^{ipn} \zeta_p, \quad \zeta_p = \sum_n e^{-ipn} \zeta_n, \quad (6)$$

$$c_n^\dagger = N^{-1/2} \sum_p e^{-ipn} c_p^\dagger, \quad c_p^\dagger = N^{-1/2} \sum_n e^{ipn} c_n^\dagger, \quad (7)$$

for operators ($c = a, b$) and scalars ($\zeta = \alpha, \beta, \gamma$), respectively.

Throughout, we indicate exciton and phonon wave vectors by latin indices and reserve the greek κ for the joint crystal momentum; however, to simplify presentation we suppress the explicit κ label on many quantities since the relevant value is generally clear from context.

III. TRIAL STATES

Our calculations are based on unit-normalized delocalized trial states. These states are built up from localized functions carrying all the information regarding exciton-phonon

correlations. This delocalized state framework is to be contrasted with common localized state approaches in which the variational functional is not a polaron band energy, but the expected value of the Hamiltonian in a trial state that is generally incompatible with the properties of Bloch states and generally yields localized functions as minimal solutions. In view of the relation of this work to its predecessors (I and II) using simpler trial states, and the relation between our sequence of delocalized state calculations with roughly parallel work in the localized state framework,^{20–41} here we approach the definition of our trial states in a somewhat formal way in order to clarify these relationships.

Our normalized trial Bloch states can be constructed in the form⁴⁸

$$|\Psi(\kappa)\rangle = \frac{|\kappa\rangle}{\langle\kappa|\kappa\rangle^{1/2}}, \quad (8)$$

in which the delocalized vector $|\kappa\rangle$ is generated from a form factor $|\phi\rangle$ through a projection operation

$$|\kappa\rangle = \hat{\Xi}^\kappa |\phi\rangle \quad (9)$$

$[(\hat{\Xi}^\kappa)^\dagger = \hat{\Xi}^\kappa]$. The delocalizing operator $\hat{\Xi}^\kappa$ is given by

$$\hat{\Xi}^\kappa \equiv N^{-1} \sum_n \exp[-i(\hat{P} - \kappa)n], \quad (10)$$

in which N is the number of lattice sites and $\hat{P}$ is the operator representing the joint crystal momentum of the exciton-phonon system

$$\hat{P} = \sum_k k a_k^\dagger a_k + \sum_q q b_q^\dagger b_q. \quad (11)$$

The joint crystal momentum operator commutes with the Hamiltonian, and the operator $e^{-i\hat{P}n}$ is straightforwardly shown to induce concerted exciton and phonon translations by n lattice sites. The effect of the delocalizing operator is to displace replicas of the operand by all possible lattice translations, weighting each by an appropriate phase, and collecting the entire set of such displaced replicas into a single superposition state. The resulting superposition state satisfies the Bloch condition

$$e^{-i\hat{P}r}|\kappa\rangle = e^{-i\kappa r}|\kappa\rangle \quad (12)$$

for any lattice vector r , and any quantity measured relative to a fixed frame is found to be uniform throughout the lattice.

These procedures apply and the resulting properties follow for any form factor $|\phi\rangle$. Indeed, while in many cases $|\phi\rangle$ can be viewed as a localized state, the delocalizing operation applies with equal effect to extended states, e.g., wave trains that are not compatible with the Bloch condition. The delocalizing operator $\hat{\Xi}^\kappa$ contains no information specific to the Hamiltonian $\hat{H}$, and, in particular, contains no variational quantities; it does nothing but render the input function $|\phi\rangle$ into a form consistent with the symmetry requirements of energy-momentum eigenstates of crystalline solids. All system-specific information, and, in particular, all variational quantities are contained in the form factor $|\phi\rangle$; generally $|\phi\rangle$

does not bear any dependence on the crystal momentum label κ until a variation is implemented on the delocalized state, optimizing the form factor for a particular value of κ . Every state so constructed is a fitting candidate for energy band calculations regardless of the depth of insight invested in the localized function $|\phi\rangle$; the latter may be quite simple, yielding results of little practical value, or arbitrarily complex, yielding results of little practical utility. The art to the science lies in the choice of “form factor” $|\phi\rangle$.

It is, perhaps, self evident that good choices of form factor would be variational states that are in some meaningful sense “good” approximate solutions in their own right, but that lack compatibility with the properties of Bloch states. It is thus that our attention is focused on states that occupy a central position in the development of the theory of polarons, in particular the small polaron form, the Pekar–Davydov form, and our own generalization of the latter. These have all been previously developed in the localized framework, where they are generally understood as describing the internal structure of a quasiparticle whose external dynamics is particlelike with respect to a centroid. The delocalization index “ n ” appearing in Eq. (10) and in our trial Bloch states is a surrogate for the centroid degree of freedom; hence we will occasionally refer to this index as an “external” label.

Our form factors can be viewed as superpositions of products of exciton and phonon components. In all that we do, the elemental phonon component is a product over coherent states selected to represent the quantum state of each phonon mode. Such coherent state products can be written⁴⁹

$$|\{\zeta_q\}\rangle = \exp\left[-N^{-1/2} \sum_q (\zeta_q b_q^\dagger - \zeta_q^* b_q)\right] |0\rangle, \quad (13)$$

in which ζ_q is the complex amplitude characterizing the state of the mode labeled by q . When all $\{\zeta_q\}$ are free to range over the complex numbers, all possible classical lattice configurations are represented as minimum-uncertainty quantum states, making such coherent states natural choices for use in characterizing polaronic lattice distortions.

A hierarchy of trial states can be established based on the characteristics of the phonon coherent state amplitudes and their relationship with the exciton components with which they are paired. In the following we include beside each form factor a bracketed quantity indicating the number of complex variational amplitudes required to completely specify it.

The simplest nontrivial form factor is what we shall here call the small polaron state

$$|\phi\rangle = a_m^\dagger | \{g e^{-iqm}\} \rangle \quad [0]. \quad (14)$$

This is one state from the N -fold degenerate system that is obtained in the $J \rightarrow 0$ limit. This state represents an exciton completely localized at site m , and the lattice completely undistorted except at site m where the Einstein oscillator amplitude is given by the coupling constant g .

Next in the hierarchy is the form factor underlying the variational calculation of Merrifield

$$|\phi\rangle = a_m^\dagger |\{\beta_q\}\rangle, \quad \text{or} \quad |\phi\rangle = a_m^\dagger |\{\gamma_q e^{-iqm}\}\rangle \quad [N]. \quad (15)$$

These states each represent an exciton completely localized at site m , paired with a lattice distortion as given by the set of phonon amplitudes $\{\beta_q\}$ or $\{\gamma_q e^{-iqm}\}$. Since the effect of the phase e^{-iqm} is to perform a real-space translation of m lattice sites on the phonon component, the universe of realizable lattice configurations in both cases is the same, and the two forms are physically equivalent; a lattice distortion $\{\beta_q\}$ centered at m in the former, for example, is represented in the latter by a set of amplitudes $\{\gamma_q\}$ centered at the origin. If these states are used as they stand in the localized framework, the result is identical to Eq. (14) since the complete localization of the exciton component implies $\langle \phi | \hat{H}_{\text{ex}} | \phi \rangle = 0$. If the variation is performed in the delocalized framework, however, first applying the delocalizing operator $\hat{\Xi}^\kappa$ before optimizing the phonon amplitudes, $\langle \Psi(\kappa) | \hat{H}_{\text{ex}} | \Psi(\kappa) \rangle \neq 0$, allowing the finite mobility of the exciton to be manifested in the phonon amplitudes $\{\beta_q\}$. The shape of the self-consistent lattice distortion may be either compact as in the small polaron case or broad as is more typical of the large polaron case. A detailed study of polaron structure by the Merrifield method has been given in Paper I.

An important generalization of both the small polaron and Merrifield states is that associated with Davydov (localized framework) and Toyozawa (delocalized framework). This form factor abandons the use of the phase e^{-iqm} to associate a lattice distortion with the site of exciton creation and accounts for the finite mobility of the exciton by allowing for spatial spreading of the exciton component

$$|\phi\rangle = |\alpha\rangle \otimes |\{\beta_q\}\rangle \quad [2N], \quad (16)$$

$$|\alpha\rangle = \sum_m \alpha_m a_m^\dagger |0\rangle. \quad (17)$$

This class of state subsumes a wide variety of structures from completely localized to completely delocalized, and has been used as the basis of dynamical theories as well as time-independent analyses. If this state is used as it stands in the localized framework, the result is a lattice distortion intimately related to the distribution of exciton amplitudes in real space; this relationship is manifested in similarities of shape ("locking" to be addressed later; see Sec. VIII) and less subtly in the fact that the lattice distortion is centered on the centroid of the exciton distribution. It is through such considerations that the soliton concept arises. As in the Merrifield case, the delocalization that is required by the Bloch state construction has significant consequences for polaron structure, yielding features and trends that cannot be contained in the localized construct. A detailed study of polaron structure by the Toyozawa method has been given in Paper II.

An alternate generalization of the Merrifield state would be to retain the use of the phase e^{-iqm} to associate a lattice distortion with the site of exciton creation within a state that allows for exciton spreading

$$|\phi\rangle = \sum_m \alpha_m a_m^\dagger |0\rangle |\{\gamma_q e^{-iqm}\}\rangle \quad [2N]. \quad (18)$$

Provided that the exciton amplitudes α_m exhibit a nontrivial spread in real space, the exciton-phonon correlations implicit in this state are quite distinct from those in Eq. (16). As in Eq. (16), variation in the localized framework identifies a unique shape function given by the set of variational amplitudes $\{\gamma_q\}$. Unlike Eq. (16), however, the lattice distortion associated with this shape function is not a single deformation centered on the distribution of exciton amplitudes; instead, through the action of the phase e^{-iqm} , a replica of this shape function is centered upon each exciton creation operator, in effect creating N distinguishable lattice distortions. This is a strong structural difference between the kind of exciton-phonon correlations implicit in Eq. (16) and (18) that remains functionally distinct as long as (i) there is nontrivial spreading of the exciton amplitudes in real space, and (ii) there is nontrivial q dependence in $\{\beta_q\}$ or $\{\gamma_q\}$.

In the following, we refer to correlations carried by centroid-centered coherent state amplitudes such as the $\{\beta_q\}$ in Eq. (16) as *global* correlations, and those carried by exciton-centered coherent state amplitudes such as the $\{\gamma_q e^{-iqm}\}$ in Eq. (8) as *local* correlations.

The most general one-exciton state in which the lattice components are represented by phonon coherent state products is the state

$$|\phi\rangle = \sum_m \alpha_m a_m^\dagger |0\rangle |\{\beta_{qm}\}\rangle \quad [N(N+1)], \quad (19)$$

in which the coherent state amplitudes $\{\beta_{qm}\}$ are permitted a general dependence on q and m . This state has received some attention in the localized framework,^{34,39,40} but has not seen any application as a form factor in a delocalized state. This limited attention is largely due to the vastly larger number of variational parameters required to express this general spatial dependence of β_{qm} , as well as the greater complexity of the formal description required to contain the solution.

It is in this context that Brown and Ivic²⁰⁻²² attempted to simplify the latter method in such a way that its outstanding feature—a unified description of the principal exciton-phonon correlation channels—would be preserved within a more practical framework. This was done by decomposing the amplitude β_{qm} into a part sensitive to global exciton-phonon correlations as in Eqs. (16), and a part sensitive to local exciton-phonon correlations as in Eq. (18),

$$|\phi\rangle = \sum_m \alpha_m a_m^\dagger |0\rangle |\{\beta_q - \gamma_q e^{iqm}\}\rangle \quad [3N]. \quad (20)$$

The global amplitude β_q can be related to the spatial average of β_{qm} , and the local amplitude $\gamma_q e^{-iqm}$ can be viewed as an Ansatz for the spatial variation of β_{qm} around this mean value. The latter spatial dependence may appear somewhat *ad hoc*; however, it is motivated by the physical notion of associating a lattice distortion with each lattice site as in Eq. (18).

Applying the delocalizing operation $\hat{\Xi}^\kappa$ to Eq. (20) yields the delocalized states that are the basis of our variation

$$|\kappa\rangle = N^{-1/2} \sum_{nn_a} e^{i\kappa n} \alpha_{n_a-n}^\kappa a_{n_a}^\dagger \times \exp \left\{ - \sum_{n_b} [(\beta_{n_b-n}^\kappa - \gamma_{n_b-n_a}^\kappa) b_{n_b}^\dagger - \text{H.c.}] \right\} |0\rangle. \quad (21)$$

Although self-consistency imposes complex relationships among all the variational amplitudes, it is particularly evident in this form that the α and β amplitudes are qualitatively distinct from the γ amplitudes. Both $\{\alpha_{n_a-n}\}$ and $\{\beta_{n_b-n}\}$ relate elementary exciton or phonon components to the delocalization index n , which as a surrogate for the centroid of the form factor is associated not with an elementary component but with a functional of all of the variational amplitudes. On the other hand, the amplitudes $\{\gamma_{n_b-n_a}\}$ express a relation between elementary exciton and phonon components directly, without reference to external labels.

Owing to practical considerations, the form actually used in the following is the mixed real-space/Fourier representation

$$|\kappa\rangle = N^{-1/2} \sum_{nn_a} e^{i\kappa n} \alpha_{n_a-n}^\kappa a_{n_a}^\dagger \times \exp \left\{ -N^{-1/2} \sum_q [(\beta_q^\kappa e^{-iqn} - \gamma_q^\kappa e^{-iqn_a}) b_q^\dagger - \text{H.c.}] \right\} |0\rangle. \quad (22)$$

IV. FORMULATION

We proceed to evaluate the expectation values of the three terms in the Holstein Hamiltonian

$$\langle \kappa | \hat{H}^{\text{ex}} | \kappa \rangle = -J \sum_{nm} e^{-i\kappa n} \alpha_m^* (\alpha_{m-n+1}^* S_{nm}^{+1} + \alpha_{m-n-1}^* S_{nm}^{-1}), \quad (23)$$

$$\langle \kappa | \hat{H}^{\text{ph}} | \kappa \rangle = N^{-1} \sum_{nmq} e^{-i\kappa n} \alpha_m^* \alpha_{m-n}^* S_{nm}^0 [|\beta_q|^2 e^{iqn} + |\gamma_q|^2 - \beta_q^* \gamma_q^* e^{iqm} - \beta_q^* \gamma_q e^{iq(n-m)}], \quad (24)$$

$$\langle \kappa | \hat{H}^{\text{ex-ph}} | \kappa \rangle = -g N^{-1} \sum_{nmq} e^{-i\kappa n} \alpha_m^* \alpha_{m-n}^* S_{nm}^0 [e^{iq(n-m)} \times (\beta_q^* + \beta_{-q} e^{-iqn}) - (\gamma_q^* + \gamma_{-q})], \quad (25)$$

$$\langle \kappa | \kappa \rangle = \sum_{nm} e^{-i\kappa n} \alpha_m^* \alpha_{m-n}^* S_{nm}^0, \quad (26)$$

where S_{nm}^l is the Debye–Waller factor, which has the usual physical meaning of quantifying overlaps between lattice wave functions. Here the bookkeeping associated with such

overlaps is more complex than in more familiar cases owing to the distinct spatial relationships embodied in the two classes of phonon amplitudes

$$S_{(n_1-m_1), (m_2-m_1)}^{(n_2-m_2)} \equiv \langle \{\beta_q e^{-iqn_1} - \gamma_q e^{-iqn_2}\} \{ \beta_q e^{-iqm_1} - \gamma_q e^{-iqm_2} \} \rangle, \quad (27)$$

which takes the functional form

$$S_{nm}^l = \exp \left\{ N^{-1} \sum_q [|\beta_q|^2 (e^{iqn} - 1) + |\gamma_q|^2 (e^{iql} - 1) + \frac{1}{2} (e^{-iqn} + e^{-iql} - 2) (\beta_q^* \gamma_q^* e^{iq(l+m)} + \beta_q^* \gamma_q e^{iq(n-m)})] \right\}. \quad (28)$$

This Debye–Waller factor satisfies the property

$$S_{nm}^{l*} = S_{-n, m-n+l}^{-l}, \quad (29)$$

for any $\{\beta_q, \gamma_q\}$, which is instrumental in demonstrating other symmetries. It is worth noting that although there is a formal symmetry in the way the two correlation channels contribute to the Debye–Waller factor, there is a definite asymmetry in the manner in which these two channels contribute to the expected value of the energy. The more familiar form of the Debye–Waller factor is recovered when one or the other of the two correlation channels is eliminated,

$$S_{rm}^l |_{\gamma_q=0} \equiv S_{r0}^0 = S_{nm}^r |_{\beta_q=0} \equiv S_{00}^r = S_r \equiv \exp \left[N^{-1} \sum_q |\zeta_q|^2 (e^{iqr} - 1) \right], \quad (30)$$

where $\zeta_q = \beta_q$ or γ_q .

It is the complexity of the Debye–Waller factor that is ultimately the limiting factor in numerical computation. Including the suppressed κ -dependence, the complete Debye–Waller matrix consists of N^4 complex quantities ($3N^3$ actually used in this calculation since only $S_{nm}^{l=0, \pm 1}$ appear in the variational equations), each of which requires evaluating N expressions. Since the phonon amplitudes change en route to convergence, $O\{3N^3\}$ such expressions must be evaluated at every iteration step for each κ just to compute the required Debye–Waller factors. The form of the Debye–Waller factor is a source of some numerical difficulty as well; the nesting of exponentials and the exponentiation of differences involved taxes numerical precision in some regimes, but on the whole, calculations are manageable despite these sensitivities.

Minimization of E^κ with respect to β_q^* leads to

$$\beta_q = \frac{gL_q + \gamma_q \left[\frac{1}{2} (L_{-q}^* - L_q) E^\kappa - U_q + L_q \right]}{M_q + H_q - M_q E^\kappa}, \quad (31)$$

where

$$L_q = \sum_{nm} e^{-i\kappa n} \alpha_m \alpha_{m-n}^* S_{nm}^0 e^{iq(n-m)}, \quad (32)$$

$$M_q = \sum_{nm} e^{-i\kappa n} \alpha_m \alpha_{m-n}^* S_{nm}^0 e^{iqn} = M_q^*, \quad (33)$$

$$\begin{aligned} H_q = & -J \sum_{nm} e^{-i\kappa n + iqn} \alpha_m (\alpha_{m-n+1}^* S_{nm}^{+1} + \alpha_{m-n-1}^* S_{nm}^{-1}) \\ & + N^{-1} \sum_{nmp} e^{-i\kappa n + iqn} \alpha_m \alpha_{m-n}^* S_{nm}^0 \{ [|\beta_p|^2 e^{ipn} \\ & + |\gamma_p|^2 - \beta_p \gamma_p^* e^{ipm} - \beta_p^* \gamma_p e^{ip(n-m)}] - g[e^{ip(n-m)} \\ & \times (\beta_p^* + \beta_{-p} e^{-ipn}) - (\gamma_p^* + \gamma_{-p})] \} = H_q^*, \quad (34) \end{aligned}$$

$$\begin{aligned} U_q = & -\frac{1}{2} J \sum_{nm} e^{-i\kappa n + iq(n-m)} \alpha_m [\alpha_{m-n+1}^* S_{nm}^{+1} (e^{-iqn} \\ & + e^{-iq} - 2) + \alpha_{m-n-1}^* S_{nm}^{-1} (e^{-iqn} + e^{iq} - 2)] \\ & + \frac{1}{2} N^{-1} \sum_{nmp} e^{-i\kappa n + iq(n-m)} \alpha_m \alpha_{m-n}^* S_{nm}^0 (e^{-iqn} - 1) \\ & \times \{ [|\beta_p|^2 e^{ipn} + |\gamma_p|^2 - \beta_p \gamma_p^* e^{ipm} - \beta_p^* \gamma_p e^{ip(n-m)}] \\ & - g[e^{ip(n-m)} (\beta_p^* + \beta_{-p} e^{-ipn}) - (\gamma_p^* + \gamma_{-p})] \}. \quad (35) \end{aligned}$$

Similarly, minimization of E^κ with respect to γ_q^* yields

$$\gamma_q = \frac{-g \langle \kappa | \kappa \rangle + \beta_q \left[\frac{1}{2} (L_{-q} - L_q^*) E^\kappa - U_q^* + L_q^* \right]}{\langle \kappa | \kappa \rangle + V_q}, \quad (36)$$

where

$$\begin{aligned} V_q = & -J \sum_{nm} e^{-i\kappa n} \alpha_m [\alpha_{m-n+1}^* S_{nm}^{+1} (e^{iq} - 1) \\ & + \alpha_{m-n-1}^* S_{nm}^{-1} (e^{-iq} - 1)] = V_q^*. \quad (37) \end{aligned}$$

Under the Merrifield method, there were no internal exciton amplitudes to be optimized, and under the Toyozawa method, the convenient approach was to take advantage of certain symmetries to perform all calculations in momentum space, choosing the Fourier amplitudes as the working variables in both the exciton and phonon systems. Here, owing to the complex structure of the Debye–Waller factor S_{nm}^l , there is no advantage to a total momentum space description. Both formal presentation and numerical computation are facilitated, in fact, by using the real-space exciton amplitudes as the working variables in the exciton system while retaining the momentum-space description in the phonon system.

The optimal values of the internal exciton amplitudes are determined by minimizing E^κ with respect to α_l^*

$$\alpha_l = -\frac{F_l}{G_l}, \quad (38)$$

where

$$\begin{aligned} F_l = & -J \left(\sum_{n \neq 1} e^{-i\kappa n} \alpha_{n+l-1} S_{n,n+l-1}^{+1} \right. \\ & \left. + \sum_{n \neq -1} e^{-i\kappa n} \alpha_{n+l+1} S_{n,n+l+1}^{-1} \right) \\ & + \sum_{n \neq 0} e^{-i\kappa n} \alpha_{n+l} S_{n,n+l}^0 \left\{ -E^\kappa + N^{-1} \sum_p [|\beta_p|^2 e^{ipn} \right. \\ & + |\gamma_p|^2 - \beta_p \gamma_p^* e^{ip(n+l)} - \beta_p^* \gamma_p e^{-ipl}] \\ & \left. - g N^{-1} \sum_p [e^{-ipl} (\beta_p^* + \beta_{-p} e^{-ipn}) - (\gamma_p^* + \gamma_{-p})] \right\}, \quad (39) \end{aligned}$$

$$\begin{aligned} G_l = & -J (e^{-i\kappa} S_{+1,l}^{+1} + e^{i\kappa} S_{-1,l}^{-1}) + S_{0,l}^0 \left\{ -E^\kappa + N^{-1} \right. \\ & \times \sum_p [|\beta_p|^2 + |\gamma_p|^2 - \beta_p \gamma_p^* e^{ipl} - \beta_p^* \gamma_p e^{-ipl}] - g N^{-1} \\ & \left. \times \sum_p [e^{-ipl} (\beta_p^* + \beta_{-p}) - (\gamma_p^* + \gamma_{-p})] \right\} = G_l^*. \quad (40) \end{aligned}$$

The above self-consistency equations suggest that a general solution consists of a triple of complex amplitudes β_q^κ , γ_q^κ , and α_k^κ , the latter being the Fourier transform of the α_n^κ actually used. Numerical solutions, however, appear to converge to real Fourier amplitudes, even in regimes where the detail of the optimal amplitudes is rather complicated. This is indicated numerically by real parts that converge to smoothly varying finite-valued amplitudes typically orders of magnitude greater than the limits of computational precision, while the corresponding imaginary parts are irregular and characterized by magnitudes at the limits of computational precision, the latter being the larger of machine precision or a manually fixed convergence error criterion. Reexamination of the general self-consistency equations shows that the system remains self-consistent for strictly real β_q^κ , γ_q^κ , and α_k^κ (the latter implying the real-space symmetry $\alpha_n^{\kappa*} = \alpha_{-n}^\kappa$), leading us to conclude that the optimal Fourier amplitudes are in all cases real. (Instrumental in the latter analytic demonstration is the fact that for real β_q^κ and γ_q^κ , the complex Debye–Waller factor possesses the additional symmetry $S_{nm}^{l*} = S_{-n-m}^{-l}$.) Due to this finding, the majority of our calculations, including all displayed here, were made using a faster algorithm based on real Fourier amplitudes and the slightly simpler self-consistency equations that apply to them.

We note that by considering the $q=0$ case of the above self-consistency relations, it can be shown that

$$\beta_{q=0} - \gamma_{q=0} = g. \quad (41)$$

This is the realization in the present context of the lattice sum rule,

$$\sum_{n_b} (\beta_{n_b-n} - \gamma_{n_b-n_a}) = g, \quad (42)$$

requiring that the sum of all real-space oscillator amplitudes equal the exciton-phonon coupling constant. Here, the condition applies to the superposition of contributions from the global and local exciton-phonon correlation channels, allowing the condition to be met more flexibly than under either the Merrifield method or the Toyozawa method.

It should be noted that by construction the variational energy E^κ is independent of the scaling of the internal exciton amplitudes by an arbitrary complex constant; consequently the normalization and phase of the exciton amplitudes are arbitrary for each κ . It is straightforwardly verified that the variational amplitudes $\{\beta_q, \gamma_q\}$ are also independent of such scaling. For consistency across illustrations, we have adopted the *ad hoc* convention $\alpha_{n=0}^\kappa = N$.

V. NUMERICAL SOLUTIONS

A complete solution to the variational problem as here posed consists of $4N^2$ real quantities, the two real correlation amplitudes β_q^κ and γ_q^κ , and the real and imaginary parts of the internal exciton amplitudes $\text{Re}\{\alpha_n^\kappa\}$ and $\text{Im}\{\alpha_n^\kappa\}$. Such a solution can be conveyed through four variational surfaces indicating the value of each quantity for each possible pairing of the appropriate internal label (q or n) with the external label κ . Since space considerations strongly limit the number of such solutions that can be presented, we have made our selection to illustrate typical weak, moderate, and strong coupling structures along a fixed- J transit of the system parameter space in a rather strongly adiabatic regime.

As in Papers I and II, the structure of these solutions is affected by two significant parametric relationships:

The first is the adiabaticity criterion $J > 1/4$, with which is associated a wave vector κ_c (determined by $2J[1 - \cos(\kappa_c)] = 1$) marking the point at which the free-exciton band penetrates the one-phonon continuum. In any adiabatic circumstance, polaron structure at long-wavelengths ($|\kappa| < \kappa_c$) tends to differ from that at short wavelengths ($|\kappa| > \kappa_c$) in characteristic ways, particularly when exciton-phonon coupling is weak. The solutions we display correspond to the $J=9$ case, to which corresponds $\kappa_c = 0.1066\pi$, indicating that roughly the inner 10% of the Brillouin zone may show behavior distinct from the outer 90%.

The other significant parametric relationship is embodied in the self-trapping line, an imprecisely-known curve traversing the heart of the polaron parameter space and marking the transition from large polaron structure on its weak-coupling side to small polaron structures on its strong-coupling side. In our present calculation, as in Papers I and II, this transition is associated with characteristic discontinuous behavior that, while artifactual, assists in marking the approximate location of the real, physical self-trapping line. Under the present method, self-trapping related discontinuities first appear at $J_c = 7.34$ ($g_c = 3.69$), and are present for all higher values of J . When $J=9$ as in the displayed solutions, this discontinuous behavior locates the self-trapping line within a narrow interval around $g=4$. Consequently, the solutions

FIG. 1. Complete variational solutions for the case $g=5$ and $J=9$; (a) β_q^κ , (b) γ_q^κ , (c) $\text{Re}\{\alpha_n^\kappa\}$, (d) $\text{Im}\{\alpha_n^\kappa\}$. The apparently finite amplitudes in (d) are smaller than the error tolerance set for the computation, and so are zero for the purposes of calculation; note that formally $\alpha_{n=0}^\kappa$ is real by symmetry.

displayed for $g=1$ and $g=3$ may be understood as large polaron solutions, and the solution for $g=5$ as a small polaron solution.

Proceeding now from strong to weak coupling, we consider the solution for $J=9$, $g=5$ shown in Fig. 1. This cir-

cumstance falls above the self-trapping transition, and is characterized by very compact spatial structure in every part of the total solution. The real part of the exciton amplitude is essentially independent of κ with most of the amplitude localized on a single site, and most of the remainder concentrated on the nearest neighbors. The imaginary part $\text{Im}\{\alpha_n^{\kappa}\}$ in this case is small beyond the limits of our computation, the apparently finite amplitudes evident in Fig. 1(d) being equivalent to zero under the applicable precision criteria. This spatial structure is mirrored in phonon amplitudes; both β_q^{κ} and γ_q^{κ} are quite flat, essentially independent of κ , with the weak modulation in q being nearly sinusoidal, reflecting a slight spreading of the lattice distortion to nearest neighbors but very little beyond. Most of the phonon amplitude is carried by the β amplitude, with only a small portion being carried by the γ amplitude.

Our next solution falls below the self-trapping transition, at $J=9$, $g=3$ (see Fig. 2). This solution is marked by a host of features typical of the intermediate-coupling regime. The real part of the exciton amplitudes is nearly independent of κ and symmetric about its centroid in real space, spanning a nontrivial number of lattice sites with a rather peaked, pulse-like profile. The imaginary part of the exciton amplitude is small, but finite, accounting for less than 0.2% of the total exciton density; however, this small part is antisymmetric about its centroid with its most significant excursions coincident with those of the real part. Moreover, this small imaginary part varies with κ , indicating a momentum sensitivity consistent with the imaginary part of a particle probability amplitude. The β amplitude is characterized by two prominent features, one a pulse-shaped component that appears to be strongly correlated with the exciton amplitudes, the other a wavelike component having wave vector $q=\kappa$ that appears to be essentially uncorrelated with the exciton amplitudes and is suggestive of free phonons. With decreasing coupling and passage through the self-trapping transition, the γ amplitudes have grown both in absolute and relative strength, and have acquired a distinctive shape. The γ amplitudes vary decidedly in κ , reflecting a momentum sensitivity, but this sensitivity appears in two ways: A weak feature along the $q=\kappa$ line suggesting involvement with the free phonon component of the β amplitudes, and a κ -dependent pulse-shaped component suggesting involvement with the correlated exciton-phonon pulse already discussed. Very weakly evident in all components are suggestions of qualitatively distinct structure in the inner tenth of the Brillouin zone.

Our final complete solution is from the weak coupling regime (Fig. 3). Exciton amplitudes display the appropriate symmetries and are essentially real, with the imaginary part accounting for $\sim 0.7\%$ of the total density. The exciton profile is again pulse shaped and nearly independent of κ , except for “breaks” in the vicinity of $\kappa=\pm\kappa_c$. The β amplitude is roughly similar to the preceding case, with some important differences: The free-phonon component has grown more sharp and more intense both on an absolute scale and relative to the coexisting pulse-shaped component. The pulse-shaped component has weakened considerably, primarily due to the

smaller value of g that is associated with the characteristic magnitude of this component by the sum rule; however, the pulse-shaped component has become more complicated, showing a dependence on κ that is related to the structure of the γ component. The characteristic features of the γ component have also grown more sharp and more intense. The free-phonon component is now sharply resolved and the κ -dependent pulse-shaped component has grown sufficiently to significantly affect the detail of the β component. All components show distinct breaks in the vicinity of $\kappa=\pm\kappa_c$ with distinct structure clearly evident in the inner tenth of the Brillouin zone.

Overall, it must be said that the α and β components of these solutions compare well with the shapes and trends in the corresponding solution components as computed by the Toyozawa method. However, there is no correspondent in the Toyozawa or Merrifield methods to the γ component that by our direct computation has been shown to be qualitatively distinct and of nontrivial magnitude, at least in the adiabatic weak-coupling regime.

Numerical solutions at more moderate values of J resemble those already shown for $J=9$, with the characteristic features of those solutions softening with decreasing J . Also, with decreasing J , the relative contribution of the γ -amplitude diminishes, such that there is an increasing similarity between the non- γ parts of the solution and the solutions computed by the Toyozawa method. It is important to note, however, that qualitative similarity is a very limited guide. In the $J=2$ case, for example, the α and β components of the numerical solutions are very similar to those shown in Figs. 5–8 of Paper II, and the new γ component moderate to weak; yet, as seen in the sections to follow, some physical quantities nonetheless show distinct qualitative and quantitative improvement by including the latter contribution.

The trend of the present method to show improvement relative to the Toyozawa method in some portion of the overall solution continues in the small polaron regime, but with magnitude of the improvement diminishing with decreasing polaron size. This is expected, since it can be seen from the structure of the trial states that the β and γ amplitudes are completely redundant when the exciton component is limited to a single lattice site. Since the “weight” of the distinction between the β and γ components is thereby shown to be limited crucially by the spread of the exciton component, it is perhaps not surprising to find β and γ components that are qualitatively similar.

One of the more subtle signatures of overall improvement is a reduction in precision-related sensitivities in numerical computation. Generally speaking, convergence under the present method is better behaved and can be pursued more effectively to weaker exciton-phonon coupling strengths than under the Toyozawa method. Also, certain peculiarities of solutions under the Toyozawa method are greatly improved. For example, the “tandem singularity” found along the $q=\kappa$ line of the lattice component and the $k=\kappa$ line of the exciton component is almost completely eliminated, and the growing irregularity of the exciton com-

ponent in the weak coupling regime is greatly reduced. These findings confirm that, as speculated, those peculiarities were artifacts of the Toyozawa method.³

VI. PHASE DIAGRAM

The preceding specific complete solutions exemplify the characteristic structures found in varying degrees of resolution and intensity throughout the parameter space of the Holstein Hamiltonian. Of course, many more solutions were actually computed and examined whose properties cannot be so completely detailed here. We use the device of a phase diagram to convey information about the entire class of solutions in a broader way.

The phase diagram as presented in Fig. 4 reflects the collected wisdom of each of our three calculations regarding the location of the self-trapping transition. The most prominent feature of the phase diagram at each level of calculation (i.e., by the Merrifield, Toyozawa, or global-local method) is a wedge or tongue-shaped region within which the dependence of the variational energy on J , g , and κ is not smooth. The nature of this nonanalyticity is such that within the indicated regions there exists a function $\kappa^*(J, g)$, different for each calculation method, identifying the location of a cusp in the dependence of the variational energy on κ ; i.e., at fixed J and g

$$\left. \frac{\partial E^\kappa}{\partial \kappa} \right|_{\kappa \rightarrow \kappa^*+} \neq \left. \frac{\partial E^\kappa}{\partial \kappa} \right|_{\kappa \rightarrow \kappa^*-}. \quad (43)$$

When such a $\kappa^*(J, g)$ exists, the minimum-energy states at small κ ($|\kappa| < \kappa^*$) are large polaronlike, while the minimum-energy states at high κ ($|\kappa| > \kappa^*$) are small polaronlike. The traditional self-trapping transition associated with the notion of a discrete jump in the polaron effective mass corresponds to the limit $\kappa^* \rightarrow 0$; i.e., to the point at which the large polaron region $\kappa \in (-\kappa^*, +\kappa^*)$ is squeezed out of existence. The set of points satisfying the condition $\kappa^*(J, g) = 0$ thus constitutes the traditional “self-trapping line.” The self-trapping line so defined corresponds to the strong-coupling boundary of the broader κ -dependent transition region associated with each calculation method.

On formal grounds, it is expected that there is no true nonanalyticity to be found in the physical system, suggesting that the discontinuous behaviors we associate with self-trapping phenomena are artifacts of insufficiently flexible methodologies.^{50–53} Our sequence of variational calculations supports this view, showing how incremental refinement of the variational states results in shrinkage of the fraction of the parameter space exhibiting self-trapping related discontinuities; for example, considering the sector of parameter space displayed in Fig. 4, more than half of the displayed area is affected by self-trapping discontinuities under the Merrifield method, shrinking to $\sim 1.4\%$ under the Toyozawa method, and to only 0.08% under the present method. Moreover, this shrinkage is accompanied by a shift of the onset of discontinuities to more extreme parameter values; the values $J_c = 7.34$, $g_c = 3.69$ characterizing the present method leave a large (J, g) domain free of self-trapping artifacts.

FIG. 2. Complete variational solutions for the case $g=3$ and $J=9$; (a) β_q^κ , (b) γ_q^κ , (c) $\text{Re}\{\alpha_n^\kappa\}$, (d) $\text{Im}\{\alpha_n^\kappa\}$.

VII. ENERGY BANDS AND EFFECTIVE MASS

The structure of polaron energy bands at general parameter values is strongly influenced by the limiting behaviors at small g and small J . While each of these limits can be un-

FIG. 3. Complete variational solutions for the case $g=1$ and $J=9$; (a) β_q^κ , (b) γ_q^κ , (c) $\text{Re}\{\alpha_n^\kappa\}$, (d) $\text{Im}\{\alpha_n^\kappa\}$.

derstood straightforwardly, it is a nontrivial matter that a variational solution should be consistent with both.

At $g=0^+$, the free exciton energy band enters the one-phonon continuum at κ_c , such that the energies of the joint ground states of the exciton-phonon system are given by

FIG. 4. Phase diagram. Nested wedge- or tongue-shaped sectors indicate those regions in which variational solutions exhibit self-trapping related discontinuities: Outermost boundary—Merrifield method, $J_c=0.89$, $g_c=1.90$. Intermediate boundary—Toyozawa method, $J_c=2.9$, $g_c=2.66$. Innermost boundary—global-local method, $J_c=7.34$, $g_c=3.69$. The scatter-plot of points indicate certain parameter values that receive particularly detailed attention throughout this paper.

$$E^\kappa - E^0 = 2J[1 - \cos(\kappa)] \quad \text{for } |\kappa| < \kappa_c, \\ = 1 \quad \text{for } |\kappa| > \kappa_c, \quad (44)$$

where κ_c is given by the relation $2J[1 - \cos(\kappa_c)] = 1$. The changes in band structure that occur as the exciton-phonon coupling is turned on display some of the characteristic features of level repulsion. Since the wave vector κ_c marks a crossing of the bare exciton and bare phonon level sets, energies in the vicinity of κ_c respond more strongly to weak exciton-phonon coupling than do energies at higher or lower κ . The first such effect is a rounding of the angular feature at $\pm \kappa_c$, and for a significant interval of coupling strength, the primary effect of increasing coupling is the progressive rounding of this feature and a gradual smoothing of the overall energy band spreading outward to higher and lower κ from these points. Only after reaching a significantly finite value of the exciton-phonon coupling strength does this smoothing of the energy band progress to the point that the band begins to narrow.

Quite distinct from this is the archetypical small polaron energy band, which takes the simple form

$$E^\kappa = -g^2 - 2J e^{-g^2} \cos(\kappa). \quad (45)$$

This is the result of applying the displaced-oscillator transformation at small J and neglecting all finite- J corrections.⁵⁴ More generally, of course, the dependence of the energy band on the transfer integral is substantially more complex as is evident already even in the Merrifield method; however, it is generally expected that the above small polaron form is recovered at finite J for coupling strengths that are “large enough.”

Qualitatively, then, one expects band shapes similar to Eq. (44) at weak coupling to distort into shapes similar to Eq. (45) at strong coupling and this is, generally speaking, what we find.

FIG. 5. Shifted energy bands $E^{\kappa} - E^0$ for $J=9.0$, $g=1, 3, 3.5, 3.85, 4.0, 5.0$ as computed by the present method. The dotted, nearly parabolic curve at the center is the appropriate portion of the free exciton band $2J[1 - \cos(\kappa)]$. The segmented appearance of some curves is an artifact of finite lattice size. $K = \kappa/\pi$.

Figure 5 shows a sequence of polaron energy bands for $J=9$ for assorted coupling strengths. This particular sequence clearly shows how the principal effects of the exciton-phonon interaction at weak coupling are confined to a small region near κ_c , and that only minor changes occur at either large or small κ until the smoothing of the level-crossing feature spreads essentially over the entire band. Consequently, the polaron bandwidth is saturated essentially at unity until $g \approx 3$, then decreases rapidly, encountering the self-trapping transition when $g \approx 4$, after which narrowing continues beyond the resolution of the figure. Above the self-trapping transition the energy band is nearly sinusoidal and strongly narrowed suggesting a small polaron form; however, nontrivial finite- J corrections remain.

Figure 6 compares energy bands computed by the

FIG. 6. Energy bands E^{κ} for $J=2.0$, $g=1, 2, 3$ as computed by the present method (solid lines) and the Toyozawa method (dashed lines). The $g=2.0$ solid-dashed pair has been shifted by $+1.1$ and the $g=3.0$ pair shifted by $+4.95$ to allow all curves to be compared in a single illustration. $K = \kappa/\pi$.

FIG. 7. Polaron bandwidths $E^{\kappa=\pi} - E^{\kappa=0}$ as computed by the present method vs exciton-phonon coupling strength g ; curves left to right: $J=2.0, 2.9$, and 9.0 . Bandwidths calculated using the Toyozawa method are indicated with $\times$ symbols for the $J=2$ case.

present method with energy bands computed by the Toyozawa method for $J=2$ and various values of g . The weak-coupling comparison shows that there is strong agreement between the two methods near the Brillouin zone center, but that the present method yields a considerable lowering of the energy near the Brillouin zone edge, resulting in a flatter band for essentially the same effective mass. The intermediate coupling comparison shows that measurable quantitative improvement in the energy band is achieved at all κ , still with the largest improvement being realized in the outer zone. At strong coupling both energy bands are essentially flat on the scale of the illustration, with the present method yielding measurable quantitative improvement that is essentially uniform in κ .

Figure 7 shows the dependence of the polaron bandwidth on g for J 's ranging from 2 (see Fig. 6) to 9 (see Fig. 5). Also shown for comparison is the bandwidth for the $J=2$ case according to the Toyozawa method. Considering the role of the one-phonon continuum in determining the structure and energies of the higher-momentum polaron Bloch states, it is expected that the width of the polaron band should always be less than unity at finite exciton-phonon coupling. The failure of the Merrifield method to meet this expectation is so egregious that there is little to be gained from considering it except to observe that this is one of the energy band characteristics that is most dramatically improved by the Toyozawa method. Even so, the failure of the Toyozawa method to meet this expectation is still quite significant; as shown in the figure, the Toyozawa method's overshoot of the expected maximum bandwidth is about 15% for the $J=2$ case, and worsens with increasing J . This stands in significant contrast to the results of the present method; the Toyozawa method's significant overshoots of the expected maximum bandwidth are completely eliminated at lower values of J . All is not perfect however, since the present method also overshoots the expected maximum bandwidth, though such overshoots appear at larger values of

FIG. 8. Solid curve: The global ground-state energy E^0 for $J=2$ as computed by the global-local method. Dotted curves: The small g asymptote as in Eq. 46, and the exact $J=0$ ground-state energy, $-g^2$. Dashed curve: E^0 estimate by the Merrifield method. Dash-dotted curve: E^0 estimate by the Toyozaawa method; on the scale of the figure, the Toyozaawa and global-local estimates are nearly identical in this regime, though the global-local energy is lower in every case.

J and are smaller in magnitude than is characteristic of the Toyozaawa method. Still, consistency with the saturation criterion is sufficiently well satisfied to inspire confidence in the picture of bandwidths so captured.

Figure 8 shows the dependence of the global ground-state energy E^0 on the coupling strength for $J=2$. The overall behavior of the ground-state energy is to trend between two g^2 dependences with differing coefficients and offsets. Within the Merrifield method, one can show that the leading dependence of the ground-state energy on the coupling constant is given for any J by

$$E^0 \approx -2J - \frac{g^2}{\sqrt{1+4J}}. \quad (46)$$

This is, in fact, what we find to within numerical precision within the weak coupling regime of our present method, in excellent agreement with the generally less satisfactory Merrifield method.

The situation at strong coupling is less well characterized by the readily determined asymptotes. Both the small polaron construct Eq. (45) and the Merrifield method yield ground states that trend as $E^0 \sim -g^2$ at strong coupling. As seen in Fig. 8, however, both the Toyozaawa method and the global-local method yield ground states that are substantially lower in energy than either the small polaron estimate or the Merrifield estimate, even in states well above the self-trapping transition that are properly characterized as “small-polaron.” Moreover, the magnitude of this discrepancy at any particular value of g increases with increasing J . It would appear reasonable to expect the true ground-state energy to approach $-g^2$ as $g \rightarrow \infty$ as the trend in the figure suggests, since in this limit we expect the exciton amplitudes to narrow completely, under which circumstances both the Toyozaawa method and the present method reduce to the Merrifield method. Thus, although the self-trapped states we

FIG. 9. The ratio of the polaron effective mass to the bare effective mass (m_{eff}/m_0) is plotted against exciton-phonon coupling on a logarithmic scale for $J=2, 2.9, 4, 7.34$, and 9 . The three smaller- J curves can be compared with the corresponding curves in Paper II, and the $J=2$ curve may be compared as well with the corresponding curve in Paper I.

discuss are small polaron states characterized by internal exciton amplitudes that are highly localized, it is evident that there is generally a substantial energy cost associated with complete localization.

The polaron effective mass is the traditional indicator of the self-trapping transition, the transition being evidenced by a jump discontinuity in the effective mass, and the onset of the transition being marked by the parameter values at which such jumps first appear. The method applied in this paper yields a “critical” value of the exciton transfer integral $J_c \approx 7.34$, such that for any $J < 7.34$, the dependence of the effective mass on the coupling constant g is smooth and continuous, while for $J > 7.34$ the tell-tale jump discontinuity appears. This behavior is illustrated in Fig. 9, where effective mass curves for cases below, at, and above the critical point are displayed. These computations were based on the formula

$$\frac{m_{\text{eff}}}{m_0} = \frac{2J}{\left. \frac{\partial^2 E^\kappa}{\partial \kappa^2} \right|_{\kappa=0}}, \quad (47)$$

using a discrete representation of the κ derivative at the Brillouin zone center. Though still discontinuous at sufficiently large J , the effective mass that results from the present calculation is considerably more smooth than that which results from either the Merrifield ($J_c \approx 0.89$) or Toyozaawa ($J_c \approx 2.9$) method.

VIII. SOLITONS

Polaron Hamiltonians such as the one in this paper, and particularly the analogous Hamiltonian built upon acoustic rather than optical phonons, have been the basis of a great deal of research relating to the possibility that such systems might support weakly scattered, long-lived collective excitations known as “solitons.” The most transparent favorable connection between our results and those of soliton theory is

our finding that “locked” exciton-phonon structures appear over significant regions of the polaron parameter space. Locked exciton-phonon structures are found in both nonlinear Schrödinger and discrete nonlinear Schrödinger descriptions, ranging from broad, smooth “true” solitons to highly discrete “pinned” states essentially localized on a single lattice site. Over much of the regime where soliton theory finds such locked structures, they are characterized by shapes that are dependent primarily on the ratio of the tunneling energy to the binding energy, or, in terms of our parameters, the ratio $2J/g^2$. We find that locked exciton-phonon structures of considerable breadth in real space appear systematically in the weak coupling region, provided that the exciton transfer integral J is sufficiently large; that is to say, provided the system is sufficiently adiabatic. Although such components can be inferred in the background of more complex phonon structures at moderate values of g and J , it is not until the small- g , large- J regime is well penetrated that the locked component can be unambiguously resolved.

The trial states of Paper II were particularly closely related to those commonly employed in the theory of Davydov solitons, and an attempt was made in that paper to interpret elements of polaron structure in the light of “soliton theory.” This attempt was continued in a separate paper,⁵⁵ where several distinct signatures expected of solitonlike structures were assessed and found not to hold; these were:

- (1) Exciton amplitudes exhibiting a $\text{sech}(x/\lambda)$ profile. (Instead, a strongly exponential dependence was found.)
- (2) The width of the exciton density scaling roughly as $2J/g^2$. (Instead, a much weaker dependence on the coupling constant was found.)
- (3) A specific locking relation $\beta_n^\kappa = g|\alpha_n^\kappa|^2$ between the phonon amplitudes and the exciton density, at least at small κ . (Instead, it was found that the notion of a proportionality between the phonon amplitudes and the exciton density could not be supported.)

The introduction of the γ amplitudes complicates this assessment in many ways. The first is that localized states such as underlie the Bloch states of this paper have received very little attention as the basis of soliton theories, and then only for the acoustic phonon case. More general are developments based on Eq. (19), leading to a tangled system of evolution equations that have received very little analysis.^{34,39,40} More special is the development of Brown and Ivic,^{20–22} which corresponds to replacing our present family of N independent γ amplitudes by a single parameter. For our present purposes, we note that the latter development reduces to the usual Davydov soliton theory when the dressing parameter is small, and that this is found to occur in the lower right region of the phase diagram as presented in Fig. 4. In this regime, Brown and Ivic find an approximate nonlinear Schrödinger equation that differs from the usual one in slightly renormalizing the values of the effective parameters.

A second complication is that here exciton-phonon correlations are carried not in a single amplitude type, but two. Indications from both Brown and Ivic and the detail of our present results as shown in Figs. 1–3 suggest that correla-

FIG. 10. Exciton amplitudes for $J=9$, $\kappa_c=0.1066\pi$. (a) $\alpha_n^{\kappa=0}$ plotted on a logarithmic scale for $g=1, 3, 4$, and 5 . Vertical dotted lines indicate the value of π/κ_c , which here is 9.38 . (b) sample curves showing some quasi-exponential shape functions.

tions sensitive to the shape of the exciton profile are exhibited to a greater degree in the β amplitudes, so we focus our attentions accordingly.

We show in Fig. 10(a) unnormalized exciton amplitudes $\alpha_n^{\kappa=0}$ from weak to strong coupling at a large fixed value of J ; this scans across the far right of the phase diagram from bottom to top, showing the characteristic contraction of the exciton profile with increasing g . Exciton amplitudes are scaled such that the peaks of all profiles are the same magnitude, and these are then plotted on a logarithmic scale in order to better discriminate distinct quasi-exponential shapes, and to remove the distortions associated with the squaring of the exciton amplitude that is sometimes relevant to shape. Rather than curve fit, we have also plotted in the companion Fig. 10(b) a family of quasi-exponential shape functions. Some observations are immediately evident—the computed exciton profiles are all plainly inconsistent with a Gaussian dependence except over a narrow interval near the peak of the weak-coupling curves, and the strong-coupling curve (above the self-trapping transition) is unquestionably exponential. Much more intriguing are the shapes found at weaker values of coupling, at ($g=4$) or below the self-trapping transition ($g=1,3$). These curves are Gaussian over a narrow interval around the peak of the amplitude profile, but quickly turn over into a clear exponential dependence for

FIG. 11. Exciton amplitude profiles $\alpha_n^{\kappa=0}$ for $g=1$, subject to the normalization condition $\sum_n |\alpha_n^{\kappa=0}|^2 = 1$. Points near the bottom of the figure indicate for $J=0.5, 1, 3$ the value of the length scale π/κ_c relative to the discrete space variable n . κ_c does not exist for $J=0.2$ (the free exciton band does not penetrate the one-phonon continuum) and π/κ_c for $J=9$ falls beyond the edge of the figure.

a decade or two in amplitude before saturating in the wings. (The saturation effect appears to be a mixture of a subtle intrinsic effect and a finite-lattice effect.) This Gaussian-to-exponential turnover is one of the characteristics of a $\text{sech}(x/\lambda)$ profile, and it appears that a $\text{sech}(x/\lambda)$ describes the situation rather well at weak values of coupling. One of the characteristics of the $\text{sech}(x/\lambda)$, however, is that the same parameter λ controls the curvature of the profile at the peak and the decay of the profile in the wings. Close inspection of all curves suggests that while this one-scale-fits-all dependence may be satisfactory at weak coupling, it does not consistently describe the full set of shapes found. An example of an alternative that exhibits the correct overall trends, but is unrelated to any soliton theory, is the Kubo function^{56–59}

$$f(x) = \exp\left\{-\frac{1}{\lambda a} [e^{-a|x|} - 1 + a|x|]\right\}. \quad (48)$$

This function is Gaussian ($\sim \exp\{-x^2/2\lambda\}$) near the peak and exponential ($\sim \exp\{-|x|/\lambda\}$) in the wings, with the cross-over occurring around $|x| \sim 1/a$.

We may also consider the width dependence of the exciton profiles, which we do by estimating the length scale on which the exponential part of each profile decays (i.e., the λ in the above considerations). This scale changes by a factor of three from $g=1$ –5, whereas the characteristic soliton dependence $\lambda \approx 2J/g^2$ would suggest that a factor of 25 should be found.

In Fig. 11 we show unit-normalized $\alpha_n^{\kappa=0}$ from small to large values of J for a fixed, small value of g ; this scans across the bottom of the phase diagram from left to right, showing the characteristic spreading of the exciton profile with increasing J . When these curves are examined in the same manner as those in Fig. 10 and the width measures λ of the quasi-exponential shape function determined, we find that these widths are not in proportion to J as would be

FIG. 12. The locking ratio $\beta_n^{\kappa=0}/(g|\alpha_n^{\kappa=0}|^2)$ for $g=1, 3, 4$, and 5 ; a locking ratio equal to unity for all n would indicate consistency with the locking relation typical of soliton theory. $J=9$ for all curves.

expected if a solitonlike measure $2J/g^2$ were the controlling factor. Instead, for $J=1, 3, 9$, for example, the actual widths are in the proportions 1:1.7:3, which suggests $\lambda \sim \sqrt{J}$, and not $\lambda \sim J$, as suggested by soliton theory. A scaling of the width according to $\sqrt{J}$, is what would be expected, however, if the controlling length scale were π/κ_c , which is well approximated by $\sqrt{J}$ in this range.

From these findings we may say that the exciton profile appears to be well characterized by a solitonlike $\text{sech}(x/\lambda)$ shape at weak coupling, but that this agreement deteriorates with increasing coupling, as does the correspondence of the width of the exciton profile with the typical findings of soliton theory.

Soliton theory also typically involves a definite relation describing the locking of the exciton and lattice components. In the case of theories based on the traditional Davydov Ansatz, containing only the β amplitudes, the central relation is $\beta_n = g|\alpha_n|^2$. This was tested for in Ref. 55, with the finding that the obvious similarity in shape exhibited by the exciton and lattice components could not be contained in a proportionality between the exciton density and the phonon amplitudes. We can test for the same property here. Figure 12 shows the ratio $\beta_n^{\kappa=0}/(g|\alpha_n^{\kappa=0}|^2)$ for the same sequence of curves shown in Fig. 10(a), but with each exciton profile appropriately normalized for this purpose. Although it is evident that the quality of the locking is rather poor, and in this respect shows the properties of solitons to compare rather unfavorably with our present results, the comparison in Fig. 12 is nonetheless more favorable than was found under the Toyozawa method.

In Paper II, we gave considerable attention to polaron Wannier states, the localized states that energy band theory identifies with the complete set of delocalized Bloch states.^{48,60–64} We defer the explicit construction of polaron Wannier states by the present method to later work;⁶⁵ however, certain general properties of Wannier states are worthy of note in relation to the balance of this section.

In the weak coupling limit ($g=0^+$), exact polaron Wan-

nier states can be constructed without appeal to any approximation method. In the nonadiabatic regime ($J < 1/4$), these states are trivially identical to the Wannier states of the rigid lattice, and are completely localized on a single lattice site. In the adiabatic regime, however, the exact polaron Wannier states are generally broad, complex states consisting of a localized component upon an essentially uniform background. The half-width of the localized component can be identified with the length scale π/κ_c . It is reasonable to expect that polaron Wannier states should grow more compact with increasing exciton-phonon coupling strength, and this is, in fact, what was found in the finite- g calculations of Paper II. These findings suggest that the length scale π/κ_c constitutes an upper bound for the half-width of polaron Wannier states at finite coupling.

In Figs. 11 and 10(a) we have included elements that allow the computed $\kappa=0$ exciton amplitude profiles to be compared with the Wannier length scale π/κ_c ; in every case the bulk of the computed exciton profiles fall within the appropriate Wannier width, and from the scaling of our quasi-exponential width estimates with the transfer integral $J(\lambda \sim \sqrt{J})$, it appears that the Wannier length scale is nontrivially involved in determining the width of localized components over a substantial range of parameters.

Thus, despite the intriguing appearance of a sechlike shape at weak coupling, it would appear that the localized, highly correlated exciton-phonon structures internal to our polaron Bloch states are more consistent with a band-theoretic, Wannier-state interpretation than with a soliton-theoretic interpretation.

IX. CONCLUSIONS

In this paper we have presented band-theoretic results in both broad and very specific form as follow from the application of the global-local variational method to the Holstein Hamiltonian. The present method self-consistently combines the local correlation channel characteristic of small polarons with the global correlation channel characteristic of large polarons. This generalizes the Toyozawa method which includes the global correlation channel only. As discussed in Sec. II, our trial states contain many well-known constructs that have been employed in both localized- and delocalized-state approaches to polaron theory. In view of our serial development beginning with a reexamination of the Merrifield method (Paper I) and our full implementation of the Toyozawa method (Paper II), our focus has been on the relationship of our present results to those of the immediately preceding works.

The results of the Toyozawa method are largely corroborated in the sense that features that appeared to be robust physical features under that method are resolved with increased clarity, while other features suspected to be method-related artifacts are here found to be strongly reduced, eliminated, or shifted to more extreme parameter ranges. In hand with this broad qualitative refinement of polaron structure is a broad quantitative refinement; for example, the shifting of persistent artifacts to more extreme parameter ranges has the

effect of improving the quantitative accuracy at more moderate parameter values. It is thus that many aspects of polaron structure are improved through the explicit introduction of the local correlation channel, though improvements are generally more incremental than they are dramatic.

Improvements can be characterized in several broadly typical ways. First, owing to the fact that higher wave vectors are more sensitive to structure on the smallest scales, the most obvious improvements appear as a preferential lowering of the energy of higher crystal momentum states. This results in polaron bands that typically are more narrow than those that follow from the Toyozawa method. Second, quantitative measures of the “gaps” between predictions of the Toyozawa method and the present method appear to increase with J . Third, owing to the fact that the global and local correlation channels become redundant when the internal exciton amplitudes are highly localized, there is little improvement rendered in the small polaron regime. Fourth, for exciton transfer integrals in the range $J \in (2.9, 7.34)$, i.e., between the onsets of self-trapping related discontinuities in the Toyozawa and present methods respectively, distortions related to discontinuities within the Toyozawa method are smoothed, resulting in improved estimates of polaron effective masses and global ground-state energies. Fifth, at larger values of J , both the Toyozawa and the present methods exhibit self-trapping related discontinuities, placing them in some respects on a qualitatively similar footing; however, self-trapping artifacts in the present method occupy a smaller fraction of the parameter space and affect a smaller fraction of the Brillouin zone, qualitatively reflecting the fact that the present method continues to provide quantitatively superior results despite the persistence of self-trapping related artifacts.

There are more subtle manifestations of the improvement of the present method over that of Toyozawa; these include the essentially complete removal of a minor singular artifact characteristic of the latter method, and improved behavior in the numerically challenging weak coupling regime. The latter improvements include smoother convergence at weaker values of coupling, and solutions less affected by κ -dependent irregularities that seem endemic to the weak-coupling regime of the Toyozawa method. As important, perhaps, is the fact that the global-local method realizes these quantitative and qualitative improvements without revealing any new singular or problematic behaviors.

Comparison of the internal structure of our polaron Bloch states to that found by the Toyozawa method is complicated by the fact that here we use two classes of phonon amplitude while the Toyozawa uses only one. Still, the weight of the local amplitudes $\{\gamma_q e^{-iqm}\}$ relative to the global amplitudes $\{\beta_q\}$ is typically relatively small, allowing the global amplitudes to be fairly compared with those of the Toyozawa method. The structure of our global amplitudes is essentially the same as that of the phonon amplitudes of the Toyozawa method, with small differences reflecting the involvement of the local amplitudes. The exciton amplitudes in our present method have the same structural role as in the Toyozawa method, and when compared on an equal basis

betray little qualitative change to casual inspection.

We have taken a closer look at the internal structure of our polaron Bloch states with the particular aim of deciding whether or not the pulse-shaped and obviously strongly correlated exciton-phonon structure prominent within them could be meaningfully identified with the well-known soliton solutions that follow from similar analyses in the localized state framework. We considered this question previously in the context of the Toyozawa method by subjecting our variational solutions to several litmus tests of solitonlike structure, finding that each such test failed to hold true. The present circumstance is very similar; we again find these tests to fail, but in degrees less severe than characterized the results of the Toyozawa method. The root of this slight improvement lies primarily in one intriguing quality: Though little qualitative change is revealed to casual inspection, detailed examination shows that the exciton amplitudes of the Toyozawa method tend to be strongly exponential in shape, while those of the present method prove to be less sharply peaked (at least at weak coupling), and in limited but significant respects to compare favorably with the $\text{sech}(x/\lambda)$ profiles expected of solitons. Despite this, the bulk of our findings cannot be reconciled with a soliton-theoretic interpretation.

Energy band theory's own localized states are the Wannier states which, being rigorously determined by the complete set of Bloch states, can be constructed (albeit somewhat laboriously) from the same variational data that we have discussed thus far. In Paper II we presented specific polaron Wannier states computed using the Toyozawa method. As with many other energy band characteristics we have considered, we expect measurable improvement to follow using the present method, particularly in the weak coupling regime where our present results find significant incremental narrowing of polaron energy bands at higher κ . Specific examples will be presented elsewhere.⁶⁵

As noted in Sec. III, the form factor upon which the present method is based is not yet the most general that could be used within the hierarchy of one-exciton states paired with phonon coherent states. Further generalization in this direction would be to allow for more complex spatial dependences than we have included in our trial phonon amplitudes; however, it would appear likely that our decomposition of the most general phonon coherent state amplitude β_{qm} into a global and a local component captures at least the main consequences of a dependence of β_{qm} on the site index m . Considering that the onset of self-trapping artifacts is at $J_c = 7.34$ already almost 30 times greater than the transfer integral marking the boundary between the adiabatic and nonadiabatic regimes ($J = 1/4$), it would appear that most circumstances of practical relevance are already rendered with high accuracy by the present method; it is questionable whether further refinement would be warranted by most practical requirements. Rather, the success of our present efforts suggests that more rewarding avenues of generalization lie in broadening the scope of the method; for example, incorporating phonon dispersion,⁶⁶ modeling for other phonon types,^{41,42} and generalizing to more than one space dimension.⁶⁷

It is evident throughout our calculations that the wave vector κ_c plays a central role in numerous aspects of polaron structure. In the absence of phonon dispersion ($\omega_q = \omega_0$), κ_c is coincident with the first crossing of the bare exciton and phonon level sets. However, the role of κ_c in the theory is not to mark the crossing of the bare level sets, but to indicate the point at which the zero-phonon, free exciton state (at $g = 0^+$) ceases to be the joint exciton-phonon state of lowest energy. In the presence of phonon dispersion, κ_c does not generally coincide with the crossing of the bare exciton and phonon level sets. It becomes possible even at $g = 0^+$ to construct joint exciton-phonon states having energies smaller than either isolated free excitons or phonons over nontrivial intervals of κ . A simple example is the case of acoustic phonons ($\omega_q \in [0, \omega_B]$), where κ_c is easily shown to be the Cherenkov wave vector; in this situation the joint exciton-phonon $g = 0^+$ states below κ_c are still zero-phonon, free-exciton states, while the states above κ_c are one-exciton/one-phonon states in which both the exciton and phonon carry finite quasimomentum. Thus, though dispersion is a factor to be accommodated with appropriate care, the wave vector κ_c can be expected to continue to play a qualitatively similar role in the quantitative characterization of polaron structure.

These observations raise pointed questions regarding the generalization of our results to two and three space dimensions. The meaning and role of the wave vector κ_c persists in higher dimensions, though its value is generally direction-dependent [e.g., $\kappa_c = (\kappa_{c,x}, \kappa_{c,y}, \kappa_{c,z})$ on the surface $2J[3 - \cos \kappa_{c,x} - \cos \kappa_{c,y} - \cos \kappa_{c,z}] = \omega_0$ in 3D]. The Wannier function construction considered explicitly in Refs. 3 and 55 and briefly in Sec. VIII suggests that the Wannier function constitutes the "smallest" exciton packet that can be constructed within a given band, and that the width of this packet at $g = 0^+$ is $O\{\pi/|\kappa_c|\}$ (in a chosen direction). Our present calculations show that this length scale continues to characterize polaron structure over a substantial range of coupling strengths in the adiabatic regime. On the other hand, well-known arguments rooted in the adiabatic limit^{31,68} suggest that at least for systems sufficiently adiabatic, finite-radius polarons should be unstable; i.e., that all polarons are either infinite radius ("delocalized") or zero radius ("completely localized"). A limitation of such scaling arguments is the continuum approximation, under which the distinction between a completely localized state and one spanning a small but finite number of lattice sites is lost. The generalization of the present work to higher dimensions can be implemented without appealing either to the adiabatic limit or to continuum approximations, and so can be expected to clarify both the nature of the self-trapping transition and the structure of the optimal polaron states, determining, for example, whether self-trapping is an essentially universal or a more limited phenomenon, and whether the optimal states are essentially completely localized or possess nontrivial spatial structure.^{10,66,67} These and other issues are the subject of ongoing investigation.⁶⁵

ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of Aldo Romero in portions of this work. This work was supported in part by the National Science Foundation under Grant No. DMR 91-18052 and in part by the United States Department of Energy under Grant No. DE-FG03-86ER13606.

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