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Dynamics of a Holstein polaron with off-diagonal coupling

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Dynamics of a one-dimensional Holstein polaron with off-diagonal exciton-phonon coupling is studied by employing the Dirac-Frenkel time-dependent variational principle. The trial state used is the Davydov D_2 Ansatz with two sets of variational parameters, one for each constituting particle in the linearly coupled exciton-phonon system. Validity of the approach is carefully checked by quantifying how faithfully the trial state follows the Schrödinger equation. A close examination of variational outputs reveals fine details of polaron dynamics and intricacies of dynamic exciton-phonon correlations. In the absence of diagonal coupling, the change in the polaron effective mass hinges on the sign of the transfer integral due to the antisymmetric nature of the off-diagonal coupling. The role of the off-diagonal coupling switches from being an agent of transport at moderate coupling strengths to that of localization at large coupling strengths. Increasing the phonon bandwidth leads to a reduced polaron effective mass at the zone center and an overall lowering of the polaron band.

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I. INTRODUCTION

Relaxation dynamics of photoexcited entities such as polarons in liquids and solids has attracted much recent interest thanks to the advent of the ultrafast laser spectroscopy.¹⁻³ Emerging technological capabilities to control femtosecond pulse durations and down-to-one-hertz bandwidth resolutions reveal previously elusive details on vibrational dynamics and excitation relaxation. For example, progress in femtosecond spectroscopic techniques has made it possible to observe a coherent phonon wave packet oscillating along an adiabatic potential surface associated with a self-trapped exciton in a crystal with strong exciton-phonon interactions.⁴

It is the aim of an ultrafast optical experiment to provide information on the details of temporal evolution on a femtosecond scale, which, in turn, offers insights into fundamental processes governing the dynamics. Developments in ultrafast laser physics and technologies now allow studies of nonequilibrium carrier/exciton dynamics that is previously inaccessible to traditional linear optical spectroscopy. In comparison, theoretical studies of polaron dynamics have not received much deserved attention. The aim of this work is to help fill the void in polaron dynamics studies in the presence of simultaneous diagonal and off-diagonal exciton-phonon coupling. We define diagonal coupling as a nontrivial dependence of the exciton site energies on the lattice coordinates, and off-diagonal coupling as a nontrivial dependence of the exciton transfer integral on the lattice coordinates.⁵ Similar off-diagonal interactions between electronic and lattice degrees of freedom were emphasized as modulations of electron-electron interactions by ion vibrations in Mahan's much famed graduate textbook on many-particle physics.⁶ Simultaneous presence of diagonal and off-diagonal coupling seems crucial to characterize solid-state excimers, where

a variety of experimental and theoretical considerations imply a strong dependence of electronic tunneling upon certain coordinated distortions of neighboring molecules in the formation of bound excited states.^{7,8} Mishchenko and Nagaosa have shown that off-diagonal coupling allows coexistence of free and self-trapped states even in quasi-one-dimensional compound A-PMDA consisting of alternating donor and acceptor molecules.⁹ It has also been proposed¹⁰ that off-diagonal coupling modulates the hopping integral of the Zhang-Rice singlet and the superexchange interaction in the low-doping regime of high-temperature superconductivity. In general, Hamiltonians containing off-diagonal exciton-phonon coupling seldom appear in the polaron literature due to inherent difficulties to obtain reliable solutions.⁶ Early treatments of off-diagonal coupling include the Munn-Silbey theory,^{11,12} which is based upon a perturbative approach with added constraints on canonical transformation coefficients determined by a self-consistency equation. An explicit expression has been later derived for the temperature dependence of the polaron bandwidths by treating diagonal and off-diagonal coupling on an equal footing.¹³ Most recently, the global-local (GL) Ansatz,^{14,15} formulated by Zhao *et al.* in the early 90s, has been used in combination with the dynamic coherent potential approximation (with the Hartree approximation) to arrive at a state-of-the-art ground-state wave function as well as higher eigenstates.¹⁶

On the polaron dynamics front, the time-dependent Schrödinger equation has been numerically integrated in real space for a few phonon periods by Ku and Trugman to probe the time evolution of electron and phonon densities and electron-phonon correlation functions.¹⁷ Based on a stochastic approach to non-Markovian open systems, a dynamical framework has been developed to describe the quantum dynamics of an electronic excitation coupled to a continuous, structured phonon bath.¹⁸ A time-dependent Merrifield-type trial state with zero crystal momentum has been employed recently to obtain an approximative solution

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to the Schrödinger equation governing the ultrafast relaxation process of a photo-excited state in a molecular ring.^{19–22} Results show that temporal changes of the exciton coherence size and related energy relaxation strongly depend on the exciton transfer integral, the exciton-phonon coupling strength, and the phonon bandwidth. The applicability of the Merrifield wave function, however, is restricted to the narrow-band regime where the electronic coupling between neighboring molecules is sufficiently weak leaving exciton-phonon coupling at a dominant role. In addition, the Merrifield *Ansatz* is incapable to provide a minimally workable description of the polaron ground state in the presence of off-diagonal interactions.²³ Fortunately, several trial wave functions with sufficient flexibilities and varying degrees of sophistication are available to describe the polaron state with off-diagonal coupling in a translationally invariant manner. Examples^{14,24} include the Toyozawa *Ansatz*, the GL *Ansatz*, and a delocalized form of the Davydov D₁ *Ansatz* that has been constructed recently.²⁵ By using these *Ansätze*, the ground state polaron energy band and the self-trapping phenomenon of a static Holstein polaron were investigated yielding far superior results.^{14,15,23}

Closely related to those polaron trial states are the Davydov *Ansätze*. Seeking to explain storage and transport of biological energy in protein, Davydov proposed in the early seventies that quantum units of peptide vibrational energy might become “self-localized” through interactions with lattice phonons.^{26,27} Following this suggestion, many studies have been carried out on the “Davydov soliton,” an essentially one-dimensional object that maintains dynamic integrity by balancing the effects of nonlinearity against those of dispersion. The original Davydov *Ansätze* include two forms of varying sophistication, namely, the D₁ (Refs. 28–34) and D₂ *Ansätze*, with the latter being a simplified version of the former. In this work the Davydov D₂ *Ansatz* is employed to study time evolution of the Holstein polaron with off-diagonal exciton-phonon coupling, and our method of choice is the Dirac-Frenkel time-dependent variational approach, a powerful apparatus to reveal accurate dynamics of quantum many-body systems.³⁵ Time-dependent variational parameters which specify the trial state are obtained from solving a set of coupled differential equations generated by the Lagrangian formalism of the Dirac-Frenkel variation. Despite that the D₂ *Ansatz* derives its name from the Davydov solitons, quantum dynamics of the D₂ trial state simulated in this work does not resemble that of solitons in any way. Solitons are quasi-classical entities, and they move like a classical object with a well-defined centroid location and group velocity. The trial wave function here is fully quantum mechanical, and in much of the phase diagram, the difference is minimal between the trial wave function and the exact solution to the Schrödinger equation.

The paper is organized as follows. In Sec. II we introduce the model Hamiltonian and discuss the nature of the trial states we use for dynamics studies. The procedure of the time-dependent variation is explained next. In Sec. III selected results from our investigation on the dynamics of the Holstein polaron are displayed and discussed. Conclusions are drawn in Sec. IV.

II. METHODOLOGY

In this paper we adopt the Holstein molecular crystal model which describes a lattice of two-level molecules interacting with a bath consisting of nuclear degrees of freedom. The Holstein Hamiltonian can be written as^{6,36–38}

$$\hat{H} = \sum_n \Omega_n(\mathbf{Q}) \hat{a}_n^\dagger \hat{a}_n + \sum_{m \neq n} J_{m,n}(\mathbf{Q}) \hat{a}_m^\dagger \hat{a}_n + \hat{H}_{\text{ph}}, \quad (1)$$

where $\hat{a}_n^\dagger$ ($\hat{a}_n$) are the exciton creation (annihilation) operators on the n th site (for the n th molecule), $\mathbf{Q}$ represents the nuclear coordinates, and $\hat{H}_{\text{ph}}$ is the bath (phonon) Hamiltonian. In the original formulation by Holstein, Einstein phonons are adopted, and $\hat{H}_{\text{ph}}$ is written as

$$\hat{H}_{\text{ph}} = \omega_0 \sum_n \hat{b}_n^\dagger \hat{b}_n, \quad (2)$$

where ω_0 is the dispersionless phonon frequency, and $\hat{b}_n^\dagger$ ($\hat{b}_n$) are the phonon creation (annihilation) operators on the n th site. In this paper, we set $\hbar = 1$.

For simplicity, we consider a one-dimensional ring of N identical molecules with N an even integer. Expanding $\Omega_n(\mathbf{Q})$ and $J_{m,n}(\mathbf{Q})$ to first order in coordinates $\mathbf{Q}$ and neglecting $J_{m,n}$ for $|m - n| > 1$, one obtains^{11,23,38}

$$\begin{aligned} \hat{H} = & \Omega \sum_n \hat{a}_n^\dagger \hat{a}_n + \hat{H}_{\text{ex-ph}}^{\text{diag}} \\ & - J \sum_n \hat{a}_n^\dagger (\hat{a}_{n+1} + \hat{a}_{n-1}) + \hat{H}_{\text{ex-ph}}^{\text{o.d.}} + \hat{H}_{\text{ph}}, \end{aligned} \quad (3)$$

where $\Omega = \Omega_n(\mathbf{Q} = \mathbf{0})$ for all sites on the homogeneous ring, J is the nearest-neighbor transfer integral $J_{m,n}(\mathbf{Q} = \mathbf{0}) = -J\delta_{m,n \pm 1}$, and $\hat{H}_{\text{ex-ph}}^{\text{diag}}$ and $\hat{H}_{\text{ex-ph}}^{\text{o.d.}}$ are the diagonal and off-diagonal parts of the exciton-phonon coupling Hamiltonian, respectively,

$$\hat{H}_{\text{ex-ph}}^{\text{diag}} = -g\omega_0 \sum_n \hat{a}_n^\dagger \hat{a}_n (\hat{b}_n + \hat{b}_n^\dagger), \quad (4)$$

$$\begin{aligned} \hat{H}_{\text{ex-ph}}^{\text{o.d.}} = & \frac{1}{2} \phi \omega_0 \sum_{n,l} [\hat{a}_n^\dagger \hat{a}_{n+1} (\hat{b}_l + \hat{b}_l^\dagger) (\delta_{n+1,l} - \delta_{n,l}) \\ & + \hat{a}_n^\dagger \hat{a}_{n-1} (\hat{b}_l + \hat{b}_l^\dagger) (\delta_{n,l} - \delta_{n-1,l})]. \end{aligned} \quad (5)$$

Here g and ϕ are the dimensionless diagonal and off-diagonal exciton-phonon coupling constants, respectively.

Note that in Eq. (3), the exciton number operator $\hat{N}_{\text{ex}} \equiv \sum_n \hat{a}_n^\dagger \hat{a}_n$ commutes with the Hamiltonian $\hat{H}$, i.e., $[\hat{N}_{\text{ex}}, \hat{H}] = 0$. And in this paper, we confine our study to the one-exciton subspace. Thus, $\Omega \sum_n \hat{a}_n^\dagger \hat{a}_n$ equals to a constant operator and can be removed from Eq. (3), and the Hamiltonian $\hat{H}$ can be simplified as

$$\hat{H} = \hat{H}_{\text{ex}} + \hat{H}_{\text{ph}} + \hat{H}_{\text{ex-ph}}^{\text{diag}} + \hat{H}_{\text{ex-ph}}^{\text{o.d.}}, \quad (6)$$

where $\hat{H}_{\text{ph}}$, $\hat{H}_{\text{ex-ph}}^{\text{diag}}$, and $\hat{H}_{\text{ex-ph}}^{\text{o.d.}}$ have been given in Eqs. (2), (4), and (5), respectively, and $\hat{H}_{\text{ex}}$ is the simplified form of the exciton Hamiltonian:

$$\hat{H}_{\text{ex}} = -J \sum_n \hat{a}_n^\dagger (\hat{a}_{n+1} + \hat{a}_{n-1}). \quad (7)$$

The phonon frequency in Eqs. (2), (4), and (5) is assumed to be independent with the phonon momentum q . In the presence of phonon dispersion, Eqs. (2), (4), and (5) can be written in the momentum space as:

$$\hat{H}_{\text{ph}} = \sum_q \omega_q \hat{b}_q^\dagger \hat{b}_q, \quad (8)$$

$$\hat{H}_{\text{ex-ph}}^{\text{diag}} = -g \sum_{n,q} \omega_q \hat{a}_n^\dagger \hat{a}_n (e^{iqn} \hat{b}_q + e^{-iqn} \hat{b}_q^\dagger), \quad (9)$$

$$\begin{aligned} \hat{H}_{\text{ex-ph}}^{\text{o.d.}} = & \frac{1}{2} \phi \sum_{n,q} \omega_q \{ \hat{a}_n^\dagger \hat{a}_{n+1} [e^{iqn} (e^{iq} - 1) \hat{b}_q + \text{H.c.}] \\ & + \hat{a}_n^\dagger \hat{a}_{n-1} [e^{iqn} (1 - e^{-iq}) \hat{b}_q + \text{H.c.}] \}. \end{aligned} \quad (10)$$

Here H.c. stands for Hermitian conjugate, ω_q is the phonon frequency for momentum q , and $\hat{b}_q^\dagger$ ($\hat{b}_q$) is the creation (annihilation) operator of a phonon with momentum q

$$\hat{b}_q^\dagger = N^{-1/2} \sum_n e^{iqn} \hat{b}_n^\dagger, \quad \hat{b}_n^\dagger = N^{-1/2} \sum_q e^{-iqn} \hat{b}_q^\dagger \quad (11)$$

with

$$q = \frac{2\pi}{N} l, \quad \left(l = -\frac{N}{2} + 1, \dots, -1, 0, 1, \dots, \frac{N}{2} \right). \quad (12)$$

In this paper, we assume a linear dispersion phonon band

$$\omega_q = \omega_0 [1 + D(2|q|/\pi - 1)], \quad (13)$$

where D is a constant between 0 and 1, the bandwidth of the phonon frequency is $2D\omega_0$. We note that our model is capable to include multiple phonon branches with various dispersion relations, and each with its specific form of interactions with the exciton.

The time-dependent Schrödinger equation which governs the time evolution of the polaron state can be solved approximately by the Dirac-Frenkel variational principle in which the polaron wave function is approximated by a trial state (such as the Davydov D_1 or D_2 Ansatz), and the parameters specifying the trial state are obtained from a set of coupled differential equations mandated by the time-dependent variation.²⁶⁻³⁴ In this work, we adopt the D_2 Ansatz to probe the dynamics of the Holstein polaron with off-diagonal exciton-phonon coupling. The D_2 Ansatz, which is a simplification of the D_1 Ansatz, is defined in the real space as

$$\begin{aligned} |D_2(t)\rangle \equiv & \sum_n \psi_n(t) \hat{a}_n^\dagger |0\rangle_{\text{ex}} \\ & \times \exp \left\{ \sum_n [\lambda_n(t) \hat{b}_n^\dagger - \lambda_n^*(t) \hat{b}_n] \right\} |0\rangle_{\text{ph}}, \end{aligned} \quad (14)$$

where $\psi_n(t)$ and $\lambda_n(t)$ are the variational parameters representing the exciton amplitude and phonon displacement at the n th site, respectively. The D_2 Ansatz can also be defined in the

momentum space as

$$\begin{aligned} |D_2(t)\rangle \equiv & \sum_k \psi_k(t) \hat{a}_k^\dagger |0\rangle_{\text{ex}} \\ & \times \exp \left\{ \sum_q [\lambda_q(t) \hat{b}_q^\dagger - \lambda_q^*(t) \hat{b}_q] \right\} |0\rangle_{\text{ph}}, \end{aligned} \quad (15)$$

where $\hat{a}_k^\dagger$ ($\hat{a}_k$) is the creation (annihilation) operator of a exciton with momentum k

$$\hat{a}_k^\dagger = N^{-1/2} \sum_n e^{ikn} \hat{a}_n^\dagger, \quad \hat{a}_n^\dagger = N^{-1/2} \sum_k e^{-ikn} \hat{a}_k^\dagger, \quad (16)$$

Here $\psi_k(t)$ and $\lambda_q(t)$ are the variational parameters representing the exciton amplitude of momentum k and the phonon displacement of momentum q , respectively. The following Fourier transformation conventions are used

$$\psi_k = N^{-1/2} \sum_n e^{-ikn} \psi_n, \quad \psi_n = N^{-1/2} \sum_k e^{ikn} \psi_k \quad (17)$$

and

$$\lambda_q = N^{-1/2} \sum_n e^{-iqn} \lambda_n, \quad \lambda_n = N^{-1/2} \sum_q e^{iqn} \lambda_q. \quad (18)$$

In the actual numerical implementation, we use a crossover of Eqs. (14) and (15), i.e., $\psi_n(t)$ (the amplitude of exciton in real space) and $\lambda_q(t)$ (the amplitude of phonon in momentum space) are enlisted to specify the trial state

$$\begin{aligned} |D_2(t)\rangle \equiv & \sum_n \psi_n(t) \hat{a}_n^\dagger |0\rangle_{\text{ex}} \\ & \times \exp \left\{ \sum_q [\lambda_q(t) \hat{b}_q^\dagger - \lambda_q^*(t) \hat{b}_q] \right\} |0\rangle_{\text{ph}}. \end{aligned} \quad (19)$$

The equations of motion for the variational parameters $\psi_n(t)$ and $\lambda_q(t)$ can be derived by various methods. The approach we adopt in this paper is the Lagrangian formalism of the Dirac-Frenkel variation.^{35,39,40} For the D_2 Ansatz, the Lagrangian L is formulated as

$$\begin{aligned} L = & \langle D_2(t) | \frac{i\hbar}{2} \frac{\overleftrightarrow{\partial}}{\partial t} - \hat{H} | D_2(t) \rangle \\ = & \frac{i\hbar}{2} \left[\langle D_2(t) | \frac{\overrightarrow{\partial}}{\partial t} | D_2(t) \rangle - \langle D_2(t) | \frac{\overleftarrow{\partial}}{\partial t} | D_2(t) \rangle \right] \\ & - \langle D_2(t) | \hat{H} | D_2(t) \rangle. \end{aligned} \quad (20)$$

The Dirac-Frenkel variational principle will lead to equations of motion for $\psi_n(t)$ and $\lambda_q(t)$

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\psi}_n^*} \right) - \frac{\partial L}{\partial \psi_n^*} = 0, \quad \frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\lambda}_q^*} \right) - \frac{\partial L}{\partial \lambda_q^*} = 0. \quad (21)$$

Details on derivation of the time evolution equations of the D_2 Ansatz for an extended Holstein Hamiltonian with off-diagonal coupling are given in Appendix.

FIG. 1. Time evolution of the D_2 variation parameters in real space for $D = 0.5$, $J = 1.0$, $g = 1/8$, and $\phi = 0$. (a) A contour plot of the exciton amplitude $|\psi_n(t)|$; (b) a contour plot of the phonon displacement $|\lambda_n(t)|$.

III. RESULTS AND DISCUSSIONS

A. Diagonal cases

Figures 1–3 show the time evolution of the D_2 variational parameters, namely, the exciton amplitude $\psi_n(t)$ and phonon displacement $\lambda_n(t)$, for the three cases with only diagonal coupling ($\phi = 0$). The first two cases have an identical phonon bandwidth of ω_0 , and the third case has a much wider bandwidth of $1.8\omega_0$. The exciton transfer integral is fixed at $J = 1.0$ for all three cases. The system we consider is a molecular ring of 32 identical sites. The initial state of the system is prepared to have one exciton at site $n = 0$, i.e., $\psi_n(t = 0) = \delta_{n,0}$ (see the center black dots at $t = 0$ in Figs. 1(a), 2(a), and 3(a)), and there are no phonon displacements on the entire ring at $t = 0$, i.e., $\lambda_n(t = 0) = 0$ for all n . The incident exciton at $n = 0$ generates wave fronts which propagate in both directions until the fronts meet on the other side of the ring, analogous to a circular, propagating wave front which expands in radius with time after a calm water surface is disturbed at a center point.

Comparing Figs. 1 and 2, one finds that the two figures are very similar to each other except that, as indicated by the color-bar scales in Figs. 1(b) and 2(b), the phonon displacement $\lambda_n(t)$ in Fig. 2(b) is about $\sqrt{2}$ times of that in Fig. 1(b). This can be explained by the fact that the diagonal exciton-phonon interaction $g^2\omega_0$ is negligible compared to the exci-

FIG. 2. Time evolution of the D_2 variation parameters in real space for $D = 0.5$, $J = 1.0$, $g = 0.1768$, and $\phi = 0$. (a) A contour plot of the exciton amplitude $|\psi_n(t)|$; (b) a contour plot of the phonon displacement $|\lambda_n(t)|$.

ton transfer J . As such, the two cases shown in Figs. 1 and 2 belong to the weak-coupling regime with the exciton amplitude only slightly disturbed by the phonon distortions it causes, which explains the resemblance between the two panels. While the parameter sets of $(D, J, \phi) = (0.5, 1.0, 0)$ are the same for Figs. 1 and 2, the g value in Fig. 2 ($\sqrt{2}/8$) is $\sqrt{2}$ times of that in Fig. 1 ($1/8$). In the absence of off-diagonal coupling ($\phi = 0$), the equation of motion for the phonon amplitude $\lambda_q(t)$, Eq. (A7), is reduced to

$$-i\dot{\lambda}_q(t) = g\omega_q \sum_n |\psi_n(t)|^2 e^{-iqn} - \omega_q \lambda_q(t). \quad (22)$$

Initially, the phonon amplitudes are small compared with the exciton counterparts, given the same initial condition $\lambda_n(t = 0) = 0$ for all n . With very similar distributions of $|\psi_n(t)|$ as shown in Figs. 1(a) and 2(a), it is plausible that, according to Eq. (22), $\dot{\lambda}_q(t)$, $\lambda_q(t)$, and therefore $\lambda_n(t)$, scale approximately with g . In these two weak-coupling cases, the exciton wave packets travel much faster than the sound speed which is determined by the phonon bandwidth D . The fast-moving exciton amplitude also generates phonon distortions (blue-colored) along its trail way ahead of the arrival of an independent phonon wave packet (yellow-colored and V-shaped) originated at the site of exciton creation.

Figures 1(a) and 2(a) capture the collisional events of two exciton wave packets traveling in opposite directions. The left-moving and right-moving wave packets of the exciton

FIG. 3. Time evolution of the D₂ variation parameters in real space for $D = 0.9$, $J = 0.6$, $g = 0.1768$, and $\phi = 0$. (a) A contour plot of the exciton amplitude $|\psi_n(t)|$; (b) a contour plot of the phonon displacement $|\lambda_n(t)|$.

depart from the site of creation, i.e., the point (0, 0) in Figs. 1(a) and 2(a), with the same speed and make a quick rendezvous at the opposite site of the ring ($n = 16$), causing a collisional event. The collision brings the recombined exciton density to a sufficiently high level, and triggers another pair of localized phonon wave packets as clearly demonstrated in Figs. 1(b) and 2(b).

The group velocity of the exciton wave packets, which can be expressed as $\partial E_{\text{ex}}(k)/\partial k$ with $E_{\text{ex}}(k)$ the bare exciton band, is proportional to the exciton transfer integral J according to Eq. (7). This can be readily verified by comparing Fig. 3(a) with Figs. 1(a) and 2(a). Unlike the reduced exciton movements in Fig. 3(a) ($J = 0.6$), the phonons gain much greater mobility due to an enlarged phonon bandwidth ($D = 0.9$). Compared to Figs. 1 and 2, the speed of localized phonon wave packets in Fig. 3 is therefore much closer to that of the exciton propagation. As a result, phonon distortions are found mostly along the trail of the phonon wave packets traveling at a speed of $v_q = \partial \omega_q / \partial q$. Near the same phonon trail which starts at point (0,0), the site of exciton creation, substantial exciton amplitudes appear in Fig. 3(a) due to diagonal exciton-phonon coupling despite the considerable difference in speed between the exciton and the phonons. This demonstrates clearly that the exciton-phonon coupling is a two-way street, and between the exciton and the phonons, either entity can be the cause or the consequence of the other.

B. Off-diagonal cases

In this subsection, time evolution of the Holstein polaron in the presence of off-diagonal coupling is investigated for a few cases of zero phonon bandwidth and zero or narrow exciton bandwidth. The off-diagonal coupling strength is set at $\phi = 1$, and its diagonal counterpart zero, in order to demonstrate the effect of the off-diagonal coupling on polaron dynamics. From Eq. (10), the off-diagonal coupling exists only when the exciton amplitudes are nonzero on at least two adjacent sites. For simplicity, in all the six examples of simulation in this subsection, we assume the simplest initial state of the system that can include the off-diagonal coupling: $\psi_0(t=0) = \psi_1(t=0) = 1/\sqrt{2}$, $\psi_{n \neq 0,1}(t=0) = 0$, and $\lambda_n(t=0) = 0$ for all n .

Due to the particular choice of g , the diagonal exciton-phonon coupling Hamiltonian $\hat{H}_{\text{ex-ph}}^{\text{diag}}$ vanishes. And if J is zero or very small, the exciton Hamiltonian $\hat{H}_{\text{ex}}$, Eq. (7), is negligible. Thus, there are only two dominant, competing terms in the total system Hamiltonian Eq. (6), namely, the phonon Hamiltonian $\hat{H}_{\text{ph}}$, Eq. (8), and the off-diagonal exciton-phonon coupling Hamiltonian $\hat{H}_{\text{ex-ph}}^{\text{o.d.}}$, Eq. (10). Three values of transfer integral J are taken, $J = 0$ and $J = \pm 0.1$. Let us first consider the case of zero exciton bandwidth. Albeit an agent of excitonic localization, the off-diagonal coupling turns itself into the only transport mechanism in the absence of direct exciton transfer integral. Time evolution of the exciton amplitude $|\psi_n(t)|$ and phonon displacement $|\lambda_n(t)|$ are displayed in Fig. 4. At $t = 0$, there are no phonon displacements on the molecular ring, and the exciton amplitudes are evenly created on a pair of adjacent sites $n = 0$ and $n = 1$. Due to the existence of the off-diagonal coupling, the lattice deformation soon gains at the expense of the exciton energy. As shown in Fig. 4(b), the phonon displacements $|\lambda_n(t)|$ in the vicinity of $n = 0$ and $n = 1$ increase from zero and reach their maximum values at $t = \pi/\omega_0$, then decrease to zero at $t = 2\pi/\omega_0$. And in the second cycle of period $2\pi/\omega_0$, $|\lambda_n(t)|$ increase from zero again and reach their second maximum at $t = 3\pi/\omega_0$. Delocalization of the exciton also benefits from the presence of off-diagonal coupling as the exciton amplitude is substantially expanded from the sites of creation, a phenomenon known in the literature as the phonon-assisted transport.

As shown in Fig. 4, the off-diagonal coupling ϕ supports excitonic transfer in the absence of the direct transfer integral ($J = 0$). At $t = 0$, the exciton is created evenly on sites $n = 0$ and $n = 1$, i.e., $\psi_n = (\delta_{n,0} + \delta_{n,1})/\sqrt{2}$ and there are no initial phonon displacements over the entire chain. During the first phonon period ($t < t_0 = 2\pi/\omega_0$), the exciton is mostly localized around the site of creation. Back-and-forth exciton movements are detected in the second period ($t_0 < t < 2t_0$) and after. Similar behavior is also found for the phonon displacement $|\lambda_n(t)|$ which is shown in the lower panel of Fig. 4. As a consequence of the off-diagonal coupling ϕ , the exciton amplitude spreads to sites other than the initial location of creation sites despite the absence of a direct J .

Since exciton transport is usually induced by a direct transfer integral J , it is beneficial to quantify individual contributions from the transfer integral and the off-diagonal

FIG. 4. Time evolution of the D₂ variation parameters in real space for $D = 0$, $J = 0$, $g = 0$, and $\phi = 1$. (a) A contour plot of the exciton amplitude $|\psi_n(t)|$; (b) a contour plot of the phonon displacement $|\lambda_n(t)|$.

coupling when both mechanisms are present. Leaving the off-diagonal coupling strength unchanged (i.e., $\phi = 1$), time evolution of the variational parameters is displayed in Figs. 5 and 6 for $J = -0.1$ and $J = 0.1$, respectively. Similar to the case of $J = 0$, the exciton amplitude for $J = -0.1$ is confined to the sites of creation initially. Thanks to the combined effect of exciton transfer integral J and off-diagonal coupling ϕ , after $t = 2t_0$ the exciton amplitude in Fig. 5 starts to delocalize more rapidly than that in Fig. 4, a trend that is also reflected in the corresponding phonon displacement. However, the contribution of transfer integral $J = 0.1$ is in contrast to that of $J = -0.1$, and in comparison with Fig. 4, both the exciton amplitude and the phonon displacement in Fig. 6 prefer to be localized next to the sites of exciton creation. This behavior will become clear to us when the energy band near the zone center is analyzed by the Toyozawa *Ansatz*.

The Toyozawa *Ansatz*, which can be viewed as a translationally invariant rendering of the Davydov D₂ *Ansatz*, is borrowed to calculate the ground-state energy band. Since the polaron crystal momentum commutes with the Hamiltonian, the Toyozawa *Ansatz* can be taken as the lowest energy polaron state $|K\rangle$ with momentum K

$$|K\rangle = N^{-1} \sum_n e^{iKn} |\Lambda_n^K\rangle \sum_m \psi_{m-n}^K a_m^\dagger |0\rangle_{\text{ex}}. \quad (23)$$

Here $|\Lambda_n^K\rangle$ is the phonon wave function centered at site n containing a coherent state on each site n_2 with a displacement

FIG. 5. Time evolution of the D₂ variation parameters in real space for $D = 0$, $J = -0.1$, $g = 0$, and $\phi = 1$. (a) A contour plot of the exciton amplitude $|\psi_n(t)|$; (b) a contour plot of the phonon displacement $|\lambda_n(t)|$.

$$\lambda_{n_2-n}^K:$$

$$|\Lambda_n^K\rangle = \exp \left[- \sum_{n_2} (\lambda_{n_2-n}^K b_{n_2}^\dagger - \lambda_{n_2-n}^{K*} b_{n_2}) \right] |0\rangle_{\text{ph}}. \quad (24)$$

Here $|\Lambda_n^K\rangle$ represents a lattice distortion forming a potential well centered at n and trapping the exciton with an amplitude distribution of ψ_l^K , and it 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 for each momentum K , and the polaron energy bands are displayed in the upper two panels of Fig. 7 for a number of parameter sets. In the absence of the transfer integral, the minima of the band are found at $K = \pm\pi/2$, and depending on the sign of the transfer integral J , the minima can go both ways: a positive (negative) J will move the minima toward (away from) the zone center. Another outcome of the polaron band study is that the polaron effective mass at the zone center differs for the three values of J . The case of $J = -0.1$ (solid line), for example, has the smallest effective mass among the three, and therefore, the excitonic polaron is the most mobile. This explains those features of more rapid delocalization in polaron dynamics as mentioned earlier in Fig. 5. On the other hand, addition of $J = 0.1$ increases the polaron effective mass at $K = 0$, and consequently, the polaron becomes less mobile.

The effect of the off-diagonal coupling ϕ is shown in the middle panel of Fig. 7. In the absence of the transfer

FIG. 6. Time evolution of the D_2 variation parameters in real space for $D = 0$, $J = 0.1$, $g = 0$, and $\phi = 1$. (a) A contour plot of the exciton amplitude $|\psi_n(t)|$; (b) a contour plot of the phonon displacement $|\lambda_n(t)|$.

integral J and diagonal coupling g , the polaron energy is found to decrease with a nonmonotonically varying band width, and the polaron band is found to have a maximum width at approximately $\phi_c = \sqrt{2}$. Width of the polaron energy band is displayed in the lower panel of Fig. 7(c) as a function of ϕ . It is found that width-vs- ϕ relation $B(\phi)$ can be fitted nicely with

$$B(\phi) = 0.7324\phi^2 e^{-\frac{1}{2}\phi^2} \quad (25)$$

As mentioned earlier, off diagonal coupling can be simultaneously an agent for exciton transport and localization. For large coupling strengths $\phi > \phi_c$, the localization effect of ϕ takes over as the dominant mechanism in the transport-localization duality, and the difference between diagonal and off-diagonal coupling in reducing the polaron bandwidth gradually diminishes with further increase in ϕ .

If a finite phonon bandwidth is allowed, other interesting features in the exciton-phonon dynamics, such as increased polaron mobility, can be discovered from our study. It is clearly seen from Fig. 8(a) that an increase of the phonon bandwidth leads to a reduced polaron effective mass at the zone center and an overall lowering of the polaron band, in agreement with the findings in Ref. 41. As shown in Fig. 8(a), calculated polaron bandwidths increase almost linearly with the phonon bandwidth D .

FIG. 7. Polaron energy bands and bandwidths of a one-dimensional molecular ring calculated with the Toyozawa Ansatz. The diagonal coupling strength g and the phonon bandwidth D are both set to zero. Other control parameters for the upper and middle panels are: (a) $J = -0.1$, $\phi = 1.0$ (solid line); $J = 0.0$, $\phi = 1.0$ (dashed line); $J = 0.1$, $\phi = 1.0$ (dashed-dotted line); (b) $J = 0.0$, $\phi = 0.6$ (solid line); $J = 0.0$, $\phi = 1.4$ (dashed line); $J = 0.0$, $\phi = 2.0$ (dashed-dotted line). Width of the polaron energy band in the absence of J and g is displayed in the lower panel (c) as a function of ϕ .

C. Validity of the trial state

Questions on the validity of the Davydov Ansatz and their translationally invariant variants have been around for decades.^{28,42} To our knowledge, this work constitutes the first instance to use a time-dependent trial state to simulate the dynamics of an off-diagonally coupled exciton-phonon com-

FIG. 8. Polaron energy bands and bandwidths of a one-dimensional molecular ring calculated for various phonon dispersions using the Toyozawa *Ansatz*. Parameters chosen are $J = 0.1$, $g = 1/8$, $\phi = 1$. In the upper panel (a), from top downward, $D = 0.0, 0.1, 0.5$, and 1.0 . In the lower panel (b), calculated polaron bandwidths (diamonds, with the solid line as its fitting) are displayed as a function of D . The dotted line shows the slope at $D = 0$ as a guide to the eye. The polaron bandwidth is found to increase almost linearly with the phonon bandwidth.

plex, therefore making it essential to check the validity of the *Ansatz*. Since a trial wave function $|\varphi(t)\rangle$ does not strictly obey the Schrödinger equation, a deviation vector $|\delta(t)\rangle$ can be defined to quantify the accuracy of $|\varphi(t)\rangle$ as follows:

$$|\delta(t)\rangle \equiv i \frac{\partial}{\partial t} |\varphi(t)\rangle - H |\varphi(t)\rangle. \quad (26)$$

The amplitude of the deviation vector $|\delta(t)\rangle$, which has the dimension of energy, serves as a good indicator of how faithfully the trial state follows the Schrödinger equation:

$$\Delta(t) \equiv \sqrt{\langle \delta(t) | \delta(t) \rangle}. \quad (27)$$

Figures 9(a)–9(d) display system energies E_{ph} , E_{ex-ph} , and E_{tot} and the deviation-vector amplitude $\Delta(t)$ for four parameter sets labeled by (D, J, g, ϕ) . Since the Hamiltonian is time-independent, the total energy of the system E_{tot} , shown in Fig. 9 as the dashed-dotted line, is a conserved quantity during the time evolution. Meanwhile, the amplitude of deviation $\Delta(t)$ is mostly negligible compared with other characteristic energy components (e.g., E_{ph} and E_{ex-ph}) of the system, infer-

FIG. 9. System energies, E_{ph} (solid), E_{ex-ph} (dashed), and E_{tot} (dotted), and amplitude of the deviation vector $\Delta(t)$ (dashed-dotted) of a 32-site molecular ring calculated by the D_2 *Ansatz*. Parameters chosen are, from top down: (a) $D = 0$, $J = 0$, $g = 0$, $\phi = 0.4$; (b) $D = 0$, $J = 0$, $g = 0$, $\phi = 1$; (c) $D = 0$, $J = -0.1$, $g = 0$, $\phi = 1$; (d) $D = 0$, $J = 0.1$, $g = 0$, $\phi = 1$.

ring a respectable accuracy of the D_2 *Ansatz* in the presence of diagonal and off-diagonal coupling.

Moreover, a global measure of the D_2 *Ansatz* accuracy may be revealed by defining the relative deviation⁴²

$$\sigma \equiv \frac{\max\{\Delta(t)\}}{\text{avg}\{E_{ph(t)}\}}, \quad t \in [0, t_{\max}], \quad (28)$$

where $t_{\max}$ is the duration of dynamics simulation. Figures 10(a)–10(f) display the relative deviation σ of the D_2 *Ansatz* as a function of the diagonal coupling strength g and off-diagonal coupling strength ϕ for a number of exciton transfer integral J . Influence of the excitonic initial state on the dynamics is taken into account here. Two types of initial states are used in Fig. 10, a single-site occupied initial state (left panels), and one with two sites evenly occupied (right panels). Smaller values of the relative deviation σ are found for the initial state with two sites evenly occupied (right panels). Of course, other initial exciton states, such as optically allowed exciton states⁴³ and states with spatially Gaussian distributions, can be explored to fit specific circumstances. For large values of diagonal and off-diagonal coupling strengths, the D_2 *Ansatz* deviates little from the exact solutions for the time-dependent Schrödinger equation of the

FIG. 10. Relative deviation σ of the D_2 Ansatz as a function of g and ϕ . The phonon bandwidth chosen is $D = 0.5$. For (a) and (d), $J = 0.1$; for (b) and (e), $J = 0.3$; for (c) and (f), $J = 0.5$. Relative deviation σ is calculated with $t_{\max} = 10(2\pi/\omega_0)$. For (a), (b), and (c), the exciton is created at $t = 0$ on site $n = 0$, i.e., $\psi_n = \delta_{n,0}$, and for (d), (e), and (f), it is created on sites $n = 0$ and $n = 1$, i.e., $\psi_n = (\delta_{n,0} + \delta_{n,1})/\sqrt{2}$. Initially, the phonons are their vacuum state.

Holstein system, thereby confirming the validity of our time-dependent variational approach. However, more sophisticated trial states, similar to the aforementioned Davydov D_1 Ansatz, are needed in the regime of large transfer integrals and weak diagonal and off-diagonal couplings.

IV. CONCLUSION

In this paper we simulate polaronic dynamics in a one-dimensional molecular chain following the Dirac-Frenkel time-dependent variational approach. A versatile trial state by the name of Davydov D_2 Ansatz has been adopted to capture the exciton-phonon dynamics. Special attention is paid to the time evolution of the variational parameters that characterize the propagation of the exciton and accompanying phonons from an initial location of exciton creation to the entire aggregate. Validity of our time-dependent variational approach has been carefully looked into by quantifying, in real time, how closely the trial state follows the Schrödinger equation. The D_2 Ansatz is shown to be rather efficient for computation, and extending the approach to higher spatial dimensions would be a feasible generalization. For most of the parameter regimes, the D_2 Ansatz is found to be a reasonable approximation with respectable accuracy in describing the dynamics of the Holstein polaron. Of course, there is plenty room for improvements in the parameter regime with large transfer integrals and weak diagonal and off-diagonal

couplings. In the absence of diagonal coupling, the sign of the transfer integral determines whether the polaron effective mass is increased or decreased due to the antisymmetric nature of the off-diagonal coupling. The role of the off-diagonal coupling switches from being an agent of transport at moderate coupling strengths to that of localization at large coupling strengths. Increasing the phonon bandwidth would lead to a reduced polaron effective mass at the zone center and an overall lowering of the polaron band. Our findings can be applied to understand optical and transport processes in materials where off-diagonal exciton-phonon coupling is important.^{13,44-46}

The trial state used in this work is a localized variational wave function, and it is interesting to work out detailed dynamics of its translationally invariant counterpart, the Toyozawa Ansatz, and its more sophisticated variants. As off-diagonal coupling is believed to be one of the mechanisms responsible for the highly efficient energy transport in light-harvesting systems in photosynthesis, the method developed here can be borrowed, for example, to study exciton transfers in purple bacteria.⁴⁷ Our approach here can be also readily extended to include other forms of exciton-phonon interactions, such as symmetric off-diagonal coupling,^{12,48} and even higher-order couplings. Work in this direction is now in progress.

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APPENDIX: TIME EVOLUTION EQUATIONS OF THE D_2 TRIAL STATE

From the definition of D_2 Ansatz, Eq. (19), one obtains

$$\begin{aligned} \langle D_2(t) | \frac{\partial}{\partial t} | D_2(t) \rangle - \langle D_2(t) | \frac{\partial}{\partial t} | D_2(t) \rangle \\ = \sum_n [\psi_n^*(t) \dot{\psi}_n(t) - \dot{\psi}_n^*(t) \psi_n(t)] \\ - \sum_n |\psi_n(t)|^2 \sum_q [\lambda_q^*(t) \dot{\lambda}_q(t) - \dot{\lambda}_q^*(t) \lambda_q(t)], \quad (A1) \end{aligned}$$

and

$$\begin{aligned} \langle D_2(t) | \hat{H} | D_2(t) \rangle \\ = \langle D_2(t) | \hat{H}_{\text{ex}} | D_2(t) \rangle + \langle D_2(t) | \hat{H}_{\text{ph}} | D_2(t) \rangle \\ + \langle D_2(t) | \hat{H}_{\text{ex-ph}}^{\text{diag}} | D_2(t) \rangle + \langle D_2(t) | \hat{H}_{\text{ex-ph}}^{\text{o.d.}} | D_2(t) \rangle, \quad (A2) \end{aligned}$$

with

$$\langle D_2(t) | \hat{H}_{\text{ex}} | D_2(t) \rangle = -J \sum_n \psi_n^*(t) [\psi_{n+1}(t) + \psi_{n-1}(t)], \quad (A3)$$

$$\langle D_2(t) | \hat{H}_{\text{ph}} | D_2(t) \rangle = \sum_n |\psi_n(t)|^2 \sum_q \omega_q |\lambda_q(t)|^2, \quad (A4)$$

$$\begin{aligned} \langle D_2(t) | \hat{H}_{\text{ex-ph}}^{\text{diag}} | D_2(t) \rangle \\ = -g \sum_n |\psi_n(t)|^2 \sum_q \omega_q [\lambda_q(t) e^{iqn} + \lambda_q^*(t) e^{-iqn}], \end{aligned} \quad (\text{A5})$$

and

$$\begin{aligned} \langle D_2(t) | \hat{H}_{\text{ex-ph}}^{\text{o.d.}} | D_2(t) \rangle \\ = \frac{1}{2} \sum_n \psi_n^*(t) \psi_{n+1}(t) \sum_q \phi \omega_q (1 - e^{-iq}) \\ [\lambda_q(t) e^{iq(n+1)} - \lambda_q^*(t) e^{-iqn}] \\ + \frac{1}{2} \sum_n \psi_n^*(t) \psi_{n-1}(t) \sum_q \phi \omega_q (1 - e^{iq}) \\ [\lambda_q^*(t) e^{-iqn} - \lambda_q(t) e^{iq(n-1)}]. \end{aligned} \quad (\text{A6})$$

Equations of motion for $\lambda_q(t)$ and $\psi_n(t)$ are then obtained by substituting Eqs. (A1)–(A6) into Eqs. (20) and (21),

$$\begin{aligned} -i\dot{\lambda}_q(t) = \frac{1}{2} \phi \omega_q (1 - e^{-iq}) \sum_n [\psi_n^*(t) \psi_{n+1}(t) + \text{c.c.}] e^{-iqn} \\ + \omega_q [g \sum_n |\psi_n(t)|^2 e^{-iqn} - \lambda_q(t)] \end{aligned} \quad (\text{A7})$$

and

$$\begin{aligned} -i\dot{\psi}_n(t) = \psi_{n+1}(t) \left\{ J - \frac{1}{2} \sum_q \phi \omega_q (1 - e^{-iq}) \right. \\ \left. [\lambda_q(t) e^{iq(n+1)} - \lambda_q^*(t) e^{-iqn}] \right\} \\ + \psi_{n-1}(t) \left\{ J - \frac{1}{2} \sum_q \phi \omega_q (1 - e^{iq}) \right. \\ \left. [\lambda_q^*(t) e^{-iqn} - \lambda_q(t) e^{iq(n-1)}] \right\} \\ - \psi_n(t) \left\{ \sum_q \omega_q |\lambda_q(t)|^2 \right. \\ - g \sum_q \omega_q [\lambda_q(t) e^{iqn} + \lambda_q^*(t) e^{-iqn}] \\ \left. - \frac{i}{2} \sum_q [\dot{\lambda}_q(t) \lambda_q^*(t) - \dot{\lambda}_q^*(t) \lambda_q(t)] \right\} \end{aligned} \quad (\text{A8})$$

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