

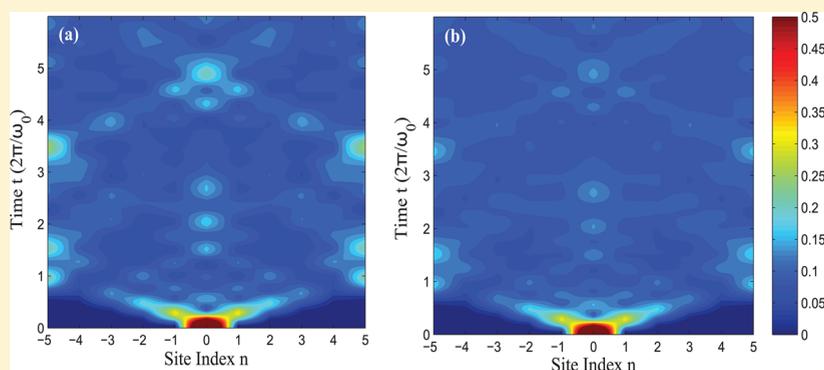
# Dynamics of a One-Dimensional Holstein Polaron with the Hierarchical Equations of Motion Approach

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**ABSTRACT:** Dynamics of a one-dimensional Holstein molecular crystal model is investigated by making use of the hierarchical equations of motion (HEOM) introduced by Tanimura and Kubo [*J. Phys. Soc. Jpn.* **1989**, *104*, 101]. Our extended, numerically exact HEOM approach is capable of treating exciton–phonon coupling in a nonperturbative manner and is applicable to any temperature. It is revealed that strong exciton phonon coupling leads to excitonic localization, while a large exciton transfer integral facilitates exciton transport. Temperature effects on excitonic scattering have also been examined. A proof of concept, our work also serves as a benchmark for future comparisons with other numerical approaches to Holstein polaron dynamics.

Modeling the dynamics of the Holstein polaron, a quasiparticle that comprises an electronic excitation interacting with a phonon cloud in its environs, is of great importance to understanding transport mechanisms of charge carriers in organic materials. Relaxation dynamics of polarons in solids and liquids have garnered increasing attention due to the rapid progress in ultrafast laser spectroscopy.<sup>1</sup> Recent advent of femtosecond spectroscopic techniques have made it possible to probe, for example, sustained intrachain electronic and vibrational coherences in resonant energy transfer along conjugated polymer chains of MEH-PPV (poly[2-methoxy-5-(2'-ethylhexoxy)-1,4-phenylenevinylene]).<sup>2</sup> Such quantum coherence phenomena may play an essential role in efficient energy transfer in organic photovoltaic (OPV) devices.

Theoretical study of the Holstein polaron dynamics can be traced back to the seminal work of Holstein.<sup>3</sup> Despite successful interpretation of the temperature dependence of band narrowing as well as the crossover from bandlike to hopping transport with increasing temperature, the theory was at a perturbative level and applicable only to narrow band systems. Various numerical approaches have since been constructed to study static and dynamic properties of the Holstein polaron in the past decades. Approaches designed to probe properties of the ground state and the low-lying excited states include exact diagonalization (ED),<sup>4,5</sup>

quantum Monte Carlo (QMC),<sup>6,7</sup> variational methods,<sup>8–10</sup> density matrix renormalization group (DMRG),<sup>11,12</sup> and variational exact diagonalization (VED).<sup>13,14</sup> Contrastingly, theoretical treatments of polaron dynamics have not received much-deserved attention due to the elusiveness of reliable solutions.

In the 1970s, Davydov proposed the concept of “Davydov soliton” and a mechanism to account for the biological energy transfer in proteins,<sup>8</sup> according to which energy released by an enzymatic reaction can be stored and transported in the form of a soliton. Subsequently developed were two Ansätze with varying sophistication, specifically, the Davydov  $D_1$ <sup>15–17</sup> and  $D_2$  trial state, with the latter being a simplified version of the former. Following the Dirac–Frenkel time-dependent variational principle, a time-dependent Merrifield-type trial state<sup>18</sup> with zero crystal momentum was proposed to study ultrafast relaxation dynamics of a photoexcited one-dimensional polaron.<sup>19</sup> Time-dependent variational parameters specifying the trial state were obtained by solving a set of coupled differential equations. The Merrifield-type wave function, however, is only

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applicable to the narrow band regime, and realistic initial states often come in a localized form. The Davydov Ansatz and their variants that can take into account arbitrary initial states and have built-in flexibility and variable sophistication for each practical occasion have recently been engineered for dynamics of the Holstein model as well as the energy transfer in light-harvesting systems.<sup>20–23</sup> Criteria were also established to gauge how faithfully the trial wave functions follow the Schrödinger equation. It is found that the Davydov D<sub>1</sub> Ansatz and its variants are sufficiently accurate in all parameter space but the very weak coupling regime, in which the form of the trial state is not well-suited to capture the plane-wave phonon wave functions. In parallel, a dynamical framework based on a stochastic approach to non-Markovian open quantum systems has been developed to efficiently describe the quantum dynamics of an electronic excitation coupled to a continuous phonon environment.<sup>24</sup> In addition, Spano has intensively studied the spectral signatures of polarons in organic semiconductors using a reduced basis set consisting of all one- and two-particle vibronic states.<sup>25,26</sup>

Starting from generic system-bath interaction Hamiltonian, Tanimura derived the hierarchical equations of motion (HEOM) for the reduced density matrix.<sup>27–32</sup> It eliminates several well-recognized limitations of the reduced equations of motion approaches, involving rotating wave approximation, the white-noise (Markovian) approximation, and the perturbative approximant that is associated with the dynamical positivity problem. The HEOM method takes into account non-Markovian effects and nonperturbative system-bath interactions at finite temperature in a numerically exact manner,<sup>33,34</sup> and has been widely used to study multidimensional spectroscopy,<sup>35–37</sup> electron transfer processes,<sup>38,39</sup> energy transfer processes in photosynthetic antenna systems,<sup>40–42</sup> and quantum information.<sup>43–45</sup> Furthermore, Yan and co-workers have extended the HEOM to the Fermionic systems,<sup>46</sup> as well as substantially increased the efficiency of the approach by applying the Pade spectrum decompositions of quantum distribution functions.<sup>47,48</sup> The purpose of this paper is to adapt a novel HEOM formalism to study the Holstein polaron model for a broad range of exciton–phonon coupling strengths. While the applicability of the previous versions of HEOM for a Brownian system or a variant of the spin-Boson model is limited to finite temperatures, that of the present one is valid even at zero temperature, because the HEOM in this work is expressed in terms of discretized phonon modes instead of the Matsubara expansion.

The one-dimensional Holstein molecular crystal model of *N* sites with the periodic boundary condition can be written as<sup>3,49,50</sup>

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

where

$$\hat{H}_{\text{ex}} = -J \sum_n \hat{a}_n^\dagger (\hat{a}_{n+1} + \hat{a}_{n-1}) \quad (2)$$

is the Hamiltonian for a single Frenkel exciton band in a rigid chain,  $\hat{a}_n$  ( $\hat{a}_n^\dagger$ ) is the annihilation (creation) operator of an exciton at the *n*th site, and *J* is the nearest-neighbor transfer integral. The bath degrees of freedom are described by

$$\hat{H}_{\text{ph}} = \sum_q \omega_q \hat{b}_q^\dagger \hat{b}_q \quad (3)$$

where  $\hat{b}_q$  ( $\hat{b}_q^\dagger$ ) is the boson annihilation (creation) operator of a phonon with momentum *q* and frequency  $\omega_q$ . The exciton–phonon interaction is assumed to have a site diagonal form:

$$\hat{H}_{\text{ex-ph}} = -g \sum_{q,n=1}^N \omega_q \hat{a}_n^\dagger \hat{a}_n (\hat{b}_q e^{iqn} + \hat{b}_q^\dagger e^{-iqn}) \quad (4)$$

where *g* is the dimensionless exciton–phonon coupling strength.

Here we assume a linear dispersion phonon band  $\omega_q = \omega_0 [1 + W(2|q|/\pi - 1)]$  with  $q = (2\pi/N)l$  [ $l = -(N/2) + 1, \dots, -1, 0, 1, \dots, (N/2)$ ], where the central frequency of the phonon band  $\omega_0$  is taken as the energy unit, i.e.,  $\omega_0 = 1$  and the bandwidth of the phonon frequency is  $2W\omega_0$ . It is noted that our model can include multiple phonon branches with arbitrary dispersion relations, each of which is described by different exciton–phonon interactions.

Let us consider the exciton eigenstate at the *n*th site  $|n\rangle = \hat{a}_n^\dagger |0\rangle_{\text{ex}}$  where  $|0\rangle_{\text{ex}}$  represents the exciton vacuum. Then the reduced density matrix element for the exciton system is expressed in the path integral form with the factorized initial state as

$$\rho(n, n'; t) = \int \mathcal{D}n \int \mathcal{D}n' \rho(n_0, n'_0; t_0) \times e^{iS[n;t]} F(n, n'; t) e^{-iS[n';t]} \quad (5)$$

where *S*[*n*] is the action of the exciton system, and *F*[*n, n'*] is the Feynman-Vernon influence functional given by

$$F[n, n'] = \exp\left\{-\sum_q \omega_q^2 \int_{t_0}^t ds \int_{t_0}^s ds' V_q^{*\times}(s) \times [V_q^\times(s') \coth(\beta\omega_q/2) \cos(\omega_q(s-s')) - iV_q^\circ(s') \sin(\omega_q(s-s'))]\right\} \quad (6)$$

Here,  $\beta$  is the inverse of temperature ( $\beta = 1/k_B T$ ), and we define

$$V_q^\times \equiv V_q(n) - V_q(n') \quad (7)$$

$$V_q^\circ \equiv V_q(n) + V_q(n') \quad (8)$$

with  $V_q^*$  matrix representation of the operator  $\hat{V}_q^\dagger = g \sum_n \hat{a}_n^\dagger \hat{a}_n e^{iqn}$ .

Taking the derivative of eq 5, we have

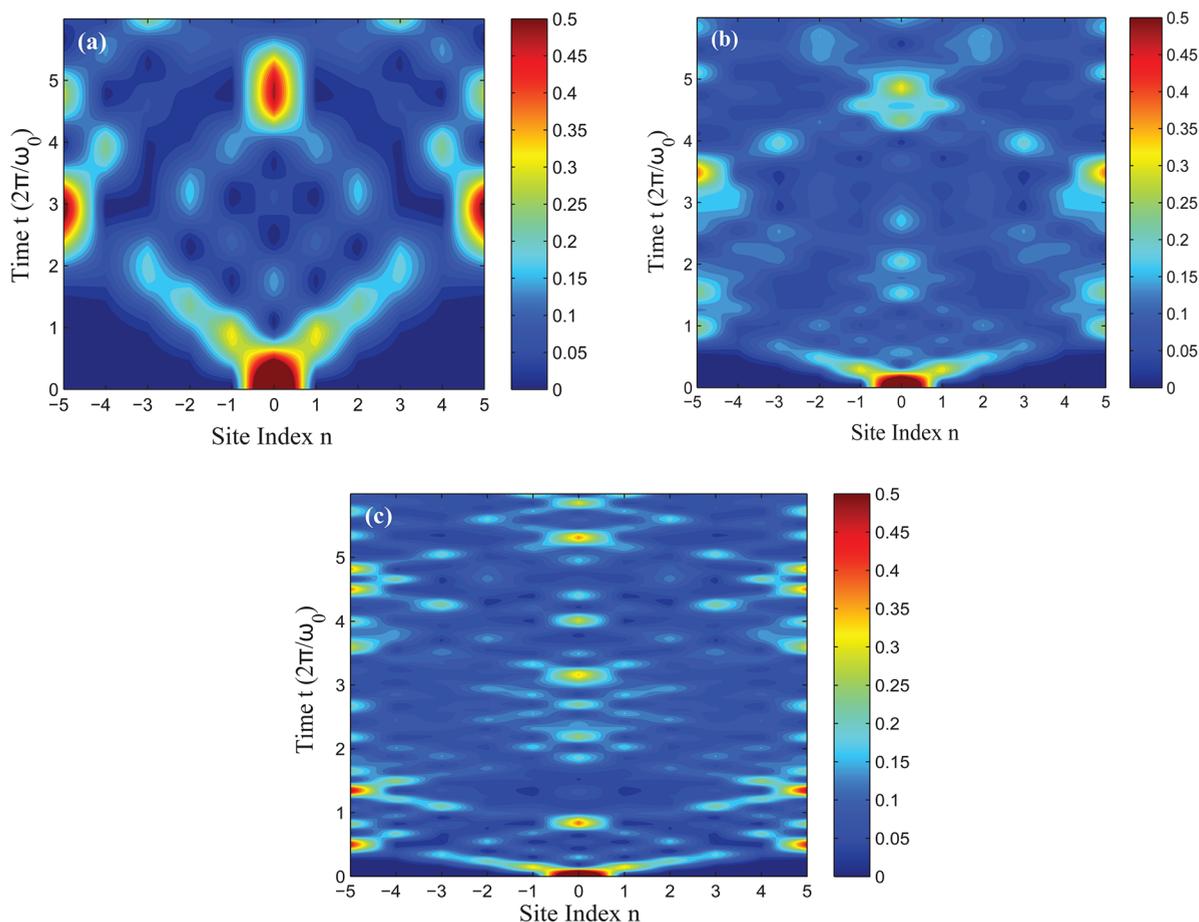
$$\frac{\partial}{\partial t} \rho(n, n'; t) = -i\mathcal{L}\rho(n, n'; t) - \sum_q \Phi_q(t) \int \mathcal{D}n \int \mathcal{D}n' \times \rho(n_0, n'_0; t_0) \int_0^t ds' [e^{i\omega_q(t-s)} \Theta_{q+}(s') + e^{-i\omega_q(t-s)} \Theta_{q-}(s')] \times e^{iS[n;t]} F(n, n'; t) e^{-iS[n';t]} \quad (9)$$

with the following superoperator defined as

$$\hat{\Phi}_q(t) = \omega_q^2 V_q^{*\times}(t)/2 \quad (10)$$

$$\hat{\Theta}_{q\pm}(t) = \hat{V}_q^\times(t) \coth(\beta\omega_q/2) \mp \hat{V}_q^\circ(t) \quad (11)$$

In order to derive the equation of motion, we introduce the auxiliary operator  $\rho_{m_1 \pm, m_2 \pm, \dots, m_N \pm}(n, n'; t)$  by its matrix element as



**Figure 1.** Time evolution of exciton population for (a)  $J = 0.2$ ,  $W = 0.5$ ,  $g = 0.1$ ; (b)  $J = 0.5$ ,  $W = 0.5$ ,  $g = 0.1$ ; (c)  $J = 1.0$ ,  $W = 0.5$ ,  $g = 0.1$ . The temperature is set to zero ( $\beta = \infty$ ).

$$\rho_{m_{1\pm}, m_{2\pm}, \dots, m_{N\pm}}(n, n'; t) = \int \mathcal{D}n \int \mathcal{D}n' \rho(n_0, n'_0; t_0) \times \prod_{q=1}^N \left( \int_{t_0}^t ds e^{i\omega_q(t-s)} \Theta_{q+}(s) \right)^{m_{q+}} \left( \int_{t_0}^t ds e^{-i\omega_q(t-s)} \Theta_{q-}(s) \right)^{m_{q-}} \times e^{iS[n,t]} F(n, n') e^{-iS[n'; t]} \quad (12)$$

for non-negative integers  $m_{1\pm}, m_{2\pm}, \dots, m_{N\pm}$ . Note that  $\hat{\rho}_{0, \dots, 0}(t) = \hat{\rho}(t)$  and other auxiliary density matrices contain the complete set of the information on the Liouville space wavepackets. Differentiating  $\rho_{m_{1\pm}, m_{2\pm}, \dots, m_{N\pm}}(n, n'; t)$  with respect to  $t$ , we can obtain the following hierarchy of equations in operator form

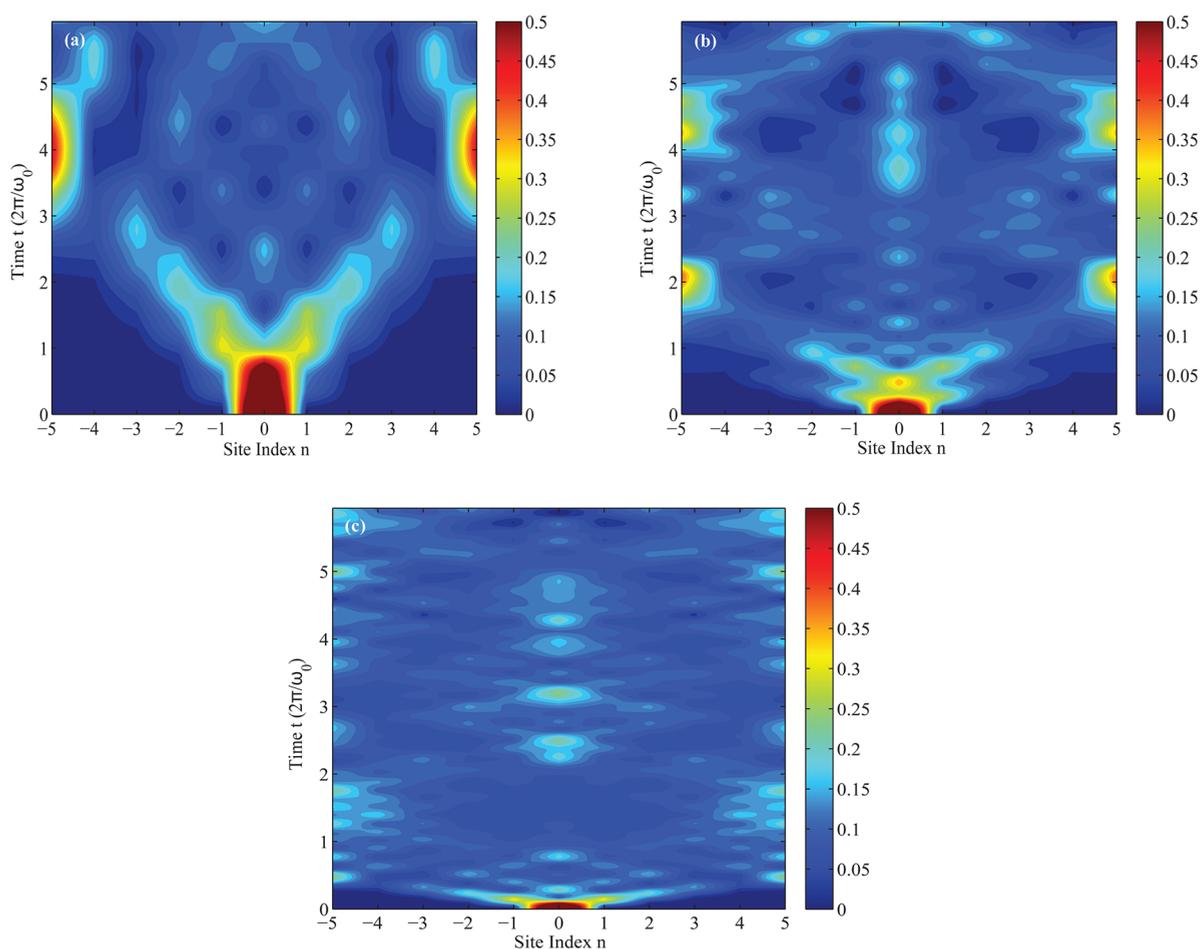
$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_{m_{1\pm}, \dots, m_{N\pm}}(t) &= -i\mathcal{L} \hat{\rho}_{m_{1\pm}, \dots, m_{N\pm}}(t) - i \sum_q \omega_q (m_{q-} - m_{q+}) \\ &\times \hat{\rho}_{m_{1\pm}, \dots, m_{N\pm}}(t) \\ &+ \hat{\rho}_{m_{1\pm}, \dots, m_{q+}, m_{q-}+1, m_{q-}, \dots, m_{N\pm}}(t) \\ &+ \sum_q (m_{q+} \hat{\Theta}_q + \hat{\rho}_{m_{1\pm}, \dots, m_{q+}-1, m_{q-}, \dots, m_{N\pm}}(t) \\ &+ m_{q-} \hat{\Theta}_q - \hat{\rho}_{m_{1\pm}, \dots, m_{q+}, m_{q-}-1, \dots, m_{N\pm}}(t)) \end{aligned} \quad (13)$$

The HEOM consists of an infinite number of equations, but they can be truncated at a finite number of hierarchy elements by the terminator as

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\rho}_{m_{1\pm}, \dots, m_{N\pm}}(t) &= -(i\mathcal{L} + i \sum_q \omega_q (m_{q-} - m_{q+})) \\ &\times \hat{\rho}_{m_{1\pm}, \dots, m_{N\pm}}(t) \end{aligned} \quad (14)$$

In principle, the HEOM provides an asymptotic approach that allows us to calculate various physical quantities with any desired accuracy by adjusting the number of hierarchical elements; the error introduced by the truncation can be made negligibly small by choosing the number of hierarchical elements to sufficiently large. The total number of hierarchy elements is evaluated as  $L_{\text{tot}} = (N_{\text{trun}} + 2N)! / N_{\text{trun}}! (2N)!$ , while the total number of termination elements is  $L_{\text{term}} = (N_{\text{trun}} + 2N - 1)! / (2N - 1)! N_{\text{trun}}!$ , where  $N_{\text{trun}}$  is the depth of hierarchy for  $m_{q\pm}$  ( $q = 1, \dots, N$ ). In practice, we can set the termination elements to zero and thus the number of hierarchy elements for calculation can be reduced as  $L_{\text{calc}} = L_{\text{tot}} - L_{\text{term}}$ . The system we consider is a molecular ring of  $N$  identical sites, and we vary the truncation number of hierarchy  $N_{\text{trun}}$  to confirm the convergence of the reduced density matrix. The initial state of system is prepared to have one exciton at site  $n = 0$ , i.e., we set the  $\rho_{0, \dots, 0}(0, 0) = 1$ , and all the other matrix elements of  $\hat{\rho}_{m_{1\pm}, m_{2\pm}, \dots, m_{N\pm}}$  are set to 0.

Figure 1 displays the time evolution of exciton population for various values of the transfer integral  $J$  at zero temperature. The phonon bandwidth  $W$  and exciton–phonon coupling  $g$  are set to 0.5 and 0.1, respectively. As shown in Figure 1a–c, the incident exciton at  $n = 0$  generates left- and right-moving wave packets of the exciton and make a quick rendezvous at the opposite site of



**Figure 2.** Time evolution of exciton population for (a)  $J = 0.2$ ,  $W = 0.5$ ,  $g = 0.2$ ; (b)  $J = 0.5$ ,  $W = 0.5$ ,  $g = 0.2$ ; (c)  $J = 1.0$ ,  $W = 0.5$ ,  $g = 0.2$ . The temperature is set to zero ( $\beta = \infty$ ).

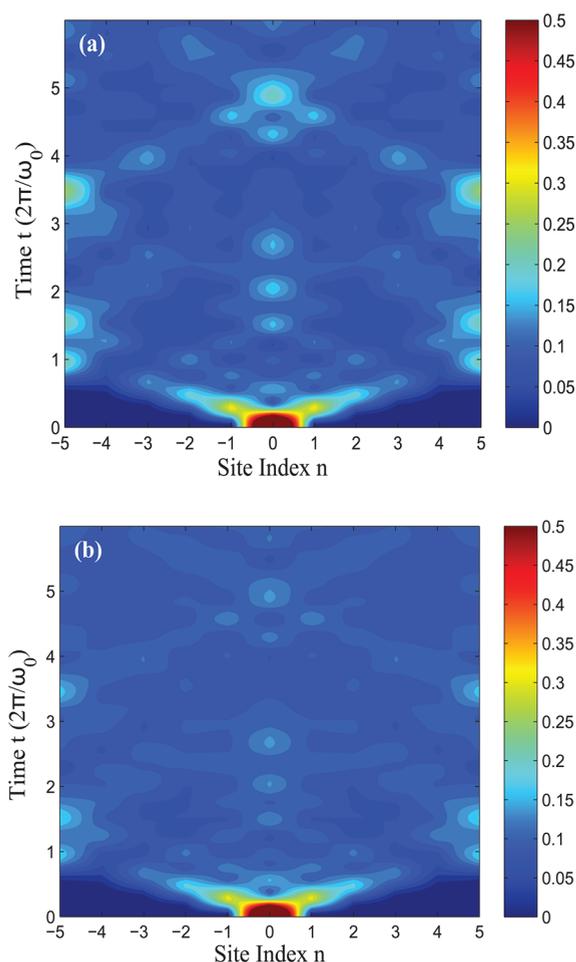
the ring, where the recombined exciton density is sufficiently high to trigger another pair of wave packets of the exciton. The exciton wave packets propagate from the initial site  $n = 0$  to the entire chain with a speed that is proportional to transfer integral  $J$  (the velocities of exciton propagation for Figure 1a–c are 2, 5, 10 in units of  $\omega_0/2\pi$ ). This is because the group velocity of the exciton wave packets, 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  $J$  (cf. eq 2).

The time evolution of exciton population in the intermediate exciton–phonon coupling regime ( $g = 0.2$ ) is shown in Figure 2. The rest of the parameters are the same as in the case of Figure 1. For small and intermediate transfer integrals ( $J = 0.2$  and  $0.5$ ), the exciton wave packets for  $g = 0.2$  are found to be much slower than that for the weak coupling case,  $g = 0.1$  as revealed by a comparison of the top two panels of Figures 1 and 2. Interestingly, for a large transfer integral ( $J = 1.0$ ), increase of exciton–phonon coupling from 0.1 to 0.2 has a minor effect on the speed of the exciton wave packets. This is because the exciton–phonon interaction  $g^2\omega_0$  for  $g = 0.2$  remains weak in comparison to the exciton transfer integral  $J$ . However, the V-shape propagation pattern after the first collision event at the opposite site of the ring in Figure 1c is significantly weakened in Figure 2c.

Next, we discuss the temperature effect on the evolution of the exciton population. Figure 3 illustrates the time-dependent exciton population at two temperatures ( $\beta = 2$  and  $\beta = 1.25$ ). The

rest of the parameter values are  $J = 0.5$ ,  $W = 0.5$ , and  $g = 0.1$ . Similarly to the case shown in Figure 1b, the left and right moving wave packets of the exciton depart from the site of creation and make a V-shape propagation until they collide at the opposite site of the ring. As time goes on, we can see clear differences in the exciton population (cf. Figure 1b and Figure 3a,b). The bright spots shown in Figure 1b are significantly quenched in Figure 3a,b due to heightened thermal fluctuations.

To summarize, we have derived a novel HEOM formalism that can treat a one-dimensional Holstein polaron in a non-perturbative manner and at any temperature. We have achieved this goal by expressing the HEOM in terms of discretized phonon modes in place of the Matsubara expansion. It is revealed that strong exciton phonon coupling leads to exciton localization, while a large exciton transfer integral facilitates exciton transport. Temperature effects on excitonic scattering have also been examined. We would like to emphasize that our work here is a proof of concept, one that also serves as a benchmark for future comparisons with other numerically intensive approaches to polaron dynamics.<sup>23</sup> Applying our theory to the study of one-dimensional Holstein model driven away from equilibrium by an external electric field is straightforward.<sup>51</sup> It is also of great interest to use our HEOM formalism to probe quantum dynamics of related Hamiltonians involving the Hubbard–Holstein model<sup>52,53</sup> and the t-J-Holstein model.<sup>54</sup> The fundamental connection between electronic correlation and decoherence induced by electron–phonon coupling in mole-



**Figure 3.** Time evolution of exciton population for (a)  $J = 0.5$ ,  $W = 0.5$ ,  $g = 0.1$ ,  $\beta = 2$ ; (b)  $J = 0.5$ ,  $W = 0.5$ ,  $g = 0.1$ ,  $\beta = 1.25$ .

cules and materials remains the key issue of investigation in condensed matter physics. Extensions of our HEOM approach in these directions are in progress.

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### Notes

The authors declare no competing financial interest.

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