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Delocalized Davydov D_1 Ansatz for the Holstein polaron

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An efficient, yet very accurate trial wave function, constructed from projecting the well-known Davydov D_1 Ansatz onto momentum eigenstates, is employed to study the ground state properties of the generalized Holstein Hamiltonian with simultaneous diagonal and off-diagonal coupling. Ground-state energies have been obtained with a precision matching that of the computationally much more demanding density-matrix renormalization group method. The delocalized D_1 Ansatz lowers the ground-state energies at the Brillouin zone boundary significantly compared with the Toyozawa and Global-Local Ansätze in the weak coupling regime, while considerable improvement is demonstrated to have been achieved over the entire Brillouin zone in the strong coupling regime. Unique solutions are obtained with the delocalized D_1 for different initial conditions when the transfer integral is 20 times the phonon frequency at the zone center, implying the absence of any self-trapping discontinuity. The scaled correlation variance is found to fit satisfactorily well with the predictions of the perturbation theories. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4802961>]

I. INTRODUCTION

A polaron is a quasiparticle consisting of an exciton or an electron and the phonon cloud that surrounds it. The concept of polaron was first introduced by Landau in 1933.¹ Since then, much attention has been devoted to understanding the role of polaron in determining electric and optical properties of a variety of materials, such as lithium halide,² C_{60} ,^{3,4} oxide materials,⁵ manganites, and conductive organic oligomers.^{6,7} Some recent experiments, such as infrared spectroscopy and transport measurements, have demonstrated the existence of polarons and bipolarons even in high- T_c superconductors.^{8,9} Polarons also play an important role in phonon-assisted optical transitions due to effects of nonadiabaticity in exciton-phonon systems,¹⁰ and may produce a considerable increase of total electric current in organic molecular crystals.¹¹ The development of the ultrafast laser spectroscopy^{12,13} provided further opportunities for polaron dynamics studies.

A simple Hamiltonian by the name of the Holstein molecular crystal model^{14,15} has been extensively used to study polaron properties of molecular and biological systems. Based on the Holstein Hamiltonian, various numerical methods have been proposed to study static and dynamic properties of the Holstein polaron, such as the ground-state energy, the effective polaron mass and radius,^{16–21} adiabatic behavior,²² low-energy excitations,^{19,23} and the phase diagram.²⁴ As an exact solution to the Holstein Hamiltonian remains elusive, the weak-coupling perturbation theory (WCPT)²⁵ and the strong-coupling perturbation theory (SCPT)²⁶ were used to deal with the weak and strong exciton-phonon coupling regimes, respectively. In the weak coupling regime where the ground state is well described by an electron with a slightly renormalized mass, the Migdal ap-

proximation, which used the first term in an expansion utilizing the exciton-phonon coupling constant as a small parameter, is very accurate for this weakly-coupled system. Suitable to describe polaron properties in the strong-coupling limit is the Lang-Firsov (LF) canonical transformation²⁶ which diagonalizes the Holstein Hamiltonian exactly if the exciton hopping is neglected. However, neither of these methods is applicable in the intermediate coupling regime. Berciu and Goodvin proposed an improved momentum-average (MA) approximation for the Green's function of a single Holstein polaron which has been proven to be quite accurate over most of the parameter space, including the intermediate exciton-phonon coupling.²⁷ A number of numerical methods, such as variants of the dynamical coherent potential approximation (DPCA),^{28–30} the quantum Monte Carlo (QMC) methods,^{31–33} exact diagonalization (ED),^{34,35} the method of relevant coherent states,²² density-matrix renormalization group (DMRG),³⁶ and the dynamical mean field theory (DMFT)³⁷ have also been adopted to study the polaron properties. Among these numerical methods, the DMRG³⁶ method yields the most accurate results. However, a high-performance computing system is necessary to carry out the DMRG calculations.

In addition to the aforementioned numerical methods, the variational approach is also an effective tool to deal with the Holstein Hamiltonian so long as a proper trial wave function is chosen. Barišić¹⁹ studied the localized and translationally invariant polaron wave functions. Bonča *et al.*^{17,18,23} proposed a simple, computationally efficient variational method based on the exact diagonalization technique (VED), which can be used to describe the ground state as well as the low-lying excited state^{17,23} and is able to cover the entire coupling and frequency range.²¹ Although it has demonstrated advantages in selecting the variational space, truncation of the Hilbert space is still needed. An improved method to select

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the variational space for VED is proposed, which can speed up considerably the convergence, especially in the strong coupling regime.²⁰ Previously, Zhao *et al.* undertook a series of trial wave functions based upon phonon coherent states, such as the Toyozawa *Ansatz*^{38–40} and the Global-Local (GL) *Ansatz*,^{40–42} to analyze the polaronic ground state properties with simultaneous diagonal and off-diagonal exciton-phonon coupling. The Toyozawa *Ansatz*, for example, requires only limited computational resources, and can deal with large clusters with the number of sites greater than 1000. However, its accuracy in the weak coupling regime at the Brillouin zone boundary has room for improvements due to the excessive simplification of exciton-phonon correlations. The GL *Ansatz* possesses an improved accuracy which is comparable with that of the computationally much more expensive DMRG method,²⁸ as it includes explicit correlations between the exciton and the phonons.⁴¹ However, the GL *Ansatz* is not without shortcomings. For example, it is difficult to achieve iterative convergence for the GL *Ansatz* in the weak coupling regime.

Deficiencies of the aforementioned *Ansätze* call for more sophisticated trial wave functions. The delocalized D₁ *Ansatz* can be a candidate as it is considered as a substantial improvement over the GL *Ansatz*. For the phonon description in the GL *Ansatz*, we only consider the position of the phonon and the relative distance between the exciton and the phonon, while in the delocalized D₁ *Ansatz*, both the positions of the exciton and the phonon play a role. Therefore, the delocalized D₁ *Ansatz* can better describe the exciton-phonon correlations, especially in the presence of the off-diagonal exciton-phonon coupling. In this work we shall restrict our attention to the static properties of the Holstein Hamiltonian, such as the ground state energy bands and exciton-phonon correlations, and we expect the delocalized D₁ *Ansatz* to provide more accurate description of the ground state of the Holstein polaron.

The rest of paper is structured as follows. In Sec. II, the Holstein Hamiltonian with simultaneous diagonal and off-diagonal exciton-phonon coupling will be presented. In Sec. III, the variational method, as well as the trial wave functions used will be shown in detail. We will compare the GL *Ansatz* with the delocalized D₁ *Ansatz*, and show the advantages of the delocalized D₁ *Ansatz* over the GL *Ansatz* mathematically. In Sec. IV, we will show the detailed results of the delocalized D₁ *Ansatz* and analyze the influence of the diagonal and off-diagonal coupling to the ground state of the polaron. Conclusions are drawn in the final Sec. V.

II. THE MODEL HAMILTONIAN

The Holstein molecular crystal model with diagonal and off-diagonal exciton-phonon coupling in one dimension^{14,15} has the form

$$\hat{H} = \hat{H}^{\text{ex}} + \hat{H}^{\text{ph}} + \hat{H}_{\text{diag}}^{\text{ex-ph}} + \hat{H}_{\text{off-diag}}^{\text{ex-ph}}, \quad (1)$$

$$\hat{H}^{\text{ex}} = -J \sum_n a_n^\dagger (a_{n+1} + a_{n-1}), \quad (2)$$

$$\hat{H}^{\text{ph}} = \hbar\omega \sum_n b_n^\dagger b_n, \quad (3)$$

$$\hat{H}_{\text{diag}}^{\text{ex-ph}} = -g\hbar\omega \sum_n a_n^\dagger a_n (b_n^\dagger + b_n), \quad (4)$$

$$\begin{aligned} \hat{H}_{\text{off-diag}}^{\text{ex-ph}} = & \frac{1}{2}\phi\hbar\omega \sum_n (a_n^\dagger a_{n-1} + a_{n-1}^\dagger a_n \\ & - a_{n+1}^\dagger a_n - a_n^\dagger a_{n+1})(b_n^\dagger + b_n), \end{aligned} \quad (5)$$

where $a_n^\dagger$ creates an exciton in the rigid-lattice Wannier state at site n , and $b_n^\dagger$ creates a quantum of vibrational energy of the Einstein oscillator at site n . The Einstein frequency is given by ω , J is the exciton transfer integral between nearest neighbor sites, g is the diagonal coupling strength, and ϕ is the off-diagonal coupling strength characterizing phonon-assisted transfer between nearest-neighbor sites. All of the methods employed in this work can also be applied to common generalizations of this Hamiltonian, involving, for example, phonon dispersion, exciton transfers beyond nearest neighbors, and long-range exciton-phonon coupling. $\hbar = \omega = 1$ is used throughout this article; consequently, all energies are understood to be measured in units of the optical phonon energy $\hbar\omega$.

Throughout this article, we use the Fourier conventions for ladder operator $c^\dagger$ and scalar γ as follows:

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

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

We indicate the exciton and the phonon wave vectors by Latin indices k and q , and reserve the Greek κ for the joint crystal momentum; however, to simplify the presentations we suppress the explicit κ label on many quantities since the relevant value is generally clear from the context.

III. METHODOLOGY

The one-dimensional Holstein Hamiltonian with simultaneous diagonal and off-diagonal exciton-phonon coupling has been previously studied using a variational wave function pioneered by Toyozawa.^{38,43} Further improvements have also been made by extending the Toyozawa *Ansatz* to GL *Ansatz* with additional exciton-phonon correlations.^{40,42} Our central interest in this work is the polaron ground-state energy band, computed as

$$E(\kappa) = \langle \Psi(\kappa) | \hat{H} | \Psi(\kappa) \rangle, \quad (8)$$

where $|\Psi(\kappa)\rangle$ is an appropriately normalized delocalized trial wave function, and $\hat{H}$ is the system Hamiltonian given by Eq. (1). As the trial wave functions are characterized by many parameters, the basic idea of the variational approach is to find the optimal set of parameters to minimize the energy $E(\kappa)$. It should be noted that the total crystal momentum commutes with the system Hamiltonian, so the trial wave functions are the eigenfunctions of the total crystal momentum. Therefore, variations for distinct κ are independent. The set of $E(\kappa)$ constitutes a variational estimate (an upper bound) for the polaron energy band.^{43,44}

The relaxation iteration technique, an efficient method for identifying energy minima of a complex variational system,^{45,46} is adopted in this work to obtain numerical solutions to a set of self-consistency equations derived from the variational principle. A major issue with this approach is stability of the iteration. A proper solution obtained by this or any other variational methods must be stable relative to small changes in the variational parameters. 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 be generated for randomly chosen initial data, in practice the best convergence results are achieved when the search is initialized with input that is already close to the solution being sought. For our problem, the mathematical dilemma of finding suitable initial guesses for the nonlinear iterative scheme can be avoided for the most parts 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 most of the phase diagram and may initialize the iteration using a reliable ground state already determined at some nearby points 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 the parameter space using solutions from one step to initialize the next, the whole parameter space can be explored.

A. The delocalized D_1 Ansatz

The most general one-exciton Davydov trial state in which the lattice components are represented by products of phonon coherent states is the Davydov D_1 Ansatz

$$|\Phi\rangle = \sum_m \alpha_m a_m^\dagger |0\rangle |\beta_{qm}\rangle, \quad (9)$$

where the coherent-state phonon displacements β_{qm} are permitted a general dependence on phonon momentum q and exciton site m . The D_1 Ansatz has earlier been studied in framework of the localized states and soliton theory, but has not been applied as a form factor in a delocalized state. This limited attention is largely due to the challenges introduced by a large number of variational parameters required to express the general spatial dependence of β_{qm} as well as the greater complexity of the formal description required to obtain the solution. In this paper, we overcome these problems, and analyze the polaron state with the delocalized D_1 Ansatz which is a Bloch state with a designated crystal momentum.

To arrive at the delocalized D_1 Ansatz, we use the momentum projection operator which can be written as

$$\mathcal{P}^\kappa = \sum_n e^{i(\kappa - \hat{k})n}, \quad (10)$$

where $\hat{k} = \sum_k k \hat{a}_k \hat{a}_k + \sum_q q \hat{b}_q \hat{b}_q$ is the crystal momentum operator. In general, the localized D_1 Ansatz, Eq. (9), can be projected onto momentum eigenstates to form the delocalized

D_1 Ansatz used in this work:

$$\begin{aligned} |\kappa\rangle &= \mathcal{P}^\kappa |\Phi\rangle, \\ &= \sum_n e^{i\kappa n} \sum_{n_1} \alpha_{n_1-n}^\kappa a_{n_1}^\dagger \\ &\quad \exp \left[- \sum_{n_2} (\beta_{n_1-n, n_2-n}^\kappa) b_{n_2}^\dagger - \text{H.c.} \right] |0\rangle \\ &= \sum_n e^{i\kappa n} \sum_{n_1} \alpha_{n_1-n}^\kappa a_{n_1}^\dagger \\ &\quad \exp \left[- \frac{1}{\sqrt{N}} \sum_q (\beta_{n_1-n, q}^\kappa e^{-iqn} b_q^\dagger - \text{H.c.}) \right] |0\rangle. \end{aligned} \quad (11)$$

As $|\kappa\rangle$ is non-normalized, $|\Psi(\kappa)\rangle$ is constructed

$$|\Psi(\kappa)\rangle = |\kappa\rangle \langle \kappa | \kappa \rangle^{-1/2}, \quad (12)$$

where

$$\langle \kappa | \kappa \rangle = N \sum_n e^{i\kappa n} \sum_{n_1} \alpha_{n_1}^{\kappa*} \alpha_{n_1-n}^\kappa S_{n, n_1, 0}^\kappa \quad (13)$$

with

$$\begin{aligned} S_{n, n_1, m}^\kappa &= \exp \left[\sum_{n_2} \beta_{n_1, n_2}^{\kappa*} \beta_{n_1+m-n, n_2-n}^\kappa \right. \\ &\quad \left. - \frac{1}{2} |\beta_{n_1, n_2}^\kappa|^2 - \frac{1}{2} |\beta_{n_1+m-n, n_2-n}^\kappa|^2 \right], \end{aligned} \quad (14)$$

where H.c. represents Hermitian conjugate, $|0\rangle$ is the product of the exciton and phonon vacuum states, α_n^κ is the exciton amplitude, and the phonon displacement $\beta_{n_1-n, n_2-n}^\kappa$ depends on n_1 and n_2 , respectively, the sites at which an electronic excitation and a phonon are generated.

B. The Toyozawa Ansatz

There are other delocalized trial states that are based on certain variations of the D_1 Ansatz albeit with substantial simplifications. In the Toyozawa Ansatz, for example, the phonon displacements only depend on the phonon location. As a result, the number of variational parameters in the Toyozawa Ansatz gets reduced considerably, and the process of variation becomes much easier to handle. The Toyozawa Ansatz can be written as

$$|\Psi(\kappa')\rangle_T = |\kappa'\rangle \langle \kappa' | \kappa' \rangle^{-1/2}, \quad (15)$$

$$\begin{aligned} |\kappa'\rangle &= \sum_n e^{i\kappa'n} \sum_{n_1} \psi_{n_1-n}^{\kappa'} a_{n_1}^\dagger \\ &\quad \exp \left[- \sum_{n_2} (\lambda_{n_2-n}^{\kappa'}) b_{n_2}^\dagger - \text{H.c.} \right] |0\rangle, \end{aligned} \quad (16)$$

where $\psi_{n_1-n}^{\kappa'}$ is the exciton amplitude analogous to $\alpha_{n_1-n}^\kappa$ in the delocalized D_1 Ansatz, and $\lambda_{n_2-n}^{\kappa'}$ is the phonon displacement. In fact, $\lambda_{n_2-n}^{\kappa'}$ is just one column of the phonon

TABLE I. Comparison of the ground-state energies. Listed are results for a lattice of 32 sites calculated using three trial wave functions, namely, the Toyozawa *Ansatz*, GL *Ansatz*, and delocalized D₁ *Ansatz*. Also listed for comparison in the absence of off-diagonal coupling are HA-DCPA results taken from Ref. 28 and DMRG results taken from Ref. 36, both computed for a lattice of 32 sites. Results from the VED approach¹⁷ and the perturbation theories^{25,26} are shown at the end. All energies are given in units of phonon energy $\hbar\omega$. If off-diagonal coupling is included, the minimum of the energy is not always at $\kappa = 0$. For $J = 1$, $g = 0$, and $\phi = 1$, the minimum energy is found at $\kappa = 0$ (3rd column), while for $J = 0$, $g = 0$ and $\phi = 1$, the energy band displays a bimodal structure, and the minimum energy occurs at $\kappa = \pi/2$ (4th column). Also shown for comparison in the 3rd and 4th columns are HA-DCPA results calculated in this work.

Methods	$J = 1, g = 1, \phi = 0$	$J = 1, g = \sqrt{2}, \phi = 0$	$J = 1, g = 0, \phi = 1$	$J = 0, g = 0, \phi = 1$
HA-DCPA	-2.46506 (Ref. 28)	-2.98602 (Ref. 28)	-2.21557	-1.05788
Toyozawa	-2.46870	-2.99173	-2.20311	-1.06525
GL	-2.46931	-2.99802	-2.20854	-1.10573
Delocalized D ₁	-2.46968	-2.99882	-2.21281	-1.15690
DMRG (Ref. 36)	-2.46968	-2.99883		
WCPT (Ref. 25)	-2.44721	-2.89442		
SCPT (Ref. 26)	-3.08959	-3.05279		
VED (Ref. 17)	-2.469684723933	-2.998828186867		

displacement matrix $\beta_{n_1-n, n_2-n}^\kappa$ in the delocalized D₁ *Ansatz* [cf. Eq. (11)].

C. The global-local *Ansatz*

The GL *Ansatz*^{40-42,47} was introduced as an extension of the Toyozawa *Ansatz*^{38,39,43} to include explicit correlations between the electronic excitation and the phonon displacements. The general phonon displacement in the delocalized D₁ *Ansatz* $\beta_{n_1-n, n_2-n}^\kappa$ is replaced by $\lambda_{n_2-n}^{\kappa''} - \gamma_{n_2-n_1}^{\kappa''}$. The GL *Ansatz* can be written as

$$|\Psi(\kappa'')\rangle_{\text{GL}} = |\kappa''\rangle \langle \kappa'' | \kappa'' \rangle^{-1/2}, \quad (17)$$

$$|\kappa''\rangle = \sum_n e^{i\kappa''n} \sum_{n_1} \psi_{n_1-n}^{\kappa''} a_{n_1}^\dagger \exp \left[- \sum_{n_2} (\lambda_{n_2-n}^{\kappa''} - \gamma_{n_2-n_1}^{\kappa''}) b_{n_2}^\dagger - \text{H.c.} \right] |0\rangle. \quad (18)$$

The two-parameter phonon displacement, $\lambda_{n_2-n}^{\kappa''} - \gamma_{n_2-n_1}^{\kappa''}$ in the GL *Ansatz*, generalizes its one-parameter counterpart $\lambda_{n_2-n}^{\kappa'}$ in the Toyozawa *Ansatz*.^{40,41} The new set of variational parameters, $\gamma_{n_2-n_1}^{\kappa''}$, supplies a direct correlation between the exciton amplitude and the phonon field for the polaron trial wave function, which captures the dependence of phonon field on the relative separation $n_2 - n_1$ between the electronic excitation and the phonon. These additional exciton-phonon correlations bear close resemblance to the Jastrow-type wave function,^{41,48} well known for simplifying a many-body wave function into a pairwise construction.

IV. RESULTS AND DISCUSSIONS

A. The polaron ground-state energy band

The ground-state energies calculated by the three trial states of the hierarchy with varying sophistication are compared in Table I. DMRG results³⁶ are generally regarded as

a benchmark in the computation of the ground-state energy, and results from perturbation theories^{25,26} and the variational method based on ED,¹⁷ are also listed for comparison. For the purely diagonal coupling case, the minimum of the energy band always corresponds to $\kappa = 0$. However, it should be noted that the minimum of the energy is not always at $\kappa = 0$ if off-diagonal coupling is included, as will be illustrated in detail later. In the first three columns in Table I, ground-state energies with $\kappa = 0$ are compared, while in the last column, ground-state energies with $\kappa = \pi/2$ are compared. Also listed for comparison are DCPA results under the Hartree approximation (HA-DCPA) taken from Ref. 28 (1st and 2nd columns) and those computed here for a lattice of 32 sites (3rd and 4th columns). From Table I, it is apparent that the precision of the ground-state energies calculated from the delocalized D₁ *Ansatz* in this work matches well with those calculated from the computationally much more expensive DMRG method, and compared with the GL and Toyozawa *Ansätze*, the delocalized D₁ *Ansatz* exhibits considerable improvements.

Figure 1(a) displays the relative polaron energy bands $E(\kappa) - E(0)$ calculated by the delocalized D₁ *Ansatz* for $J = 10$, $\phi = 0$, and $g = 1, 3, 3.65, 4.1, 4.3, 5$. The exciton-phonon coupling is known to have a significant influence on the polaron formation and the ground-state energy band. The diagonal coupling strength g can decrease the polaron energy as well as the width of the energy band. In the weak coupling regime, the band has a nearly cosine-shaped dispersion near the band center, and a flat region at the band boundary, in agreement with Ref. 16. For weak exciton-phonon coupling strengths, however, the relative polaron energy band $E(\kappa) - E(0)$ is hardly changed at either the Brillouin zone boundary or the zone center as g is increased. As a result, the polaron bandwidth retains its saturation value of unity until the coupling strength g reaches a critical value $g_c \approx 4.1$ which is associated with self-trapping and characterizes the crossover between the large and small polarons.⁴² For $g > g_c$, the energy band is strongly flattened throughout the entire Brillouin zone which indicates the formation of small polaron.

FIG. 1. (a) Relative polaron energy band $E(k) - E(0)$ calculated by the delocalized D_1 Ansatz for $J = 10$, $\phi = 0$, and $g = 1$ (black), 3 (red), 3.65 (blue), 4.1 (green), 4.3 (cyan), and 5 (magenta); (b) Polaron energy bands calculated variationally using the delocalized D_1 Ansatz (solid), the GL Ansatz (dashed) and Toyozawa Ansatz (dotted) for the case $J = 3$, $g = 2$, $\phi = 0$; and (c) the polaron energy bands calculated variationally using the delocalized D_1 Ansatz (solid), GL Ansatz (dashed) and Toyozawa Ansatz (dotted) for the case of $J = 3$, $g = 3$, $\phi = 0$. A lattice of 32 sites is used for all calculations.

Numerical solutions to the self-consistency equations derived from the delocalized D_1 Ansatz are compared with those got from the Toyozawa and GL Ansätze in Figs. 1(b) and 1(c). As shown previously,^{40–42,47} the GL Ansatz shows a great advantage over the Toyozawa Ansatz as judged by the lower ground-state energies obtained with the GL Ansatz. In Figs. 1(b) and 1(c), the ground-state energies calculated by the delocalized D_1 Ansatz are shown to be significantly lowered compared to those calculated by the Toyozawa and GL Ansätze. This is because of full consideration of the general correlations between the exciton and the phonons on various sites in the phonon displacement. In the weak coupling regime, the three Ansätze show similar results near the Brillouin zone center, but significant differences appear near the Brillouin zone edge. The delocalized D_1 Ansatz yields the

FIG. 2. Ground-state band widths as a function of diagonal coupling strength g in the absence of off-diagonal coupling for (a) $J = 2$ and (b) $J = 9$. Methods used are: the delocalized D_1 Ansatz (black), GL Ansatz (blue), and Toyozawa Ansatz (red).

lowest ground-state energy. In the strong coupling regime, the ground-state energy bands are shrunk to be essentially flat, with the delocalized D_1 Ansatz yielding quantitative improvement.

Figure 2 displays the polaron band widths as a function of g . As the Toyozawa Ansatz and GL Ansatz are found to be associated with difficulties in achieving convergence in the weak coupling regime, less data points are displayed in Fig. 2 for these two trial states than for the delocalized D_1 Ansatz. However, the number of the points is still large enough to reveal the trends in the band width. It is clear that in the limit of weak coupling the band widths of the GL Ansatz and the delocalized D_1 Ansatz will tend to be unity, i.e., the Einstein phonon energy. This can be explained by level repulsion from the one-phonon continuum. With an increase in the coupling strength g , the band width will decrease. The Toyozawa Ansatz, however, displays an unphysical variation of the band width with respect to the coupling strength as has been pointed out previously,^{40,42} i.e., it initially increases with increasing g , and then falls down when g is larger than 1.3. As a result, the Toyozawa Ansatz displays considerable overshoots of the expected bandwidth for a wide range of the coupling strength as shown in Fig. 2(a) for the case of $J = 2$. Much better results have been obtained on the band

FIG. 3. (a) Polaron ground-state energy bands calculated by the delocalized D_1 Ansatz for $J = 0$, $g = 0$, and $\phi = 1$. (b) Polaron energy bands calculated by the delocalized D_1 Ansatz for $J = 1$, $g = 0$, and $\phi = 0.1$ (black), $\phi = 1$ (red), $\phi = 1.4$ (green), and $\phi = 1.7$ (blue).

width using the GL Ansatz, but it has been pointed out earlier that such overshoots still appear at much larger values of J ,^{40,42} as shown in Fig. 2(b). In comparison, the bandwidth calculated by the delocalized D_1 Ansatz is further lowered, which has effectively avoided the overshoots.

The effect of off-diagonal exciton-phonon coupling is most evident when J and g is absent, as displayed in Fig. 3(a). Without the influence of the transfer integral J and the diagonal exciton-phonon coupling g , the ground state polaron energy band exhibits a bimodal variation symmetric about $\kappa = 0$, π , and $\pm \frac{\pi}{2}$, which results from the particular form of off-diagonal exciton-phonon coupling that effectively doubles the lattice constant from a to $2a$, just as the Peierls distortion. Therefore, the period in the momentum space is shortened from $2\pi/a$ to π/a (here we set $a = 1$).

Next we consider the influence of the off-diagonal coupling in the presence of the transfer integral J , as shown in Fig. 3(b). It is clear that the delocalized D_1 Ansatz can deal with weak off-diagonal coupling where the one-phonon continuum has strong influences on the ground state polaron band at the Brillouin zone boundary. When the off-diagonal coupling is very weak, the energy band shows a unimodal structure. With an increase in the off-diagonal exciton-phonon coupling strength, the polaron ground-state energy band will

FIG. 4. Polaron ground-state energy bands calculated by the GL Ansatz (black) and the delocalized D_1 Ansatz (red) for $J = 1$, $g = 0$, and (a) $\phi = 1.1$, (b) $\phi = 1.5$, and (c) $\phi = 2.5$.

be lowered and the band width will shrink; moreover, bimodal structures will emerge when the off-diagonal coupling strength exceeds a critical value ϕ_c .

The comparisons of the ground-state energies calculated with the delocalized D_1 Ansatz and the GL Ansatz are shown in Fig. 4. The delocalized D_1 Ansatz demonstrates superiority over the GL Ansatz, thanks to the inclusion of more extensive correlations between the electronic excitation and the phonon displacement. When the exciton-phonon coupling is weak, the advantages of the delocalized D_1 Ansatz over the GL Ansatz become much more prominent near the Brillouin zone boundary where the effect of the phonon continuum is stronger as shown in Fig. 4(a). In the strong off-diagonal coupling regime, the energy band calculated by the delocalized D_1 Ansatz is lower than that by the GL Ansatz over the entire Brillouin zone as displayed in Fig. 4(c). In addition, it is clearly shown in Fig. 4(b) that the critical value ϕ_c calculated by the delocalized D_1 Ansatz is smaller than that calculated by the GL Ansatz, which indicates that the delocalized D_1

FIG. 5. Exciton amplitude and phonon displacement calculated by the delocalized D₁ Ansatz, when $g = 0.2$, $\phi = 0$, and $J = 0.1$. (a) Exciton amplitude and (b) the center one row of phonon displacement matrix which satisfies $n_1 = n$.

Ansatz is more sensitive to the minute changes of the band structure.

B. Exciton amplitude and phonon displacement

In Figs. 5–7, the variational parameters obtained from our self-consistency equations are displayed and compared. When J and g are much smaller than the phonon frequency, e.g., $J = 0.1$ and $g = 0.2$, the exciton amplitude α_n^κ of the delocalized D₁ Ansatz behaves in the site space as a δ function localized at site $n = 0$ throughout the Brillouin zone as shown in Fig. 5(a). From Eq. (11), it can be seen that in this case the exciton amplitude works as a window function, and the effect of the phonon displacement on the Ansatz can only appear at the sites satisfying $n_1 = n$. In Fig. 5(b) there is one row of nonzero β matrix elements β_{0,n_2-n}^κ for all crystal momenta. It shows that the phonon displacement at $n_1 = n$, β_{0,n_2-n}^κ , is also

FIG. 6. Exciton amplitude and phonon displacement calculated by the delocalized D₁ Ansatz, for $g = 2$, $\phi = 0$, and $J = 3$. (a) The exciton amplitude α_n^κ . (b) The phonon displacement matrix for $\kappa = 0$, i.e., $\beta_{n_1-n,n_2}^{\kappa=0}$. (c) The phonon displacement matrix $\beta_{n_1-n,n,0}^{\kappa=0,\pi}$. The black solid line corresponds to the crystal momentum $\kappa = 0$ and the red dash line corresponds to $\kappa = \pi$.

localized at site $n_2 = n$, and does not change with the crystal momentum κ . This behavior is similar to the variational results using the Toyozawa and GL *Ansätze*. As a result, the difference in the ground-state energies for three *Ansätze* in this case is inconspicuous. We can thus conclude that the polaronic properties are mainly determined by the central row of the phonon displacement matrix, β_{0,n_2-n} , in the delocalized D_1 *Ansatz*, reminiscent of the phonon displacement described by the Toyozawa *Ansatz* and GL *Ansatz* which depends solely on the phonon site.

As shown in Fig. 6(a), the exciton amplitude matrix $\alpha_{n_1-n}^\kappa$ also has nonzero elements beyond $n_1 = n$, which indicates that the exciton is not completely localized. The phonon displacement matrix has nonzero elements other than β_{0,n_2-n}^κ as well in certain parameter space. As a consequence, the Toyozawa *Ansatz* whose phonon displacement component only corresponds to the central row of the phonon displacement matrix $\beta_{n_1-n,n_2-n}^\kappa$ in the delocalized D_1 *Ansatz* is not sufficiently accurate in those regimes. It follows that the GL *Ansatz* or the delocalized D_1 *Ansatz* is needed to improve the accuracy, as has been demonstrated in Fig. 1. For the GL *Ansatz*, the phonon displacement that depends on the relative separation between the exciton and the phonon is represented by an additional set of variational parameters $\gamma_{n_1-n_2}^{\kappa''}$, as depicted in Fig. 7 for $J = 3$ and $g = 2$. This extra array of phonon-displacement parameters, $\gamma_{n_1-n_2}^{\kappa''}$, has substantial contributions mainly along the $n_1 = n_2$ line despite visible oscillations up to a few sites away from the line. Upon changing the control parameters J and g , the shape of $\gamma_{n_1-n_2}^{\kappa''}$ remains nearly unchanged. Similar trends can also be found in the delocalized D_1 *Ansatz*. Figure 6(b) displays the converged variational parameters for the phonon displacement in the delocalized D_1 *Ansatz* for the total crystal momentum $\kappa = 0$. The peaks appear mainly along the diagonal line of the parameter matrix $\beta_{n_1-n,n_2-n}^\kappa$, which corresponds to the condition $n_1 = n_2$. This helps us understand why the GL *Ansatz* can describe the polaron properties much better than the Toyozawa *Ansatz*. However, there are also many components in matrix $\beta_{n_1-n,n_2-n}^\kappa$ that the GL *Ansatz* can not deal with by its simple summation of $\gamma_{n_1-n_2}^{\kappa''}$ and $\lambda_{n_2-n}^{\kappa''}$.

Figure 6(c) displays the phonon displacement $\beta_{n_1-n,n_2-n}^\kappa$ for two values of crystal momenta $\kappa = 0, \pi$, and $n_2 = n$. It is obvious that the distribution of the phonon displacement is more concentrated near $n_2 = n_1$ (or, $n_1 = n$) for $\kappa = 0$ than that for $\kappa = \pi$, indicating that it is much harder for the GL *Ansatz* to deal with the crystal momentum $\kappa = \pi$. It is concluded that the inadequacy of the GL *Ansatz* is more severe at the Brillouin zone boundary $\kappa = \pi$, where the ground state energies of the delocalized D_1 *Ansatz* also show more improvements over those of the GL *Ansatz*, as shown in Fig. 1.

C. Phase diagram

Reference 24 provided a detailed phase diagram of the Holstein polaron in one dimension. Here a simple sketch is used to show the discontinuity regions in the phase diagram in order to compare the relative validities of the *Ansätze*. Due to insufficient sophistication of the GL and Toyozawa *Ansätze*

FIG. 7. Phonon displacement $\gamma_{n_1-n_2}^{\kappa''}$ which depends on the relative separation between the exciton and phonon in the GL *Ansatz*, when $g = 2$, $\phi = 0$, and $J = 3$.

and many trial wave functions that came before the two *Ansätze*, self-trapping discontinuities in the g - J phase diagram are known to exist in general.^{38,41,47} The most prominent feature of the phase diagram for the Toyozawa and GL *Ansätze* is a tongue-shaped region, such as those shown in the inset of Fig. 8, within which the dependence of the ground state energy on J , g , and κ is not smooth. The discontinuities associated with the tongue-shaped regions can be elaborated as follows. Within those regions there exists a function $\kappa^*(J, g)$, identifying the location of a cusp in the dependence of the

FIG. 8. The ground-state energies calculated from two types of initialization, i.e., initial small (solid) and large (dashed) polaron states, using the relaxation iteration technique and the delocalized D_1 *Ansatz*, for $J = 20$, $\phi = 0$, and g varying from 5.2 to 5.7. Two curves are found to coincide with each other. The most prominent feature of the phase diagram for the Toyozawa and GL *Ansätze* is a tongue-shaped region, as shown in the inset, within which the dependence of the ground state energy on J , g , and κ is not smooth. For the delocalized D_1 *Ansatz*, however, despite examining a large span in the J - g parameter space, we have not detected any discontinuity region.

variational energy on κ ;⁴⁷ i.e., at fixed J and g ,

$$\frac{\partial E(\kappa)}{\partial \kappa} \Big|_{\kappa \rightarrow \kappa^{*+}} \neq \frac{\partial E(\kappa)}{\partial \kappa} \Big|_{\kappa \rightarrow \kappa^{*-}}, \quad (19)$$

where the function $\kappa^*(J, g)$ differs for each type of trial wave functions [cf. Eqs. (16) and (18)]. If such a function $\kappa^*(J, g)$ exists, the minimum-energy states at small κ ($|\kappa| < \kappa^*$) are large polaron-like, while the minimum-energy states at large κ ($|\kappa| > \kappa^*$) are small polaron-like, and these two kinds of solutions can be obtained from different initial conditions in the variation process. It follows that in the absence of $\kappa^*(J, g)$, variationally optimized ground-state energies will be unique and there will be no discontinuities in the phase diagram. The exact solution of the two-site Holstein model has been shown to display no discontinuities in the effective mass,⁴⁹ and it is expected on formal grounds that no true nonanalyticity exists in this physical system.^{50,51} The discontinuities shown by the variational methods based on the Toyozawa and GL *Ansätze* are believed to be artifacts due to the insufficient flexibility of the trial wave functions.

For the delocalized D₁ *Ansatz*, despite examining a large span in the J - g parameter space, we have not detected any discontinuity region. Figure 8 depicts the minimum-energy calculated via two different paths, employing either the small polaron state or the large polaron state as the initial state for variation respectively, when $J = 20$ and $\kappa = 0$. The result shows that even when J is 20 times the phonon frequency, the polaron energies of two states coincide and the self-trapping discontinuity does not appear. This is a very pronounced improvement for the delocalized D₁ *Ansatz* compared with the Toyozawa or GL *Ansätze*.

D. Correlation function and the polaron size

In order to study the exciton-phonon correlations directly, we have calculated the correlation function, which is defined as

$$C_r = \frac{1}{2g} \sum_n \langle a_n^\dagger a_n (b_{n+r}^\dagger + b_{n+r}) \rangle, \quad (20)$$

and normalized such that $\sum_r C_r = 1$. The correlation function describes the static correlation between the exciton and the oscillator displacement. Here we only consider the correlation functions at $\kappa = 0$, which are shown in Figure 9. It is obvious that when the diagonal exciton-phonon coupling is very weak, the correlations between the exciton and the phonon are widely distributed over many sites. With an increase in the diagonal exciton-phonon coupling strength, C_r tends to be 1 on $r = 0$, which indicates that the exciton tends to be localized. This is because the lattice displacement is so large that it traps the exciton at a certain site.

The polaron size can be quantified by the variance of the correlation function⁵²

$$\sigma^2 = \sum_r r^2 C_r. \quad (21)$$

From the weak-coupling and strong-coupling perturbation theories,⁵³ we can get the polaron size in certain limits, as

FIG. 9. The correlation function at $\kappa = 0$ calculated by the delocalized D₁ *Ansatz* for $J = 2$, and $g = 0.1$ (black), $g = 1$ (red), $g = 2$ (green), and $g = 3$ (blue).

shown below:

$$\lim_{g \rightarrow 0} \sigma^2 = \sigma_0^2 = 2J/\hbar\omega, \quad (22)$$

$$\lim_{J/\hbar\omega \rightarrow \infty} (\sigma^2/\sigma_0^2) = 0, \quad g > g_{st}, \quad (23)$$

where g_{st} is the diagonal exciton-phonon coupling strength corresponding to the self-trapping. The self-trapping trends are well located by the empirical curve $g_{st} = 1 + \sqrt{J/\hbar\omega}$.⁵⁴ Here g_{st} characterizes the crossover which separates the large polaron states with a small effective mass from the self-trapping state with a large effective mass, and Barišić has demonstrated that at a certain diagonal coupling strength similar to g_{st} , the energetic difference between the ground state and the first excited state reaches a minimum, which indicates that the polaron crossover is related to dramatic changes in the ground state and the first excited state of the Holstein polaron.¹⁹ The scaled correlation variance σ^2/σ_0^2 is shown in Fig. 10, from which we can see that the results of the delocalized D₁ *Ansatz* fit well with the perturbation theories. In addition, it is easy to see from Fig. 10 that large polarons which extend to more sites will change into small polarons gradually with an increase in the diagonal coupling strength.

The scaled correlation variance σ^2/σ_0^2 for the GL *Ansatz* has been discussed in Ref. 52, and it has been noted that the polaron size revealed by the GL *Ansatz* deviates quite obviously from that estimated by the weak-coupling perturbation theory. As shown in Fig. 10, the GL result (filled triangles) displays a small arc in the intermediate coupling regime, instead of tending toward the limit of $\sigma^2/\sigma_0^2 = 1$. This discrepancy has been attributed to the deficiencies of the GL *Ansatz* as well as the finite-size effects.⁵² From our results in this work, we can see that the delocalized D₁ *Ansatz*, empowered by a more flexible set of built-in exciton-phonon correlations, has overcome the deficiencies of the GL *Ansatz*.

An empirical function to characterize the changes of the polaron size as one goes from the weak coupling regime to

FIG. 10. Scaled correlation variance σ^2/σ_0^2 as a function of the scaled coupling strength g/g_{st} . The zero-momentum scaled correlation variance, $\sigma^2/\sigma_0^2(\kappa=0)$, calculated by the GL *Ansatz* and the delocalized D_1 *Ansatz* are displayed, respectively, as filled triangles and circles for the case of $J = 2$. The solid and dashed lines are two auxiliary functions corresponding to, respectively, Eq. (25) and $\sigma^2/\sigma_0^2 = \sqrt{1 - g/g_{st}}$ for $g < g_{st}$, while for $g > g_{st}$, both lines are reduced to $\sigma^2/\sigma_0^2 = 0$. As discussed in the text, the dashed line represents the empirical function proposed in Ref. 52 to capture the main trends in convergence toward the limit of adiabatic strong-coupling, and the solid line, the one proposed in this work.

the strong coupling regime has also been proposed in Ref. 52, which can be written as

$$\frac{\sigma^2}{\sigma_0^2} = \begin{cases} \sqrt{1 - \frac{g}{g_{st}}}, & g < g_{st}, \\ 0, & g > g_{st}. \end{cases} \quad (24)$$

From the results of the delocalized D_1 *Ansatz* shown in Fig. 10, we can see the empirical function above can hardly describe the weak coupling regime well. We thus propose a new empirical function

$$\frac{\sigma^2}{\sigma_0^2} = \begin{cases} \frac{1 - \left(\frac{g}{g_{st}}\right)^2 + \sqrt{1 - \left(\frac{g}{g_{st}}\right)^2}}{2}, & g < g_{st}, \\ 0, & g > g_{st}. \end{cases} \quad (25)$$

This new function fits the scaled correlation variance much better in the weak coupling regime than the former one, although the description of the strong coupling regime still has room for improvements.

V. CONCLUSIONS

In this paper we have investigated the ground-state properties of polaron using the delocalized D_1 *Ansatz*, the most sophisticated in a hierarchy of variational trial states that derive their origin from the Davydov solitons. The delocalized D_1 *Ansatz* lowered the ground-state energies at the Brillouin zone boundary significantly compared with the Toyozawa and GL *Ansätze* in the weak coupling regime, while considerable improvement is demonstrated to be achieved over the entire Brillouin zone in the strong coupling regime. The ground-state energy calculations are carried out with a precision matching that of the computationally much more expensive DMRG

method. The delocalized D_1 *Ansatz* also effectively decreases the overshoots of the band width shown by the Toyozawa and GL *Ansätze*. Recently, a localized form of the Davydov D_1 *Ansatz*, which extends the Silbey-Harris polaron *Ansatz*, has been used to develop an analytical theory of the ground state properties of the spin-boson model, revealing a continuous phase transition for the deep sub-Ohmic regime.⁵⁵ Furthermore, a time-dependent form of the Davydov D_1 *Ansatz* has been employed to study the dynamic properties of the spin-boson model,⁵⁶ confirming a finding that coherent dynamics can persist even in the ultrastrong coupling regime in a deep sub-Ohmic spin-boson model.⁵⁷ The success of applying the Davydov D_1 *Ansatz* to the spin-boson model demonstrates its ample adaptability.

The discussions about the exciton amplitude and phonon displacement of different *Ansätze* show that the Toyozawa and GL *Ansätze* can hardly capture the full characteristics of the exciton and phonons especially in the weak exciton-phonon coupling regime, compared with the delocalized D_1 *Ansatz*. We further explored the much-mentioned self-trapping discontinuities which always appear for the Toyozawa and GL *Ansätze*. Unique solutions are obtained with the delocalized D_1 for various initial conditions when J is 20 times the phonon frequency and $\kappa = 0$, implying the absence of any the self-trapping discontinuity, a finding that also indicates that the existence of the discontinuity in the Toyozawa and GL *Ansätze* are totally due to their insufficiencies. We have effectively demonstrated the remarkable superiority of the delocalized D_1 *Ansatz*.

Finally, we have also investigated exciton-phonon interactions through the calculation of correlation function and polaron size. The scaled correlation variance is found to fit satisfactorily well with the predictions of the perturbation theories. A gradual transformation from large polarons, which extend to more sites, to small polarons is found when increasing the diagonal coupling strength. We have also demonstrated that the delocalized D_1 *Ansatz*, by the virtue of more flexible exciton-phonon correlations, can overcome the deficiencies of the GL *Ansatz*.

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APPENDIX: THE VARIATIONAL PROCEDURE

In this Appendix, we show the derivation of the self-consistency equations for the variational parameters in the delocalized D_1 *Ansatz*. First, the expectation value of the Hamiltonian is calculated. Then the variational approach is applied to minimize the expectation values of the Hamiltonian in the framework of the delocalized D_1 *Ansatz* state. Upon the completion of the variational process, optimal values of the variational parameters are determined, then the polaron properties,

such as the ground state energy and correlations, can be calculated.

We proceed to evaluate the expectation values of the four term of the generalized Holstein Hamiltonian

$$H = H_{\text{ex}} + H_{\text{ph}} + H_{\text{ex-ph}}^{\text{diag}} + H_{\text{ex-ph}}^{\text{od}}, \quad (\text{A1})$$

$$\begin{aligned} H_{\text{ex}} &= \langle \kappa | \hat{H}_{\text{ex}} | \kappa \rangle \\ &= -J \sum_n e^{i\kappa n} \sum_{n_1} \alpha_{n_1}^{\kappa*} (\alpha_{n_1+1-n}^{\kappa} S_{n,n_1,1}^{\kappa} \\ &\quad + \alpha_{n_1-1-n}^{\kappa} S_{n,n_1,-1}^{\kappa}), \end{aligned} \quad (\text{A2})$$

$$\begin{aligned} H_{\text{ph}} &= \langle \kappa | \hat{H}_{\text{ph}} | \kappa \rangle \\ &= \hbar\omega \sum_n e^{i\kappa n} \sum_{n_1} \alpha_{n_1}^{\kappa*} \alpha_{n_1-n}^{\kappa} S_{n,n_1,0}^{\kappa} \\ &\quad \sum_{n_2} \beta_{n_1,n_2}^{\kappa*} \beta_{n_1-n,n_2-n}^{\kappa}, \end{aligned} \quad (\text{A3})$$

$$\begin{aligned} H_{\text{ex-ph}}^{\text{diag}} &= \langle \kappa | \hat{H}_{\text{ex-ph}}^{\text{diag}} | \kappa \rangle \\ &= -g\hbar\omega \sum_n e^{i\kappa n} \sum_{n_1} \alpha_{n_1}^{\kappa*} \alpha_{n_1-n}^{\kappa} S_{n,n_1,0}^{\kappa} \\ &\quad (\beta_{n_1,n_1}^{\kappa*} + \beta_{n_1-n,n_1-n}^{\kappa}), \end{aligned} \quad (\text{A4})$$

$$\begin{aligned} H_{\text{ex-ph}}^{\text{od}} &= \langle \kappa | \hat{H}_{\text{ex-ph}}^{\text{od}} | \kappa \rangle, \\ &= -\frac{1}{2}\phi\hbar\omega \sum_n e^{i\kappa n} \sum_{n_1} \alpha_{n_1}^{\kappa*} \\ &\quad \{ \alpha_{n_1+1-n}^{\kappa} S_{n,n_1,1}^{\kappa} [(\beta_{n_1,n_1+1}^{\kappa*} + \beta_{n_1+1-n,n_1+1-n}^{\kappa}) \\ &\quad - (\beta_{n_1,n_1}^{\kappa*} + \beta_{n_1+1-n,n_1-n}^{\kappa})] + \alpha_{n_1-1-n}^{\kappa} S_{n,n_1,-1}^{\kappa} \\ &\quad [(\beta_{n_1,n_1}^{\kappa*} + \beta_{n_1-1-n,n_1-n}^{\kappa}) - (\beta_{n_1,n_1-1}^{\kappa*} \\ &\quad + \beta_{n_1-1-n,n_1-1-n}^{\kappa})] \}, \end{aligned} \quad (\text{A6})$$

$$D = \langle \kappa | \kappa \rangle = \sum_n e^{i\kappa n} \sum_{n_1} \alpha_{n_1}^{\kappa*} \alpha_{n_1-n}^{\kappa} S_{n,n_1,0}^{\kappa}, \quad (\text{A7})$$

where $S_{n,n_1,m}^{\kappa}$ is the Debye-Waller factor, defined as

$$\begin{aligned} S(n, n_1, m) &= S_{n,n_1,m}^{\kappa} \\ &= \exp \left(\sum_{n_2} \beta_{n_1,n_2}^{\kappa*} \beta_{n_1+m-n,n_2-n}^{\kappa} \right. \\ &\quad \left. - \frac{1}{2} |\beta_{n_1,n_2}^{\kappa}|^2 - \frac{1}{2} |\beta_{n_1+m-n,n_2-n}^{\kappa}|^2 \right). \end{aligned} \quad (\text{A8})$$

The expectation value of the Hamiltonian in the delocalized D_1 Ansatz state can then be calculated by $E(\kappa) = H/D$.

To simplify the expressions, we define several auxiliary parameters:

$$A(n, n_1, m) = \alpha_{n_1}^{\kappa*} \alpha_{n_1+m-n}^{\kappa}, \quad (\text{A9})$$

$$B(n, n_1, m) = \sum_{n_2} \beta_{n_1,n_2}^{\kappa*} \beta_{n_1+m-n,n_2-n}^{\kappa}, \quad (\text{A10})$$

$$AS(n, n_1, m) = A(n, n_1, m) * S(n, n_1, m). \quad (\text{A11})$$

The Debye-Waller factor can be written as

$$\begin{aligned} S(n, n_1, m) &= \exp \left[B(n, n_1, m) - \frac{1}{2} B(0, n_1, 0) \right. \\ &\quad \left. - \frac{1}{2} B(0, n_1 + m - n, 0) \right]. \end{aligned} \quad (\text{A12})$$

The expressions of the energy can be written as

$$\begin{aligned} H_{\text{ex}} &= -J \sum_n e^{i\kappa n} \sum_{n_1} (AS(n, n_1, 1) \\ &\quad + AS(n, n_1, -1)), \end{aligned} \quad (\text{A13})$$

$$H_{\text{ph}} = \hbar\omega \sum_n e^{i\kappa n} \sum_{n_1} AS(n, n_1, 0) B(n, n_1, 0), \quad (\text{A14})$$

$$\begin{aligned} H_{\text{ex-ph}}^{\text{diag}} &= -g\hbar\omega \sum_n e^{i\kappa n} \sum_{n_1} AS(n, n_1, 0) (\beta_{n_1,n_1}^{\kappa*} \\ &\quad + \beta_{n_1-n,n_1-n}^{\kappa}), \end{aligned} \quad (\text{A15})$$

$$\begin{aligned} H_{\text{ex-ph}}^{\text{od}} &= -\frac{1}{2}\phi\hbar\omega \sum_n e^{i\kappa n} \\ &\quad \sum_{n_1} \{ AS(n, n_1, 1) [(\beta_{n_1,n_1+1}^{\kappa*} + \beta_{n_1+1-n,n_1+1-n}^{\kappa}) \\ &\quad - (\beta_{n_1,n_1}^{\kappa*} + \beta_{n_1+1-n,n_1-n}^{\kappa})] \\ &\quad + AS(n, n_1, -1) [(\beta_{n_1,n_1}^{\kappa*} + \beta_{n_1-1-n,n_1-n}^{\kappa}) \\ &\quad - (\beta_{n_1,n_1-1}^{\kappa*} + \beta_{n_1-1-n,n_1-1-n}^{\kappa})] \}, \end{aligned} \quad (\text{A16})$$

$$D = \sum_n e^{i\kappa n} \sum_{n_1} AS(n, n_1, 0). \quad (\text{A17})$$

Minimization of $E(\kappa)$ with respect to $\alpha_i^{\kappa*}$ leads to

$$\frac{\partial E}{\partial \alpha_i^{\kappa*}} = 0. \quad (\text{A18})$$

From Eq. (A18), one arrives at

$$\frac{\partial H}{\partial \alpha_i^{\kappa*}} - E \frac{\partial D}{\partial \alpha_i^{\kappa*}} = 0. \quad (\text{A19})$$

Finally, one can get the self-consistency equations $\alpha_i^{\kappa} = f_i(\alpha, \beta)$ from the derivatives below:

$$\begin{aligned} \frac{\partial H_{\text{ex}}}{\partial \alpha_i^{\kappa*}} &= -J \sum_n e^{i\kappa n} (\alpha_{i+1-n}^{\kappa} S(n, i, 1) \\ &\quad + \alpha_{i-1-n}^{\kappa} S(n, i, -1)), \end{aligned} \quad (\text{A20})$$

$$\frac{\partial H_{\text{ph}}}{\partial \alpha_i^{\kappa*}} = \hbar\omega \sum_n e^{i\kappa n} \alpha_{i-n}^{\kappa} S(n, i, 0) B(n, i, 0), \quad (\text{A21})$$

$$\frac{\partial H_{\text{ex-ph}}^{\text{diag}}}{\partial \alpha_i^{\kappa*}} = -g\hbar\omega \sum_n e^{i\kappa n} \alpha_{i-n}^{\kappa} S(n, i, 0) (\beta_{i,i}^{\kappa*} + \beta_{i-n,i-n}^{\kappa}), \quad (\text{A22})$$

$$\begin{aligned} \frac{\partial H_{\text{ex-ph}}^{\text{od}}}{\partial \alpha_i^{\kappa*}} = & -\frac{1}{2}\phi\hbar\omega \sum_n e^{i\kappa n} \{ \alpha_{i+1-n}^{\kappa} S(n, i, 1) \\ & [(\beta_{i,i+1}^{\kappa*} + \beta_{i+1-n,i+1-n}^{\kappa}) - (\beta_{i,i}^{\kappa*} + \beta_{i+1-n,i-n}^{\kappa})] \\ & + \alpha_{i-1-n}^{\kappa} S(n, i, -1) [(\beta_{i,i}^{\kappa*} + \beta_{i-1-n,i-n}^{\kappa}) \\ & - (\beta_{i,i-1}^{\kappa*} + \beta_{i-1-n,i-1-n}^{\kappa})] \}, \end{aligned} \quad (\text{A23})$$

$$\frac{\partial D}{\partial \alpha_i^{\kappa*}} = \sum_n e^{i\kappa n} \alpha_{i-n}^{\kappa} S(n, i, 0). \quad (\text{A24})$$

Minimization of $E(\kappa)$ with respect to $\beta_{i,j}^{\kappa*}$ leads to

$$\frac{\partial E}{\partial \beta_{i,j}^{\kappa*}} = 0. \quad (\text{A25})$$

From which, we can get

$$\frac{\partial H}{\partial \beta_{i,j}^{\kappa*}} - E \frac{\partial D}{\partial \beta_{i,j}^{\kappa*}} = 0. \quad (\text{A26})$$

Finally, one can get the self-consistency equations $\beta_{i,j}^{\kappa} = g_{i,j}(\alpha, \beta)$ from the derivatives below:

$$\begin{aligned} \frac{\partial H_{\text{ex}}}{\partial \beta_{i,j}^{\kappa*}} = & -J \sum_n e^{i\kappa n} \left[AS(n, i, 1) \left(\beta_{i+1-n,j-n}^{\kappa} - \frac{1}{2} \beta_{i,j}^{\kappa} \right) \right. \\ & + AS(n, i+n-1, 1) \left(-\frac{1}{2} \beta_{i,j}^{\kappa} \right) \\ & + AS(n, i, -1) \left(\beta_{i-1-n,j-n}^{\kappa} - \frac{1}{2} \beta_{i,j}^{\kappa} \right) \\ & \left. + AS(n, i+n+1, -1) \left(-\frac{1}{2} \beta_{i,j}^{\kappa} \right) \right], \end{aligned} \quad (\text{A27})$$

$$\begin{aligned} \frac{\partial H_{\text{ph}}}{\partial \beta_{i,j}^{\kappa*}} = & \hbar\omega \sum_n e^{i\kappa n} \left\{ AS(n, i, 0) \left[B(n, i, 0) \left(\beta_{i-n,j-n}^{\kappa} \right. \right. \right. \\ & \left. \left. - \frac{1}{2} \beta_{i,j}^{\kappa} \right) + \beta_{i-n,j-n}^{\kappa} \right] + AS(n, i+n, 0) \\ & \left. B(n, i+n, 0) \left(-\frac{1}{2} \beta_{i,j}^{\kappa} \right) \right\}. \end{aligned} \quad (\text{A28})$$

$$\begin{aligned} \frac{\partial H_{\text{ex-ph}}^{\text{diag}}}{\partial \beta_{i,j}^{\kappa*}} = & -g\hbar\omega \sum_n e^{i\kappa n} \left\{ AS(n, i, 0) \left[(\beta_{i,i}^{\kappa*} + \beta_{i-n,i-n}^{\kappa}) \right. \right. \\ & \left. \left(\beta_{i-n,j-n}^{\kappa} - \frac{1}{2} \beta_{i,j}^{\kappa} \right) + \delta_{j,i} \right] + AS(n, i+n, 0) \\ & \left. (\beta_{i+n,i+n}^{\kappa*} + \beta_{i,i}^{\kappa}) \left(-\frac{1}{2} \beta_{i,j}^{\kappa} \right) \right\}. \end{aligned} \quad (\text{A29})$$

$$\begin{aligned} \frac{\partial H_{\text{ex-ph}}^{\text{od}}}{\partial \beta_{i,j}^{\kappa*}} = & -\frac{1}{2}\phi\hbar\omega \sum_n e^{i\kappa n} \left\{ AS(n, i, 1) \left([(\beta_{i,i+1}^{\kappa*} \right. \right. \\ & \left. + \beta_{i+1-n,i+1-n}^{\kappa}) - (\beta_{i,i}^{\kappa*} + \beta_{i+1-n,i-n}^{\kappa})] \right. \\ & \left. \left(\beta_{i+1-n,j-n}^{\kappa} - \frac{1}{2} \beta_{i,j}^{\kappa} \right) + \delta_{j,i+1} - \delta_{j,i} \right) \\ & + AS(n, i+n-1, 1) [(\beta_{i+n-1,i+n}^{\kappa*} + \beta_{i,i}^{\kappa}) \\ & - (\beta_{i+n-1,i+n-1}^{\kappa*} + \beta_{i,i-1}^{\kappa})] \left(-\frac{1}{2} \beta_{i,j}^{\kappa} \right) \\ & + AS(n, i, -1) \left([(\beta_{i,i}^{\kappa*} + \beta_{i-1-n,i-n}^{\kappa}) \right. \\ & \left. - (\beta_{i,i-1}^{\kappa*} + \beta_{i-1-n,i-1-n}^{\kappa})] \right. \\ & \left. \left(\beta_{i-1-n,j-n}^{\kappa} - \frac{1}{2} \beta_{i,j}^{\kappa} \right) + \delta_{j,i} - \delta_{j,i-1} \right) \\ & + AS(n, i+n+1, -1) [(\beta_{i+n+1,i+n+1}^{\kappa*} + \beta_{i,i+1}^{\kappa}) \\ & \left. - (\beta_{i+n+1,i+n}^{\kappa*} + \beta_{i,i}^{\kappa})] \left(-\frac{1}{2} \beta_{i,j}^{\kappa} \right) \right\}, \end{aligned} \quad (\text{A30})$$

$$\begin{aligned} \frac{\partial D}{\partial \beta_{i,j}^{\kappa*}} = & \sum_n e^{i\kappa n} \left[AS(n, i, 0) \left(\beta_{i-n,j-n}^{\kappa} - \frac{1}{2} \beta_{i,j}^{\kappa} \right) \right. \\ & \left. + AS(n, i+n, 0) \left(-\frac{1}{2} \beta_{i,j}^{\kappa} \right) \right]. \end{aligned} \quad (\text{A31})$$

A relaxation iteration scheme is employed to obtain solutions to the self-consistency equations for α_n^{κ} and $\beta_{n_1, n_2}^{\kappa}$.

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