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Finite temperature dynamics of a Holstein polaron: The thermo-field dynamics approach

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Combining the multiple Davydov D_2 Ansatz with the method of thermo-field dynamics, we study finite temperature dynamics of a Holstein polaron on a lattice. It has been demonstrated, using the hierarchy equations of motion method as a benchmark, that our approach provides an efficient, robust description of finite temperature dynamics of the Holstein polaron in the simultaneous presence of diagonal and off-diagonal exciton-phonon coupling. The method of thermo-field dynamics handles temperature effects in the Hilbert space with key numerical advantages over other treatments of finite-temperature dynamics based on quantum master equations in the Liouville space or wave function propagation with Monte Carlo importance sampling. While for weak to moderate diagonal coupling temperature increases inhibit polaron mobility, it is found that off-diagonal coupling induces phonon-assisted transport that dominates at high temperatures. Results on the mean square displacements show that band-like transport features dominate the diagonal coupling cases, and there exists a crossover from band-like to hopping transport with increasing temperature when including off-diagonal coupling. As a proof of concept, our theory provides a unified treatment of coherent and incoherent transport in molecular crystals and is applicable to any temperature. *Published by AIP Publishing.*
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I. INTRODUCTION

Thanks to their promising potentials in cost reduction, functionalization versatility, thin film flexibility, and processability, organic solar cells (OSCs) based on π -conjugated polymers are highly regarded among next-generation renewable energy technologies.^{1–4} However, OSCs are yet to achieve the photocurrent efficiencies of their inorganic counterparts, thereby limiting their large-scale commercial applications. One hotly debated issue is the paradoxical observations of sometimes delocalized “band-like” transport but other times thermalized hopping by strongly localized charge carriers.⁵ A consensus has yet to emerge on fundamental mechanisms of charge transport in organic semiconductors despite the fact that an in-depth understanding of these mechanisms will immensely facilitate design of solar-to-electronic energy conversion devices with high efficiency and robustness.

Polaronic self-trapping was first predicted by Landau in the 1930s, but theoretical study of charge transport in organic semiconductors did not gather steam until the pioneering work of Holstein, who introduced the one-dimensional (1D) Holstein molecular crystal model⁶ to account for exciton-phonon dynamics in molecular crystals. Among various factors that affect electron-phonon interplay in organic semiconductors, electronic transfer integrals and electron-phonon coupling strengths are key parameters that determine charge transport mechanisms. While Holstein’s theory of small polarons can

qualitatively explain the experimental findings of band narrowing as well as the crossover from band-like to hopping transport with increasing temperature, it is perturbative with respect to the electronic bandwidth and limited to the case of diagonal electron-phonon coupling. A variety of studies have revealed that taking into account the simultaneous presence of diagonal and off-diagonal coupling seems essential to characterize charge transport mechanisms in organic semiconductors.^{7–12} Early treatments of off-diagonal coupling by Munn and Silbey^{8,9} suggest that off-diagonal coupling increases the polaron binding energy and may introduce new minima and bandwidth broadening to the polaron energy band.¹⁰ A microscopic theory based on the Holstein-Peierls-type Hamiltonian^{13,14} claims to reproduce transport properties in naphthalene using parameters obtained from *ab initio* calculations. Recently, mixed quantum-classical non-adiabatic dynamics was proposed to explain temperature-dependent charge transport properties of organic semiconductors.¹⁵

Because of the enormous size of the Hilbert space of an electron-phonon system, it is a non-trivial task to accurately treat polaron dynamics at finite temperatures in the presence of diagonal and off-diagonal coupling. Methods treating finite-temperature dynamics can be mainly classified into two categories: one uses the quantum master equation (QME) method and provides a reduced description by tracing out bath degrees of freedom (DOFs) and the other is the wave function method that propagates the wave function from different initial conditions with bath modes sampled according to a certain statistical distribution. Typical examples of QME methods include the hierarchical equations of motion (HEOM)^{16–18} and the quasi-adiabatic path integral (QUAPI).¹⁹ However,

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it is well known that HEOM and QUAPI methods become numerically very expensive at low temperatures, and they yield no information on phonon-manifold dynamics. Furthermore, the HEOM approach is mainly restricted to systems with certain forms of phonon spectral densities despite the fact that several extensions have been formulated to alleviate this shortcoming.^{20–22} For the wave function propagation methods, the multi-configuration time-dependent Hartree (MCTDH) method and its multilayer variants,^{23–26} and most recently for the Holstein polaron and the spin-boson model, the hierarchy of time-dependent variational wave functions of varying sophistication by the names of the Davydov D_1 , $\tilde{D}$, and D_2 *Ansätze*,^{27–30} are among the most successful examples of accurate ultra-low temperature dynamics. Due to a high demand of statistical samplings, wave function propagation methods such as MCTDH can be computationally prohibitive at high temperatures.³¹ An alternative to circumvent this problem is the method of thermo-field dynamics (TFD),³² a finite temperature representation of quantum mechanics, which employs temperature-dependent “vacuum” expectation values to treat statistical averages of observables. Borrelli and Gelin are the first to develop the TFD theory for excitonic systems with applications made to a spin-boson problem.³³ It is highly promising to combine TFD with basis set methods to provide an accurate description of polaron dynamics at any temperature.

Previously, by using the Dirac-Frenkel time-dependent variational principle, dynamics of the Holstein polaron have been extensively studied with the hierarchy of time-dependent Davydov trial states (the so-called D_1 and D_2 *Ansätze* with the latter as a simplified version of the former) that can be traced to the Davydov soliton. Due to the construct of the coherent state, both D_1 and D_2 *Ansätze* are well suitable to describe the polaron dynamics for strong exciton-phonon coupling cases. Recently, a multitude of the Davydov trial states, i.e., a superposition of the D_1 or the D_2 *Ansatz*, referred to as the “multi- D_1 ” or “multi- D_2 ” *Ansatz*, have been developed to treat polaron dynamics at zero temperature, and its validity has been adequately demonstrated.^{34,35} The multiple Davydov *Ansätze* provide an efficient, yet accurate, tool to characterize the dynamics of coupled electron-boson systems for broad parameter regimes of transfer integrals and electron-phonon coupling strengths. Moreover, the multiple Davydov *Ansätze* (also termed the multi-polaron *Ansätze* for a multiplicity of two) have been applied to study the ground-state properties of the dissipative two-level system—the spin boson model.^{36–38} However, how to extend the description by multi- D_1 /(D_2) *Ansätze* to finite temperatures remains an issue to be addressed. In this work, a novel description of finite-temperature polaron dynamics is proposed by seamlessly integrating the multi- D_2 *Ansatz* into the TFD framework.

The rest of this paper is organized as follows. The TFD theory and its application to Holstein polaron dynamics by using the multi- D_2 *Ansatz* are elaborated in Sec. II. In Sec. III, we compare simulation results with those calculated by the HEOM and discuss the temperature effect on dynamic properties of the Holstein polaron. Conclusions are drawn in Sec. IV.

II. METHODOLOGY

A. Thermo-field dynamics

The TFD method is a promising finite temperature description of many-body quantum dynamics, but its impact has been largely limited to fields of theoretical physics.^{39–43} The basic idea of the TFD is to express the statistical average of any physical quantity Q in terms of a “thermal vacuum state” $|O(\beta)\rangle$,^{32,44,45}

$$\langle Q \rangle = Z^{-1}(\beta) \text{Tr}\{Q e^{-\beta H}\} = \langle O(\beta) | Q | O(\beta) \rangle, \quad (1)$$

where $Z(\beta) = \text{Tre}^{-\beta H}$ is the partition function of the relevant quantum system described by the Hamiltonian H , and $\beta = 1/K_B T$. Here, $|O(\beta)\rangle$ is the temperature-dependent “vacuum” state, which is defined as³²

$$\begin{aligned} |O(\beta)\rangle &= Z(\beta)^{-1/2} \sum_k e^{-\beta E_k/2} |k, \tilde{k}\rangle \\ &= Z(\beta)^{-1/2} e^{-\frac{1}{2}\beta H} |\mathbf{I}\rangle; |\mathbf{I}\rangle = \sum_k |k, \tilde{k}\rangle, \end{aligned} \quad (2)$$

where $|k\rangle$ is the eigenstate of the Hamiltonian H with eigenvalue E_k , and $|\tilde{k}\rangle$ is the eigenstate of the corresponding fictitious Hamiltonian $\tilde{H}$, which is defined in the tilde Hilbert space and can be derived from the original Hamiltonian H using some mapping.^{32,45,46}

Following Suzuki,⁴⁶ the time evolution of a system described by the Hamiltonian H at finite temperatures follows the TFD Schrödinger equation with a modified Hamiltonian $\hat{H}(\hat{H} = H - \tilde{H})$,

$$i \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle, \quad (3)$$

where we have defined a time-dependent state $|\psi(t)\rangle = \rho(t)^{1/2} |I\rangle$, with $\rho(t)$ denoting the density matrix of the relevant quantum system H . Finally, the expectation value of any operator Q acting in the relevant system Hilbert space $\{|k\rangle\}$ can be evaluated as

$$\langle Q(t) \rangle = \langle \psi(t) | Q | \psi(t) \rangle = \text{Tr}\{\rho(t) Q\}. \quad (4)$$

The evaluation of $\langle Q(t) \rangle$ using the temperature-dependent TFD wave function $\psi(t)$ and that using the corresponding density matrix $\rho(t)$ is equivalent.

The initial state for the system at thermal equilibrium in the TFD framework can be written as

$$|\psi(0)\rangle = \rho(0)^{1/2} |\mathbf{I}\rangle = Z(\beta)^{-1/2} e^{-\frac{1}{2}\beta H} |\mathbf{I}\rangle. \quad (5)$$

For a typical molecular system where the electronic energy gap is much larger than the vibrational energies, we can safely assume that the system resides in the electronic ground state, $|g\rangle$. The initial density matrix under this approximation can be written as

$$\rho(0) = Z(\beta)^{-1} e^{-\beta H} \approx |g\rangle \langle g| \rho_{\text{ph}}, \quad (6)$$

where ρ_{ph} is the density matrix of the bath DOFs usually described by a collection of harmonic oscillators,

$$\rho_{\text{ph}} = Z_{\text{ph}}(\beta)^{-1} e^{-\beta H_{\text{ph}}} \quad (7)$$

with

$$H_{\text{ph}} = \sum_q \omega_q b_q^\dagger b_q, \quad (8)$$

where $b_q^\dagger(b_q)$ is the boson creation (annihilation) operator of the q th mode with frequency ω_q . For a process of photon excitation, the system is prepared in an electronic excited state $|e\rangle = X^\dagger |g\rangle$, where $X^\dagger$ is the transition dipole operator that couples the electronic ground state $|g\rangle$ with the electronic excited state $|e\rangle$. Finally, the initial TFD wave function can be defined as

$$|\psi(0)\rangle = |e\rangle |\tilde{e}\rangle \rho_{\text{ph}}^{1/2} |\mathbf{I}\rangle = |\mathbf{e}\rangle Z_{\text{ph}}(\beta)^{-1/2} e^{-\beta H_{\text{ph}}/2} |\mathbf{I}\rangle, \quad (9)$$

where $|\mathbf{e}\rangle = |e\rangle |\tilde{e}\rangle$, and $|\mathbf{I}\rangle$ only applies to the phonon DOFs. The state $Z_{\text{ph}}(\beta)^{-1/2} e^{-\beta H_{\text{ph}}/2} |\mathbf{I}\rangle$ is often referred to as the temperature-dependent “vacuum” state $|\mathbf{0}(\beta)\rangle$. It is further noted that $|\mathbf{0}(\beta)\rangle$ can be rewritten as³²

$$|\mathbf{0}(\beta)\rangle = e^{-iG} |\mathbf{0}\rangle, \quad (10)$$

where $|\mathbf{0}\rangle = |0\tilde{0}\rangle$ is the ground state of the combined vibrational subsystem (H_{ph} and $\tilde{H}_{\text{ph}}$), and G is the Bogoliubov unitary transformation operator defined by

$$G = G^\dagger = -i \sum_q \theta_q (b_q \tilde{b}_q - b_q^\dagger \tilde{b}_q^\dagger) \quad (11)$$

with

$$\theta_q = \text{arctanh}(e^{-\beta \omega_q/2}). \quad (12)$$

The temperature effect is thus taken into account by coupling the physical system to the fictitious tilde system through the temperature-dependent mixing angle θ_q .

In order to facilitate solving of the Schrödinger equation (3) with the initial condition (9), we introduce a new state⁴⁷

$$|\varphi(t)\rangle = e^{iG} |\psi(t)\rangle \quad (13)$$

whose time evolution is obtained by the transformed Schrödinger equation

$$i \frac{\partial}{\partial t} |\varphi(t)\rangle = \hat{H}_\theta |\varphi(t)\rangle \quad (14)$$

with the initial condition $|\varphi(0)\rangle = |\mathbf{0}\rangle$ and the transformed Hamiltonian $\hat{H}_\theta = e^{iG} \hat{H} e^{-iG}$. The expectation value of an observable Q is thus rewritten as

$$\langle Q(t) \rangle = \langle \varphi(t) | Q_\theta | \varphi(t) \rangle \quad (15)$$

with

$$Q_\theta = e^{iG} Q e^{-iG}. \quad (16)$$

It is noted that the results obtained through Eqs. (14) and (16) are equivalent to those obtained through Eqs. (3) and (4) and are the starting point of the TFD method.

B. The Holstein model

The Hamiltonian of the one-dimensional Holstein molecular crystal model can be partitioned as follows:

$$H = H_{\text{ex}} + H_{\text{ph}} + H_{\text{ex-ph}}^{\text{diag}} + H_{\text{ex-ph}}^{\text{o.d.}}, \quad (17)$$

where the exciton Hamiltonian H_{ex} , the bath (phonon) Hamiltonian H_{ph} , and the exciton-phonon coupling Hamiltonian $H_{\text{ex-ph}}$ can be defined, respectively, as

$$\begin{aligned} H_{\text{ex}} &= J \sum_n a_n^\dagger (a_{n+1} + a_{n-1}), \\ H_{\text{ph}} &= \sum_q \omega_q b_q^\dagger b_q, \\ H_{\text{ex-ph}}^{\text{diag}} &= \frac{g}{\sqrt{N}} \sum_{n,q} \omega_q a_n^\dagger a_n (e^{iqn} b_q + e^{-iqn} b_q^\dagger), \\ H_{\text{ex-ph}}^{\text{o.d.}} &= \frac{\phi}{2\sqrt{N}} \sum_{n,q} \omega_q \left\{ a_n^\dagger a_{n+1} [e^{iqn} (e^{iq-1}) b_q + \text{H.c.}] \right. \\ &\quad \left. + a_n^\dagger a_{n-1} [e^{iqn} (1 - e^{-iq}) b_q + \text{H.c.}] \right\}. \end{aligned} \quad (18)$$

Here H.c. denotes the Hermitian conjugate, $a_n^\dagger(a_n)$ is the exciton creation (annihilation) operator for the n th molecule, and $b_q^\dagger(b_q)$ is the creation (annihilation) operator of a phonon with frequency ω_q ,

$$b_q^\dagger = N^{-1/2} \sum_n e^{iqn} b_n^\dagger, \quad b_n^\dagger = N^{-1/2} \sum_q e^{-iqn} b_q^\dagger. \quad (19)$$

The fictitious Hamiltonian $\tilde{H}$ of the Holstein model is constructed by substituting all physical operators in Eq. (17) to corresponding tilde forms,³² i.e.,

$$\tilde{H} = \tilde{H}_{\text{ex}} + \tilde{H}_{\text{ph}} + \tilde{H}_{\text{ex-ph}}^{\text{diag}} + \tilde{H}_{\text{ex-ph}}^{\text{o.d.}} \quad (20)$$

with

$$\begin{aligned} \tilde{H}_{\text{ex}} &= J \sum_n \tilde{a}_n^\dagger (\tilde{a}_{n+1} + \tilde{a}_{n-1}), \\ \tilde{H}_{\text{ph}} &= \sum_q \omega_q \tilde{b}_q^\dagger \tilde{b}_q, \\ \tilde{H}_{\text{ex-ph}}^{\text{diag}} &= \frac{g}{\sqrt{N}} \sum_{n,q} \omega_q \tilde{a}_n^\dagger \tilde{a}_n (e^{iqn} \tilde{b}_q + e^{-iqn} \tilde{b}_q^\dagger), \\ \tilde{H}_{\text{ex-ph}}^{\text{o.d.}} &= \frac{\phi}{2\sqrt{N}} \sum_{n,q} \omega_q \left\{ \tilde{a}_n^\dagger \tilde{a}_{n+1} [e^{iqn} (e^{iq} - 1) \tilde{b}_q + \text{H.c.}] \right. \\ &\quad \left. + \tilde{a}_n^\dagger \tilde{a}_{n-1} [e^{iqn} (1 - e^{-iq}) \tilde{b}_q + \text{H.c.}] \right\}. \end{aligned} \quad (21)$$

The parameters J , g , and ϕ are the transfer integral, the diagonal coupling strength, and the off-diagonal coupling strength, respectively, and N is the number of sites in the Holstein model. In this paper, a linear phonon dispersion is assumed,

$$\omega_q = \omega_0 [1 + W(2|q|/\pi - 1)], \quad (22)$$

where ω_0 denotes the central energy of the phonon band and is used as the energy unit ($\omega_0 = 1$), W is the bandwidth between 0 and 1, and the momentum is set to be $q = 2\pi l/N$ with $(l = -\frac{N}{2} + 1, \dots, \frac{N}{2})$.

Following the TFD procedure, we need to solve the Schrödinger equation (3) with the initial condition

$$|\psi(0)\rangle = \rho_{\text{ph}}^{1/2} |I\rangle |n\rangle |\tilde{n}\rangle = |\mathbf{0}(\beta)\rangle |n\rangle |\tilde{n}\rangle, \quad (23)$$

where ρ_{ph} and $|\mathbf{0}(\beta)\rangle$ are defined in Eqs. (7) and (10), and $|n\rangle (|\tilde{n}\rangle)$ is the initial condition for the exciton part of $H(\tilde{H})$. In

a basis-set representation, the TFD wave function $|\psi(t)\rangle$ is an array of the dimension $(N_{\text{ex}} \times N_{\text{ph}})^2$ with $N_{\text{ex}}(N_{\text{ph}})$ denoting the number of the electronic (vibrational) basis function, which has exactly the same dimensions as those of the density matrix. It is noted that Eq. (23) introduces the temperature effect using only vibrational DOFs, which reveals that the tilde part of the exciton Hamiltonian ($|\tilde{n}\rangle$) can be dropped (see Ref. 47). This statement is rigorously proven by Borrelli and Gelin,³³ who showed that the Schrödinger equation given by

$$i \frac{\partial}{\partial t} |\psi(t)\rangle = \tilde{H} |\psi(t)\rangle, \quad (24)$$

with the initial condition

$$|\psi(0)\rangle = \rho_{\text{ph}}^{1/2} |I\rangle |n\rangle = |\mathbf{0}(\beta)\rangle |n\rangle, \quad (25)$$

reproduces the expectation value $\langle Q(t) \rangle$ [cf. Eq. (4)] obtained by the TFD Schrödinger equation (3) with Hamiltonian $\tilde{H}$. In Eq. (24), the new Hamiltonian operator $\tilde{H}$ is defined as

$$\tilde{H} = H - \tilde{H}_{\text{ph}}, \quad (26)$$

where H is defined in Eq. (17), and $\tilde{H}_{\text{ph}}$ is any operator acting in the tilde vibrational space. It is noted that the specific form of $\tilde{H}_{\text{ph}}$ does not affect the expectation value $\langle Q(t) \rangle$. For simplicity, we choose (see Ref. 33)

$$\tilde{H}_{\text{ph}} = \sum_q \omega_q \tilde{b}_q^\dagger \tilde{b}_q. \quad (27)$$

Finally, we arrive at the Schrödinger equation by applying the Bogoliubov transformation to Eq. (24),

$$i \frac{\partial}{\partial t} |\varphi(t)\rangle = \tilde{H}_\theta |\varphi(t)\rangle, \quad |\varphi(0)\rangle = |\mathbf{0}\rangle |n\rangle, \quad (28)$$

and the transformed Hamiltonian has the form

$$\begin{aligned} \tilde{H}_\theta &= e^{iG} \tilde{H} e^{-iG} \\ &= J \sum_n a_n^\dagger (a_{n+1} + a_{n-1}) + \sum_q \omega_q (b_q^\dagger b_q - \tilde{b}_q^\dagger \tilde{b}_q) \\ &\quad \times \frac{g}{\sqrt{N}} \sum_{n,q} \cosh \theta_q \omega_q a_n^\dagger a_n (e^{iqn} b_q + e^{-iqn} \tilde{b}_q^\dagger) \\ &\quad \times \frac{g}{\sqrt{N}} \sum_{n,q} \sinh \theta_q \omega_q a_n^\dagger a_n (e^{iqn} \tilde{b}_q^\dagger + e^{-iqn} \tilde{b}_q) \\ &\quad + \frac{\phi}{2\sqrt{N}} \sum_{n,q} \cosh \theta_q \omega_q \left\{ a_n^\dagger a_{n+1} [e^{iqn} (e^{iq} - 1) b_q + \text{H.c.}] \right. \\ &\quad \left. + a_n^\dagger a_{n-1} [e^{iqn} (1 - e^{-iq}) b_q + \text{H.c.}] \right\} \\ &\quad + \frac{\phi}{2\sqrt{N}} \sum_{n,q} \sinh \theta_q \omega_q \left\{ a_n^\dagger a_{n+1} [e^{iqn} (e^{iq} - 1) \tilde{b}_q^\dagger + \text{H.c.}] \right. \\ &\quad \left. + a_n^\dagger a_{n-1} [e^{iqn} (1 - e^{-iq}) \tilde{b}_q^\dagger + \text{H.c.}] \right\}, \end{aligned}$$

where the following relations have been used:³²

$$\begin{aligned} e^{iG} b_q e^{-iG} &= b_q \cosh(\theta_q) + \tilde{b}_q^\dagger \sinh(\theta_q), \\ e^{iG} \tilde{b}_q e^{-iG} &= \tilde{b}_q \cosh(\theta_q) + b_q^\dagger \sinh(\theta_q), \\ e^{iG} (b_q^\dagger b_q - \tilde{b}_q^\dagger \tilde{b}_q) e^{-iG} &= b_q^\dagger b_q - \tilde{b}_q^\dagger \tilde{b}_q. \end{aligned} \quad (29)$$

It is noted that for practical numerical calculations, the high-frequency modes can be dropped from the tilde Hamiltonian since $\theta_k \ll 1$, $\sinh(\theta_k) \approx 0$, and $\cosh(\theta_k) \approx 1$ even at

room temperature. This yields an additional reduction in the dimension in comparison with the standard Liouville equation.

C. The multi-D₂ Ansatz

Solving Eq. (28) requires an efficient numerical approach because the number of vibrational DOFs is now doubled due to the coupling to the fictitious bath. For this purpose, we write $|\varphi(t)\rangle$ in terms of the time-dependent version of the multi-D₂ Ansatz

$$\begin{aligned} |D_2^M(t)\rangle &= \sum_{n=1}^N a_n^\dagger |0\rangle_{\text{ex}} \sum_{i=1}^M \Psi_{i,n}(t) \exp \left[\sum_q (\lambda_{i,q} b_q^\dagger - \lambda_{i,q}^* b_q) \right] |0\rangle \\ &\quad \times \exp \left[\sum_q (\tilde{\lambda}_{i,q} \tilde{b}_q^\dagger - \tilde{\lambda}_{i,q}^* \tilde{b}_q) \right] |\tilde{0}\rangle. \end{aligned} \quad (30)$$

Here, $\Psi_{i,n}$ and $\lambda_{i,q}(\tilde{\lambda}_{i,q})$ are variational parameters denoting the exciton probability and phonon displacement, respectively, and n and i label the site index in the molecular ring and rank of the coherent superposition state, respectively. Following the Dirac-Frenkel time-dependent variational principle,⁴⁸ the Lagrangian L is constructed as follows:

$$\begin{aligned} L &= \frac{i\hbar}{2} \left[\langle D_2^M(t) | \frac{\partial}{\partial t} | D_2^M(t) \rangle - \langle D_2^M(t) | \frac{\partial}{\partial t} | D_2^M(t) \rangle \right] \\ &\quad - \langle D_2^M(t) | \tilde{H}_\theta | D_2^M(t) \rangle, \end{aligned} \quad (31)$$

from which the equations of motion for $\alpha(t)$ and its time derivative $\dot{\alpha}(t)$ can be obtained as

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\alpha}^*} \right) - \frac{\partial L}{\partial \alpha^*} = 0, \quad (32)$$

where α represents variational parameters $\Psi_{i,n}$ and $\lambda_{i,q}(\tilde{\lambda}_{i,q})$. The readers are referred to Appendix A for a derivation of the equations of motion for variational parameters.

D. Observables

From Eq. (30), the norm of the multi-D₂ Ansatz can be calculated as

$$N(t) = \langle D_2^M(t) | D_2^M(t) \rangle = \sum_{i,j} \sum_n \Psi_{j,n}^* \Psi_{i,n} S_{j,i}, \quad (33)$$

where $S_{j,i}$ is the Debye-Waller factor defined in Eq. (A3). Then the reduced single-exciton density matrix $\rho_{mn}(t)$ can be written as

$$\rho_{mn} = \langle D_2^M(t) | e^{iG} a_m^\dagger a_n e^{-iG} | D_2^M(t) \rangle = \sum_{i,j} \Psi_{j,m}^* \Psi_{i,n} S_{j,i}. \quad (34)$$

Among physical observables of interest in the Holstein model are the exciton probability $P_{\text{ex}}(t, n)$ and the phonon displacement $X_{\text{ph}}(t, n)$. Once the reduced density matrix is computed, the exciton probabilities $P_{\text{ex}}(t, n) = \rho_{nn}(t) (n = 1, 2, \dots, N)$ can be obtained from the diagonal elements of the reduced density matrix. The phonon displacement $X_{\text{ph}}(t, n')$ in real space at the

n' th site is calculated by

$$\begin{aligned}
 X_{\text{ph}}(t, n') &= \langle D_2^M(t) | e^{iG} (b_{n'} + b_{n'}^\dagger) e^{-iG} | D_2^M(t) \rangle \\
 &= \frac{1}{\sqrt{N}} \langle D_2^M | \left[\sum_q e^{-iqn'} (\cosh \theta_q b_q^\dagger + \sinh \theta_q \tilde{b}_q) \right. \\
 &\quad \left. + \sum_q e^{iqn'} (\cosh \theta_q b_q + \sinh \theta_q \tilde{b}_q^\dagger) \right] | D_2^M \rangle \\
 &= \frac{1}{\sqrt{N}} \sum_{q,i,j,n} e^{iqn'} \cosh \theta_q [\lambda_{i,q} \Psi_{j,n}^* \Psi_{i,n} S_{j,i}] \\
 &\quad + \frac{1}{\sqrt{N}} \sum_{q,i,j,n} e^{iqn'} \sinh \theta_q [\tilde{\lambda}_{j,q}^* \Psi_{j,n}^* \Psi_{i,n} S_{j,i}] \\
 &\quad + \frac{1}{\sqrt{N}} \sum_{q,i,j,n} e^{-iqn'} \cosh \theta_q [\lambda_{j,q}^* \Psi_{j,n}^* \Psi_{i,n} S_{j,i}] \\
 &\quad + \frac{1}{\sqrt{N}} \sum_{q,i,j,n} e^{-iqn'} \sinh \theta_q [\tilde{\lambda}_{i,q} \Psi_{j,n}^* \Psi_{i,n} S_{j,i}].
 \end{aligned}$$

III. RESULTS AND DISCUSSIONS

In this section, our TFD results on Holstein polaron dynamics will be displayed and compared with those from the

numerically exact HEOM approach. Time-dependent exciton probabilities and phonon displacements at different temperatures for both diagonal and off-diagonal coupling cases will be scrutinized in detail in Sec. III B. In Sec. III C, mean square displacements will be utilized to analyze the transport mechanism.

A. Comparisons with the HEOM method

We first check the validity of our approach by comparing results obtained by the multi- D_2 Ansatz with those by the numerically exact HEOM method.²¹ Figure 1 displays the time-dependent exciton probability at zero temperature (left panels) and $T = 1$ (right panels) for the weak diagonal coupling case of $g = 0.3$. At $T = 0$, it is found that the exciton probability calculated by the $D_2^{M=24}$ Ansatz is in perfect agreement with that from the HEOM method [see Figs. 1(a) and 1(b)], a result also reflected in Fig. 1(c), where the exciton probability difference between the two methods is shown to be about four orders of magnitude smaller than the value of $P_{\text{ex}}(t, n)$. At $T = 1$, the exciton probability difference $\Delta P_{\text{ex}}(t, n)$ is two orders of magnitude smaller than the value of $P_{\text{ex}}(t, n)$. The reliability of our approach is further confirmed in Fig. 2, where for the case of weak off-diagonal coupling $\phi = 0.3$, the exciton probability

FIG. 1. Time evolution of the exciton probability $P_{\text{ex}}(t, n)$ at $T = 0$ (left panels) and $T = 1$ (right panels) for the case of $J = 0.2$, $W = 0.5$, $g = 0.3$, $\phi = 0$, $N = 10$ is displayed in panels [(a) and (b)] and [(d) and (e)], respectively, corresponding to results obtained with the $D_2^{M=24}$ Ansatz and the HEOM method, respectively. The differences $\Delta P_{\text{ex}}(t, n)$ between the HEOM method and the $D_2^{M=24}$ Ansatz are also displayed in panels (c) and (f).

FIG. 2. Time evolution of the exciton probability $P_{\text{ex}}(t, n)$ at $T = 0$ (left panels) and $T = 1$ (right panels) for the case of $J = 0.1$, $W = 0$, $g = 0$, $\phi = 0.3$, $N = 10$ is displayed in panels [(a) and (b)] and [(d) and (e)], respectively, corresponding to the results obtained with the $D_2^{M=20}$ Ansatz and the HEOM method, respectively. The differences $\Delta P_{\text{ex}}(t, n)$ between the HEOM method and the $D_2^{M=20}$ Ansatz are also displayed in panels (c) and (f).

difference between the $D_2^{M=20}$ Ansatz and the HEOM method is found to be negligible.

It should be mentioned that the comparisons between the TFD approach and the HEOM method are restricted to small systems and weak diagonal/off-diagonal coupling because the memory requirement for the HEOM method to achieve convergence becomes unmanageable for systems with multiple electronic states and moderate-to-strong electron-phonon coupling strengths. Furthermore, all explicit information regarding the bosonic dynamics is completely lost when the boson DOFs are traced out in reduced density matrix approaches. However, recent studies seem to show that explicit evaluation of coupled electronic-vibrational states is essential to decipher interesting phenomena such as long-lived quantum beating in two-dimensional (2D) electronic spectra of light harvesting systems^{49,50} and efficient singlet fission processes in organic crystals.^{51–54} The wave function propagation method, on the other hand, tracks the time evolution of boson DOFs explicitly, before employing Monte Carlo importance sampling to characterize temperature effects. The latter step usually requires averaging over a large number of realizations at high temperatures. Our method here

combining the multi- D_2 Ansatz with the TFD technique circumvents aforementioned difficulties by providing a numerically accurate and computationally efficient description of finite-temperature polaron dynamics over broad parameter regimes ranging from weak to strong exciton-phonon coupling strengths.

B. Exciton probabilities and phonon displacements

Exciton probabilities and phonon displacements obtained can be utilized to characterize dynamical properties of the Holstein polaron at finite temperatures. Figure 3 displays the time evolution of the exciton probability $P_{\text{ex}}(t, n)$ (left panels) and the phonon displacement (right panels) in a weak diagonal coupling case of $g = 0.4$ obtained with the $D_2^{M=16}$ Ansatz at four temperatures $T = 0, 0.5, 1$, and 2 . For zero temperature, the exciton propagates from the initial site $n = 0$ to the entire chain with a velocity $v \approx \omega_0/2\pi$, which generates phonon distortions in its wake [see Figs. 3(a) and 3(e)]. It is also found that an independent phonon wave packet originated at the site of excitation travels at a speed of $v_q = \partial\omega_q/\partial q = 2W$. As can be readily seen from Figs. 3(a)–3(d), the exciton becomes less

FIG. 3. Time evolution of the exciton probability $P_{\text{ex}}(t, n)$ (left panels) and the phonon displacement $X_{\text{ph}}(t, n)$ (right panels) obtained with the $D_2^{M=16}$ Ansatz at different temperatures $T = 0, 0.5, 1, 2$, respectively. The other parameters are $J = 0.1$, $W = 0.5$, $g = 0.4$, $\phi = 0$, and $N = 16$.

mobile with increasing temperature, a phenomenon closely related to the polaron band narrowing effect.^{6-9,13} The phonon wave packets (center V-shaped) induced by the exciton-phonon interaction also travel at a slower velocity with the increase of the temperature, while the outer independent V-shaped phonon wave packets are nearly unaltered [see Figs. 3(e)–3(h)].

Figure 4 shows the exciton probability and the phonon displacement calculated for an intermediate diagonal coupling case of $g = 0.8$. The speed of the exciton wave packets

$v \approx \omega_0/4\pi$ at $T = 0$ is found to be nearly half of that for the weak diagonal coupling case of $g = 0.4$ [see Figs. 3(a) and 4(a)]. Similar to the case of $g = 0.4$, the exciton becomes more localized with the increase of the temperature as depicted in Figs. 4(a)–4(d). The exciton wave packet as well as the phonon distortion induced by the exciton-phonon coupling at $T = 2$ is completely confined to the initial excitation site [see Figs. 4(d) and 4(h)]. This can be understood again by invoking the polaron band narrowing effect and the much-reduced effective transfer integral at elevated temperatures.

FIG. 4. Time evolution of the exciton probability $P_{\text{ex}}(t, n)$ (left panels) and the phonon displacement $X_{\text{ph}}(t, n)$ (right panels) obtained with the $D_2^{M=16}$ Ansatz at different temperatures $T = 0, 0.5, 1, 2$, respectively. The other parameters are $J = 0.1$, $W = 0.5$, $g = 0.8$, $\phi = 0$, and $N = 16$.

To illustrate the bandwidth narrowing effect, it is helpful to investigate the polaron band structures as a function of temperature. For this purpose, the Munn-Silbey approach with a self-consistent treatment of temperature-dependent canonical transformation coefficients^{55,56} is well suited, and it will be utilized to obtain the polaron bands at finite temperatures (see Appendix B for details on the Munn-Silbey approach). Polaron bands as well as their bandwidths are illustrated in Fig. 5 as a function of temperature. As can be readily seen in Figs. 5(a) and 5(b), which correspond to the cases

of Figs. 3 and 4, the polaron band becomes narrower with the increase of the temperature. The bandwidths as a function of temperature as shown in Fig. 5(c) clearly demonstrate the band narrowing effect, which is also consistent with temperature-dependent exciton propagation behaviors in Figs. 3 and 4. As revealed in Refs. 55 and 56, increasing temperature leads to a greater momentum-space variation in variational parameters (A -matrix, see the notation therein), which in turn is transformed into weaker dispersion of the energy band. Such changes in polaron band structures have a great

FIG. 5. Polaron band structures at temperatures $T = 0, 0.5, 1.0, 2.0$ for the cases of (a) $J = 0.1$, $W = 0.5$, $g = 0.4$, $\phi = 0$, (b) $J = 0.1$, $W = 0.5$, $g = 0.8$, $\phi = 0$, and (c) polaron bandwidths as a function of temperature.

impact on transport properties. Overall, the band narrowing effect can be explained by a reduced renormalized transfer integral and an increased polaron binding energy at higher temperatures.^{55,56}

We then study the temperature-dependent polaron dynamics for the off-diagonal coupling case. Figure 6 presents the time evolution of the exciton probability $P_{ex}(t, n)$ (left panels) and the phonon displacement $X_{ph}(t, n)$ (right panels) for the off-diagonal coupling strength $\phi = 0.6$ at four temperatures $T = 0, 0.5, 1$, and 2 . At zero temperature, the exciton probability is found to be mostly localized at the initial excitation site $n = 0$ during the first phonon period ($t < 2\pi/\omega_0$), and correspondingly, minor lattice distortions emerge in this time period regime, as shown in Fig. 6(e). Then the exciton probability quickly spreads out from the initial creation site due to the combined effect of the transfer integral J and the off-diagonal coupling strength ϕ . As demonstrated in Figs. 6(a)–6(d), the

exciton propagation first slows down with the increase of the temperature, and then it slightly becomes faster with further increase of the temperature. While the off-diagonal coupling will increase the scattering that inhibits the transport at low temperatures, it may also induce phonon-assisted transport that dominates at high temperatures.^{9,56}

It is noted that the dynamical disorder model (i.e., the off-diagonal coupling case discussed here) is widely applied to investigate charge transport mechanisms in organic semiconductors. For example, by employing the mixed quantum-classical Ehrenfest dynamics to this model, Troisi and Orlandi¹⁵ proposed that large phonon-induced fluctuations in the intermolecular transfer integral will localize the charge carrier and reduce the mobility. However, similar to most approaches of mixed quantum-classical dynamics, the Ehrenfest method does not adequately take into account the decoherence process.⁵⁷ To avoid this problem, Yao *et al.*⁵⁸ introduced a phenomenological parameter, the decoherence time, to account for the decoherence process in Troisi's dynamic disorder model. Their results show that there exists a transition from coherent to incoherent transport at a sufficiently short decoherence time. Our approach proposed here, on the other hand, provides a unified treatment of the coherent and incoherent charge transport in a fully quantum mechanical manner, which may open a new avenue to study charge transport mechanisms in organic semiconductors.

C. Mean square displacements

In this section, we utilize the mean square displacement (MSD) to characterize transport properties of the exciton. The MSD for a 1D chain is defined as

$$\text{MSD}(t) = \sum_{n=-N/2}^{N/2} n^2 P_{ex}(t, n). \quad (35)$$

Charge transport in organic molecular crystals usually exhibits a band-like transport behavior (negative temperature dependence of the diffusion coefficient) at low temperatures and a hopping-like transport behavior (positive temperature dependence of the diffusion coefficient) at high temperatures. In Figs. 7(a) and 7(b), we display the MSD as a function of time for various values of the temperature. For the diagonal coupling case as shown in Fig. 7(a), the MSD shows ballistic behavior for all temperatures considered. It is found that the amplitude of the MSD decreases with the temperature, exhibiting band-like transport behavior. When the off-diagonal coupling is included [see Fig. 7(b)], the MSD shows diffusive behavior for all temperatures. Although the diffusive regime at high temperatures ($T > 1.6$) is weakly temperature dependent, it is found that the amplitude of the MSD decreases first and then increases with the increase of the temperature. For even larger temperatures ($T > 2.5$), due to the relatively large strength of disorder included by the combined effect of the temperature and the off-diagonal coupling, the MSD has a rather weak temperature dependence. For the temperature regimes considered ($T \leq 2.5$), we find a critical area of transition from band-like to hopping-like transport that corresponds to a transition temperature of $T = 1$. While the diagonal coupling always acts as a localization factor, the

FIG. 6. Time evolution of the exciton probability $P_{\text{ex}}(t, n)$ (left panels) and the phonon displacement $X_{\text{ph}}(t, n)$ (right panels) obtained with the $D_2^{M=16}$ Ansatz at different temperatures $T = 0, 0.5, 1, 2$, respectively. The other parameters are $J = 0.1$, $W = 0.0$, $g = 0.0$, $\phi = 0.6$, and $N = 16$.

off-diagonal coupling can be an agent for exciton transport which leads to a lower band contribution and a higher hopping contribution.^{9,56,58} It is thus expected that larger off-diagonal coupling will likely shift the band to hopping transport transition to a lower temperature.^{9,56} The results obtained here are in qualitative agreement with those from Ref. 56, which exhibits nonmonotonic changes of the diffusion coefficient as a function of temperature. It is also interesting to compare our results

here with those by other numerical methods such as Green's function approach⁵⁹ and the variational exact diagonalization method.⁶⁰ In the Green's function approach,⁵⁹ a mixed quantum-classical algorithm is employed to calculate the non-local electron Green's function and the corresponding electrical conductivity via the Kubo formula for an extended Holstein model with off-diagonal electron-phonon coupling only. It is found that the paradoxical transport regime can be understood

FIG. 7. MSD as a function of time at different temperatures for the cases of (a) $J = 0.1$, $W = 0$, $g = 0.4$, $\phi = 0$ and (b) $J = 0.1$, $W = 0$, $g = 0.4$, $\phi = 0.6$.

from the coexistence of Bloch states and incoherent states induced by large thermal lattice fluctuations. Our results show that the band-like features dominate the diagonal coupling cases, and the inclusion of off-diagonal coupling induces a crossover from band-like to hopping transport with increasing temperature. The variational exact diagonalization method⁶⁰ allows for analysis of real-time dynamics of a highly excited charge carrier that is diagonally coupled to phonons and sheds light on how the energy transfer to phonons depends on energy scales of the electron and the phonons as well as the electron-phonon coupling. Our theory proposed here can be easily used to study non-equilibrium dynamics and bath-induced relaxation processes, which will be the subject of future work.

IV. CONCLUSIONS

In summary, we have proposed a novel description of finite temperature dynamics of a Holstein polaron by combining the TFD method with the multiple Davydov D_2 Ansatz. The temperature effect is accounted for through the coupling of the system to a fictitious bosonic bath, and the corresponding TFD Schrödinger equation is then solved using the multiple Davydov D_2 Ansatz. The validity of our approach is checked by comparing the exciton probabilities calculated by the multiple D_2 Ansatz with those from the hierarchy equations of motion method, which confirms the efficiency and robustness of our approach for describing finite temperature polaron dynamics in the presence of diagonal and off-diagonal

exciton-phonon coupling. For weak to moderate diagonal coupling strengths, the exciton becomes less mobile with the increase of the temperature, exhibiting a band-like transport behavior. The off-diagonal coupling, on the other hand, acting as an agent for exciton transport, may induce a crossover from band-like to hopping transport with increasing temperature. Taking into account the competitive effects of the diagonal coupling in hindering delocalization and of the off-diagonal coupling in promoting transport is thus essential to accurately characterize exciton (charge) transport properties in organic crystals.

Several comments are in order on possible extensions of our approach and its applications. It is straightforward to include other forms of exciton-phonon interactions, such as symmetric off-diagonal coupling,^{55,61} and multiple phonon branches, each with individual coupling to the electronic DOFs. For realistic organic semiconductor materials, an external electric field can be built up in the donor-acceptor interface which induces a drift of charge carriers. Our approach here can be readily extended to include an external electric field by employing a Holstein model with a phase-factor modified transfer integral.^{62,63} A polaron is also known to play an important role in determining electrodynamic properties of superlattices, where a dimensional crossover of the polaron from 3D to quasi-2D is often found, and strong electron-phonon coupling has been suggested to provide alternative pathways to efficient thermoelectric materials.⁶⁴ Our efficient dynamics simulation can be extended to two dimensions and help explain thermopower enhancements in those materials. Recent studies have shown that low frequency intermolecular vibrations are expected to alter the electronic coupling, thus may play an important role in the highly efficient single fission (SF) process of single crystal materials.^{65,66} Our method proposed here can also be applied to investigate temperature dependence of SF processes. Finally, it is also of great interest to use our approach to simulate linear and non-linear spectra, by both perturbative^{67–69} and non-perturbative methods.⁷⁰ Work in these directions is in progress.

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APPENDIX A: THE TIME-DEPENDENT VARIATIONAL APPROACH FOR THE HOLSTEIN MODEL

The equations of the motion are derived for the variational parameters $\Psi_{i,n}$ and $\lambda_{i,q}(\tilde{\lambda}_{i,q})$ by adopting the Dirac-Frenkel time-dependent variational principle, in which the Lagrangian is formulated as

$$L = \frac{i\hbar}{2} \left[\left\langle D_2^M(t) \right| \frac{\vec{\partial}}{\partial t} \left| D_2^M(t) \right\rangle - \left\langle D_2^M(t) \right| \frac{\overleftarrow{\partial}}{\partial t} \left| D_2^M(t) \right\rangle \right] - \left\langle D_2^M(t) \right| \hat{H}_\theta \left| D_2^M(t) \right\rangle, \quad (\text{A1})$$

where the first term reads

$$\begin{aligned} \frac{i}{2} \left[\langle D_2^M(t) | \frac{\vec{\partial}}{\partial t} | D_2^M(t) \rangle - \langle D_2^M(t) | \frac{\overleftarrow{\partial}}{\partial t} | D_2^M(t) \rangle \right] &= \frac{i}{2} \sum_{i,j} \sum_n (\Psi_{jn}^* \dot{\Psi}_{in} - \dot{\Psi}_{jn}^* \Psi_{in}) S_{ji} + \frac{i}{2} \sum_{i,j} \sum_n \Psi_{jn}^* \Psi_{in} \\ &\times \sum_q \left[\frac{\dot{\lambda}_{jq}^* \lambda_{jq} + \lambda_{jq}^* \dot{\lambda}_{jq} - \dot{\lambda}_{iq} \lambda_{iq}^* - \lambda_{iq} \dot{\lambda}_{iq}^*}{2} + \lambda_{jq}^* \dot{\lambda}_{iq} - \lambda_{iq} \dot{\lambda}_{jq}^* \right] S_{ji} \frac{i}{2} \sum_{i,j} \sum_n \Psi_{jn}^* \Psi_{in} \\ &\times \sum_q \left[\frac{\dot{\tilde{\lambda}}_{jq}^* \tilde{\lambda}_{jq} + \tilde{\lambda}_{jq}^* \dot{\tilde{\lambda}}_{jq} - \dot{\tilde{\lambda}}_{iq} \tilde{\lambda}_{iq}^* - \tilde{\lambda}_{iq} \dot{\tilde{\lambda}}_{iq}^*}{2} + \tilde{\lambda}_{jq}^* \dot{\tilde{\lambda}}_{iq} - \tilde{\lambda}_{iq} \dot{\tilde{\lambda}}_{jq}^* \right] S_{ji} \end{aligned} \quad (\text{A2})$$

with the Debye-Waller factor S_{ji} defined as

$$S_{ji} = \exp \left\{ \sum_q \left[\lambda_{jq}^* \lambda_{iq} - \frac{1}{2} (|\lambda_{iq}|^2 + |\lambda_{jq}|^2) \right] + \sum_q \left[\tilde{\lambda}_{jq}^* \tilde{\lambda}_{iq} - \frac{1}{2} (|\tilde{\lambda}_{iq}|^2 + |\tilde{\lambda}_{jq}|^2) \right] \right\}, \quad (\text{A3})$$

and the second term is

$$\begin{aligned} \langle D_2^M(t) | \bar{H}_\theta | D_2^M(t) \rangle &= J \sum_{i,j} \sum_n \Psi_{j,n}^* (\Psi_{i,n+1} + \Psi_{i,n-1}) S_{j,i} + \sum_{i,j} \sum_n \Psi_{j,n}^* \Psi_{i,n} \sum_q \omega_q \lambda_{j,q}^* \lambda_{i,q} S_{j,i} - \sum_{i,j} \sum_n \Psi_{j,n}^* \Psi_{i,n} \sum_q \omega_q \tilde{\lambda}_{j,q}^* \tilde{\lambda}_{i,q} S_{j,i} \\ &+ \frac{g}{\sqrt{N}} \sum_{i,j} \sum_n \Psi_{j,n}^* \Psi_{i,n} \sum_q \cosh \theta_q \omega_q (e^{iqn} \lambda_{i,q} + e^{-iqn} \lambda_{j,q}^*) S_{j,i} + \frac{g}{\sqrt{N}} \sum_{i,j} \sum_n \Psi_{j,n}^* \Psi_{i,n} \\ &\times \sum_q \sinh \theta_q \omega_q (e^{iqn} \tilde{\lambda}_{j,q} + e^{-iqn} \tilde{\lambda}_{i,q}) S_{j,i} + \frac{\phi}{2\sqrt{N}} \sum_{i,j} \sum_n \sum_q \cosh \theta_q \omega_q S_{j,i} \\ &\times \left\{ \Psi_{j,n}^* \Psi_{i,n+1} [e^{iqn} (e^{iq} - 1) \lambda_{i,q} + e^{-iqn} (e^{-iq} - 1) \lambda_{j,q}^*] + \Psi_{j,n}^* \Psi_{i,n-1} [e^{iqn} (1 - e^{-iq}) \lambda_{i,q} + e^{-iqn} (1 - e^{iq}) \lambda_{j,q}^*] \right\} \\ &+ \frac{\phi}{2\sqrt{N}} \sum_{i,j} \sum_n \sum_q \sinh \theta_q \omega_q S_{j,i} \left\{ \Psi_{j,n}^* \Psi_{i,n+1} [e^{iqn} (e^{iq} - 1) \tilde{\lambda}_{j,q}^* + e^{-iqn} (e^{-iq} - 1) \tilde{\lambda}_{i,q}] \right. \\ &\left. + \Psi_{j,n}^* \Psi_{i,n-1} [e^{iqn} (1 - e^{-iq}) \tilde{\lambda}_{j,q}^* + e^{-iqn} (1 - e^{iq}) \tilde{\lambda}_{i,q}] \right\}. \end{aligned} \quad (\text{A4})$$

The equations of motion for $\Psi_{i,n}$ are

$$\begin{aligned} -i \sum_i \dot{\Psi}_{in} S_{ki} - \frac{i}{2} \sum_i \Psi_{in} \sum_q (2\lambda_{kq}^* \dot{\lambda}_{iq} - \dot{\lambda}_{iq} \lambda_{kq}^* - \lambda_{iq} \dot{\lambda}_{kq}^*) S_{ki} - \frac{i}{2} \sum_i \Psi_{in} \sum_q (2\tilde{\lambda}_{kq}^* \dot{\tilde{\lambda}}_{iq} - \dot{\tilde{\lambda}}_{iq} \tilde{\lambda}_{kq}^* - \tilde{\lambda}_{iq} \dot{\tilde{\lambda}}_{kq}^*) S_{ki} \\ = -J \sum_i (\Psi_{i,n+1} + \Psi_{i,n-1}) S_{ki} - \sum_i \Psi_{in} \sum_q \omega_q \lambda_{kq}^* \lambda_{i,q} S_{ki} + \sum_i \Psi_{in} \sum_q \omega_q \tilde{\lambda}_{kq}^* \tilde{\lambda}_{i,q} S_{ki} \\ - \frac{g}{\sqrt{N}} \sum_i \Psi_{in} \sum_q \cosh \theta_q \omega_q (e^{iqn} \lambda_{i,q} + e^{-iqn} \lambda_{kq}^*) S_{ki} - \frac{g}{\sqrt{N}} \sum_i \Psi_{in} \sum_q \sinh \theta_q \omega_q (e^{iqn} \tilde{\lambda}_{kq}^* + e^{-iqn} \tilde{\lambda}_{i,q}) S_{ki} \\ - \frac{\phi}{2\sqrt{N}} \sum_i \sum_q \cosh \theta_q \omega_q \Psi_{i,n+1} [e^{iqn} (e^{iq} - 1) \lambda_{i,q} + e^{-iqn} (e^{-iq} - 1) \lambda_{kq}^*] S_{ki} - \frac{\phi}{2\sqrt{N}} \sum_i \sum_q \cosh \theta_q \omega_q \Psi_{i,n-1} [e^{iqn} (1 - e^{-iq}) \lambda_{i,q} \\ + e^{-iqn} (1 - e^{iq}) \lambda_{kq}^*] S_{ki} - \frac{\phi}{2\sqrt{N}} \sum_i \sum_q \sinh \theta_q \omega_q \Psi_{i,n+1} [e^{iqn} (e^{iq} - 1) \tilde{\lambda}_{kq}^* + e^{-iqn} (e^{-iq} - 1) \tilde{\lambda}_{i,q}] S_{ki} \\ - \frac{\phi}{2\sqrt{N}} \sum_i \sum_q \sinh \theta_q \omega_q \Psi_{i,n-1} [e^{iqn} (1 - e^{-iq}) \tilde{\lambda}_{kq}^* + e^{-iqn} (1 - e^{iq}) \tilde{\lambda}_{i,q}] S_{ki}. \end{aligned} \quad (\text{A5})$$

The equations of motion for λ_{iq} are

$$\begin{aligned}
& -i \sum_i \sum_n \Psi_{kn}^* \dot{\Psi}_{in} \lambda_{iq} S_{ki} - i \sum_i \sum_n \Psi_{kn}^* \Psi_{in} \dot{\lambda}_{iq} S_{ki} - \frac{i}{2} \sum_i \sum_{np} \Psi_{kn}^* \Psi_{in} \lambda_{iq} S_{ki} (2\lambda_{kp}^* \dot{\lambda}_{ip} - \dot{\lambda}_{ip} \lambda_{kp}^* - \lambda_{ip} \dot{\lambda}_{kp}^* + 2\tilde{\lambda}_{kp}^* \dot{\tilde{\lambda}}_{ip} - \dot{\tilde{\lambda}}_{ip} \tilde{\lambda}_{kp}^* - \tilde{\lambda}_{ip} \dot{\tilde{\lambda}}_{kp}^*) \\
& = -J \sum_i \sum_n \Psi_{kn}^* (\Psi_{i,n+1} + \Psi_{i,n-1}) \lambda_{iq} S_{ki} - \sum_i \sum_n \Psi_{kn}^* \Psi_{in} \left[\omega_q + \sum_p \omega_p (\lambda_{kp}^* \lambda_{ip} - \tilde{\lambda}_{kp}^* \tilde{\lambda}_{ip}) \right] \lambda_{iq} S_{ki} - \frac{g}{\sqrt{N}} \sum_i \sum_n \\
& \quad \times \Psi_{kn}^* \Psi_{in} \cosh \theta_q \omega_q e^{-iqn} S_{ki} - \frac{g}{\sqrt{N}} \sum_i \sum_{np} \Psi_{kn}^* \Psi_{in} \lambda_{iq} \left[\cosh \theta_p \omega_p (e^{ipn} \lambda_{ip} + e^{-ipn} \lambda_{kp}^*) + \sinh \theta_p \omega_p (e^{ipn} \tilde{\lambda}_{kp}^* + e^{-ipn} \tilde{\lambda}_{ip}) \right] S_{ki} \\
& \quad - \frac{\phi}{2\sqrt{N}} \sum_i \sum_n \cosh \theta_q \omega_q \Psi_{kn}^* \left[\Psi_{i,n+1} e^{-iqn} (e^{-iq} - 1) + \Psi_{i,n-1} e^{-iqn} (1 - e^{iq}) \right] S_{ki} \\
& \quad - \frac{\phi}{2\sqrt{N}} \sum_i \sum_n (\Psi_{k,n+1}^* \Psi_{i,n} + \Psi_{kn}^* \Psi_{i,n+1}) \lambda_{iq} \sum_p \cosh \theta_p \omega_p \left[e^{ipn} (e^{ip} - 1) \lambda_{ip} + e^{-ipn} (e^{-ip} - 1) \lambda_{kp}^* \right] S_{ki} \\
& \quad - \frac{\phi}{2\sqrt{N}} \sum_i \sum_n (\Psi_{k,n+1}^* \Psi_{i,n} + \Psi_{kn}^* \Psi_{i,n+1}) \lambda_{iq} \sum_p \sinh \theta_p \omega_p \left[e^{ipn} (e^{ip} - 1) \tilde{\lambda}_{kp}^* + e^{-ipn} (e^{-ip} - 1) \tilde{\lambda}_{ip} \right] S_{ki}. \tag{A6}
\end{aligned}$$

The equations of motion for $\tilde{\lambda}_{iq}$ are

$$\begin{aligned}
& -i \sum_i \sum_n \Psi_{kn}^* \dot{\Psi}_{in} \tilde{\lambda}_{iq} S_{ki} - i \sum_i \sum_n \Psi_{kn}^* \Psi_{in} \dot{\tilde{\lambda}}_{iq} S_{ki} - \frac{i}{2} \sum_i \sum_{np} \Psi_{kn}^* \Psi_{in} \tilde{\lambda}_{iq} S_{ki} (2\lambda_{kp}^* \dot{\lambda}_{ip} - \dot{\lambda}_{ip} \lambda_{kp}^* - \lambda_{ip} \dot{\lambda}_{kp}^* + 2\tilde{\lambda}_{kp}^* \dot{\tilde{\lambda}}_{ip} - \dot{\tilde{\lambda}}_{ip} \tilde{\lambda}_{kp}^* - \tilde{\lambda}_{ip} \dot{\tilde{\lambda}}_{kp}^*) \\
& = -J \sum_i \sum_n \Psi_{kn}^* (\Psi_{i,n+1} + \Psi_{i,n-1}) \tilde{\lambda}_{iq} S_{ki} - \sum_i \sum_n \Psi_{kn}^* \Psi_{in} \left[\omega_q - \sum_p \omega_p (\lambda_{kp}^* \lambda_{ip} - \tilde{\lambda}_{kp}^* \tilde{\lambda}_{ip}) \right] \tilde{\lambda}_{iq} S_{ki} - \frac{g}{\sqrt{N}} \sum_i \sum_n \\
& \quad \times \Psi_{kn}^* \Psi_{in} \sinh \theta_q \omega_q e^{iqn} S_{ki} - \frac{g}{\sqrt{N}} \sum_i \sum_{np} \Psi_{kn}^* \Psi_{in} \tilde{\lambda}_{iq} \left[\cosh \theta_p \omega_p (e^{ipn} \lambda_{ip} + e^{-ipn} \lambda_{kp}^*) + \sinh \theta_p \omega_p (e^{ipn} \tilde{\lambda}_{kp}^* + e^{-ipn} \tilde{\lambda}_{ip}) \right] S_{ki} \\
& \quad - \frac{\phi}{2\sqrt{N}} \sum_i \sum_n \sinh \theta_q \omega_q \Psi_{kn}^* \left[\Psi_{i,n+1} e^{iqn} (e^{iq} - 1) + \Psi_{i,n-1} e^{iqn} (1 - e^{-iq}) \right] S_{ki} \\
& \quad - \frac{\phi}{2\sqrt{N}} \sum_i \sum_{np} (\Psi_{k,n+1}^* \Psi_{i,n} + \Psi_{kn}^* \Psi_{i,n+1}) \tilde{\lambda}_{iq} \cosh \theta_p \omega_p \left[e^{ipn} (e^{ip} - 1) \lambda_{ip} + e^{-ipn} (e^{-ip} - 1) \lambda_{kp}^* \right] S_{ki} \\
& \quad - \frac{\phi}{2\sqrt{N}} \sum_i \sum_{np} (\Psi_{k,n+1}^* \Psi_{i,n} + \Psi_{kn}^* \Psi_{i,n+1}) \tilde{\lambda}_{iq} \sinh \theta_p \omega_p \left[e^{ipn} (e^{ip} - 1) \tilde{\lambda}_{kp}^* + e^{-ipn} (e^{-ip} - 1) \tilde{\lambda}_{ip} \right] S_{ki}. \tag{A7}
\end{aligned}$$

APPENDIX B: CALCULATIONS OF POLARON BANDS USING MUNN-SILBEY APPROACH

The generalized Holstein Hamiltonian including simultaneous diagonal and off-diagonal exciton-phonon coupling can be written as

$$\begin{aligned}
H = & \sum_n \epsilon a_n^\dagger a_n + \sum_{n,m} J_{nm} a_n^\dagger a_m + \sum_q \omega_q b_q^\dagger b_q \\
& + N^{-1/2} \sum_{nmq} \omega_q f_{nm}^q a_n^\dagger a_m (b_q + b_{-q}^\dagger), \tag{B1}
\end{aligned}$$

where $a_n^\dagger (a_n)$ is the creation (annihilation) operator of an exciton with energy ϵ , and $b_q^\dagger (b_q)$ is the creation (annihilation) operator of a phonon with frequency ω_q , J_{nm} is the electronic coupling between molecules n and m , and f_{nm}^q are linear exciton-phonon coupling strength. It is more convenient to write the Hamiltonian (B1) in the momentum representation

due to its translational symmetry,

$$\begin{aligned}
H = & \sum_k \epsilon_k a_k^\dagger a_k + \sum_q \omega_q b_q^\dagger b_q \\
& + N^{-1/2} \sum_{kq} \omega_q f_{-k}^q a_{k+q}^\dagger a_k (b_q + b_{-q}^\dagger), \tag{B2}
\end{aligned}$$

where $\epsilon_k = \epsilon + J_k$, with $J_k = \sum_m e^{ik \cdot (R_n - R_m)} J_{nm}$ and $f_k^q = \sum_m e^{-ik \cdot (R_n - R_m)} f_{n-m}^q$. Here, $J_{nm} = J(\delta_{n,m+1} + \delta_{n,m-1})$ and $f_k^q = g - i\phi[\sin(k) - \sin(k-q)]$, where J , g , and ϕ are the transfer integral, the diagonal exciton-phonon coupling strength, and the off-diagonal exciton-phonon coupling strength, respectively. Applying a unitary transformation to Hamiltonian (B2), one obtains

$$H \rightarrow \tilde{H} = U^\dagger H U \tag{B3}$$

with $U = e^{N^{-1/2} \sum_{kq} A_{-k}^q (b_{-q}^\dagger - b_q) a_{k+q}^\dagger a_k}$. The transformation can also be written as

$$U = e^{\sum_{kk'} a_k^\dagger S_{kk'} a_{k'}}, \quad (\text{B4})$$

where $S_{kk'} = N^{-1/2} A_{-k}^{k-k'} (b_{k'-k}^\dagger - b_{k-k'})$, with $b_{k'-k}^\dagger$ denoting the operator creating a net phonon with momentum $k' - k$. The exciton operators are then written as

$$\begin{aligned} a_k &\rightarrow \sum_{k'} \theta_{kk'} a_{k'}, \\ a_k^\dagger &\rightarrow \sum_{k'} \theta_{kk'}^\dagger a_{k'}^\dagger, \end{aligned} \quad (\text{B5})$$

with

$$\begin{aligned} \theta_{kk'} &= [\exp(-S)]_{kk'}, \\ \theta_{kk'}^\dagger &= [\exp(S)]_{kk'}. \end{aligned} \quad (\text{B6})$$

The transformed Hamiltonian can be divided into the zeroth-order term $\tilde{H}_0$ and the first-order term V . The zeroth-order Hamiltonian $\tilde{H}_0$ has the following expression:

$$\tilde{H}_0 = \sum_k (\epsilon + \tilde{J}_k - N^{-1} \sum_q |A_k^q|^2 \omega_q) a_k^\dagger a_k + \sum_q \omega_q b_q^\dagger b_q \quad (\text{B7})$$

with the renormalized transfer integral $\tilde{J}_k = \sum_{k'} J_{k'} \langle \theta_{k'k}^\dagger \theta_{k'k} \rangle$, where the bracket denotes the thermal average. The first-order term V can be written as

$$\begin{aligned} V &= \sum_{kk'k''} (J_k T_{kk';kk''} - 2N^{-1} \sum_q \omega_q f_{-k}^q A_{-k''}^{-q} \\ &\quad \times T_{k+q,k';k,k''-q} + N^{-1/2} \sum_q \omega_q f_{-k}^q \\ &\quad \times T_{k+q,k';kk''} (b_q + b_{-q}^\dagger) a_k^\dagger a_{k''}), \end{aligned} \quad (\text{B8})$$

where $T_{kk';uu'} = \theta_{kk'}^\dagger \theta_{uu'} - \langle \theta_{kk'}^\dagger \theta_{uu'} \rangle$. Polaron bands are computed only using $\tilde{H}_0$, i.e.,

$$\epsilon_k = \epsilon + \tilde{J}_k - N^{-1} \sum_q |A_k^q|^2 \omega_q. \quad (\text{B9})$$

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