An improved variational approach to off-diagonal exciton-phonon coupling

Zhao, Yang; Li, Guangqi; Sun, Jin; Wang, Weihua

2008

Zhao, Y., Li, G., Sun, J., & Wang, W. (2008). An improved variational approach to off-diagonal exciton-phonon coupling. *Journal of Chemical Physics*, (129), 1-10.

<https://hdl.handle.net/10356/92421>

<https://doi.org/10.1063/1.2987364>

© 2008 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/10.1063/1.2987364>]. 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 17:15:02 SGT

An improved variational approach to off-diagonal exciton-phonon coupling

Yang Zhao,^{1,a)} Guangqi Li,² Jin Sun,¹ and Weihua Wang¹

¹*School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore*

²*School of Engineering and Science, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany*

(Received 3 July 2008; accepted 27 August 2008; published online 30 September 2008)

A state-of-the-art variational wave function incorporating Jastrow-type exciton-phonon correlations, the global-local *Ansatz*, is utilized to elucidate exciton-phonon correlations in a generalized form of the Holstein Hamiltonian with the simultaneous presence of diagonal and off-diagonal exciton-phonon coupling. Much lowered ground-state energies are found for the global-local *Ansatz* when compared with the previously studied Toyozawa *Ansatz*. A three-dimensional phase diagram spanned by the transfer integral and two forms of exciton-phonon coupling is given to illustrate polaronic self-trapping near the zone center. © 2008 American Institute of Physics.

[DOI: [10.1063/1.2987364](https://doi.org/10.1063/1.2987364)]

I. INTRODUCTION

Employing a state-of-the-art variational wave function, the global-local (GL) *Ansatz*,^{1,2} we revisit a classic problem of polaron theory in one dimension incorporating simultaneous diagonal and off-diagonal exciton-phonon coupling. The former interaction is defined as a nontrivial dependence of the exciton site energies on lattice coordinates, and the latter as a nontrivial dependence of the exciton transfer integral on lattice coordinates. Almost three quarters of a century have passed since the concept of polaronic self-trapping was first conceived by Landau,^{3,4} and yet many questions remain unanswered regarding some of the most simplistic polaron Hamiltonians. One of them is a Hamiltonian containing off-diagonal exciton-phonon coupling that has been inadequately addressed in the polaron literature thanks to inherent difficulties associated with obtaining accurate solutions.⁵ It is not difficult to see that off-diagonal coupling is prevalent in all forms of solids. In the theory of high-temperature superconductivity, for example, it has been recently proposed⁶ that off-diagonal coupling modulates the hopping integral of the Zhang–Rice singlet and the superexchange interaction and is especially relevant in the low-doping regime. Simultaneous diagonal and off-diagonal coupling appears to be particularly important in the characterization of solid-state excimers, where a variety of experimental and theoretical considerations suggest that a strong dependence of electronic tunneling upon certain coordinated distortions of neighboring molecules (or off-diagonal exciton-phonon coupling) is crucial to the formation of excited bound states.^{7,8}

Previously, Zhao *et al.* undertook a numerical implementation⁹ of a method proposed by Munn and Silbey¹⁰ to determine polaron properties in the presence of simultaneous diagonal and off-diagonal coupling. The Munn–Silbey method was essentially perturbative, with the

coefficients of a canonical transformation being fixed so as to limit the secular growth with the temperature of the perturbation remaining after transformation. Since the Munn–Silbey method was formulated to curb divergence at high temperatures, it is not expected to produce the best description of polaron states at low temperatures. In addition, the self-consistency equations on which the Munn–Silbey method is based do not involve the exciton transfer integral; therefore, it is questionable whether the method can be relied on beyond the narrow band regime. The central findings of our prior work on the Munn–Silbey method, that polaron binding energies may be much larger than previously thought, and polaron bands much narrower, underscores the importance of independent corroboration, since such findings are of central importance in understanding the influence of off-diagonal exciton-phonon coupling on the nature of polaron states and of polaron transport.

Our work on the Munn–Silbey method was later followed by a variational approach motivated to overcome aforementioned limitations of the Munn–Silbey method.¹¹ A flexible spanning set of orthonormal eigenfunctions of the joint exciton-phonon crystal momentum, namely, the Toyozawa *Ansatz*, is used to arrive at a variational estimate of the ground-state energy, and the complete set of polaron Bloch functions associated with this energy band, for every value of the joint crystal momentum across the entire Brillouin zone.^{11,12} The variation is implemented numerically, avoiding restrictive assumptions that have limited the scope of previous assaults on similar problems. Polaron energy bands and the structure of the associated Bloch states are studied at points in the three-dimensional parameter space of the model Hamiltonian (electronic tunneling, diagonal coupling, and off-diagonal coupling). For small electronic tunneling integrals, the Toyozawa *Ansatz* and the Munn–Silbey approach yield very similar polaron energy bands; however, these bands grow increasingly dissimilar with an increasing transfer integral. In all cases studied, we have found the

^{a)}Electronic mail: yzhao@ntu.edu.sg.

variational approach based on the Toyozawa *Ansatz* to yield polaron energy bands lower than those of the Munn–Silbey method at all crystal momenta, establishing the variational energy bands as the quantitatively superior results.

The Toyozawa *Ansatz* is not without shortcomings. The three-dimensional phase diagram spanned by the electronic tunneling, diagonal coupling, and off-diagonal coupling, for example, shows large areas in which two solutions of the polaron ground state coexist.^{11,13} For the diagonal-coupling only case, it is shown that a more sophisticated variational wave function such as the GL *Ansatz* will drastically reduce the size of such areas.² It was also concluded that discontinuities encountered in both the Merrifield *Ansatz*^{2,14,15} and the Toyozawa *Ansatz* are primarily and perhaps entirely artifacts introduced by the insufficiency in complexity of the variational *Ansätze*. Probably the most accurate variational wave function for the ground state of the Holstein Hamiltonian to our knowledge, the GL *Ansatz* has been shown to yield variational ground-state energies of very high accuracy, and when compared with computationally much more expensive approaches such as the density matrix renormalization group (DMRG) method, the difference falls below half a percentage point for all crystal momenta.² However, DMRG, due to a constantly changing basis in its iteration procedure, fails to provide a trial wave function at the end of the computation. Other inadequacies of the Toyozawa *Ansatz* include the difficulty in approximating phonon number states at weak exciton-phonon coupling by using simple linear superpositions of phonon coherent states. This also calls for extending the GL *Ansatz* to include the off-diagonal exciton-phonon coupling.

This paper is structured as follows. In Sec. II, we extend the Holstein model in one spatial dimension to include simultaneous diagonal and off-diagonal exciton-phonon interactions. In Sec. III, we give a detailed description of the GL *Ansatz*. In Sec. IV, we derive analytical expressions that constrain the variational parameters for the generalized Holstein Hamiltonian with both diagonal and off-diagonal coupling. In Sec. V, we numerically solved self-consistency equations for the variational parameters and discuss a phase diagram in a three-dimensional parameter space spanned by the electronic tunneling, diagonal coupling, and off-diagonal coupling. Conclusions are drawn in Sec. VI.

II. THE MODEL HAMILTONIAN

The Holstein molecular crystal model describes a lattice of two-level molecules interacting with a bath consisting of nuclear (intramolecular, intermolecular, and solvent) degrees of freedom

$$\hat{H} = \sum_n \Omega_n(\mathbf{q}) a_n^\dagger a_n + \sum_{m,n}^{m \neq n} J_{mn}(\mathbf{q}) a_m^\dagger a_n + \hat{H}^{\text{ph}}. \quad (1)$$

Here $a_n(a_n^\dagger)$ are exciton annihilation (creation) operators for the n th molecule, $\hat{H}^{\text{ph}}$ is the bath (phonon) Hamiltonian, and $\mathbf{q}$ represents the complete set of nuclear coordinates. Exciton-phonon interactions originate from dependence of molecular frequencies Ω_n and the intermolecular couplings J_{mn} on nuclear coordinates $\mathbf{q}$. We adopt the Hamiltonian

equation [Eq. (1)] with the Einstein phonon Hamiltonian

$$\hat{H}^{\text{ph}} = \sum_n \hbar \omega_0 b_n^\dagger b_n, \quad (2)$$

where $b_n^\dagger$ creates a phonon of frequency ω_0 on site n , and we have one Einstein oscillator per molecule. Exciton-phonon interactions enter through the nuclear coordinate influence on both molecular frequencies (diagonal coupling) and intermolecular interactions (off-diagonal coupling). Expanding $\Omega_n(\mathbf{q})$ to first order in phonon coordinate $\mathbf{q}$, the first term of Eq. (1) reads

$$\sum_n \Omega_n(\mathbf{q}) a_n^\dagger a_n = \sum_n \Omega_n(\mathbf{q}=0) a_n^\dagger a_n + \hat{H}^{\text{diag}}, \quad (3)$$

with the diagonal exciton-phonon coupling term

$$\hat{H}^{\text{diag}} = g \hbar \omega_0 \sum_n a_n^\dagger a_n (b_n^\dagger + b_n), \quad (4)$$

and g is a dimensionless diagonal coupling constant. Expanding $J_{mn}(\mathbf{q})$ to first order in phonon coordinates, we write the second term of Eq. (1) as, for example,

$$\sum_{m \neq n} J_{mn}(\mathbf{q}) a_m^\dagger a_n = \sum_{m \neq n} J_{mn}(\mathbf{q}=0) a_m^\dagger a_n + \hat{H}^{\text{od}}, \quad (5)$$

with the transfer integral $J_{mn}(\mathbf{q}=0) = -J \delta_{n,m \pm 1}$ and the off-diagonal coupling term^{9,10}

$$\begin{aligned} \hat{H}^{\text{od}} = & \frac{1}{2} \phi \hbar \omega_0 \sum_{nl} [a_n^\dagger a_{n+1} (b_l^\dagger + b_l) (\delta_{n+1,l} - \delta_{nl}) \\ & + a_n^\dagger a_{n-1} (b_l^\dagger + b_l) (\delta_{nl} - \delta_{n-1,l})]. \end{aligned} \quad (6)$$

The second term of Eq. (6) is the Hermitian conjugate of the first, and we have assumed nearest-neighbor coupling of the antisymmetric type with ϕ a dimensionless parameter controlling the off-diagonal coupling strength. Off-diagonal coupling may adopt various forms^{6,9} other than the antisymmetric type (6) and can play important roles in electronic properties of solid. Equations (4) and (6), together with $\hat{H}^{\text{ph}}$ and the zeroth-order intermolecular coupling term, result in the generalized Holstein Hamiltonian $\hat{H}^{\text{GH}}$ (the original Holstein Hamiltonian contains diagonal coupling only)¹⁶

$$\begin{aligned} \hat{H}^{\text{GH}} = & \sum_n \Omega_n(\mathbf{q}=0) a_n^\dagger a_n + \hat{H}^{\text{diag}} \\ & + \sum_{mn}^{m \neq n} J_{mn}(\mathbf{q}=0) a_m^\dagger a_n + \hat{H}^{\text{od}} + \hat{H}^{\text{ph}}. \end{aligned} \quad (7)$$

We may partition the generalized Holstein Hamiltonian $\hat{H}^{\text{GH}}$ into three terms, namely, the exciton Hamiltonian $\hat{H}^{\text{ex}}$, the phonon Hamiltonian $\hat{H}^{\text{ph}}$, and the coupling Hamiltonian $\hat{H}^{\text{cpl}}$

$$\hat{H}^{\text{GH}} \equiv \hat{H}^{\text{ex}} + \hat{H}^{\text{ph}} + \hat{H}^{\text{cpl}}, \quad (8)$$

where

$$\hat{H}^{\text{ex}} \equiv \sum_n \Omega_n(\mathbf{q}=0) a_n^\dagger a_n + \sum_{mn} J_{mn}(\mathbf{q}=0) a_m^\dagger a_n, \quad (9)$$

$$\hat{H}^{\text{cpl}} \equiv \hat{H}^{\text{od}} + \hat{H}^{\text{diag}}. \quad (10)$$

The one-dimensional generalized Holstein Hamiltonian with simultaneous diagonal and off-diagonal coupling to Einstein phonons^{1,2,17,18} has been previously modeled by the Munn–Silbey approach and by a variational wave function pioneered by Toyozawa.² The latter has been extended to treat two-dimensional particle-boson coupling and arbitrary boson dispersion relations.¹² Our results on off-diagonal coupling from the Toyozawa *Ansatz* have been recently corroborated by Kato *et al.* using a dynamic coherent potential approach (DCPA).¹⁹ The one-dimensional variational wave function known as the Toyozawa *Ansatz*² reads

$$|K\rangle = N^{-1} \sum_n e^{iKn} |\Lambda_n^K\rangle \sum_m \psi_{m-n}^K a_m^\dagger |0\rangle_e. \quad (11)$$

Here $|K\rangle$ is the lowest energy polaron state with momentum K , $|0\rangle_e$ is the exciton vacuum state, and $|\Lambda_n^K\rangle$ are phonon wave functions centered at site n containing a coherent state on each site n_2 with a displacement $\lambda_{n_2-n}^K$

$$|\Lambda_n^K\rangle = \exp\left[-\sum_{n_2} (\lambda_{n_2-n}^K b_{n_2}^\dagger - \lambda_{n_2-n}^{K*} b_{n_2})\right] |0\rangle_{\text{ph}}. \quad (12)$$

$|0\rangle_{\text{ph}}$ is the phonon vacuum state and $|\Lambda_n^K\rangle$ is different from $|\Lambda_{n'}^K\rangle$ only by a shift of $n-n'$ lattice constants. The parameters λ_l^K and ψ_l^K are obtained variationally. The phonon wave functions $|\Lambda_n^K\rangle$ represent a lattice distortion forming a potential well centered at n and trapping the exciton with an amplitude distribution of ψ_l^K . The Toyozawa *Ansatz* state (11) is not normalized: $\langle K|K\rangle = \sum_{nm} e^{-iKn} \psi_m^K \psi_{m-n}^{K*} S_n^K$, where S_n^K is the Debye–Waller factor: $S_n^K \equiv \langle \Lambda_n^K | \Lambda_{m-n}^K \rangle = \exp[N^{-1} \sum_q |\lambda_q^K|^2 (e^{iqn} - 1)]$ and λ_q^K are the Fourier transform of λ_n^K .

III. THE GLOBAL-LOCAL ANSATZ

The GL *Ansatz* was introduced to extend the Toyozawa wave function to include explicit correlations between the electronic excitation and the phonon displacements. The site-space representation of the GL polaron trial state reads

$$|\Psi(K)\rangle = N^{-1/2} \sum_n e^{iKn} \sum_{n_1} \psi_{n_1-n}^K a_{n_1}^\dagger \times \exp\left\{\sum_{n_2} [(\beta_{n_2-n_1}^K - \alpha_{n_2-n_1}^K) b_{n_2}^\dagger - \text{H.c.}]\right\} |0\rangle, \quad (13)$$

where H.c. is short for Hermitian conjugate, $|0\rangle$ is the product of the exciton and phonon vacuum states, ψ_n^K is the exciton amplitude, and the two-parameter phonon displacement, $\alpha_{n_2-n}^K - \beta_{n_2-n_1}^K$, generalizes its one-parameter counterpart λ_n^K in the Toyozawa *Ansatz* $|K\rangle$, which can also be written as

$$|K\rangle = N^{-1/2} \sum_n e^{iKn} \sum_{n_1} \psi_{n_1-n}^K a_{n_1}^\dagger \times \exp\left\{-\sum_{n_2} [(\lambda_{n_2-n}^K) b_{n_2}^\dagger - \text{H.c.}]\right\} |0\rangle. \quad (14)$$

The new set of variational parameters, $\beta_{n_2-n_1}^K$, introduces to the polaron trial state additional exciton-phonon correlations which bear close resemblance to the Jastrow-type wave functions,²⁰ well known for simplifying a many-body wave function into a pairwise construction.

The Toyozawa *Ansatz* can be obtained from a localized wave function $|L\rangle$

$$|L\rangle = \sum_m \psi_m a_m^\dagger \exp\left[-\sum_l (\lambda_l b_l^\dagger - \lambda_l^* b_l)\right] |0\rangle \quad (15)$$

via a projection operator $\hat{P}^K$

$$\hat{P}^K = \delta(K - \hat{P}), \quad (16)$$

where

$$\hat{P} = \sum_k k a_k^\dagger a_k + \sum_q q b_q^\dagger b_q. \quad (17)$$

In general, the localized wave function $|L\rangle$ can be generalized to Davydov's “D1” *Ansatz*²¹

$$\sum_{n_1} \psi_{n_1}^K a_{n_1}^\dagger \exp\left[-\sum_{n_2} (\gamma_{n_2,n_1}^K b_{n_2}^\dagger - \text{H.c.})\right] |0\rangle. \quad (18)$$

In Davydov's D1 *Ansatz*, the phonon displacement γ_{n_2,n_1}^K depends on n_1 , the location where the electronic excitation is generated. In this particular *Ansatz*, however, the general phonon displacement γ_{n_2,n_1}^K is replaced by

$$\alpha_{n_2}^K - \beta_{n_2-n_1}^K, \quad (19)$$

where $\alpha_{n_2}^K$ represents the part of the phonon displacement independent of the location of the electronic excitation (as in the Toyozawa *Ansatz*) and $\beta_{n_2-n_1}^K$ represents the part of the phonon displacement that only depends on the relative separation between the phonon and the electronic excitation. This is analogous to the Jastrow trial functions that are constructed from two-particle functions and only depend explicitly on the interparticle separations in a many-body problem.²⁰

The GL variational approach has been shown to be rather efficient while remaining quantitatively accurate compared with calculations involving far more expensive computational resources.^{22,23} For example, the GL *Ansatz* was able to match the accuracy of the computationally demanding DMRG method for a lattice of 32 sites.²

IV. THE VARIATIONAL PROCEDURE

Due to the fact that expressions and equations look more compact in the momentum space, we should perform our variational procedure in the momentum space as well. Applying the Fourier conventions

$$a_n = N^{-1} \sum_q e^{iqn} \alpha_q, \quad \alpha_q = \sum_n e^{-iqn} a_n, \quad (20)$$

$$\beta_n = N^{-1} \sum_q e^{iqn} \beta_q, \quad \beta_q = \sum_n e^{-iqn} \beta_n, \quad (21)$$

$$a_n^\dagger = N^{-1/2} \sum_k e^{-ikn} a_k^\dagger, \quad a_k^\dagger = N^{-1/2} \sum_n e^{ikn} a_n^\dagger, \quad (22)$$

$$b_n^\dagger = N^{-1/2} \sum_q e^{-iqn} b_q^\dagger, \quad b_q^\dagger = N^{-1/2} \sum_n e^{iqn} b_n^\dagger, \quad (23)$$

one finds that in the momentum-space representation the GL Ansatz state (13) can be simplified as

$$|\Psi(K)\rangle = N^{-1} \sum_{nn'k} e^{iKn-ikn'} \psi_{n'-n}^K a_k^\dagger \times \exp \left\{ N^{-1/2} \sum_q [(\beta_q^K e^{-iqn'} - \alpha_q^K e^{-iqn}) b_q^\dagger - \text{H.c.}] \right\} |0\rangle,$$

where H.c. stands for Hermitian conjugate. We note that the Ansatz above is not normalized

$$M^K \equiv \langle \Psi(K) | \Psi(K) \rangle = \sum_{nm} e^{-iKn} \psi_m \psi_{m-n}^* S_{nm}^0. \quad (24)$$

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

$$\langle \Psi(K) | \hat{H}^{\text{ex}} | \Psi(K) \rangle = -J \sum_{nm} e^{-iKn} \psi_m (\psi_{m-n+1}^* S_{nm}^{+1} + \psi_{m-n-1}^* S_{nm}^{-1}), \quad (25)$$

$$\langle \Psi(K) | \hat{H}^{\text{ph}} | \Psi(K) \rangle = N^{-1} \sum_{nmq} e^{-iKn} \psi_m \psi_{m-n}^* S_{nm}^0 [|\alpha_q|^2 e^{iqn} + |\beta_q|^2 - \alpha_q \beta_q^* e^{iqm} - \alpha_q^* \beta_q e^{iq(n-m)}], \quad (26)$$

$$\begin{aligned} \langle \Psi(K) | \hat{H}^{\text{cpl}} | \Psi(K) \rangle &= -g N^{-1} \sum_{nmq} e^{-iKn} \psi_m \psi_{m-n}^* S_{nm}^0 \\ &\times [e^{iq(n-m)} (\alpha_q^* + \alpha_{-q} e^{-iqn}) - (\beta_q^* + \beta_{-q})] \\ &- \frac{\phi}{2} \sum_{nm} e^{-iKn} \psi_m (\psi_{m-n-1}^* S_{nm}^{-1} W_{nm}^{-1} \\ &+ \psi_{m-n+1}^* S_{nm}^{+1} W_{nm}^{+1}), \end{aligned} \quad (27)$$

where S_{nm}^l generalizes the Debye–Waller factor

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

and W_{nm}^{-1} and W_{nm}^{+1} are two auxiliary functions defined as

$$W_{nm}^{-1} = N^{-1} \sum_q (1 - e^{iq}) [e^{iq(n-m)} (\alpha_q^* + \alpha_{-q} e^{-iqn}) - (\beta_q^* e^{-iq} + \beta_{-q})],$$

$$W_{nm}^{+1} = N^{-1} \sum_q (e^{-iq} - 1) [e^{iq(n-m)} (\alpha_q^* + \alpha_{-q} e^{-iqn}) - (\beta_q^* e^{iq} + \beta_{-q})].$$

The variational approach aims to minimize the expectation values of the Hamiltonian in the framework of the GL Ansatz state. Upon the conclusion of the variational process, optimal values of the variational parameters are determined, and exciton-phonon correlations in the optimal state are evaluated. We define the expectation value of the Hamiltonian in the GL Ansatz state as H^K/M^K , where

$$H^K = \langle \Psi(K) | \hat{H}^{\text{ex}} + \hat{H}^{\text{ph}} + \hat{H}^{\text{cpl}} | \Psi(K) \rangle. \quad (28)$$

Minimization of H^K/M^K with respect to α_q^* leads to

$$\frac{\partial H^K}{\partial \alpha_q^*} - \frac{H^K}{M^K} \frac{\partial M^K}{\partial \alpha_q^*} = 0. \quad (29)$$

Upon substitution of H^K and M^K , one has

$$\begin{aligned} \alpha_q &= \left(M_q + H_q - M_q \frac{H^K}{M^K} \right)^{-1} \left\{ g L_q + \frac{\phi}{2} (1 - e^{iq}) P_q^{-1} \right. \\ &\quad \left. + \frac{\phi}{2} (e^{-iq} - 1) P_q^{+1} + \beta_q \left[L_q + \frac{(N_q - L_q)}{2} \frac{H^K}{M^K} - H_q^\beta \right] \right\}, \end{aligned} \quad (30)$$

where

$$L_q = \sum_{nm} e^{-iKn} \psi_m \psi_{m-n}^* S_{nm}^0 e^{iq(n-m)}, \quad (31)$$

$$M_q = \sum_{nm} e^{-iKn} \psi_m \psi_{m-n}^* S_{nm}^0 e^{iqn}, \quad (32)$$

$$N_q = \sum_{nm} e^{-iKn} \psi_m \psi_{m-n}^* S_{nm}^0 e^{-iqm}, \quad (33)$$

$$P_q^{-1} = \sum_{nm} e^{-iKn} \psi_m \psi_{m-n-1}^* S_{nm}^{-1} e^{iq(n-m)}, \quad (34)$$

$$P_q^{+1} = \sum_{nm} e^{-iKn} \psi_m \psi_{m-n+1}^* S_{nm}^{+1} e^{iq(n-m)}, \quad (35)$$

$$\begin{aligned} H_q &= H_q^{\text{ex}} + H_q^{\text{ph}} + H_q^{\text{cpl}} = -J \sum_{nm} e^{-iKn+iqn} \psi_m (\psi_{m-n+1}^* S_{nm}^{+1} + \psi_{m-n-1}^* S_{nm}^{-1}) + N^{-1} \sum_{nmp} e^{-iKn+iqn} \psi_m \psi_{m-n}^* S_{nm}^0 \\ &\times \{ [|\alpha_p|^2 e^{ipn} + |\beta_p|^2 - \alpha_p \beta_p^* e^{ipm} - \alpha_p^* \beta_p e^{ip(n-m)}] - g [e^{ip(n-m)} (\alpha_p^* + \alpha_{-p} e^{-ipn}) - (\beta_p^* + \beta_{-p})] \} \\ &- \frac{\phi}{2} \sum_{nm} e^{-iKn+iqn} \psi_m (\psi_{m-n-1}^* S_{nm}^{-1} W_{nm}^{-1} + \psi_{m-n+1}^* S_{nm}^{+1} W_{nm}^{+1}), \end{aligned} \quad (36)$$

$$\begin{aligned}
H_q^\beta = & -\frac{1}{2}J \sum_{nm} e^{-iKn+iq(n-m)} \psi_m [\psi_{m-n+1}^* S_{nm}^{+1} (e^{-iqn} + e^{-iq} - 2) + \psi_{m-n-1}^* S_{nm}^{-1} (e^{-iqn} + e^{iq} - 2)] \\
& + \frac{1}{2}N^{-1} \sum_{nmp} e^{-iKn+iq(n-m)} \psi_m \psi_{m-n}^* S_{nm}^0 (e^{-iqn} - 1) \{ [\alpha_p]^2 e^{ipn} + |\beta_p|^2 - \alpha_p \beta_p^* e^{ipm} - \alpha_p^* \beta_p e^{ip(n-m)} \} \\
& - g[e^{ip(n-m)}(\alpha_p^* + \alpha_{-p} e^{-ipn}) - (\beta_p^* + \beta_{-p})] - \frac{\phi}{2} e^{-iKn+iq(n-m)} \sum_{nm} \psi_m [(e^{-iqn} + e^{-iq} - 2) \psi_{m-n+1}^* S_{nm}^{+1} W_{nm}^{+1} \\
& + (e^{-iqn} + e^{iq} - 2) \psi_{m-n-1}^* S_{nm}^{-1} W_{nm}^{-1}].
\end{aligned} \quad (37)$$

We note that

$$H_q|_{q=0} = H^K, \quad (38)$$

$$H_q^\beta|_{q=0} = 0, \quad (39)$$

$$L_q|_{q=0} = M_q|_{q=0} = N_q|_{q=0} = M^K. \quad (40)$$

Therefore, the sum rule for site space is recovered

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

Similarly, minimization of H^K/M^K with respect to β_q^* yields

$$\beta_q = - \frac{gM^K - \alpha_q \left[\frac{(L-q-N-q)}{2} \frac{H^K}{M^K} - H_q^\alpha + N_{-q} \right]}{M^K + H_q^{\text{od}}} - \frac{\frac{1}{2}\phi(e^{-iq} - 1)P_{q=0}^{-1} + \frac{1}{2}\phi(1 - e^{iq})P_{q=0}^{+1}}{M^K + H_q^{\text{od}}}, \quad (42)$$

where

$$\begin{aligned}
H_q^\alpha = & -\frac{1}{2}J \sum_{nm} e^{-iKn+iqm} \psi_m [\psi_{m-n+1}^* S_{nm}^{+1} e^{iq}(e^{-iqn} + e^{-iq} - 2) + \psi_{m-n-1}^* S_{nm}^{-1} e^{-iq}(e^{-iqn} + e^{iq} - 2)] \\
& + \frac{1}{2}N^{-1} \sum_{nmp} e^{-iKn+iqm} \psi_m \psi_{m-n}^* S_{nm}^0 (e^{-iqn} - 1) \{ [\alpha_p]^2 e^{ipn} + |\beta_p|^2 - \alpha_p \beta_p^* e^{ipm} - \alpha_p^* \beta_p e^{ip(n-m)} \} - g[e^{ip(n-m)}(\alpha_p^* + \alpha_{-p} e^{-ipn}) \\
& - (\beta_p^* + \beta_{-p})] \} - \frac{\phi}{2} \sum_{nm} e^{-iKn+iqm} [e^{iq}(e^{-iqn} + e^{-iq} - 2) \psi_{m-n+1}^* S_{nm}^{+1} W_{nm}^{+1} + e^{-iq}(e^{-iqn} + e^{iq} - 2) \psi_{m-n-1}^* S_{nm}^{-1} W_{nm}^{-1}],
\end{aligned} \quad (43)$$

$$H_q^{\text{od}} = - \sum_{nm} e^{-iKn} \psi_m \left[\psi_{m-n+1}^* S_{nm}^{+1} (e^{iq} - 1) \left(J + \frac{\phi}{2} W_{nm}^{+1} \right) + \psi_{m-n-1}^* S_{nm}^{-1} (e^{-iq} - 1) \left(J + \frac{\phi}{2} W_{nm}^{-1} \right) \right]. \quad (44)$$

We now turn to the minimization of H^K/M^K with respect to ψ_l^*

$$\frac{\partial H^K}{\partial \psi_l^*} - \frac{H^K}{M^K} \frac{\partial M^K}{\partial \psi_l^*} = 0. \quad (45)$$

Again substituting H^K and M^K , we arrive at

$$\psi_l = - \frac{H_l^\psi}{H_0^\psi}, \quad (46)$$

where

$$\begin{aligned}
H_l^\psi = & -J \left(\sum_{n \neq 1} e^{-iKn} \psi_{n+l-1} S_{n,n+l-1}^{+1} + \sum_{n \neq -1} e^{-iKn} \psi_{n+l+1} S_{n,n+l+1}^{-1} \right) - \frac{\phi}{2} N^{-1} \sum_{n \neq 1, q} e^{-iKn} \psi_{n+l-1} S_{n,n+l-1}^{+1} (e^{-iq} - 1) [e^{-i(l-1)q} (\alpha_q^* + \alpha_{-q} e^{-iqn}) \\
& - (\beta_q^* e^{iq} + \beta_{-q})] - \frac{\phi}{2} N^{-1} \sum_{n \neq 1, q} e^{-iKn} \psi_{n+l+1} S_{n,n+l+1}^{+1} (1 - e^{iq}) [e^{-i(l+1)q} (\alpha_q^* + \alpha_{-q} e^{-iqn}) - (\beta_q^* e^{-iq} + \beta_{-q})] + \sum_{n \neq 0} e^{-iKn} \psi_{n+l} S_{n,n+l}^0 \\
& \times \left\{ - \frac{H^K}{M^K} + N^{-1} \sum_p [|\alpha_p|^2 e^{ipn} + |\beta_p|^2 - \alpha_p \beta_p^* e^{ip(n+l)} - \alpha_p^* \beta_p e^{-ipl}] - gN^{-1} \sum_p [e^{-ipl} (\alpha_p^* + \alpha_{-p} e^{-ipn}) - (\beta_p^* + \beta_{-p})] \right\},
\end{aligned}$$

$$\begin{aligned}
H_0^\psi = & -J(e^{-iK}S_{+1,l}^{+1} + e^{iK}S_{-1,l}^{-1}) - \frac{\phi}{2}N^{-1}\sum_q e^{-iK}S_{+1,l}^{+1}(e^{-iq} - 1)[e^{-i(l-1)q}(\alpha_q^* + \alpha_{-q}e^{-iq}) - (\beta_q^*e^{iq} + \beta_{-q})] \\
& - \frac{\phi}{2}N^{-1}\sum_q e^{-iK}S_{-1,l}^{-1}(1 - e^{iq})[e^{-i(l+1)q}(\alpha_q^* + \alpha_{-q}e^{-iq}) - (\beta_q^*e^{-iq} + \beta_{-q})] + S_{0,l}^0 \\
& \times \left\{ -\frac{H^K}{M^K} + N^{-1}\sum_p [|\alpha_p|^2 + |\beta_p|^2 - \alpha_p\beta_p^*e^{ipl} - \alpha_p^*\beta_p e^{-ipl}] - gN^{-1}\sum_p [e^{-ipl}(\alpha_p^* + \alpha_{-p}) - (\beta_p^* + \beta_{-p})] \right\}.
\end{aligned}$$

A relaxation iteration scheme similar to those used in previous efforts^{2,9} has been employed to obtain solutions for three sets of variational parameters α_q^K , β_q^K , and ψ_n^K . 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 on 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. The mathematical dilemma of finding educated initial guesses for the nonlinear iterative scheme can be avoided here 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 rapid, 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 the 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 stepwise process and calculations involving classical magnetic hysteresis where the external field serves as the physical control parameter.^{24,25} In such systems, one may observe hysteresis, that is, a dependence on the path through the parameter space along which the physical parameter value of interest is approached. Such effects exist here as well, that is, there are regimes in the parameter space where trial states obtained for a given set of parameter values by iteration depend on the path of approach to those values in the parameter space.

V. RESULTS AND DISCUSSIONS

As compared with the Toyozawa *Ansatz*, the variational energies in the simultaneous presence of diagonal and off-diagonal coupling as calculated by the present GL trial state

have been significantly lowered thanks to the addition of the parameter set β_q^K , which introduces the Jastrow-type exciton-phonon correlations in the polaron wave function. Two specific cases for comparison between the two polaron trial states have been shown in Fig. 1. In the upper panel, the energy bands calculated from the GL *Ansatz* and Toyozawa's *Ansatz* are displayed for the case of $g=2.0$, $J=2.0$, and $\phi=0.5$. It shows that measurable quantitative improvements in the energy band are achieved for all crystal momenta K , with the largest improvement being realized near the zone boundary. For a case of stronger off-diagonal coupling, $g=2.0$, $J=2.0$, and $\phi=2.0$, the polaron energy bands are shown in the lower panel of Fig. 1. The polaron bands calculated by both variational methods show a large bimodal variation, and the improvement of the GL *Ansatz* over the Toyozawa *Ansatz*,

FIG. 1. Variational energy bands are compared for the GL *Ansatz* (solid) and the Toyozawa *Ansatz* (dashed). Upper panel: $g=2.0$, $J=2.0$, and $\phi=0.5$; lower panel: $g=2.0$, $J=2.0$, and $\phi=2.0$. The crystal momentum K is in units of π , and the energy E and the transfer integral J are in units of the phonon frequency ω .

about 30% of the polaron bandwidth, is relatively uniform throughout the Brillouin zone. The larger value of off-diagonal coupling here makes the polaron bands much narrower than those with weak off-diagonal coupling under similar other conditions. The significant lowering of the ground-state energy in Fig. 1 demonstrates that the GL *Ansatz* is quantitatively superior to its the Toyozawa *Ansatz*. In the absence of transfer integral J and the diagonal coupling g , the polaron energy band for a finite value of off-diagonal coupling ϕ will exhibit a bimodal variation symmetric about $K=0, \pi$, and $\pm\pi/2$, which comes from the particular form of off-diagonal exciton-phonon coupling [Eq. (6)]. Adding diagonal coupling will only reduce the bandwidth while leaving the bimodal variation intact. The effect of transfer integral will lower (raise) the energy at $K=0$ ($K=\pm\pi$). For the case of $g=2.0, J=2.0$, a crossover from the band in the upper panel of Fig. 1 to that in the lower panel occurs at a critical value of off-diagonal coupling $\phi_c=1.48$, for which we observe zero curvature of the polaron energy dispersion at $K=0$. This critical value $\phi_c=1.48$ is the same for both the Toyozawa *Ansatz* and the GL *Ansatz* under consideration here.

Previous studies have shown that there exist two regions of discontinuity where two solutions to the self-consistency equations are found depending on the manner in which these points are approached in the aforementioned iterative procedure.² The two competing solutions represent two different forms of exciton-phonon correlations; one is of the small-polaron type, and the other, of the large-polaron type. As one solution becomes more energetically favorable than the other, properties reflecting the exciton-phonon correlations in the trial state such as the polaronic effective mass will undergo a discontinuous jump, which coincides with the self-trapping transition. It is therefore very helpful to use a phase diagram to illustrate the polaron self-trapping transition in a three-dimensional parameter space spanned by the transfer integral J , the diagonal exciton-phonon coupling g , and off-diagonal exciton-phonon coupling ϕ . Such a phase diagram associated with the polaron self-trapping near the zone center in the three-dimensional space labeled by (g, ϕ, J) is shown in Fig. 2.

The ax-shaped region enveloped by solid (dashed) lines in Fig. 2 represents the zone-center self-trapping for the GL (Toyozawa) *Ansatz*. As is afforded by its greater flexibility, the self-trapping region for the GL *Ansatz* has a much-reduced volume compared with that for the Toyozawa *Ansatz*. Within the ax-shaped region bordered by solid (dashed) lines in Fig. 2, two sets of convergent solutions are found to coexist near the zone center for the self-consistency equations that govern the variational procedure of the GL (Toyozawa) *Ansatz*. One set of solutions can be interpreted as a small-polaron state, and the other, a large-polaron state. Outside the self-trapping region for each *Ansatz*, only one unique set of solutions can be obtained for the self-consistency equations near zone center. This self-trapping region divides the (g, ϕ, J) space into two distinct portions. For a given set of diagonal and off-diagonal exciton-phonon coupling, the self-consistent solutions are usually “large-polaron-like” for large values of J and are “small-polaron-

FIG. 2. Phase diagrams of the near zone-center self-trapping in g - ϕ - J space for the GL *Ansatz* (solid) and the Toyozawa *Ansatz* (dashed). Under the solid-line ax-shaped region (small J), there is a unique solution to the set of self-consistency equations derived from the GL *Ansatz*, and the crossover from small-polaron correlations to large-polaron ones is smooth. Within the ax-shaped region, two convergent solutions are found to coexist for the GL trial state.

like” for small values of J . For small J values, the structural transition of the optimized exciton-phonon complex from small-polaron correlations to large-polaron ones can be smooth and encounter no pockets of double converging solutions.

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 that is associated with the common notion of a more-or-less sharp self-trapping transition. In reality, we have encountered ax-shaped (or in the case of a two-dimensional phase diagram, wedge-shaped) regions both here and in our earlier models.^{1,2} The discontinuities encountered in both the Toyozawa *Ansatz* and the GL *Ansatz* are primarily and perhaps entirely artifacts introduced by the insufficiency in complexity of the variational *Ansätze*. Although the self-trapping transition is expected to be smooth on formal grounds,^{26,27} 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. From this viewpoint, the GL *Ansatz* is not an exception, but it has its merit that it gives a much smaller self-trapping region relative to the Toyozawa *Ansatz*. From the Toyozawa *Ansatz* to the GL *Ansatz*, the incremental refinement of the variational states results in shrinkage of the fraction of the parameter space exhibiting self-trapping related discontinuities; moreover, this shrinkage is accompanied by a shift of the onset of discontinuities to more extreme parameter values. Were the form

$$|\Psi(K)\rangle = N^{-1/2} \sum_n e^{iKn} \sum_{n_1} \psi_{n_1-n}^K a_{n_1}^\dagger \times \exp \left[- \sum_{n_2} (\gamma_{n_2-n, n_1-n}^K b_{n_2}^\dagger - \text{H.c.}) \right] |0\rangle \quad (47)$$

of delocalized Davydov’s D1 *Ansatz* [cf. Eq. (18)] solved for the generalized Holstein Hamiltonian with both diagonal and

FIG. 3. Optimized variational parameters for the case of $g=2.0$, $J=2.0$, and $\phi=0.5$: (a) α_q^K , (b) β_q^K , (c) $\text{Re}\{\alpha_n^K\}$, (d) $\text{Re}\{\beta_n^K\}$, (e) $\text{Im}\{\alpha_n^K\}$, (f) $\text{Im}\{\beta_n^K\}$, (g) $\text{Re}\{\psi_n^K\}$, and (h) $\text{Im}\{\psi_n^K\}$.

off-diagonal exciton-phonon coupling, one should expect further reductions in the volume of the ax-shaped self-trapping region accompanied by further lowering of the variational energies of the polaron bands. Work in this direction is now in progress.

Figure 3 shows the variational parameters that minimize the polaron energy band for the case of $g=2.0$, $J=2.0$, and $\phi=0.5$, for which the energy band has been displayed in the upper panel of Fig. 1. The momentum-space representations of phonon displacements α_q^K and β_q^K are displayed in Figs. 3(a) and 3(b), respectively. Both sets of the optimized phonon displacements, α_q^K and β_q^K , are found to be real in the momentum space. In fact, re-examination of the self-consistency equations shows that the system remains self-consistent for strictly real α_q^K and β_q^K , leading us to conclude that the optimal phonon displacements in the momentum space are real.

The polaron band at the zone boundary experiences more phonon displacements than at the zone center, which is reflected by the visibly larger values of α_q^K at $K=\pi$ in Fig. 3(a). This is due to stronger level repulsion from the one-phonon continuum at the zone boundary.²⁸ The one-phonon continuum plays an important role in determining the structure of the exciton-phonon entity and energies of the ground-

state polaron band, and it follows that the width of the polaron band should be always less than the frequency of the optical phonon ω at any finite exciton-phonon coupling. The substantial reduction in the polaron band widths as one goes from the Toyozawa *Ansatz* to the present GL *Ansatz*, as demonstrated in Fig. 1(a), ensures that such expectations on the polaron band widths are more likely met in the GL *Ansatz*. The second set of phonon displacements, β_q^K , is numerically found to be roughly one-tenth in size compared with the first set, α_q^K . However, it is this tiny Jastrow-type component of the phonon displacements in the present variational wave function that is responsible for significant reductions in the calculated ground-state energies.

For the case of $g=2.0$, $J=2.0$, and $\phi=0.5$, real and imaginary parts of the site-space phonon displacements α_n^K (i.e., Fourier transformations of α_q^K) are displayed in Figs. 3(c) and 3(e), respectively. Again, it is obvious that the phonon displacements at the zone boundary are significantly larger than those near the zone center. The imaginary parts of α_n^K are negligible compared with its real counterparts, and $\text{Re}\{\alpha_n^K\}$, approximately symmetric with respect to $n=0$, are found only one or two sites from the location of the exciton due to strong diagonal exciton-phonon coupling and moderate transfer integral for this case. Real and imaginary parts of the site-space phonon displacements β_n^K (i.e., Fourier transformations of β_q^K) are displayed in Figs. 3(d) and 3(f), respectively. Similar to the imaginary parts of α_n^K , $\text{Im}\{\beta_n^K\}$ are negligible compared with their real counterparts (about one-tenth as large as $\text{Re}\{\beta_n^K\}$). The distinction between the two types of phonon displacements is limited crucially by the spread of the exciton amplitude ψ_n^K , and the two displacements would become redundant if the exciton amplitude is completely localized to one single site. For this intermediate-coupling case, the Jastrow-type phonon displacements β_n^K are on average only one-tenth of α_n^K . Real and imaginary parts of the site-space exciton amplitudes ψ_n^K (i.e., Fourier transformations of ψ_k^K) are displayed in Figs. 3(g) and 3(h), respectively. The real-space exciton amplitudes ψ_n^K are predominantly real, and the imaginary components are two orders of magnitude smaller than the real counterparts. The spread of $\text{Re}\{\psi_n^K\}$ extends over three sites, visibly larger than that of $\text{Re}\{\alpha_n^K\}$.

Figure 4 shows the variational parameters that minimize the polaron energy band for the case of $g=2.0$, $J=2.0$, and $\phi=2.0$, for which the energy band has been displayed in the lower panel of Fig. 1. Due to a large overall strength of the exciton-phonon coupling combining its diagonal and off-diagonal components, the polaron energy band for this set of parameters is rather narrow, rendering the distance in energy from the ground-state band to the bottom of the one-phonon continuum more or less equal for all crystal momentum, and therefore, level repulsion from the one-phonon continuum is uniform relatively for all crystal momenta. This is reflected by the uniform values of α_q^K and β_q^K throughout the Brillouin zone. As shown in Figs. 4(a) and 4(b), the Jastrow-type phonon displacements β_q^K are about two orders of magnitude smaller than α_q^K , confirming further that this is a small-polaron case with extremely localized exciton amplitudes.

For the case of $g=2.0$, $J=2.0$, and $\phi=2.0$, real and

FIG. 4. Optimized variational parameters for the case of $g=2.0$, $J=2.0$, and $\phi=2.0$: (a) α_q^K , (b) β_q^K , (c) $\text{Re}\{\alpha_n^K\}$, (d) $\text{Re}\{\beta_n^K\}$, (e) $\text{Im}\{\alpha_n^K\}$, (f) $\text{Im}\{\beta_n^K\}$, (g) $\text{Re}\{\psi_n^K\}$, and (h) $\text{Im}\{\psi_n^K\}$.

imaginary parts of the site-space phonon displacement α_n^K (i.e., Fourier transformations of α_q^K) are displayed in Figs. 4(c) and 4(e), respectively. The imaginary parts of α_n^K are negligible compared with their real counterparts. As shown in Fig. 4(c), $\text{Re}\{\alpha_n^K\}$ are restricted almost entirely to the site of the exciton ($n=0$) thanks to a combined effect of strong diagonal and off-diagonal exciton-phonon coupling for this case. Very small leakage of $\text{Re}\{\alpha_n^K\}$ is found on sites $n = \pm 1$ and beyond. Real and imaginary parts of the site-space phonon displacements β_n^K (i.e., Fourier transformations of β_q^K) are displayed in Figs. 4(d) and 4(f), respectively. Similar to α_n^K , the Jastrow-type phonon displacements β_n^K are found to have negligible imaginary parts. $\text{Re}\{\beta_n^K\}$ may appear more delocalized due to their tiny magnitudes, but the spread of $\text{Re}\{\beta_n^K\}$ is mostly on sites $n=0, \pm 1, \pm 2$. Real and imaginary parts of the site-space exciton amplitudes ψ_n^K (i.e., Fourier transformations of ψ_k^K) are displayed in Figs. 4(g) and 4(h), respectively. As expected, strong exciton-phonon coupling limits the spread of the exciton amplitudes, and $\text{Re}\{\psi_n^K\}$ has only nonzero values at $n=0, \pm 1$. Due to the asymmetry of the off-diagonal coupling and the simultaneous presence of diagonal and off-diagonal coupling, $\text{Re}\{\psi_n^K\}$ is visibly asymmetric with respect to site $n=0$.

VI. CONCLUSIONS

In this paper we have revisited the classic polaron problem incorporating simultaneous diagonal and off-diagonal exciton-phonon coupling as formulated by the generalized Holstein Hamiltonian equation [Eq. (7)]. Our method of choice is the GL *Ansatz*. Arguably, the most accurate variational wave function available to date to describe the ground state of the Holstein polaron, the GL *Ansatz* has been shown to produce variational energies that match those from some of the most computationally intensive methods. However, the GL *Ansatz*, with its added Jastrow-type exciton-phonon correlations, was previously implemented only for diagonal exciton-phonon coupling.² In this work, the GL *Ansatz* has been expanded to treat the full effects of off-diagonal coupling. The work carried out here is a direct extension of our numerical implementation of the Toyozawa *Ansatz* to off-diagonal exciton coupling¹¹ more than a decade ago.

For the first time, a phase diagram in a three-dimensional space spanned by electronic tunneling, diagonal coupling, and off-diagonal coupling has been mapped out for the self-trapping transition near the zone center for the two *Ansatz* under discussion, namely, the Toyozawa *Ansatz* and the GL *Ansatz*. The ax-shaped region in the three-dimensional phase diagram where two convergent solutions to the self-consistency equations coexist is much reduced in volume for the GL *Ansatz* (as compared with the Toyozawa *Ansatz*). Significant lowering of the ground state energy by the GL *Ansatz* in comparison with the Toyozawa *Ansatz* in all parameter regimes demonstrates that the former is quantitatively superior. To some degree, the GL *Ansatz* also helps to circumvent the difficulty for the Toyozawa *Ansatz* to approximate phonon number states at weak exciton-phonon coupling by using simple linear superpositions of phonon coherent states.

There are a few remaining tasks on the horizon in our pursuit of hierarchical trial states of increasing sophistication to achieve a better, more precise description of the ground-state properties of the Holstein Hamiltonian. Despite its success, the GL *Ansatz* still has room for improvements, and more sophisticated trial states, such as the one constructed from the Davydov's "D1" *Ansatz* [cf. Eq. (47)], are now being developed. There are several issues that those better trials states can help to resolve with more certainty. For example, as aforementioned, there is well-known difficulty to achieve iteration convergence for weak exciton-phonon coupling (diagonal or off-diagonal) because coherent states are not good at representing phonon number states associated with the weak-coupling regime. With the GL *Ansatz* doing better than the Toyozawa *Ansatz*, we hope more sophisticated trial states will make further improvements. In the presence of off-diagonal coupling, a second polaron self-trapping transition may occur at the zone boundary. This zone-boundary self-trapping transition is not well resolved with the present *Ansatz*. It is our hope that a better variational *Ansatz* will reveal the structure of the transition clearly.

By allowing some of the variational parameters to have a time dependence, those trial states can also be used to study polaron dynamics using the Dirac–Frenkel formulation of the

time-dependent variational principle,^{29,30} a powerful technique to obtain accurate dynamics of quantum systems for which exact solutions are elusive. Previously, time evolution of the zero-crystal-momentum Merrifield *Ansatz* has been formulated.¹⁵ Progress has recently been made on the dynamics of the Davydov's "D2" *Ansatz*,³¹ a localized wave function from which the Toyozawa *Ansatz* was constructed by a projection technique. The Dirac–Frenkel variational principle is now being implemented to other trial states to reveal the full quantum dynamics of the Holstein polaron.

ACKNOWLEDGMENTS

Support from the Singapore Ministry of Education through the Academic Research Fund (Tier 2) under Project No. T207B1214 is gratefully acknowledged. One of us (Y.Z.) would like to thank X. Dai for useful discussions.

¹Y. Zhao, Ph.D. thesis, University of California, 1994.

²Y. Zhao, D. W. Brown, and K. Lindenberg, *J. Chem. Phys.* **107**, 3159 (1997); **107**, 3179 (1997); **106**, 5622 (1997); A. Romero, D. W. Brown, and K. Lindenberg, *ibid.* **109**, 6540 (1998).

³L. D. Landau, *Phys. Z. Sowjetunion* **3**, 644 (1933).

⁴S. I. Pekar, *J. Phys. (Moscow)* **10**, 341 (1946).

⁵G. D. Mahan, *Many Particle Physics* (Plenum, New York, 1981).

⁶S. Ishihara and N. Nagaosa, *Phys. Rev. B* **69**, 144520 (2004).

⁷L. A. Dissado and S. H. Walmsley, *Chem. Phys.* **86**, 375 (1984).

⁸H. Sumi, *Chem. Phys.* **130**, 433 (1989).

⁹Y. Zhao, D. W. Brown, and K. Lindenberg, *J. Chem. Phys.* **100**, 2335 (1994).

¹⁰R. W. Munn and R. Silbey, *J. Chem. Phys.* **83**, 1843 (1985); **83**, 1854 (1985).

¹¹Y. Zhao, D. W. Brown, and K. Lindenberg, *J. Chem. Phys.* **106**, 2728 (1997).

¹²Y. Zhao, G. H. Chen, and L. Yu, *J. Chem. Phys.* **113**, 6502 (2000).

¹³Y. Zhao (unpublished).

¹⁴R. E. Merrifield, *J. Chem. Phys.* **40**, 445 (1964).

¹⁵S. Tanaka, *J. Chem. Phys.* **119**, 4891 (2003).

¹⁶T. Holstein, *Ann. Phys. (N.Y.)* **8**, 325 (1959); **8**, 343 (1959).

¹⁷Y. Toyozawa, *Prog. Theor. Phys.* **26**, 29 (1961).

¹⁸V. M. Buimistrov and S. I. Pekar, *Sov. Phys. JETP* **5**, 970 (1957).

¹⁹T. Kato, F. Sasaki, and S. Kobayashi, *Chem. Phys. Lett.* **303**, 649 (1999).

²⁰R. Jastrow, *Phys. Rev.* **98**, 1479 (1955).

²¹A. S. Davydov, *Sov. Phys. JETP* **51**, 397 (1980).

²²E. Jeckelmann and S. R. White, *Phys. Rev. B* **57**, 6376 (1998).

²³J. Bonca, S. A. Trugman, and I. Batistić, *Phys. Rev. B* **60**, 1633 (1999).

²⁴Y. Zhao and H. N. Bertram, *J. Magn. Magn. Mater.* **114**, 329 (1992).

²⁵Y. Zhao and H. N. Bertram, *J. Appl. Phys.* **77**, 6411 (1995).

²⁶B. Gerlach and H. Lowen, *Phys. Rev. B* **35**, 4291 (1987).

²⁷B. Gerlach and H. Lowen, *Phys. Rev. B* **35**, 4297 (1987).

²⁸G. Whitfield and R. Puff, *Phys. Rev.* **139**, A338 (1965).

²⁹P. A. M. Dirac, *Proc. Cambridge Philos. Soc.* **26**, 376 (1930); J. Frenkel, *Wave Mechanics* (Oxford University Press, Oxford, 1934).

³⁰Y. Zhao, S. Yokojima, and G. H. Chen, *J. Chem. Phys.* **113**, 4016 (2000).

³¹R. Yu, J. Sun, and Y. Zhao (to be published).