Variational energy band theory for polarons : mapping polaron structure with the Toyozawa method

Brown, David W.; Zhao, Yang; Lindenberg, Katja

1997

Zhao, Y., Brown, D. W., & Lindenberg, K. (1997). Variational energy band theory for polarons: Mapping polaron structure with the Toyozawa method. *Journal of chemical physics*, 107(8), 3159-3178.

<https://hdl.handle.net/10356/92315>

<https://doi.org/10.1063/1.474667>

© 1997 AIP. This paper was published in *Journal of Chemical Physics* and is made available as an electronic reprint (preprint) with permission of American Institute of Physics. The paper can be found at: [Doi: <http://dx.doi.org/10.1063/1.474668>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Apr 2023 13:31:09 SGT

Variational energy band theory for polarons: Mapping polaron structure with the Toyozawa method

Yang Zhao^{a)}

Department of Physics, University of California, San Diego, La Jolla, California 92093-0354

David W. Brown

Institute for Nonlinear Science, University of California, San Diego, La Jolla, California 92093-0402

Katja Lindenberg

Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0340

(Received 6 December 1996; accepted 8 April 1997)

In this article we revisit from a contemporary perspective a classic problem of polaron theory in one space dimension following the variational approach originally taken by Toyozawa. 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 . Through this exfoliation of the exciton-phonon correlations comprising the polaron, 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. Through such examination of the complete parameter space at all κ , it is found that the common notion of a self-trapping phenomenon associated with $\kappa=0$ is a limiting aspect of a more general finite- κ phenomenon. Quantities such as phonon number distributions, complete ground state energy bands, and effective masses are obtained for all κ . The inverse problem of associating localized functions with the variational energy bands is addressed, with attention given to the concept of solitons and with the explicit construction of polaron Wannier states. The successes and failures of the Toyozawa method are assessed. © 1997 American Institute of Physics. [S0021-9606(97)50227-3]

I. INTRODUCTION

In this article, we approach a classic problem of polaron theory following the variational approach introduced by Toyozawa¹⁻⁵ and revisited in various guises by many since.⁶⁻¹⁶ We focus on phenomena specifically associated with the correlations driven by interactions of a single quasiparticle with phonons. We refer to our free quasiparticle as an “exciton,” though our results apply to a much wider class of excitations.

Our purpose is severalfold: First, though the Toyozawa method has been applied in varying degrees of completeness and sophistication through the years, there has as yet been no implementation of the method that has not been burdened either by analytical approximation or truncations perceived necessary to limit the scope of numerical computations. Computational resources now routinely available make possible a faithful numerical implementation of the method for lattices of meaningful size. Second, due to the more limited nature of the computations made heretofore and the varying priorities addressed along the way, some questions of interest today have yet to be adequately addressed or answered. Third, the method has the benefit of flexibly and clearly re-

solving the essential features of polaron structure with a degree of accuracy that is impressive despite the inherent limitations of the method.

More than merely updating the state of the art as it applies to the Toyozawa method, this article constitutes one “point” in a sequence of several increasingly refined variational attacks on a classic problem of polaron theory.¹⁷⁻¹⁹ The Merrifield method is the simplest in this sequence, and was addressed in a previous work^{17,18} in a fashion that we follow in this article as well; the results of that work provided quantitative bounds and qualitative guides for the computations implemented here. Besides providing more accurate estimates of the ground state energy, the present and subsequent works should shed light on which features of polaron structure are “robust” in that they are resolved with increasing clarity, and which features are artifacts of an insufficiently flexible approach. With this interest in mind, we draw comparisons with the more limited Merrifield approach with the aim of identifying robust trends; we shall be particularly concerned with identifying large and small polaron structures, and with assessing the nature of the self-trapping transition. The third point in the sequence is our own generalization of the Toyozawa method,^{17,19} including structure that became of interest during some of our prior studies of the interrelationships between polaron theory and soliton theory.^{12,13,16,20-41}

^{a)}Present address: Rochester Theory Center for Optical Science and Engineering, University of Rochester, Rochester, NY 14627.

Our central interest in this article 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 an appropriately normalized delocalized trial state, and $\hat{H}$ is the system Hamiltonian. The set of E^κ so produced constitutes an estimate (upper bound) for the polaron energy band.^{1,42} The trial states we use are eigenfunctions of the appropriate total momentum operator and orthogonal for distinct κ , making variations for distinct κ independent. Overlaps of $\hat{H}$ between trial states of distinct κ vanish, implying the absence of $\kappa - \kappa'$ scattering among the self-consistent states when considered from a dynamical perspective; however, since our trial states in most cases are not exact eigenstates, they retain within each κ sector a nonstationary quality associated with the error between the variational energy and the exact target value. It is a major goal of this work to implement the Toyozawa method to the limits of its flexibility in order to minimize this absolute error.

This article is organized as follows: In Sec. II we pose the model Hamiltonian, establish conventions, discuss the nature of the trial states we employ, and obtain the self-consistency equations to be solved for the optimal values of the variational parameters. In Sec. III we consider certain exact and general results that are in the nature of criteria against which our results may be judged, and others that aid in the interpretation of our solutions. In Sec. IV we discuss aspects of the numerical method, and in Sec. V we sketch a broad view of polaron structure in the context of the full system parameter space, introducing the notion of a phase diagram. In Sec. VI we look at specific sets of parameters and display the full variational solutions associated with each and, in Sec. VII, we take a more focused look at the character of the polaron energy band. In Secs. VIII and IX we return to the question of the local character of the polaron, first comparing our results with concepts from soliton theory, then introducing the notion of polaron Wannier states and displaying specific results from our variational calculations. Conclusions are summarized in Sec. X.

II. FORMULATION

As our system Hamiltonian, we choose the traditional Holstein Hamiltonian,^{43,44} for our purposes limited to one space dimension,

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

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

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

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

in which $a_n^\dagger$ creates an exciton 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 . Excitons and phonons are both treated 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. All of the methods used in this article can be applied as well to common generalizations of this Hamiltonian, involving, for example, phonon dispersion, exciton transfers beyond nearest neighbors, and/or different exciton-phonon coupling geometry. Nonlocal coupling in particular, has been treated elsewhere.^{45,46} Except where displayed for emphasis, $\hbar = \omega = 1$ throughout this article; consequently, all energies are understood to be measured in units of the optical phonon energy.

Throughout this article, we use the Fourier conventions for ladder operators $c^\dagger = a^\dagger, b^\dagger$, etc. and scalars $\gamma = \alpha, \beta$, etc.

$$c_n^\dagger = N^{-1/2} \sum_p e^{-ipn} c_p^\dagger, \quad c_p^\dagger = N^{-1/2} \sum_n e^{ipn} c_n^\dagger, \quad (6)$$

$$\gamma_n = N^{-1} \sum_p e^{ipn} \gamma_p, \quad \gamma_p = \sum_n e^{-ipn} \gamma_n. \quad (7)$$

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.

Toyozawa's Ansatz may be viewed as a time-independent translationally invariant rendering of the basic Ansatz state underlying much of the theory of the Davydov soliton,

$$|\psi\rangle = |\alpha\rangle \otimes |\beta\rangle, \quad (8)$$

where $\otimes$ denotes the direct product, $|\alpha\rangle$ and $|\beta\rangle$ are the exciton and phonon part of the Ansatz state, respectively,

$$|\alpha\rangle = \sum_n \alpha_n a_n^\dagger |0\rangle_{\text{ex}}, \quad (9)$$

$$|\beta\rangle = \exp \left[- \sum_n (\beta_n b_n^\dagger - \beta_n^* b_n) \right] |0\rangle_{\text{ph}}. \quad (10)$$

In much of what we shall refer to as “soliton theory,” states such as Eq. (8) are treated as trial wave functions in their own right *without* resort to the additional step of constructing explicitly delocalized superpositions. This distinction proves to be of considerable importance, since the product form of Eq. (8) predisposes it to the formation of permanently localized solutions even in translationally invariant polaron systems. In such solutions, the typically pulse-shaped distribution of the amplitudes β_n describes a lattice deformation fixed in the frame of the lattice, to which conforms a correspondingly pulse-shaped distribution of exciton probability amplitudes α_n .

Though rooted in the same practical notion of using the product function (8) to describe the internal correlations comprising polaron structure, the Toyozawa method lifts these correlations into an explicitly translationally invariant

trial state by superposing replicas of the form factor (8) displaced to every lattice site, weighted by an appropriate phase.

$$|\Psi(\kappa)\rangle = |\kappa\rangle \langle \kappa | \kappa \rangle^{-1/2}, \quad (11)$$

$$\begin{aligned} |\kappa\rangle &= \sum_n e^{i\kappa n} \sum_{n_1} \alpha_{n_1-n}^\kappa a_{n_1}^\dagger \exp \left[- \sum_{n_2} (\beta_{n_2-n}^\kappa b_{n_2}^\dagger \right. \\ &\quad \left. - \beta_{n_2-n}^{\kappa*} b_{n_2}) \right] |0\rangle, \\ &= N^{-1/2} \sum_{nk} e^{i(\kappa-k)n} \alpha_k^\kappa a_k^\dagger \\ &\quad \times \exp \left[- N^{-1/2} \sum_q (\beta_q^\kappa e^{-iqn} b_q^\dagger - \beta_q^{\kappa*} e^{iqn} b_q) \right] |0\rangle, \end{aligned} \quad (12)$$

where $|0\rangle$ is the vacuum state for both the exciton and the phonon field. The auxiliary vector $|\kappa\rangle$ is not normalized, but simplifies presentation of some results. The normalization condition for the total Toyozawa state does not impose any condition on the exciton amplitudes; indeed, the Toyozawa state is invariant under the scaling of all exciton amplitudes by an arbitrary but common complex constant. Since the variational calculation is insensitive to such scaling, solutions at differing κ may differ by arbitrary but distorting factors. As a practical matter, therefore, interpretation of results is facilitated by constraining the normalization of the exciton amplitudes to a common value for all κ of a particular total solution. In Figs. 4–12 below, the particular normalization convention used in each is indicated in each figure caption.

While the amplitudes $\{\alpha_n, \beta_n\}$ clearly are the vehicles for encoding the exciton-phonon correlations in both classes of trial state, it must quickly be noted that despite the obviously intimate relationship between the amplitudes of the Davydov Ansatz (8) and the apparently similar amplitudes in the Toyozawa state, the delocalizing construction creates important differences. For example, the Ansatz state $|\alpha\rangle \otimes |\beta\rangle$ admits the simple interpretation that the α 's are the exciton probability amplitudes and β 's are the mode amplitudes in the phonon coherent state, yielding readily interpretable relations such as

$$\langle a_m^\dagger a_m \rangle = |\alpha_m|^2, \quad (14)$$

$$\langle b_m \rangle = \beta_m, \quad (15)$$

$$\langle a_m^\dagger a_m b_{m+n} \rangle = |\alpha_m|^2 \beta_{m+n}. \quad (16)$$

Once this Ansatz state is incorporated into Bloch states, however, these expressions become substantially more complex [see, e.g., Eqs. (17)–(19)], with certain of these simpler forms recovered only in limits, and some not at all. The reason for this increased complexity is that any measurement of a local property in the delocalized state involves contributions from *all* displaced replicas of the form factor, not merely a single one at a fixed location as in the soliton theory. Thus, while the amplitudes α and β have parallel

roles in the two approaches and are intimately related, they do not represent the same physical quantities.

The expectation values of the several contributions to the Holstein Hamiltonian are given by

$$\langle \kappa | \hat{H}^{\text{ex}} | \kappa \rangle = -2JN^{-1} \sum_k S_{\kappa-k}^\kappa \cos k |\alpha_k^\kappa|^2, \quad (17)$$

$$\langle \kappa | \hat{H}^{\text{ph}} | \kappa \rangle = N^{-2} \sum_{kq} S_{\kappa-k-q}^\kappa |\alpha_k^\kappa|^2 \beta_q^{\kappa*}, \quad (18)$$

$$\begin{aligned} \langle \kappa | \hat{H}^{\text{ex-ph}} | \kappa \rangle &= -gN^{-2} \sum_{kq} \alpha_k^{\kappa*} \alpha_{k+q}^\kappa (S_{\kappa-k-q}^\kappa \beta_q^{\kappa*} \\ &\quad + S_{\kappa-k}^\kappa \beta_{-q}^\kappa), \end{aligned} \quad (19)$$

$$\langle \kappa | \kappa \rangle = N^{-1} \sum_k S_{\kappa-k}^\kappa |\alpha_k^\kappa|^2. \quad (20)$$

Here S_p^κ is the Fourier transform of the Debye–Waller factor S_n^κ ,

$$S_p^\kappa = \sum_n e^{-ipn} S_n^\kappa, \quad (21)$$

$$S_n^\kappa = \langle \{ \beta_m \} | \{ \beta_{m+n} \} \rangle = \exp \left[N^{-1} \sum_q |\beta_q^\kappa|^2 (e^{iqn} - 1) \right]; \quad (22)$$

because the real-space form of the Debye–Waller factor satisfies the inversion symmetry $S_n^{\kappa*} = S_{-n}^\kappa$, the Fourier transform S_p^κ is real. The Debye–Waller factor is to be distinguished from the Franck–Condon factor

$$\text{ph} \langle 0 | \{ \beta_n \} \rangle = e^{-1/2 \sum_n |\beta_n|^2}. \quad (23)$$

The latter is of importance in optical absorption, while the former has a greater role in transport problems since it quantifies the overlap of the polaron lattice distortion with itself displaced by n lattice sites. The nearest neighbor Debye–Waller factor $S_{\pm 1}^\kappa$ appears routinely in the transport terms of effective (small) polaron Hamiltonians, where they are instrumental in the renormalization of the effective mass. Longer range Debye–Waller factors appear in our calculations because the spreading of the exciton amplitudes α_n^κ allows overlaps between non-nearest-neighbor components to contribute. Note, for example, that because $N^{-1} \sum_p S_p^\kappa = S_{n=0}^\kappa = 1$, if the exciton amplitudes contract down to a single site ($\alpha_n^\kappa = \delta_{n0}$, $\alpha_k^\kappa = \text{const.}$) all the Debye–Waller factors in Eqs. (18)–(20) disappear, leaving only the nearest neighbor Debye–Waller factors in the transport term (17). The presence of long range Debye–Waller factors in our calculation has the consequence that the decomposition of the complex real-space Debye–Waller factors into amplitude and phase variables ($S e^{i\Phi}$) as in the corresponding Merrifield calculation offers no practical advantage over the real Fourier transform S_p^κ .

Minimization of E^κ with respect to $\beta_q^{\kappa*}$ yields

$$\beta_q^\kappa = \frac{L_q^\kappa}{M_q^\kappa + H_q - M_q^\kappa E^\kappa}, \quad (24)$$

where

$$L_q^\kappa = gN^{-1} \sum_k S_{\kappa-k-q}^\kappa \alpha_k^{\kappa*} \alpha_{k+q}^\kappa, \quad (25)$$

$$M_q^\kappa = N^{-1} \sum_k S_{\kappa-k-q}^\kappa |\alpha_k^\kappa|^2, \quad (26)$$

and H_q is the sum of three terms

$$H_q = H_q^{\text{ex}} + H_q^{\text{ph}} + H_q^{\text{ex-ph}}, \quad (27)$$

$$H_q^{\text{ex}} = -2JN^{-1} \sum_k S_{\kappa-k-q}^\kappa \cos k |\alpha_k^\kappa|^2, \quad (28)$$

$$H_q^{\text{ph}} = N^{-2} \sum_{kq'} S_{\kappa-k-q-q'}^\kappa |\alpha_k^\kappa|^2 |\beta_{q'}^\kappa|^2, \quad (29)$$

$$H_q^{\text{ex-ph}} = -gN^{-2} \sum_{kq'} \alpha_k^{\kappa*} \alpha_{k+q}^\kappa (S_{\kappa-k-q-q'}^\kappa \beta_{q'}^{\kappa*} + S_{\kappa-k-q}^\kappa \beta_{-q'}^\kappa). \quad (30)$$

Similarly, we minimize E^κ with respect to $\alpha_k^{\kappa*}$, obtaining

$$\alpha_k^\kappa = \frac{L_k^\kappa}{M_k^\kappa - (E^\kappa + 2J \cos k) S_{\kappa-k}^\kappa}, \quad (31)$$

where

$$L_k^\kappa = gN^{-1} \sum_q \alpha_{k+q}^{\kappa*} (S_{\kappa-k-q}^\kappa \beta_q^{\kappa*} + S_{\kappa-k}^\kappa \beta_{-q}^\kappa) \quad (32)$$

and

$$M_k^\kappa = N^{-1} \sum_q S_{\kappa-k-q}^\kappa |\beta_q^\kappa|^2. \quad (33)$$

We may obtain the sum rule from Eq. (24)

$$\beta_{q=0} = \sum_n \beta_n = g, \quad (34)$$

by noting that

$$H_q|_{q=0} = E^\kappa \langle \kappa | \kappa \rangle, \quad (35)$$

$$g^{-1} L_q|_{q=0} = M_q^\kappa|_{q=0} = \langle \kappa | \kappa \rangle. \quad (36)$$

Results of our numerical solution of the self-consistency equations are presented in sections to follow as surfaces in momentum space. While this requires a certain amount of mental Fourier inversion to interpret real-space structure, the momentum-space representation compactly reveals the principal components of polaron structure in a manner that would be significantly less clear in real space. Real-space structure is given particularly close attention in Secs. VIII and IX.

III. EXACT RESULTS AND CERTAIN GENERAL CONSIDERATIONS

Here we consider three distinct scenarios: (i) the exact solution at $J=0$ for any g , (ii) the exact solution at $g=0^+$

for any J , and (iii) an exact decoupling property of the polaron Hamiltonian valid for any J and g . While each of these can be understood straightforwardly, that our variational solutions should be consistent with all of them is a nontrivial matter. Moreover, as will become clear in the sections to follow, though each of these properties holds rigorously only in a parametric limit or in a limited part of the total solution, the characteristics they reveal are reflected in polaron structure well beyond the limiting scenarios.

A. $J=0$

It is well known that in the limit of vanishing exciton transfer integral ($J=0$) local-coupling polaron Hamiltonians are diagonalizable by the displaced oscillator transformation. In such cases the polaron energy band is lowered, but is completely flat, resulting in a complete degeneracy of all polaron states associated with a given band. Consequently all superposition states

$$|\Psi\rangle = \sum_n \psi_n a_n^\dagger \exp[-g(b_n^\dagger - b_n)] |0\rangle_{\text{ex-ph}} \quad (37)$$

constitute equally valid solutions, opening to speculation the question of which of all possible superpositions should be preferred in a small polaron scenario, e.g., whether a Bloch state ($\psi_n^\kappa = N^{-1/2} e^{i\kappa n}$) or a localized state ($\psi_n^\kappa = \delta_{n0}$).

Our variational solutions are characterized in part by the fact that the amplitudes α_k^κ , which are generally more highly structured in k than in κ , become completely flat in both k and κ as $J \rightarrow 0$. This implies that the exciton amplitudes describing the *internal* structure of the polaron become completely localized in real space, consistent with the notion of small polarons, but that the total state is at all times delocalized, consistent with the loss of absolute spatial reference in course of the Bloch state construction.

B. $g=0^+$

We stress by our notation that the weak-coupling limit to which we refer is *not* the free-exciton/free-phonon limit in which each subsystem is regarded independently of the other. Rather, we refer to the limiting character of the *joint* exciton-phonon Bloch states and their energies given fixed values of the joint crystal momentum κ as the exciton-phonon coupling vanishes. That the latter can differ significantly from the free-exciton scenario proves to have a strong influence over polaron structure at finite coupling strengths.

The exact solution at vanishing coupling is controlled by the relationship between the free-exciton energy band and the one-phonon continuum, with the result that the exact joint energy band at $g=0^+$ for any $J>1/4$ is given by

$$E_{g=0^+}(\kappa) - E_{g=0^+}(0) = 2J[1 - \cos(\kappa)] \quad \text{for } |\kappa| < \kappa_c, \quad (38)$$

$$= 1 \quad \text{for } |\kappa| > \kappa_c, \quad (39)$$

FIG. 1. The number of phonons that clothe the exciton for $g=0.4$, $J=0.5$, $\kappa_c = \pi/2$, and $g=2.5$, $J=4.0$, $\kappa_c \approx 0.16\pi$. Diamond symbols indicate the points (κ_c) at which the free-exciton energy band enters the one-phonon continuum. $K = \kappa/\pi$.

in which $\pm \kappa_c$ are the wave vectors at which the free-exciton band penetrates the one-phonon continuum, given by the relation $2J(1 - \cos \kappa_c) = 1$. Associated with these energies are the Bloch states

$$|\Psi(\kappa)\rangle = a_{k=\kappa}^+ |0\rangle \quad \text{for } |\kappa| < \kappa_c, \quad (40)$$

$$= b_{q=\kappa}^+ a_{k=0}^+ |0\rangle \quad \text{for } |\kappa| > \kappa_c, \quad (41)$$

the former being a zero-phonon state in which the exciton carries all the crystal momentum, and the latter being a state in which the exciton is at rest and all the crystal momentum is carried by a single free-phonon quantum. Figure 1 illustrates the sense in which this highly quantum mechanical property is continued to finite coupling and gradually eroded with increasing coupling strength. At the small but finite value of the coupling shown in the lower curve, the number of phonons present in the phonon cloud is essentially equal to zero near the Brillouin zone center and essentially equal to unity near the Brillouin zone edge; the transition from zero to one phonon occurs smoothly, through an interval of κ centered on κ_c . With decreasing coupling this interval narrows until the sharp transition noted above is recovered at $g=0^+$. Conversely, with increasing coupling this transition broadens until significant phonon numbers are present at all κ . Not evident in Fig. 1 is the detail with which the expected number of phonons is distributed over the many phonon modes participating in the polaron. Detailed study reveals that in weak-coupling distributions such as that shown in the lower curve of Fig. 1 the total phonon number is highly concentrated in a single phonon mode, very closely approximating the pure zero and one-phonon states expected at $g=0^+$. This changes significantly with increasing coupling; the multiphonon states suggested by the upper curve in Fig. 1 involve a fractional excitation of all phonon modes so that the phonon cloud has indefinite-number character in essentially all respects.

The (nearly) number-definite states characteristic of weak coupling are not well approximated by small polaron states due to the number-indefinite character of the single coherent state that represents the lattice component in such states. The Toyozawa Ansatz improves this situation, though indirectly and incompletely. The lattice state associated with each exciton operator $a_m^\dagger$ is no longer a single coherent state but a superposition of such states weighted by the exciton profile.

We may examine the weak-coupling limit of the high momentum states ($\kappa > \kappa_c$) by setting $\beta_q^\kappa = \beta_\kappa \delta_{q\kappa}$ and $\alpha_k^\kappa = \alpha_0^\kappa \delta_{k0}$; in such a case, the real-space exciton amplitudes are uniform, and the multimode product of phonon coherent states is reduced to the product of a single-mode coherent state with the phonon vacua of all other modes. Owing to the delocalization that is possible within the electronic component of Toyozawa's Ansatz, the result is a superposition of phonon coherent states [see Eq. (13)]

$$|\Psi_0(\kappa > \kappa_c)\rangle = N^{-1/2} \alpha_0^\kappa |0\rangle_{\text{ex}} \sum_n e^{i\kappa n} \times \exp[-N^{-1/2}(\beta_\kappa^\kappa e^{-i\kappa n} b_\kappa^\dagger - \beta_\kappa^{*\kappa} e^{i\kappa n} b_\kappa)] |0\rangle_{\text{ph}}. \quad (42)$$

Noting that the phase κn may be viewed as a discrete summation variable θ_n that (modulo 2π) samples the interval $[-\pi, +\pi]$, the phonon component of this state may be understood as a discrete approximation to the integral representation of a pure, single-phonon state^{47,48}

$$b^\dagger |0\rangle_{\text{ph}} = \frac{e^{1/2\rho^2}}{\rho} \int_{-\pi}^{+\pi} d\theta e^{i\theta} \exp[-(\rho e^{-i\theta} b^\dagger - \rho e^{i\theta} b)] |0\rangle_{\text{ph}}. \quad (43)$$

Were the variational solutions for the weak-coupling limit to converge to a state in which $\beta_q^\kappa \propto \delta_{q,\kappa}$ and $\alpha_k^\kappa \propto \delta_{k,0}$ as is suggested by the exact weak-coupling limit, the estimated energy would still be burdened by the fact that the phonon part of Eq. (42) is a discrete approximation of Eq. (43). For certain values of κ (e.g., small integer divisors of 2π) the sampling of the interval $[-\pi, +\pi]$ by such discrete sums is particularly poor. This would suggest that the quality of the variational energy bound might be irregular in κ at sufficiently weak coupling. We did *not* find such irregularities in the κ dependence of the energy band itself, which was smooth in κ within the tolerances of our computation. We *did*, however, find increasing irregularity in the κ dependences of certain variational quantities such as the exciton amplitudes α_k^κ at weak coupling and at higher κ 's where such sampling-related insufficiencies might be expected to be more pronounced. While these trends are intriguing, we cannot draw definitive conclusions about them because of the parallel complications of deteriorating numerical precision in the weak-coupling regime.

C. $q=0$

In the approach of this article, all manipulations are made on the variational trial state rather than on the Hamiltonian operator itself; however, essentially equivalent attack can be made by using the Lee–Low–Pines transformation⁴² to effect the partial diagonalization of the Hamiltonian into decoupled sectors labeled by the joint crystal momentum. In such an approach, the transformed Hamiltonian takes the form

$$\hat{H} = \sum_{\kappa} \hat{H}^{\kappa} a_{\kappa}^{\dagger} a_{\kappa}, \quad (44)$$

in which $\hat{H}^{\kappa}$ contains no dressed particle operators and describes a set of independent, highly nonlinear dressed-phonon problems parametrized by the joint crystal momentum κ . Within each sector the phonon Hamiltonian $\hat{H}_{\kappa}$ can be separated into two parts,

$$\hat{H}^{\kappa} = \hat{H}_{q=0}^{\kappa} + \hat{H}_{q \neq 0}^{\kappa}, \quad (45)$$

where

$$\hat{H}_{q=0}^{\kappa} = b_0^{\dagger} b_0 + g N^{-1/2} (b_0 + b_0^{\dagger}), \quad (46)$$

$$\begin{aligned} \hat{H}_{q \neq 0}^{\kappa} = & \sum_{q \neq 0} [b_q^{\dagger} b_q + g N^{-1/2} (b_q + b_{-q}^{\dagger})] \\ & - 2J \cos\left(\kappa - \sum_{q \neq 0} q b_q^{\dagger} b_q\right), \end{aligned} \quad (47)$$

which shows that while the finite- q modes are entangled in a complex fashion, the $q=0$ mode is decoupled from this complexity and constitutes a simple displaced oscillator. This decoupling is manifested in our computation as the “sum rule” $\beta_{q=0}^{\kappa} = g$.

Unlike the situation under the simpler Merrifield method, whose optimal phonon amplitudes are clearly both continuous and smooth at $q=0$, the self-consistency equations in the present case offer no comparable indications regarding the small- q behavior of the optimal phonon amplitudes apart from this sum rule. Indeed, we find that most of the solutions we have obtained exhibit apparent discontinuities along $q=0$ in β_q^{κ} and along $k=\kappa$ in α_k^{κ} . These discontinuities are plainly evident in many of the figures displayed in the sections to follow; even in most cases where they are not evident to the eye, their presence may be discerned on close inspection of the numerical data. These discontinuities have the appearance of removable singularities in the sense that both $\beta_{q=0}^{\kappa}$ and $\alpha_{k=\kappa}^{\kappa}$ appear to be smooth when the set of points $\{\beta_{q=0}^{\kappa}, \alpha_{k=\kappa}^{\kappa}\}$ is deleted from consideration.

These discontinuities appear together due to momentum selection rules that link the zero-momentum $\beta_{q=0}^{\kappa}$ with exciton amplitudes $\alpha_{k=\kappa}^{\kappa}$; this pairing reflects contributions to the total variational state by components in which the lattice oscillators are uniformly and statically distorted while the exciton exists in a free, plane wave state, unscattered or otherwise unencumbered by correlations with the lattice.

There is nothing in our results to suggest that this tandem discontinuity has any practical significance and it may

be an artifact of the Toyozawa method. Thus, we do not address it further in this article, except to stress that this minor feature should *not* be confused with sometimes strong features of the phonon amplitudes in the vicinity of the line $q=\kappa$; the latter features, strongly evident in the weak-coupling regime, represent important and robust contributions to polaron structure.

IV. NUMERICAL ASPECTS

Our goal is to obtain numerically exact solutions to the above self-consistency equations via relaxation techniques. We impose no restrictions on the form of β_q^{κ} and α_k^{κ} beyond those implicit in the variational Ansatz itself, and set out to solve the variational equations to desired precision.

Relaxation is an efficient iteration method for identifying energy minima of a complex variational system. The principal difficulties with this approach lie in the stability of the iteration and the quality of the convergence. Though a proper solution obtained by this or any other variational method must be stable relative to small changes in the variational parameters, and though the search for such solutions relies upon this stability property, it is possible for errors in a fraction of the total solution to spread and destabilize the iteration or otherwise limit the quality of the convergence. Thus, while in principle the same family of solutions should result for randomly chosen initial data, in practice the best convergence results when the search is initialized with input that is already “close” to the solution being sought.

For our problem, the mathematical dilemma of finding educated initial guesses for the nonlinear iterative scheme can be avoided for the most part due to the uniqueness of the physical solution and the availability of exact solutions in certain limits of physical parameters. To achieve efficient and stable iterations toward the variational ground state, one may take advantage of the continuity of the ground state with respect to small changes in system parameters over much of the phase diagram, and may initialize the iteration using a reliable ground state already determined at some nearby point in parameter space. Starting from those limits where exact solutions can be obtained analytically and executing a sequence of variations along well-chosen paths through parameter space using solutions from one step to initialize the next, the whole parameter space can be explored.

Similarities can be drawn between such a step-wise process and calculations involving classical magnetic hysteresis where the external field serves as the physical control parameter.^{49,50} Hysteresis is evident when the iterative solution exhibits a dependence on the path through parameter space along which the physical parameter of interest is approached. Insufficiency in the flexibility of Ansätze is usually responsible for such behavior, although a certain degree of rapid changes in the system with respect to physical parameters is reflected by the occurrence of apparent hysteresis.

The exact small polaron solution is available in the limit of vanishing bare bandwidth ($J \rightarrow 0$). Computation typically starts from the region where small polaron theory holds, and

FIG. 2. Phase diagram. This parameter space illustration conveys four different items of information. The thinner, more closed figure in the middle to upper right (solid curves) illustrates the boundary of the discrete self-trapping transition as found in our present calculations. The wider, more open figure (dashed curves) has the same interpretation, but is the result of calculations by the Merrifield method and is presented for comparison purposes only; the dotted curve illustrates the notion of a self-trapping line associated with the latter as discussed in Sec. VII. The scatter plot of discrete symbols indicates parameter values chosen for explicit illustration in Figs. 4–12.

the bare bandwidth is gradually increased relative to the small polaron binding energy (g^2) as the computation continues. Reversibility of the computation is tested as the parameter space is mapped; that is, a provisionally convergent solution is used to initialize a new variation at the point in parameter space that provided the initialization for the provisional solution. That particular step of computation is termed reversible if the solution for the previous set of parameters is recovered. Any point in the parameter space can be approached from various points close to it, which we shall call its “neighbors.” A completely reversible point is one that survives all the reversibility tests of its various neighbors. Most of the regions in our problem are found to be reversible except for a thin tongue (see Fig. 2) constituting a “phase boundary” between two types of polaron states. Within that tongue, two solutions are obtained depending on whether those points are reached from above or below the tongue.

For any specific calculation, the number of sites N in our one-dimensional, periodic lattice must be fixed at some reasonable value. N must be large enough to contain the largest structure to be encountered, or, in momentum space terms, to resolve the finest feature; on the other hand, little is gained and computational effort wasted if N is significantly larger than is necessary for this purpose. All the essential features of our variational solutions are adequately resolved using lattices of 32 sites, with the possible exception of the weakest values of exciton-phonon coupling as may be apparent in Figs. 8(a) and 12(a) below; in such cases, however, the variational energy does not appear to be sensitive to this potential limitation.

Good numerical convergence is achieved for most re-

gions of parameter space. Round-off errors affect computation only in the weak-coupling regime; in this regime the polaron energy is increasingly insensitive to round-off errors, allowing errors in the variational parameters themselves to grow. High-momentum states ($\kappa > \kappa_c$) are most vulnerable to such inaccuracies.

It is possible that algorithmic improvements might allow a more precise resolution of polaron structure at a given machine precision, or that better results might be achieved at higher machine precision. Test calculations performed at higher precision on different machines show better convergence for given parameters in the weak-coupling region. However, even at higher precision, a small decrease in exciton-phonon coupling in that region greatly increases demands on computational precision, such that increasing precision only slightly reduces the value of the exciton-phonon coupling at which computational reliability is lost.

The solutions for the phonon amplitudes β_q^κ appear to be real within numerical precision; however, the site-space phonon displacements β_n^κ generally are complex owing to nontrivial asymmetries in the q -dependent amplitudes over large regimes of parameter space. Prior variations have often restricted β_q^κ to be symmetric in q (β_n^κ real), which has introduced problematic artifacts.¹³ Computation also yields real exciton amplitudes α_k^κ within numerical precision for initial starts of real matrices.

V. PHASE DIAGRAM AND GENERAL RESULTS

It is convenient to use the device of a phase diagram to organize our discussion of the specific results of our computations. One would expect the principal feature of such a phase diagram to be a boundary line separating a small polaron region from a large polaron region; such a line would be expected to be associated with the common notion of a more-or-less sharp self-trapping transition. Though on formal grounds the self-trapping transition is expected to be smooth,^{51–54} it is commonplace for approximate treatments such as ours to encounter discontinuities where polaron structure changes in too complex a fashion to be represented accurately within the scope of the computational method. While such discontinuities must be understood to be artifacts of an insufficiently flexible method, they are also convenient “markers” identifying the location of significant features on the phase diagram and thus have at least conceptual utility.

Variational solutions are found to smoothly follow incremental changes in the control parameters J and g over most of the phase diagram with, however, dramatic exception in a wedge-shaped region at moderate to large values of J and g (see Fig. 2). The nature of the exception is qualitatively similar to that found using the less satisfactory Merrifield method.^{17,18} At every point within the wedge-shaped region there exists a κ^* , the particular value of which is dependent upon J and g , at which the variational energy band $E(\kappa)$ is not smooth. More specifically, the variational solutions in a neighborhood around κ^* are not unique, such that the family of solutions smoothly continuous with unique solutions at high κ cease to be the minimum energy solutions below

FIG. 3. Schematic of the typical variational situation in the transition region; features have been exaggerated for illustrative purposes and units are arbitrary. Two distinct classes of stable solutions exist, and coexist over a limited range of κ . The variational energy band is arrived at by discarding the higher-energy solutions and joining the resulting branches at their intersection κ^* . $K = \kappa/\pi$.

κ^* , and the family of solutions smoothly continuous with unique solutions a low κ cease to be the minimum energy solutions above κ^* (see Fig. 3). In such cases, the states above κ^* can be meaningfully interpreted as small polaron states, and the states below κ^* can be interpreted as large polaron states, and the “event” marked by κ^* can be understood as a κ -dependent self-trapping transition at fixed J and g .

The usual notion of a self-trapping transition is associated with discrete changes in properties of the $\kappa=0$ state as J and/or g are varied; for example, the effective mass, whose rapid change or jump is the traditional hallmark of self-trapping. Such discrete behavior yields a self-trapping “line” in parameter space separating large and small polaron structures. The κ -dependent self-trapping transition we observe, though discrete, is discrete in a different way; since κ^* s exist over a range of J and g , there is not a single transition line, but a transition *region* within which the transition *moves* through the band. At every point in this region, the band is interpretable as large-polaron-like at small κ , and small-polaron-like at large κ . The usual notion of a self-trapping transition is recovered, however, if from any point within the transition region the coupling parameter is increased sufficiently. In response to increasing coupling strength, κ^* moves toward the center of the Brillouin zone, such that $\kappa^* \rightarrow 0$ at some finite g . At this point, the $\kappa=0$ solution changes abruptly from being of large polaron character to small polaron character, with properties such as the effective mass experiencing the discrete changes one would expect.

For values of J less than the “critical value” J_c , it is still the case that solutions are “large-polaron-like” at weak coupling, and “small-polaron-like” at strong coupling; however, the transition between these two occurs smoothly. The “critical point” under the present method is given ap-

proximately by $J_c=2.9$ and $g_c=2.66$ as compared with $J_c=0.89$, $g_c=1.90$ under the Merrifield method. This, together with the fact that the “width” of the transition in J , g , and κ is significantly reduced relative to the Merrifield calculation, lends support to the notion that the discreteness of the self-trapping transition is an artifact that gets “squeezed out” to ever farther reaches of parameter space as flexibility of the variational method is meaningfully increased.

VI. SPECIFIC RESULTS

In this section we present three sets of specific variational solutions. The selection was made first with the aim of illustrating characteristic features at “small,” “medium,” and “large” values of the exciton transfer integral J . For these purposes, small J has the same meaning as nonadiabatic ($J < 1/4$), and the medium and large J solutions all lie in the adiabatic regime ($J > 1/4$). Medium and large J refer to values respectively below and above $J_c=2.9$ marking the onset of the self-trapping-related discontinuities as located by the Toyozawa method. Values of the coupling parameter g have been chosen to illustrate the range of polaron structure characteristic of each regime.

A. Small J

In this section we focus on exciton transfer integrals that are small in an absolute sense, which for our purposes means values of $J < 1/4$. Such values correspond to free-exciton bands that may approach but do not penetrate the one-phonon continuum (see Sec. III B above). Figure 4 presents results for the case of $g=0.1$, $J=0.2$, which is typical of many small- J cases, and contains a number of features worthy of note.

Most obvious, perhaps, is the fact that the shapes of the variational surfaces along the “internal” dimensions q , k , and the “external” dimension κ differ qualitatively, in keeping with the differing roles of these dependences. The profiles of β_q^κ in q and α_k^κ in k reflect the internal correlations that comprise polaron structure, while the profiles in κ reflect states of motion or polaron dynamics. The κ dependence of β_q^κ is relatively strong while that of α_k^κ is weak, suggesting that the phonon cloud is more responsive to dynamics than is the exciton component.

Both the exciton and phonon surfaces are characterized by mean values significantly above zero, implying that the real-space profiles of both components contain strong central amplitudes. The distortions of the variational surfaces around these mean amplitudes reflect the degree and manner in which the real-space amplitudes extend beyond this central peak. A sinusoidal modulation of any size in q or k maps into nearest neighbor real-space amplitudes, and distortions of more anharmonic quality reflect the spreading of the real-space amplitudes beyond nearest neighbors.

In the particular case illustrated in Fig. 4, the nearly sinusoidal variation of α_k^κ around a strong, finite background implies a strong central amplitude, small amplitudes on near-

FIG. 4. (a) Phonon amplitude β_q^κ , and (b) exciton amplitude α_k^κ for $g=0.1$, $J=0.2$. $\alpha_{n=0}^\kappa=1$.

est neighbors, and very little amplitude beyond nearest neighbors.

The accompanying phonon surface bears more careful interpretation. The strong, finite background in β_q^κ implies the existence of a strong central amplitude, but the strongly nonsinusoidal excursions near $q=\kappa$ indicate the presence of a broad background component with a prominent modulation of wave vector $q=\kappa$ that reaches its peak amplitude at the Brillouin zone boundary. This growth in the κ -dependent background component is reflective of the increasing strength of exciton-phonon interactions as the “gap” between the free-exciton energy band $2J[1 - \cos(\kappa)]$ and the one-phonon continuum decreases. This gap reaches a minimum at the zone boundary, and consequently exciton-phonon interactions are strongest there. This is essentially a level-repulsion phenomenon resulting in the modulation of the multiphonon cloud by the nearby one-phonon states at a given κ , and is thus a signature of quantum behavior. The appearance of non-negligible asymmetry in the phonon amplitudes is part of this effect, and the absence of any significant related asymmetric feature in the exciton amplitudes may be taken as one indication that the asymmetric phonon structure is in some nontrivial respect “free.”

There are no dramatic changes in the character of variational solutions as J and g are varied within this small- J regime. Overall trends are that the surfaces shown in Fig. 4 flatten as $J \rightarrow 0$ at fixed g and as g either vanishes or diverges at fixed J . The only significant qualitative deviation

FIG. 5. (a) Phonon amplitude β_q^κ , and (b) exciton amplitude α_k^κ for $g=3.0$, $J=2.0$. $\alpha_{k=0}^\kappa=1$.

from the illustrated case is that for J sufficiently small, the zone-edge features seen so prominently in Fig. 4(a) become insignificant because the energy gap between the free exciton band and the one-phonon continuum is too large for the latter to significantly affect the structure of the phonon cloud. In this *very* small- J regime, the phonon amplitudes are nearly independent of κ for all coupling strengths, and show “locking” characteristics as discussed in the next section.

B. $J=2.0$

In this section, we examine in detail the case of a medium value of the transfer integral; the value $J=2.0$, for which $\kappa_c \approx 0.23\pi$. The selection of points for presentation in this section has been made to allow direct comparison with results we have obtained previously using the Merrifield method; our present results differ rather dramatically from the latter, where the $J=2.0$ line includes strong self-trapping-related discontinuities.

Figure 5 shows the case of $g=3.0$, $J=2.0$, which is typical of the strong-coupling region. We observe that β_q^κ and α_k^κ are similar in shape, being nearly independent of the joint crystal momentum κ and being smoothly pulse-shaped around the zone center in both q and k . We describe this condition of strong similarity as a “locking” of the exciton and lattice components. This locking characteristic is reflected in the site-space β_n^κ and α_n^κ as well. This finding is at least qualitatively consistent with adiabatic polaron theories, which generally lead to coupling relations of the sort $\beta_n \propto |\alpha_n|^2$ (see Sec. VIII).

FIG. 6. (a) Phonon amplitude β_q^κ , and (b) exciton amplitude α_k^κ for $g=2.4$, $J=2.0$. $\alpha_{n=0}^\kappa=1$.

As the coupling constant is further increased, there is essentially no change in the shape of the surfaces shown in Fig. 5 except that both surfaces flatten progressively while maintaining their locked character, reflecting the monotonic real-space contraction of polaron correlations toward complete localization. As J is varied modestly at fixed g , there is again little change in the character of the variational solutions except that the real-space width of the polaron increases (decreases) as J increases (decreases).

As exciton-phonon coupling g is decreased below $g=3$, the near uniformity of the phonon amplitudes with respect to κ is lost, as Fig. 6 shows for the case of $g=2.4$, $J=2.0$. Specifically, the phonon cloud varies from being rather tightly localized in real space for states near the Brillouin zone boundary to being considerably more broad for states near the zone center. Apart from minor changes in scale, the outer zone structure is the same as that which is typical of the entire strong-coupling region, and thus reflects small-polaron structure. The broader zone-center structure is typical, as we shall see, of the long-wavelength structure found throughout the weak-coupling region, and thus reflects large-polaron structure.

Despite these obvious changes, the exciton component remains essentially completely independent of the total momentum label; thus, the noted changes in polaron structure are almost completely ascribable to changes in the phonon cloud alone. Moreover, though the clear similarities in the exciton and phonon profiles suggest the persistence of locking, the locking relation must be κ dependent, resulting in a

FIG. 7. (a) Phonon amplitude β_q^κ , and (b) exciton amplitude α_k^κ for $g=2.0$, $J=2.0$. $\alpha_{k=0}^\kappa=1$.

broader, more weakly bound phonon cloud near the Brillouin zone center than near the zone edge.

Close comparison of Figs. 5 and 6 shows that the variation of α_k^κ in k has increased in amplitude and has grown weakly nonsinusoidal, reflecting the continued spread of the real-space exciton amplitudes beyond nearest neighbors as coupling strength is decreased.

Figure 7 shows the case of $g=2.0$, $J=2.0$. At this point we can clearly resolve a ridge in β_q^κ along $q=\kappa$ for $\kappa > \kappa_c$ rising above an undulating background. As will become evident shortly, this momentum-rich feature signals the emergence of a one-phonon structure typical of the weak-coupling polaron. Important to note, however, is that despite the obvious complexity of the phonon cloud's structure, there remains in the background of the momentum-rich component a relic of the nearly κ -independent locked component that predominates at stronger coupling. Also, as in those cases, the exciton amplitudes α_k^κ remain essentially κ -independent, with their variation in k increasing in amplitude and growing still more nonsinusoidal, reflecting continued spreading of the exciton component in real space.

In the weak-coupling limit, our calculated results appear to trend toward a highly singular structure

$$\beta_q^\kappa \approx 0 \quad \text{for } |\kappa| < \kappa_c, \quad (48)$$

$$\approx \beta^\kappa \delta_{q\kappa} \quad \text{for } |\kappa| > \kappa_c. \quad (49)$$

This trend is apparent in Fig. 8, where iteration results for the case of $g=1.0$, $J=2.0$ are displayed. The δ -like com-

FIG. 8. (a) Phonon amplitude β_q^κ , and (b) exciton amplitude α_k^κ for $g=1.0$, $J=2.0$. $\alpha_{n=0}^\kappa=1$.

ponent at higher momenta sharpens progressively with decreasing coupling, reflecting the attempt of the trial state to approximate the one-phonon number state that is found in the exact weak coupling limit.

With the resolution of this one-phonon structure it is clear that there remains a weak but distinguishable low-momentum pulselike component coexisting with it. This pulselike component would appear to be a remnant of the locked component of the phonon cloud. It is also clear, however, that the detail of this apparent locking must be more complex than that found at higher coupling, since here, for the first time in this transection of the phase diagram, the exciton amplitudes show a significant dependence on κ . The feature of interest here is the “break” in this κ dependence in the vicinity of κ_c . This is the value of the crystal momentum at which the free-exciton band enters the one-phonon continuum, and the point at which the phonon cloud begins to resolve its one-phonon structure. This suggests that the resolution of the one-phonon structure coincides with the decoupling of that structure from the exciton component.

The irregularity of the more detailed features of the α_k^κ surface is typical of results at this and weaker coupling, and reflects the fact that the variational energy loses sensitivity to the details of α_k^κ with decreasing coupling (see Sec. III B).

C. Large J

In this section, we traverse the phase diagram along the vertical line $J=4.0$, for which $\kappa_c \approx 0.16\pi$; we proceed from strong to weak coupling, starting in the upper portion of the

FIG. 9. (a) Phonon amplitude β_q^κ , and (b) exciton amplitude α_k^κ for $g=2.95$, $J=4.0$. $\alpha_{n=0}^\kappa=1$.

phase diagram (see Fig. 2). Above the transition region, β_q^κ and α_k^κ are locked, and are not much different in shape from those in Fig. 5 except that the real-space width of the polaron is increased at comparable values of exciton-phonon coupling strength.

Lowering g through the upper boundary of the transition region causes abrupt changes in the variational amplitudes near $\kappa=0$, where large polaronlike structure suddenly appears, bracketed by small polaronlike structure at higher κ 's (see Fig. 9). When approached from the strong coupling side as we have described, the abrupt change first appears at $\kappa=0$, identifying the upper edge of the transition region with the traditional notion of a self-trapping transition as widely discussed in the literature. For parameter sets *within* the transition region, variational quantities are smooth within the inner and outer Brillouin zones as demarked by transition-related wave vectors $\pm\kappa^*$, but generally are not smooth at $\pm\kappa^*$; indeed, while the energy is continuous at $\pm\kappa^*$, most other quantities display jump discontinuities at these points. The polaron structure in the inner zone is in all qualitative respects the same as we have identified with large polarons, and the structure in the outer zone is likewise the same as we have identified with small polarons; thus, the wave vectors $\pm\kappa^*$ mark momentum-dependent transitions between small and large polarons structure—self-trapping—at fixed J and g .

When g is lowered below the transition region, clear distinctions remain between different types of correlation structures, though the characteristic small- and large-polaron

FIG. 10. (a) Phonon amplitude β_q^κ , and (b) exciton amplitude α_k^κ for $g=2.75$, $J=4.0$. $\alpha_{k=0}^\kappa=1$.

structures are smoothly joined in J , g , and κ . Figure 10 shows such a case for $g=2.75$, $J=4.0$. Large κ states remain small polaronlike, while the zone center states adopt large polaron correlations showing the characteristic increased width of the lattice distortion in real space and a richness of phonon momentum above κ_c . Although the complete solution here is smooth in all respects, a relic of the κ -dependent self-trapping discontinuity of Fig. 9 is clearly evident, though shifted to higher κ as is characteristic of the movement of this feature through the band with changes in coupling strength. As seems typical across much of the phase diagram, away from the transition region the exciton component seems much less sensitive to the crystal momentum label, being nearly independent of κ except for some very weak variations that correlate with the changes in overall polaron structure.

As coupling is decreased further, to $g=2.5$, the self-trapping related “break” evident at low and intermediate κ in Figs. 9 and 10, respectively, reaches the Brillouin zone boundary (see Fig. 11). Though not a sharp transition, we may say that this roughly indicates the value of coupling below which the polaron structure is essentially large polaronlike for all κ . The ridge in the phonon amplitudes along the line $q=\kappa$ signals the emergence of a one-phonon structure as in the $J=2.0$ case, and the persistence of a locked component can still be seen.

With a further decrease in coupling to $g=2.0$, the one-phonon structure is clearly resolved against a background

FIG. 11. (a) Phonon amplitude β_q^κ , and (b) exciton amplitude α_k^κ for $g=2.5$, $J=4.0$. $\alpha_{k=0}^\kappa=1$.

component that is clearly locked with the exciton amplitudes (see Fig. 12). Both the exciton and phonon components of the locked structure show large-amplitude variations in q and k that are strongly anharmonic, reflecting real-space amplitudes that span many lattice sites.

VII. ENERGY BAND AND EFFECTIVE MASS

In the previous section we have displayed complete sets of variational amplitudes for a number of representative cases. These sets consisted of $2N^2$ quantities reflecting the internal structure of the polaron in detail. In this section we examine quantities that convey less total information, but are more familiar and more directly related to observable properties. Our polaron energy band is the set of N energies $\{E(\kappa)\}$ that result from minimizing the variational energy for all κ . The energies $\{E(\kappa)\}$ are functionals of $2N$ amplitudes $\{\alpha_k^\kappa, \beta_q^\kappa\}$, and thus despite being the central quantities in the calculation convey far less information than is available. The energy band is often further reduced to one of several one-number characterizations: the polaron bandwidth, the polaron effective mass, or the ground state energy (or equivalently, the binding energy). These several one-number quantities are often viewed as being in some degree interchangeable thanks to the well-known small-polaron form of the energy band

$$E(\kappa) = -g^2 - 2Je^{-g^2} \cos(\kappa), \quad (50)$$

FIG. 12. (a) Phonon amplitude β_q^κ , and (b) exciton amplitude α_k^κ for $g=2.0$, $J=4.0$. The coexistence of a broad, locked exciton-phonon structure and free one-phonon component is clear. $\alpha_{k=0}^\kappa=1$.

$$m_{\text{eff}} = m_0 e^{g^2}, \quad (51)$$

so that in common parlance all that could be known about polaron structure is often reduced to one or two “effective” quantities.

We now consider several polaron energy bands and their most common one-number characterizations. In Fig. 13(a) we display a number of calculated polaron energy bands and related asymptotic curves.

It was stressed in our previous article implementing the Merrifield method^{17,18} that that method grossly overestimated the ground state energy at higher momenta, the variational energy near the Brillouin zone boundary being as much as five times the target value for the case illustrated in Fig. 13. This failure is almost completely eliminated in the present case despite the potential for some technical difficulties as discussed in Sec. III B. Actual computations for $g < 0.1$ found the computed energy band to differ from the exact $g=0^+$ band by less than the plot line width.

With increasing coupling strength, it is expected that the polaron energies at all κ and the overall polaron bandwidth should both decrease monotonically. This expectation is largely fulfilled in our calculation. Polaron energies at all κ decrease monotonically; however, there is a range of coupling over which polaron energies near the band edge decrease more slowly than energies near the zone center, resulting in an overall polaron bandwidth $[E(\pi) - E(0)]$ that

FIG. 13. (a) Energy bands shifted by the ground state energy of each band. $J=2.0$ for all curves. Solid curve; rigid lattice energy band, truncated due to scale. Dashed line at $E(\kappa) - E(0) = 1.0$: edge of the one-phonon continuum. Remaining curves top to bottom: $g=1, 2, 3$. The latter curve is indistinguishable from a flat line at $E(\kappa) - E(0) = 0$ because the bandwidth is less than the line thickness. (b) Solid curve: variational ground state energy $E(0)$ for $J=2.0$. Dashed curves: small g asymptote, $f(g) = -2J - \Delta^{1/3}g^2$, and the exact $J=0$ ground state, $h(g) = -g^2$. Dotted curve: ground state energy according to the Merrifield method.

first increases slightly with increasing coupling before decreasing monotonically; the maximum value reached by the polaron bandwidth in this interval is about 1.14. The $g=1.0$ curve in Fig. 13(a) exemplifies this weak-coupling transient.

Setting aside this artifactual transient, it is clear that the leading trend in the overall shape of the polaron energy band at lower coupling strengths is *not* band narrowing; the width of the polaron band is of the order of the one-phonon energy over a considerable range of coupling strengths before any narrowing trend develops. In this “prenarrowing” regime, the major trend may be described as a smoothing of the band shape primarily in the vicinity of κ_c . As this smoothing spreads from the immediate neighborhood of κ_c outward to higher and lower momenta, the effects are next apparent in a softening of the curvatures and slopes of features at the Brillouin zone center and boundary, only thereafter to materialize into a narrowing of the overall energy band. Thus, at least over a significant range of weak coupling, the common no-

tion of a polaron bandwidth proportional to an exciton transfer integral, even a reduced one, does not apply. At strong coupling, of course, the polaron band is strongly narrowed in qualitative agreement with the notion of small polarons.

Trends in the nonadiabatic regime ($J < 1/4$) are more in keeping with the notion of band narrowing even in the weak-coupling regime since such cases are more weakly affected by the one-phonon continuum.

Figure 13(b) shows the dependence of the global ground state energy $E(0)$ on the coupling strength for the energy band sequence illustrated in Fig. 13(a). 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 may show that the leading dependence of the ground state energy on the coupling constant is given by

$$E(0) + 2J \approx g^2(\Delta - 2\Delta^{1/3} + 4J\Delta) = -g^2\Delta^{1/3}, \quad (52)$$

where Δ is the limiting value of one of the self-consistent quantities of that method⁶

$$\Delta = \lim_{g \rightarrow 0} \Delta^{\kappa=0} = [1 + 4J]^{-3/2}. \quad (53)$$

For the value $J = 2.0$, $\Delta = 1/27$, suggesting a slope of $-1/3$ at weak coupling. This is, in fact, what we find with the Toyozawa method to within numerical precision, in excellent agreement with the generally *less* satisfactory Merrifield method.

At stronger values of the coupling, the differences between our present results and those of the Merrifield method are more pronounced. The Merrifield ground state, for example, never deviates far from its asymptotic dependences, and experiences a self-trapping-related discontinuity that appears as a cusp in the ground state energy near $g^2 = 6$. For the same scenario, the ground state that results from the Toyozawa method departs significantly from its asymptotic dependences and is smooth for all g . The gap between the Toyozawa ground state and its strong-coupling asymptote is significant; over the outer portion of Fig. 13(b), the gap varies between approximately 0.75–0.4 times the optical phonon energy, and 18–200 times the self-consistent polaron bandwidth as computed by the Toyozawa method. Thus, whether in absolute or relative terms, the deviation from the small-polaron form is significant well into the strong-coupling regime.

Despite the slowness with which the Toyozawa ground state appears to approach its strong-coupling asymptote, these asymptotes offer a straightforward means of describing the nature and location of the self-trapping transition that is not rooted in method-specific discontinuities known to be variational artifacts. Consider the fact that whatever the detail of the dependence of the ground state energy on J and g , it seems clear that this energy trends between the two asymptotes as discussed above with a knee in the vicinity of the intersection of these two lines. This knee may be marked by a cusp as in the Merrifield example in Fig. 13(b) or may be smooth as in the Toyozawa rendering of the same scenario. The intersection of asymptotes thus offers a rough estimate

for the location of the transition between a large polaronlike ground state at weak coupling and a small polaronlike ground state at strong coupling *without* regard to the continuity of this change. The phase diagram shown in Fig. 2 includes a curve that constitutes the locus of all J, g points corresponding to such asymptote intersections. This curve corresponds closely with the self-trapping line as determined by the Merrifield method, as may be understood from the characteristic nearness of the self-trapping cusp in the ground state energy to the asymptote intersection as seen in Fig. 13(b). There is a systematic deviation of this curve from the apparent location of the self-trapping line as determined by the Toyozawa method; this deviation can be related to the gap between the Toyozawa ground state and the strong coupling asymptote, such that improvement in the strong coupling asymptote improves the match. A significant feature of this estimated self-trapping curve is the fact that its terminus at $J = 0$ is not $g = 0^+$ but $g = 1$; that is, even for vanishingly small J , there appears to be a distinction between polaron types at strong and weak coupling. It is not part of the common vocabulary of polarons to speak of “large polarons” existing at small values of J ; however, this is the conclusion we are led to by parametric continuity of the small- g , small- J states with other large polaron states, and the evidence, albeit formal, of a change in polaron structure in the vicinity of $g = 1$. Interestingly, this conclusion was also reached in the application of a generalized soliton theory to the case of acoustic phonons;⁴⁰ there, the self-trapping curve was continued beyond the discontinuous region using a criterion based on the width of the self-consistent localized state (soliton), finding that a distinction between localized state types above and below a self-trapping line persisted nontrivially with vanishing J .

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 Toyozawa method as applied in this article yields a critical value of the exciton transfer integral $J_c \approx 2.9$, such that for any $J < 2.9$ the dependence of the effective mass on the coupling constant g is smooth and continuous, while for $J > 2.9$ the tell-tale jump discontinuity appears. This behavior is illustrated in Fig. 14, where effective mass curves for cases below, at, and above the critical point are displayed. These computations were based on the formula

$$\frac{m_{\text{eff}}}{m_0} = \frac{2J}{\left. \frac{\partial^2 E^{\kappa}}{\partial \kappa^2} \right|_{\kappa=0}}, \quad (54)$$

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 the Merrifield method; in the latter case $J_c \approx 0.89$, with the con-

FIG. 14. The ratio of the polaron effective mass to the bare exciton effective mass (m_{eff}/m_0) is plotted against exciton-phonon coupling on a logarithmic scale for $J=0^+$, 1.0, 2.0, 2.9, 4.0. For weak exciton-phonon coupling, the polaron mass approaches that of the bare exciton. For $J=4.0$, there is a discontinuous change in the polaron effective mass with increasing exciton-phonon coupling strength, while for $J=2.0$, 1.0, the change is gradual. The $J=2.9$ line (solid curve) represents the onset of the discontinuity in the polaron effective mass.

sequence that under that method even the $J=1,2$ curves of Fig. 14 exhibit discontinuities.

VIII. SOLITONS

Polaron Hamiltonians such as the one in this article, 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. Eschewing details, the basic idea is that the characteristic polaronic coupling between the otherwise linear wave equations describing the exciton and phonons introduces nonlinearities that may support soliton-like excitations in some physically significant circumstances.

The soliton theories to which we refer are approximate treatments involving dynamical equations based on (localized) Ansatz states such as shown in Eqs. (8)–(10). For that trial state and this Hamiltonian, the approximate dynamical equations that result are ($\hbar = \omega = 1$)

$$i\dot{\alpha}_n = -J(\alpha_{n+1} + \alpha_{n-1}) - g\alpha_n(\beta_n^* + \beta_n), \quad (55)$$

$$i\dot{\beta}_n = \beta_n - g|\alpha_n|^2. \quad (56)$$

By neglecting the time derivatives of the phonon amplitudes in the latter equation, one arrives at a *specific* locking relation

$$\beta_n = g|\alpha_n|^2, \quad (57)$$

from which follows a discrete nonlinear Schrödinger equation (DNLS)

$$i\dot{\alpha}_n = -J(\alpha_{n+1} + \alpha_{n-1}) - 2g^2|\alpha_n|^2\alpha_n. \quad (58)$$

With a further continuum approximation, this DNLS yields the continuous nonlinear Schrödinger equation (NLS)

$$i\dot{\alpha}(x) = -J\frac{\partial^2\alpha(x)}{\partial x^2} - 2J\alpha(x) - 2g^2|\alpha(x)|^2\alpha(x), \quad (59)$$

in which the space variable x is in units of the lattice constant. This is a completely integrable nonlinear wave equation and supports true soliton solutions typified by

$$\alpha(x) = \sqrt{\frac{\lambda}{2}} \text{sech}[x/\lambda], \quad (60)$$

in which the width parameter is given by $\lambda = 2J/g^2$.

There has been and continues to be much debate about theories of polaron systems that yield soliton excitations as an outstanding feature of their results. It is not our purpose here to elaborate on the details of such theories. Rather, we focus on identifying (i) what features of our results compare favorably with the basic characteristics of solitons, (ii) what features of our results do *not* compare favorably, and (iii) the regimes under which any favorable comparisons may apply. As we do so, it should be borne in mind that though our calculations are for the optical phonon case only, we consider only the most general characteristics of solitons that are found in both acoustical and optical formulations.

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 NLS and DNLS 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 a similar trend in our results. The shape of our solutions varies only weakly along lines that roughly parallel the self-trapping line and much more strongly along lines orthogonal to the self-trapping line. This trend is more clearly evident in solutions associated with points farther from *both* the self-trapping line *and* the $g=J=0$ corner of the parameter space.

Regarding the detail of these shapes, there is little to say about the locked structures in the strong-coupling region; all solutions in this regime resemble those shown in Fig. 5. These locked structures do not constitute solitons in the traditional sense, however, since they are *highly* localized, far from any arguable continuum limit. At best, these locked structures may be consistent with the pinned local modes that have long been known to exist in DNLS systems, and have been a subject of recent resurgent interest.^{55–61}

Of greater importance for comparison with soliton theory in the traditional sense is our finding 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.

This broad, locked component is solitonlike in several ways; (i) it spans multiple sites in real space, (ii) strong locking exists between the exciton and phonon components at all κ , (iii) the shape of the locked components is nearly independent of κ , suggesting that the internal structure of this element is relatively insensitive to external dynamics, (iv) the locked element appears to be insensitive to the presence of the coexisting one-phonon structure, and (v) the width of the locked structure increases with increasing J and decreasing g .

There are, of course, some important features of our results that do not compare favorably with soliton theory. Perhaps the most obvious is clearly evident in the same regime where the most favorable comparison is found; in the same adiabatic weak-coupling regime where solitonlike, locked exciton-phonon structures are found, we *also* find a strong component having the character of a single free-phonon quantum. Such highly quantum mechanical phonon structures are beyond the scope of soliton theory, yet these structures are present in a significant fraction of the total number of Bloch states.

Whether this strongly quantum feature is important in a practical circumstance is a matter of numbers. When the one-phonon feature is present, the overall polaron bandwidth is of the order of the one-phonon energy, and the low κ states ($|\kappa| < \kappa_c$) have large-polaron character. In order for this feature to have direct impact on observables, it is necessary for the higher-momentum Bloch states to become populated, either thermally or under the influence of applied fields. Depending on the frequencies of the phonons comprising the phonon cloud, these higher-momentum states may be frozen out ($k_B T \ll \hbar \omega$). Similarly, the same energy scale constitutes a barrier that must be overcome before any applied field can drive the polaron out of the long-wavelength regime. Whether this is possible is a matter of field strengths and mean-free paths at a practical temperature. Thus, although quite clearly at variance with the traditional soliton theory, there are practical circumstances in which the existence of such strongly quantum mechanical features, even over large fractions of the polaron band, may be of less significance than the improvements in the quality of the lowest-lying states at low κ ; in such cases the details of the polaron binding energy, effective mass, and self-trapping transition remain particularly significant.

Another problem area for the comparison with soliton theory is the lower-left corner of the phase diagram (loosely speaking, $J, g < 2$). In this regime, it is obvious from the structure of the variational solutions that the locking relation (57) breaks down, further decreasing the relevance of both the NLS and the DNLS. It remains possible that there may be pulslike exciton-phonon correlated solutions of the system of equations (55), (56) that compare favorably with our variational solutions over part of this regime; however, this has not been demonstrated and in any case would stretch the term soliton considerably beyond its traditional meaning.

The third prominent feature of our results that does *not* compare favorably with soliton theory, at least in its more traditional forms, is the existence and character of the self-trapping transition. We must emphasize that by self-trapping transitions we do *not* refer to artifactual discontinuities that are method dependent, but to the physically meaningful *rapid* changes in the character of exciton-phonon correlations that underlie such markers. The localized states born out of an Ansatz of the form (8) can be tuned from large widths (e.g., large polarons or continuum solitons) down to compact structures essentially confined to a single lattice site (e.g., small polarons) without experiencing the physically meaningful rapid changes characteristic of the self-trapping transition. The root of this lies in the fact that the self-trapping transition results from the competition between the direct, local type of exciton-phonon correlation characteristic of small polarons, and the indirect, global type of correlation characteristic of large polarons; in the traditional form of soliton theory, only the global correlation channel is operative. Consequently, there is a swath through the polaron parameter space in the vicinity of the self-trapping line within which soliton theory fares poorly.

We should note that it *is* possible to include direct, local exciton-phonon correlations in a soliton theory without resorting to delocalization. It has been shown that simultaneous local and global correlations can be included within a more general soliton theory, incorporating the notion of "partial dressing",^{37,38,40,62,63} The latter exhibits many of the qualitative features found here, *including* the existence of a self-trapping transition. Although the generalized theory improves the quality of the overall soliton picture in the polaron context, it suffers nonetheless from many of the inherent limitations of a localized state description. In a subsequent work^{17,19} we present results paralleling those of this article, in which this generalized Ansatz state is used to construct improved delocalized trial states for variational energy band calculations. That work shows that although the Toyozawa method is very successful in blending local and global exciton-phonon correlations, the direct, local correlation channel is under-represented, allowing the method to be improved by incorporating direct correlations explicitly prior to the delocalization step.

IX. WANNIER STATES

It is reasonable to ask whether there is any localized state, perhaps analogous to the soliton, in which the internal correlation properties of the energy-momentum eigenstates may be manifest. This question has the nature of an *inverse* problem. That the localized state we seek must have a decomposition over the complete set of energy-momentum eigenstates implies, of course, that it is a nonstationary state under quantum mechanics, and as a linear superposition of eigenstates should *not* evolve in the archetypically nonlinear fashion of solitary waves. Polaron dynamics *can* be addressed using the energy bands and optimized states that result from our methods;⁷⁰ however, for our present pur-

poses, we focus our attention on the structural aspects of time-independent superpositions of polaron Bloch states.

Considering desirable properties such as orthonormality, the natural construct is the Fourier transform of the polaron Bloch states in the total momentum label κ . The Wannier states^{64–69} so defined form a complete orthonormal set of localized states that are unitarily equivalent to the energy-momentum eigenstates

$$|\Phi(n)\rangle = \sum_{\kappa} \frac{e^{-i\kappa n}}{\sqrt{N}} |\Psi(\kappa)\rangle, \quad (61)$$

$$|\Psi(\kappa)\rangle = \sum_n \frac{e^{+i\kappa n}}{\sqrt{N}} |\Phi(n)\rangle. \quad (62)$$

Since distinct Wannier states differ only by their location in the lattice, one may, without loss of generality, recognize the existence of only *one* distinct Wannier state. Moreover, though we have referred to these states as local functions, we have not forced any local properties upon them. Indeed, absent further considerations, the notion of locality that attaches to the Wannier function extends no farther than the property of site-space orthonormality; that is, that $\langle\Phi(m)|\Phi(n)\rangle = \delta_{mn}$. In practice, however, by localized we usually do not refer to such formal properties as orthonormality, but to such things as the real-space width of the exciton density within the polaron, or the width of the phonon cloud. We now examine some limiting and some typical cases, displaying these properties and relating them to specific features of polaron structure and the broader theoretical context.

As in the case of the energy bands and Bloch states themselves, certain exact results are available in the limit of vanishing exciton-phonon coupling. As discussed in Sec. III B, when $J < 1/4$, the Bloch states are exactly the free-exciton Bloch states; on the other hand, when $J > 1/4$, the ground-state energy band changes abruptly at κ_c from being free-exciton-like below to being free-phonon-like above. These properties are reflected in the Wannier state

$$|\Phi(n)\rangle = \sum_{\kappa} \frac{e^{-i\kappa n}}{\sqrt{N}} a_{k=\kappa}^+ |0\rangle \quad \text{for } J < \frac{1}{4}, \quad (63)$$

$$= \sum_{\kappa < \kappa_c} \frac{e^{-i\kappa n}}{\sqrt{N}} a_{k=\kappa}^+ |0\rangle + \sum_{\kappa > \kappa_c} \frac{e^{-i\kappa n}}{\sqrt{N}} a_{k=0}^+ b_{q=\kappa}^+ |0\rangle \quad \text{for } J > \frac{1}{4}, \quad (64)$$

the meaning of which is evident in the exciton density

$$\rho_n^{\text{ex}} \equiv \langle\Phi(0)|a_n^+ a_n|\Phi(0)\rangle, \quad (65)$$

$$= \delta_{n0} \quad \text{for } J < \frac{1}{4}, \quad (66)$$

$$= \frac{\sin^2(\kappa_c n)}{\pi^2 n^2} + \frac{\pi - \kappa_c}{\pi N} \quad \text{for } J > \frac{1}{4}, \quad (67)$$

[see Fig. 15(a)]. This structure contains a localized compo-

FIG. 15. First panel: Exciton density in polaron Wannier states. Second panel: Oscillator amplitude in polaron Wannier states. Both panels: $J=4$ for all curves; center top to bottom, $g=3.2, 2.5, 2.0, 1.5, 0^+$; the $g=0^+$ curves were obtained from Eqs. (67) and (73), all others are computed directly from variational Bloch states.

nent having a width of order π/κ_c and a weight κ_c/π , and a uniform background having a weight $(\pi - \kappa_c)/\pi$. That the exciton density is normalized to unity is evident in this particular example; however, it can be shown that this normalization is independent of model parameters.

The phonon number density has a similar spatial distribution displaying a striking exciton-phonon correlation despite the absence of any dynamic interaction.

$$\rho_n^{\text{ph}} \equiv \langle\Phi(0)|b_n^+ b_n|\Phi(0)\rangle, \quad (68)$$

$$= 0 \quad \text{for } J < \frac{1}{4}, \quad (69)$$

$$= \frac{\sin^2(\kappa_c n)}{\pi^2 n^2} + \delta_{n0} \frac{\pi - 2\kappa_c}{\pi} \quad \text{for } J > \frac{1}{4}, \quad (70)$$

[see Fig. 15(b)]. Unlike the exciton density, the total phonon number depends on model parameters in a nontrivial fashion. This is particularly evident in the weak-coupling limit, where the total phonon number vanishes in the nonadiabatic regime ($J < 1/4$), but in the adiabatic regime is given by $1 - \kappa_c/\pi$ (see Fig. 16).

FIG. 16. Expectation value of phonon number operators in the $g=0^+$ polaron Wannier state. (a) The total phonon number, $\sum_n \rho_n^{\text{ph}}$, (b) the phonon number at the center of the Wannier state, $\rho_{n=0}^{\text{ph}}$.

Because it mixes zero- and one-phonon components, the $g=0^+$ polaron Wannier state is a state of indefinite phonon number; thus, though the Wannier state is *not* an eigenstate of the phonon annihilation operator (i.e., it is not a coherent state), some phonon annihilation operators have nonvanishing expectation values.

$$q_n \equiv \langle \Phi(0) | b_n^+ + b_n | \Phi(0) \rangle, \quad (71)$$

$$= 0 \quad \text{for } J < \frac{1}{4}, \quad (72)$$

$$= \frac{2}{\sqrt{N}} \left[\delta_{n0} - \frac{\sin(\kappa c n)}{\pi n} \right] \quad \text{for } J > \frac{1}{4}. \quad (73)$$

Figure 15 shows computed results for the exciton density ρ_n^{ex} and oscillator amplitude q_n for nontrivial values of J and g . The particular value $J=4$ was chosen to coincide with the “large J ” transection of the parameter space discussed in Sec. VI C, the sampling was expanded to both stronger and weaker coupling to illustrate significant features. At the strong-coupling end, above the self-trapping transition, the exciton density is essentially completely localized on a single site, with only minute spreading to nearest neighbors, consistent with our prior discussion of the character of the whole strong-coupling regime. At the weak-coupling end, the exciton density is dramatically broadened, with the finite, uniform background expected as $g \rightarrow 0^+$ already quite apparent.

Although there are clear similarities between the exciton density and the accompanying oscillator amplitude, it is not clear from Fig. 15 whether the detail of this similarity is consistent with the locking relation (57) that gives rise to the DNLS and ultimately the NLS. In Fig. 17 we show the ratio of the oscillator amplitude to the exciton density (q_n / ρ_n^{ex}) for each of the polaron Wannier states considered in Fig. 15. This locking ratio should be constant and equal to $2g$ in value if the locking relation (57) is to be recovered.

FIG. 17. Ratio of the Wannier oscillator amplitudes shown in Fig. 15(b) to the Wannier exciton density shown in Fig. 15(a). $J=4$ for all curves. Diamond symbols at $n=0$ indicate the value of the parameter $2g$ associated with each curve, which would be the expected ratio for all n if the locking relation (57) were valid. The $g=2.5, 3.2$ curves have been truncated because the erosion of numerical precision in the tails of the highly localized source distributions renders the resulting ratios unreliable.

The locking ratio at the strong-coupling end of this sequence, in the small-polaron regime above the self trapping transition, is in fact equal to $2g$ for all n for which numerical data are reliable. This is a nontrivial point of agreement between our energy band theory and the soliton theory, since the equality of the locking ratio to $2g$ extends well into the wings of the highly localized structure. With decreasing coupling strength, however, indeed, as soon as the large-polaron regime is penetrated, both the constancy of the locking ratio with respect to n and the meaningful relation of a mean locking ratio to the value $2g$ break down. It is evident enough from what has gone before that the principal reason for this breakdown of a strict locking relation is the emergence of a strong one-phonon structure in the lattice component of the polaron. This one-phonon structure is *completely* responsible for the existence of a nontrivial exciton-phonon structure at zero coupling, and hence for the existence of a nontrivial locking ratio at $g=0^+$.

X. CONCLUSIONS

In this article, we have obtained complete numerical solutions to the variational method based on Toyozawa's delocalized Ansatz in its most general form. Solutions take the form of $2N^2$ variational exciton and phonon amplitudes expressing the detail of the exciton-phonon correlations comprising the polaron. From these are constructed the N polaron band energies $E(\kappa)$, the associated Bloch states, and any other quantity of interest.

Provided that both the transfer integral J and the exciton-phonon coupling parameter g are not simultaneously too moderate in value, the shape of the optimal phonon amplitudes β_q^κ can be characterized as a mixture of three prominent elements: (i) a constant, finite background in κ and q corresponding to a strong central amplitude of the phonon

cloud in real space; (ii) a finite-width, pulse-shaped component in q that is, however, largely independent of κ , corresponding to a pulse in real space whose width increases with increasing J and decreasing g ; (iii) a ridge prominent at $\kappa > \kappa_c$ and centered on $q = \kappa$, that focuses sharply with decreasing g , corresponding to a lattice wave having a fundamental wave vector approximately equal to κ , approaching a pure one-phonon character as $g \rightarrow 0^+$.

The optimal exciton amplitudes α_k^κ show much less structure, being characterized by a finite background in k and κ and a finite width pulse in k with little dependence on κ . The latter pulse tends to appear locked to the pulselike component of the phonon cloud, and displays qualitatively similar trends with changing parameter values.

Polaron structure can be mapped on a phase diagram as shown in Fig. 2. Most of the upper portion of this diagram is occupied by highly localized, highly locked exciton-phonon structures consistent with the notion of small polarons at all κ . Most of the lower portion of this diagram is occupied by broad locked exciton-phonon structures consistent with the notion of large polarons; however, in most cases where such large polaronlike components can be resolved as such they appear *mixed* with and often *dominated* by a one-phonon component above κ_c .

If J and g are both sufficiently moderate (roughly $J, g < 2$), the several components of the phonon cloud can no longer be clearly separated from each other, and the locking characteristic relating the pulselike components of the exciton and phonon amplitudes is lost. The interpretation of such states as small or large polaron states by visual criteria is thus equivocal; however, the construction of a self-trapping line groups most such states with large polarons.

The deformation of large and small polaron states into one another through changes in parameter values is smooth for smaller values of J ; however, above $J_c = 2.9$ jump discontinuities appear in the variational solutions and in some physical quantities such as the effective mass, introducing the notion of a discrete self-trapping transition. By considering all κ and not merely $\kappa = 0$, however, we find that the traditional notion of the self-trapping transition at $\kappa = 0$ is a limit of a more general phenomenon occurring over a range of J , g , and κ . From this perspective it can be seen that over a range of parameters in the self-trapping region, the polaron band can be understood as being large polaronlike at small κ and small polaronlike at large κ , with a transition between these characteristics marked by a particular wave vector κ^* . This property of polaron energy bands is not dependent upon the existence of artifactual discontinuities, but describes a robust, physically meaningful phenomenon that exists over a finite region of parameter space in the vicinity of a self-trapping line. Setting aside the discontinuous quality of the transition in some regimes as an artifact of an insufficiently flexible variational method, a self-trapping line can be constructed by meaningful criteria that at all J separates a small-polaron regime at large g from a large-polaron regime at small to moderate g .

All of our results have been obtained using delocalized trial states, while much of the understanding afforded by our

solutions is derived from examining the local nature of the exciton-phonon correlations internal to the polaron. The whole of this effort in many respects seeks to reveal the nature of the particle whose energy momentum eigenstates are the Bloch states we have determined. Energy band theory provides an answer to the question of what this particle “is” through the construction of Wannier states. We have constructed the polaron Wannier states for a number of our variational energy bands and have probed their structure with diagnostic functions expressing the real-space shape of the exciton density and the associated lattice distortion. Unlike our decomposition of the optimal exciton and phonon amplitudes into interpretable components, the Wannier state is a construct of the entire energy band, including all components of polaron structure at all κ . It is nontrivial, therefore, that despite this great amalgamation the Wannier state profiles *as well as* the pulse-shaped components of our variational amplitudes exhibit features strongly reminiscent of the locking of electronic and lattice fields in adiabatic polaron theories based on localized trial states, among them the theories rooted in the soliton concept. At the heart of any such theory is a specific locking relation expressing the proportionality of a lattice variable and an electronic variable. We have taken an example of such a theory appropriate to the present case and tested the proportionality of the lattice distortion and the exciton density in the polaron Wannier state. The shape similarity was found to conform quite precisely to the locking relation in the small-polaron regime (i.e., above the self-trapping transition), but to deteriorate rapidly with decreasing coupling in the large polaron regime, underscoring the incongruence of the Wannier state and the soliton *per se*.

The Toyozawa method generalizes the Merrifield method by allowing for the spreading of the exciton component in the localized functions superposed to create the delocalized trial states, and leads to many quantitative and qualitative improvements in its results. The path to continued overall improvement lies in the generalization of the localized function, and guides to this may be found in theory of polarons based on localized states. It has been noted that the localized function used in the Toyozawa construction is of the same form (apart from phonon type) as used in the traditional theory of Davydov solitons. In the latter context, this localized state has been generalized in a manner that increases its flexibility, allowing it to embrace a greater range of exciton-phonon correlations. This more flexible local function is a natural candidate with which to generalize the Toyozawa method, to corroborate and/or improve its results. This generalization has been implemented, and will be reported upon separately.^{19,70}

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation under Grant No. DMR 91-18052.

¹Y. Toyozawa, Prog. Theor. Phys. **26**, 29 (1961).

²Y. Toyozawa, *Polarons and Excitons*, edited by C. G. Kuper and G. D. Whitfield (Plenum, New York, 1963), pp. 211–232.

³A. Sumi and Y. Toyozawa, J. Phys. Soc. Jpn. **35**, 137 (1973).

- ⁴Y. Toyozawa, *Relaxation of Elementary Excitations*, edited by R. Kubo and E. Hanamura (Springer-Verlag, Heidelberg-New York, 1980), pp. 3–18.
- ⁵M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa, and E. Hanamura, *Excitonic Processes in Solids* (Springer-Verlag, New York, 1986).
- ⁶R. E. Merrifield, *J. Chem. Phys.* **40**, 450 (1964).
- ⁷D. Emin, *Adv. Phys.* **22**, 57 (1973).
- ⁸H. B. Shore and L. M. Sander, *Phys. Rev. B* **7**, 4537 (1973).
- ⁹P. Gosar, *J. Phys. C* **8**, 3584 (1975).
- ¹⁰S. F. Fischer, *Organic Molecular Aggregates*, Springer Series in Solid-State Sciences, Vol. 49, edited by P. Reineker, H. Haken, and H. C. Wolf (Springer-Verlag, Berlin, 1983), pp. 107–119.
- ¹¹K. H. Höck, H. Nickish, and H. Thomas, *Helv. Phys. Acta* **56**, 237 (1983).
- ¹²G. Venzl and S. F. Fischer, *J. Chem. Phys.* **81**, 6090 (1984).
- ¹³G. Venzl and S. F. Fischer, *Phys. Rev. B* **32**, 6437 (1985).
- ¹⁴A. Klamt, *J. Phys. C* **21**, 1953 (1988).
- ¹⁵D. Feinberg, S. Ciuchi, and F. de Pasquale, *Int. J. Mod. Phys. B* **4**, 1317 (1990).
- ¹⁶B. Schopka, Ph.D. thesis, Technische Universität München, 1991 (unpublished).
- ¹⁷Y. Zhao, Ph.D. thesis, University of California, San Diego, 1994 (unpublished).
- ¹⁸Y. Zhao, D. W. Brown, and K. Lindenberg, *J. Chem. Phys.* **106**, 5622 (1997).
- ¹⁹D. W. Brown, K. Lindenberg, and Y. Zhao, *J. Chem. Phys.* **107**, 3179 (1997), following paper.
- ²⁰S. I. Pekar, *J. Phys. (Moscow)* **10**, 341 (1946).
- ²¹S. I. Pekar, *Zh. Eksp. Teor. Fiz.* **16**, 335 (1946).
- ²²L. D. Landau and S. I. Pekar, *Zh. Eksp. Teor. Fiz.* **18**, 419 (1948).
- ²³S. I. Pekar, *Untersuchungen Über die Elektronentheorie der Kristalle* (Akademie-Verlag, Berlin, 1954).
- ²⁴E. I. Rashba, *Opt. Spektrosk.* **2**, 75 (1957).
- ²⁵E. I. Rashba, *Opt. Spektrosk.* **2**, 88 (1957).
- ²⁶A. S. Davydov, *Phys. Status Solidi* **36**, 211 (1969).
- ²⁷A. S. Davydov and N. I. Kislukha, *Phys. Status Solidi B* **59**, 465 (1973).
- ²⁸D. Emin and T. Holstein, *Phys. Rev. Lett.* **36**, 323 (1976).
- ²⁹A. S. Davydov and N. I. Kislukha, *Zh. Eksp. Teor. Fiz.* **71**, 1090 (1976) [*Sov. Phys. JETP* **44**, 571 (1976)].
- ³⁰A. S. Davydov, *Phys. Scr.* **20**, 387 (1979).
- ³¹T. Holstein, *Mol. Cryst. Liq. Cryst.* **77**, 235 (1981).
- ³²E. I. Rashba, *Excitons*, edited by E. I. Rashba and M. D. Sturge (North-Holland, New York, 1987), pp. 273–332.
- ³³T. Holstein and L. Turkevich, *Phys. Rev. B* **38**, 1901 (1988).
- ³⁴T. Holstein and L. Turkevich, *Phys. Rev. B* **38**, 1922 (1988).
- ³⁵M. J. Skrinjar, D. V. Kapor, and S. D. Stojanovic, *Phys. Rev. A* **38**, 6402 (1988).
- ³⁶Q. Zhang, V. Romero-Rochin, and R. Silbey, *Phys. Rev. A* **38**, 6409 (1988).
- ³⁷D. W. Brown and Z. Ivic, *Phys. Rev. B* **40**, 9876 (1989-I).
- ³⁸Z. Ivic and D. W. Brown, *Phys. Rev. Lett.* **63**, 426 (1989).
- ³⁹X. Wang, D. W. Brown, and K. Lindenberg, *Phys. Rev. Lett.* **62**, 1796 (1989).
- ⁴⁰D. W. Brown, K. Lindenberg, and X. Wang, *Davydov's Soliton Revisited: Self-Trapping of Vibrational Energy in Protein*, NATO ASI Series B: Physics, Vol. 243, edited by P. Christiansen and A. C. Scott (Plenum, New York, 1990), pp. 63.
- ⁴¹X. Wang, D. W. Brown, and K. Lindenberg, *Davydov's Soliton Revisited: Self-Trapping of Vibrational Energy in Protein*, NATO ASI Series B: Physics, Vol. 243, edited by P. Christiansen and A. C. Scott (Plenum, New York, 1990) pp. 83.
- ⁴²T. D. Lee, F. E. Low, and D. Pines, *Phys. Rev.* **90**, 297 (1953).
- ⁴³T. Holstein, *Ann. Phys. (N.Y.)* **8**, 325 (1959).
- ⁴⁴T. Holstein, *Ann. Phys. (N.Y.)* **8**, 343 (1959).
- ⁴⁵Y. Zhao, D. W. Brown, and K. Lindenberg, *J. Chem. Phys.* **100**, 2335 (1994).
- ⁴⁶Y. Zhao, D. W. Brown, and K. Lindenberg, *J. Chem. Phys.* **106**, 2728 (1997).
- ⁴⁷C. W. Gardiner, *Handbook of Stochastic Methods for Physics, Chemistry, and the Natural Sciences* (Springer-Verlag, Berlin, 1983).
- ⁴⁸J. W. Negele and H. Orland, *Quantum Many-Particle Systems* (Addison-Wesley, Redwood City, CA, 1988).
- ⁴⁹Y. Zhao and H. Neal Bertram, *J. Magn. Magn. Mater.* **114**, 329 (1992).
- ⁵⁰Y. Zhao and H. Neal Bertram, *J. Appl. Phys.* **77**, 6411 (1995).
- ⁵¹B. Gerlach and H. Lowen, *Phys. Rev. B* **35**, 4291 (1987).
- ⁵²B. Gerlach and H. Lowen, *Phys. Rev. B* **35**, 4297 (1987).
- ⁵³H. Lowen, *Phys. Rev. B* **37**, 8661 (1988).
- ⁵⁴B. Gerlach and H. Lowen, *Rev. Mod. Phys.* **63**, 63 (1991).
- ⁵⁵J. Klafter and J. Jortner, *J. Chem. Phys.* **77**, 2816 (1982).
- ⁵⁶S. Takeno, *Prog. Theor. Phys.* **71**, 395 (1984).
- ⁵⁷S. Takneo, *J. Phys. Soc. Jpn.* **61**, 2821 (1992).
- ⁵⁸L. Bonci, P. Grigolini, R. Roncaglia, and D. Vitali, *Phys. Rev. A* **47**, 3538 (1993).
- ⁵⁹R. S. MacKay and S. Aubry, *Nonlinearity* **7**, 1623 (1994).
- ⁶⁰S. Aubry, *Physica D* **71**, 196 (1994).
- ⁶¹See, for example, *Proceedings of Fluctuations, Nonlinearity and Disorder*, Heraclion, Crete, 30 September–4 October 1996, edited by G. P. Tsironis *et al.*, to appear in *Physica D*.
- ⁶²D. Yarkony and R. Silbey, *J. Chem. Phys.* **65**, 1042 (1976).
- ⁶³D. R. Yarkony and R. Silbey, *J. Chem. Phys.* **67**, 5818 (1977).
- ⁶⁴G. H. Wannier, *Phys. Rev.* **52**, 191 (1937).
- ⁶⁵W. Kohn, *Phys. Rev.* **115**, 809 (1959).
- ⁶⁶Gabriel Weinreich, *Solids: Elementary Theory for Advanced Students* (Wiley, New York, 1965).
- ⁶⁷O. Madelung, *Introduction to Solid-State Theory* (Springer-Verlag, New York, 1978).
- ⁶⁸D. W. Brown, *Nonlinear Excitations in Biomolecules*, Centre de physique des Houches **2**, 279 (1995).
- ⁶⁹D. W. Brown, *Proc. SPIE* **25/26**, 40 (1995).
- ⁷⁰A. Romero, D. W. Brown, and K. Lindenberg (unpublished).