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Direct evaluation of boson dynamics via finite-temperature time-dependent variation with multiple Davydov states

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Recent advances in quantum optics allow for exploration of boson dynamics in dissipative many-body systems. However, the traditional descriptions of quantum dissipation using reduced density matrices are unable to capture explicit information of bath dynamics. In this work, efficient evaluation of boson dynamics is demonstrated by combining the multiple Davydov *Ansatz* with finite-temperature time-dependent variation, going beyond what state-of-the-art density matrix approaches are capable to offer for coupled electron-boson systems. To this end, applications are made to excitation energy transfer in photosynthetic systems, singlet fission in organic thin films, and circuit quantum electrodynamics in superconducting devices. Thanks to the multiple Davydov *Ansatz*, our analysis of boson dynamics leads to clear revelation of boson modes strongly coupled to electronic states, as well as in-depth description of polaron creation and destruction in the presence of thermal fluctuations. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5017713>

I. INTRODUCTION

Central to the exciton dynamics in condensed phase systems is the interaction between the electronic and the bath degrees of freedom (DOFs) such as molecular vibrations and photons.^{1,2} In the weak coupling regime, this interaction has been usually considered as being responsible for energy dissipation. On the other hand, in the strong coupling and non-Markovian regime, this interaction serves to create a mixture of exciton with other quasiparticles and significantly modify exciton dynamics and spectroscopic signatures of such molecular systems. Developments of quantum optical technology² and ultrafast nonlinear spectroscopy^{3–9} have shed light on various properties of quantum mixing between these DOFs. The concept of the polaronic states (also referred to in the literature as vibronic excitons^{10–12}) created by the resonance between electronic excitation and intramolecular vibrational state^{10–27} was accepted as a plausible explanation for long-lived quantum beating in the two-dimensional (2D) electronic spectra of photosynthetic light harvesting complexes.^{28–33} The concept of polaron is also applied to the interpretation of oscillatory behavior in the 2D electronic spectra of singlet fission in organic thin films.^{34–38} Recent experiments in cavity quantum electrodynamics (QED) provide a realistic physical setup where the light-matter interaction is much larger than the atomic and cavity frequencies.^{39–41} In this strong light-matter coupling regime, the description of atoms and photons as distinct entities breaks down, and a description in terms of quantum mechanically mixed atomic and photon states, i.e., polaritons is required.⁴²

In general, descriptions of the quantum dissipative system involving interactions between the electronic and bath DOFs can be divided into two main classes: the reduced density matrix approach and the wave function propagation method. In the former, the interplay between electronic states and the bath DOFs can be characterized by the two-body correlation function of the collective energy gap coordinate or the corresponding spectral density.³ This approach provides insight into the influence of thermal fluctuations on the exciton-boson mixture in a natural manner. In the reduced density matrix formalism, all explicit information of the bath DOFs is lost, and the coupling between the electronic and bath DOFs is only reflected in the electronic populations. However, recent progress in the cavity QED makes it possible to address the dynamics of the photonic DOFs.^{43,44} Moreover, ultrafast spectroscopic studies have pointed to participation of intramolecular vibrations in the singlet fission.^{34,45,46} Thus, it becomes increasingly important to evaluate explicit boson dynamics of a many-body boson-electronic system, and better understandings of electronic-vibrational interactions may help control dynamics and design promising new photovoltaic materials. Alternatively, the wave function propagation method gives access to the dynamics of all bath DOFs explicitly.¹ One of the established wave function propagation approaches is to employ the Dirac-Frenkel time-dependent variational principle with the Davydov *Ansätze*^{48–51} or their extension in the form of superpositions of the Davydov *Ansatz*.^{52–56} In an early effort, the explicit boson dynamics was investigated by the variational approach with the single Davydov *Ansätze* in the Holstein molecular crystal model in order to capture the temporal interplay between the electronic and vibrational DOFs.⁵¹ Recently, the multiple Davydov *Ansatz* has been utilized, which offered significant improvements in the resulting dynamics.⁵⁴ This approach was extended to the boson

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dynamics in the Holstein molecular crystal model under an external electronic field to analyze the effects of exciton-phonon coupling on Bloch oscillations.⁵⁷ In addition, Kühn and co-workers have investigated impacts of the polaronic states on excitation energy transfer (EET) dynamics in the Fenna-Matthews-Olson (FMO) protein complex by tracking the time evolution of the bath DOFs based on the multilayer multiconfigurational time-dependent Hartree (ML-MCTDH) approach.^{24,25} Their calculations clearly showed the importance of phonons to local electronic ground states in the polaronic states. However, the zero temperature assumption may lead to an unreliable prediction for their role at finite temperatures because the electronic and vibrational quantum mixtures are fragile against thermal fluctuations.²² In a preceding paper,⁵⁸ we extended this variational approach to finite temperature dynamics of the spin-boson model by adopting a Monte Carlo importance sampling method. The time-dependent variational approach with multiple Davydov states remains surprisingly efficient even at an elevated temperature and thus can explore effects of thermal fluctuations on the exciton-boson quasiparticle by tracking dynamics of the bath DOFs.

In this work, we are concerned with explicit boson dynamics at finite temperatures that can be uncovered by the multiple Davydov *Ansätze*. We will demonstrate that our methodology can reveal interesting bath information that is previously unavailable to state-of-the-art density matrix approaches. To this end, applications are made to three examples, i.e., photosynthetic excitation energy transfer (EET), singlet fission process in organic materials, and circuit QED. The EET dynamics and singlet fission processes have been of great interest because of their potential importance to effective energy conversion. Recently, impacts of vibration-induced fluctuations on fission dynamics have been investigated with the multi-level Redfield theory.³⁵ The singlet population as functions of the time and the frequency of the vibrational mode has been probed, but how the vibrational modes evolve remains unknown. Meanwhile, the circuit QED attracts great interest in the community of quantum optics for its importance to implementing qubits. The quantized electromagnetic (EM) field, i.e., photons, can be used to manipulate qubits. The photon-number distribution as functions of the frequency and the coupling strength in the stationary state has been recently investigated via a semi-analytical variational method,⁴² but questions remain on how the distribution approaches to the stationary state. Thanks to advances in experimental techniques, the coupling between the qubit and the EM field reaches the ultra-strong coupling regime,^{39–41} where the rotating wave approximation (RWA) breaks down.^{90–92} Existing methods such as those of the quasi-adiabatic propagator path integral (QUAPI) and the hierarchy equations of motion (HEOM) are valid only for weak and intermediate coupling,^{47,55} but fail in the strong coupling regime, because the demand of memory size increases exponentially at strong coupling.⁴⁷ The method of the multi-D₂ *Ansatz*, on the other hand, can effectively and accurately treat both weak and strong coupling regimes in a unified manner. The results from the multi-D₂ *Ansatz* were found to agree well with those from the other methods such as HEOM in the weak to intermediate coupling

regime.⁵⁹ Moreover, the demand of the memory size of the multi-D₂ *Ansatz* is insensitive to the coupling strength. In this work, it will be demonstrated using the aforementioned three examples that information on the system and its boson environment can be obtained simultaneously in efficient dynamics simulation.

The rest of the paper is organized as follows. In Sec. II, we introduce the Hamiltonian and the Davydov *Ansätze* with the Monte Carlo importance sampling method. In Secs. III A–III C, we apply our approach to explicit boson dynamics in photosynthetic EET, singlet fission, and circuit QED. Finally, Sec. IV is devoted to concluding remarks.

II. FORMULATION

In this section, we present a brief introduction to finite temperature time-dependent variation with the multiple Davydov *Ansätze* and define some operators for investigating boson dynamics. For this purpose, we consider the EET Hamiltonian in a dimer as an example. The Hamiltonian of a light harvesting system consisting of two pigments is expressed as^{1,4}

$$\hat{H} = \frac{\epsilon}{2}\sigma_z + \Delta\sigma_x + \sum_m |m\rangle\langle m| \sum_k g_{m,k}(b_{m,k}^\dagger + b_{m,k}) + \hat{H}_b, \quad (2.1)$$

where σ_i ($i = x, z$) are the Pauli operators defined as $\sigma_x = |1\rangle\langle 2| + |2\rangle\langle 1|$ and $\sigma_z = |1\rangle\langle 1| - |2\rangle\langle 2|$ with $|n\rangle$ ($n = 1, 2$) representing electronic localized states. ϵ is the energetic difference between the two electronic states. Δ is the electronic coupling strength between two electronic states. The bath Hamiltonian is $\hat{H}_b = \sum_m \sum_k \omega_k b_{m,k}^\dagger b_{m,k}$. The dynamics of the k th mode of the m th electronic state is described by the creation operator, $b_{m,k}^\dagger$, and the annihilation operator, $b_{m,k}$. The system-bath coupling is usually characterized by the spectral density. The spectral density, $J_m(\omega)$, is given in terms of the displacement $g_{m,k}$ as

$$J_m(\omega) = \sum_k g_{m,k}^2 \delta(\omega - \omega_k). \quad (2.2)$$

The Schrödinger equation for the Hamiltonian in Eq. (2.1) is solved by employing the time-dependent variational approach with the multi-D₂ *Ansatz*^{54,56,57,59} in order to simulate the quantum dynamics of both the electronic and bath DOFs in the non-Markovian regime. The corresponding trial wave functions take the form

$$|D_2^M(t)\rangle = \sum_i \sum_{n=1}^2 c_{i,n}(t) |n\rangle e^{\sum_m \sum_k (f_{i,m,k}(t)b_{m,k}^\dagger - f_{i,m,k}^*(t)b_{m,k})} |0\rangle_b, \quad (2.3)$$

where $|0\rangle_b$ is the vacuum state of the boson bath. The variational parameter $c_{i,n}(t)$ is the amplitude in the electronic state $|n\rangle$, $f_{i,m,k}(t)$ represents the phonon displacement with i and k denoting the i th coherent state and k th bath mode, and M is the *Ansatz* multiplicity, which labels the number of single Davydov states included. For $M = 1$, the multi-D₂ *Ansatz* reduces to the traditional single D₂ *Ansatz*. The time-dependent variational parameters, $c_{i,n}(t)$ and $f_{i,m,k}(t)$, are determined by adopting the Lagrangian formalism of the Dirac-Frenkel

time-dependent variational principle.^{1,60,61} Detailed derivations of the equations of motion for the variational parameters can be found in Ref. 54.

In order to include temperature effects in the dynamics described by the multi-D₂ *Ansatz*, initial conditions for variational parameters are chosen with the Monte Carlo importance sampling in accordance with the equilibrium distribution.^{58,59,62} The equilibrium density matrix of the bath at a finite temperature is a diagonal matrix and can be expressed as^{63,64}

$$\hat{\rho}_{\text{vib}}^{\text{eq}} = \int d^2\alpha p(\alpha; \beta) |\alpha\rangle\langle\alpha|, \quad (2.4)$$

where $|\alpha\rangle$ denotes a direct product of coherent states $(\alpha_{1,1}, \alpha_{1,2}, \dots, \alpha_{1,N_b}, \alpha_{2,1}, \alpha_{2,2}, \dots, \alpha_{2,N_b})$ for the $2N_b$ discrete bath modes and is expressed as $|\alpha\rangle = \exp(\sum_l \alpha_l b_l^\dagger - \text{H.c.}) |0\rangle_b$. Each α_i runs over all of the feasible coherent states. The element of area $d^2\alpha_i$ on the complex plane of α_i denotes $d\text{Re}(\alpha_i) \cdot d\text{Im}(\alpha_i)$, in which $\text{Re}(\alpha_i)$ and $\text{Im}(\alpha_i)$ are the real and imaginary parts of α_i , respectively. $p(\alpha; \beta)$ represents the diagonal elements of the density matrix in the coherent state representation and can be expressed as⁶⁵

$$p(\alpha; \beta) = \prod_k^{N_b} \left[\frac{e^{\beta\omega_k} - 1}{\pi} \exp(-|\alpha_k|^2(e^{\beta\omega_k} - 1)) \right]. \quad (2.5)$$

As shown in Eq. (2.5), $p(\alpha; \beta)$ is a positive definite function of α and can be seen as a probability density. The observable $\langle O(t) \rangle$ at finite temperature can be calculated by the technique of Monte Carlo importance sampling as^{58,59}

$$\langle \hat{O}(t) \rangle = \frac{1}{N_s} \sum_i^{N_s} \langle D_2^M(t; \alpha_i) | \hat{O} | D_2^M(t; \alpha_i) \rangle, \quad (2.6)$$

where N_s is the sampling number, and the configuration α_i for the bath is numerically generated according to $p(\alpha; \beta)$ by the importance sampling, where $p(\alpha; \beta)$ is the Gaussian distribution used as the weighting function in the importance sampling procedures. Initial condition parameters are $c_{1,1}(0) = 1$, $c_{1,2}(0) = 0$, $c_{i,n}(0) = 0$ for $i \neq 1$ and $f_{i,m,k}(0) = \alpha_{m,k}$ for all i, m , and k .

The reduced density matrix element of the diabatic basis is given by

$$\begin{aligned} \rho_{nm}(t) &= \frac{1}{N_s} \sum_i^{N_s} \langle D_2^M(t; \alpha_i) | n \rangle \langle m | D_2^M(t; \alpha_i) \rangle \\ &= \sum_{i,j}^M \langle c_{i,n}^*(t) c_{j,m}(t) S_{i,j}(t) \rangle_{\text{avg}}, \end{aligned} \quad (2.7)$$

where $\langle \dots \rangle_{\text{avg}}$ denotes averaging over realizations and $S_{i,j}(t)$ is known as the Debye-Waller factor,

$$S_{i,j}(t) = e^{\sum_{m,k} (f_{i,m,k}^*(t) f_{j,m,k}(t) - |f_{i,m,k}(t)|^2/2 - |f_{j,m,k}(t)|^2/2)}. \quad (2.8)$$

To investigate impacts of thermal fluctuations on the mixed electronic and vibrational states, we explicitly track the boson DOFs. For this purpose, the phonon number is calculated by the expectation value of the Hamiltonian operator^{24,25}

$$H_{mg,k} = \omega_k b_{m,k}^\dagger b_{m,k} (1 - |m\rangle\langle m|), \quad (2.9)$$

where the expectation value gives the energy of the vibrational level on the electronic ground state for the m th pigment, regardless of the electronic excitation of the other pigments ($m \neq n$). The phonon displacement can be obtained by the Hamiltonian

$$H_{me,k} = [\omega_k b_{m,k}^\dagger b_{m,k} + g_{m,k}(b_{m,k}^\dagger + b_{m,k})] |m\rangle\langle m|, \quad (2.10)$$

where the expectation value of this operator characterizes the energy of the vibrational level on the electronic excited state for the m th pigment. By using the multiple Davydov *Ansätze*, the expectation values of the phonon number and the phonon displacement for time t can be evaluated as follows:

$$\begin{aligned} \chi_{mg,k}(t) &= \frac{1}{N_s} \sum_i^{N_s} \langle D_2^M(t; \alpha_i) | H_{mg,k} | D_2^M(t; \alpha_i) \rangle \\ &= \sum_{i,j}^M \sum_n^2 \langle c_{i,n}^*(t) c_{j,n}(t) \omega_k f_{i,m,k}^*(t) f_{j,m,k}(t) S_{i,j}(t) \rangle_{\text{avg}} \\ &\quad \times (1 - \delta_{n,m}), \end{aligned} \quad (2.11)$$

$$\begin{aligned} \chi_{me,k}(t) &= \frac{1}{N_s} \sum_i^{N_s} \langle D_2^M(t; \alpha_i) | H_{me,k} | D_2^M(t; \alpha_i) \rangle \\ &= \sum_{i,j}^M \langle c_{i,m}^*(t) c_{j,m}(t) [\omega_k f_{i,m,k}^*(t) f_{j,m,k}(t) \\ &\quad + g_{m,k}(f_{i,m,k}^*(t) + f_{j,m,k}(t))] S_{i,j}(t) \rangle_{\text{avg}}. \end{aligned} \quad (2.12)$$

III. APPLICATION TO THREE MODELS AND RESULTS

In this section, we present the results of our boson dynamics analysis based on the multi-D₂ *Ansatz* as it is applied to several models. The reliability of the variational approach with the multi-D₂ *Ansatz* at finite temperatures is established through a comparison with the benchmark results obtained from the iterative QUAPI technique or the reaction coordinate mapping master equation (RCME) approach,^{26,66} which leads to numerically exact dynamics in this theoretical model. Subsection III A treats the photosynthetic EET involving one single vibrational mode. In Subsection III B, we focus on the model of the singlet fission process, in which a singlet excited state is converted into two triplet excited states.^{67,68} Subsection III C then presents results for a model of the circuit QED in superconducting devices.

A. Photosynthetic excitation energy transfer

In this subsection, we apply our variational approach to the phonon dynamics in photosynthetic EET. We consider EET dynamics in a hetero-dimer. To describe EET dynamics, we restrict the electronic state of the pigments in a molecular dimer system to the ground state and the first excited state. Thus, the Hamiltonian of the light harvesting system consisting of two pigments is expressed as Eq. (2.1). For simplicity, we consider a single intramolecular vibration on each of the pigments, with frequency ω_{vib} and the Huang-Rhys factor S . We model the

spectral density using the Brownian oscillator model³ with the vibrational relaxation rate, γ_{vib} , such that

$$J_m(\omega) = \frac{4\lambda_{\text{vib}}^m \gamma_{\text{vib}} \omega_{\text{vib}}^2 \omega}{(\omega^2 - \omega_{\text{vib}}^2)^2 + 4\gamma_{\text{vib}}^2 \omega^2}, \quad (3.1)$$

where $\lambda_{\text{vib}}^m = \omega_{\text{vib}} S_m$ has been introduced. To obtain numerical solutions to the equations of motion of the variational parameters, the continuum spectral density of Eq. (3.1) needs to be discretized. In this study, the method of linear discretization is employed, in which one divides the frequency domain $[\omega_{\text{min}}, \omega_{\text{max}}]$ into N_b equal intervals $\Delta\omega$, where N_b is the number of discrete vibrational modes. We restrict the frequency of the discrete modes to a narrow range around the value of ω_{vib} in order to reduce the computational cost. The reduction of the low-frequency discrete modes does not give large deviations from the exact dynamics.²⁴ This is also demonstrated through a comparison with the benchmark results in this section. The k th frequency is given by $\omega_k = k\Delta\omega = k(\omega_{\text{max}} - \omega_{\text{min}})/N_b$. From Eq. (2.2), the displacement of $g_{m,k}$ for each ω_k is then given by $g_{m,k}^2 = J_m(\omega_k)\Delta\omega$.

We focus on a dimer that produces no beating of electronic origin in the absence of polaronic contributions. The dimer is inspired by bacteriochlorophylls (BChls) 3 and 4 (pigments 1 and 2, respectively) in the FMO complex of *Chlorobaculum tepidum*,^{22,69–71} which serve as the two lowest energy exciton states in the single-excitation manifold. For simplicity, the energetic difference between two electronic states and their electronic coupling are set to $\epsilon = 150 \text{ cm}^{-1}$ and $\Delta = -50 \text{ cm}^{-1}$, respectively. The molecular dynamics simulation of light-harvesting complex II of *Rhodospirillum rubrum* predicts a large value of the Huang-Rhys factors in BChls ($S = 0.5$).⁷² Accurate vibrational structure calculations of excited states is difficult and so we also consider estimates based on experimental measurements. In this study, we choose $S_1 = S_2 = S = 0.025$,¹⁷ which is within the range of experimentally measured values.^{73,74}

First, we focus on the dynamics of intramolecular vibrations of pigments 1 and 2 at 77 K, as shown in Fig. 1. The low-frequency vibrational modes of BChl in solutions or protein environments have been investigated in a number of

FIG. 1. Illustration of quantum mechanical mixing among vibronic transitions of pigments 1 and 2 in a weakly coupled dimer. For pigment m , $|\varphi_{ma}\rangle$ with $a = g$ and $a = e$ denotes the ground and first excited electronic states, respectively. $|\chi_{av}^m\rangle$ represents the vibrational configuration of pigment m with the v th vibrational energy level on electronic state a . Arrows colored by same color represent pairs of the resonant vibronic transitions.

experiments, revealing the most strongly coupled vibrational mode at approximately 180 cm^{-1} .^{73,74} Thus, to describe the effects of the Franck-Condon active vibrational modes, we consider a single vibrational mode with frequency $\omega_{\text{vib}} = 180 \text{ cm}^{-1}$ in this subsection. In this situation, the gap between the two electronic energy eigenstates resonates with the vibrational frequency, $[\epsilon^2 + 4\Delta^2]^{1/2} \simeq \omega_{\text{vib}}$, and hence, the effects of the vibrational mode are expected to be maximized under given conditions.¹⁷ The vibrational relaxation rate is set to $\gamma_{\text{vib}}^{-1} = 2 \text{ ps}$.

Figure 2(a) presents time evolution of the donor (pigment 1) population affected by intramolecular vibrations of pigments 1 and 2. Our results by the multi-D₂ Ansatz are quantitatively consistent with the numerically exact results of the RCME approach. The population dynamics in Fig. 2(a) involves two oscillating components: a faster oscillation with a small amplitude and a slow oscillation with a large amplitude. The faster oscillating component is due to the EET between 0-0 vibronic transition, $|\varphi_{1g}\rangle|\chi_{g0}^1\rangle \leftrightarrow |\varphi_{1e}\rangle|\chi_{e0}^1\rangle$ and the 0-0 vibronic transition, $|\varphi_{2g}\rangle|\chi_{g0}^2\rangle \leftrightarrow |\varphi_{2e}\rangle|\chi_{e0}^2\rangle$ which is induced by the coupling strength, $\Delta\langle\chi_{e0}^1|\chi_{g0}^1\rangle\langle\chi_{e0}^2|\chi_{g0}^2\rangle = \Delta e^{-S} = 0.987\Delta$, for $S = 0.025$. The slower oscillating component arises from the two interactions. As shown, in red arrows, in Fig. 1, one is the interaction between the 0-0 vibronic transition, $|\varphi_{1g}\rangle|\chi_{g0}^1\rangle \leftrightarrow |\varphi_{1e}\rangle|\chi_{e0}^1\rangle$ and the 0-1 vibronic transition, $|\varphi_{2g}\rangle|\chi_{g0}^2\rangle \leftrightarrow |\varphi_{2e}\rangle|\chi_{e1}^2\rangle$ which is a result of

FIG. 2. Panel (a) shows the time evolution of the electronic donor population affected by intramolecular vibration at 77 K. The dashed line indicates the benchmark result by RCME. Panels (b)–(d) present the time evolution of vibrational energies $\chi_{2e,k}(t)$, $\chi_{1g,k}(t)$ and $\chi_{1e,k}(t)$ in the presence of two vibrations, respectively. Note that the vibrational excitation, $\chi_{2g,k}(t)$, of pigment 2 is close to zero and not shown. The Franck-Condon transition energy of each pigment and their electronic coupling are set to $\epsilon = 150 \text{ cm}^{-1}$ and $\Delta = -50 \text{ cm}^{-1}$, respectively. The Huang-Rhys factor, the frequency of vibration, and the dephasing time are $S = 0.025$, $\omega_{\text{vib}} = 180 \text{ cm}^{-1}$, and $\gamma_{\text{vib}}^{-1} = 2 \text{ ps}$, respectively. The multiplicity is set to $M = 2$. The spectral density is discretized into 50 equally spaced modes in the interval $[120:220] \text{ cm}^{-1}$. Statistical averages are taken over a maximum of 50 realizations.

the coupling strength, $\Delta\langle\chi_{e0}^1|\chi_{g0}^1\rangle\langle\chi_{e1}^2|\chi_{g0}^2\rangle = -\Delta e^{-S}\sqrt{S} = -0.156\Delta$. The other one is the interaction between the 0-1 vibronic transition, $|\varphi_{1g}\rangle|\chi_{g1}^1\rangle \leftrightarrow |\varphi_{1e}\rangle|\chi_{e0}^1\rangle$ and the 0-0 vibronic transition, $|\varphi_{2g}\rangle|\chi_{g0}^1\rangle \leftrightarrow |\varphi_{2e}\rangle|\chi_{e0}^1\rangle$ and participates in the 1-st vibrational level on the electronic ground state, as shown, in blue arrows, in Fig. 1.

In order to elucidate the relation between the population oscillation and the phonon excitations, Figs. 2(b)–2(d) exhibit time evolution of $\chi_{2e,k}(t)$, $\chi_{1g,k}(t)$, and $\chi_{1e,k}(t)$, respectively. As shown in Fig. 2(b), the discrete modes of the pigment 2 around $\omega_{\text{vib}} = 180 \text{ cm}^{-1}$ are excited just after the photoexcitation. The peak position of the phonon excitation on the state $|\varphi_{2e}\rangle$ consequently splits into two peaks: $\omega_k \approx 170 \text{ cm}^{-1}$ and $\omega_k \approx 190 \text{ cm}^{-1}$. This peak splitting indicates the creation of the polaronic states, $|e_1^+\rangle$ and $|e_1^-\rangle$ by the resonance between $|\varphi_{1e}\rangle|\chi_{e0}^1\rangle$ and $|\varphi_{2e}\rangle|\chi_{e1}^2\rangle$ (red arrows in Fig. 1). This is a novel feature of explicit boson dynamics calculations because the reduced density matrix approach cannot reveal the formation of polaronic states directly. The polaronic states survive for at least 5 ps due to the long vibrational relaxation time, $\gamma_{\text{vib}}^{-1} = 2 \text{ ps}$. In Fig. 2(c), the phonon excitation of discrete modes of the pigment 1 around 180 cm^{-1} is revealed, indicating for the EET driven by the resonance between the 1-0 vibronic transition, $|\varphi_{1g}\rangle|\chi_{g1}^1\rangle \leftrightarrow |\varphi_{1e}\rangle|\chi_{e0}^1\rangle$ and the 0-0 vibronic transition, $|\varphi_{2g}\rangle|\chi_{g0}^2\rangle \leftrightarrow |\varphi_{2e}\rangle|\chi_{e0}^2\rangle$ (blue arrows in Fig. 1). This clearly shows the importance of the phonon dynamics on the electronic ground state. This observation is consistent with the ML-MCTDH results in Refs. 24 and 25 and corroborates the argument by Ishizaki and co-workers.²² After 1 ps, the peak splitting due to the creation of the polaronic states can be observed, as with Fig. 2(b). The phonon displacement $\chi_{1e,k}(t)$ in Fig. 2(d) corresponds to vibrational excitation on the electronic excited state of pigment 1. This vibrational excitation leads to the EET accelerated by the resonance between the 1-1 vibronic transition, $|\varphi_{1g}\rangle|\chi_{g1}^1\rangle \leftrightarrow |\varphi_{1e}\rangle|\chi_{e1}^1\rangle$ and the 0-1 vibronic transition, $|\varphi_{2g}\rangle|\chi_{g0}^2\rangle \leftrightarrow |\varphi_{2e}\rangle|\chi_{e1}^2\rangle$ as shown, in magenta arrows, in Fig. 1. The phonon number, $\chi_{2g,k}(t)$, of pigment 2 is negligibly small (not shown) as the state $|\varphi_{1g}\rangle|\chi_{g1}^1\rangle$ does not participate in the resonant vibronic transitions in the model dimer studied here.

Next, we investigate how thermal fluctuations affect the polaronic states. For simplicity, we consider a molecular dimer affected by only intramolecular vibration of pigment 2 and focus on the EET between 0-0 vibronic transition ($|\varphi_{1g}\rangle|\chi_{g0}^1\rangle \leftrightarrow |\varphi_{1e}\rangle|\chi_{e0}^1\rangle$) and the 0-1 vibronic transition ($|\varphi_{2g}\rangle|\chi_{g0}^2\rangle \leftrightarrow |\varphi_{2e}\rangle|\chi_{e1}^2\rangle$) as shown, in red arrows, in Fig. 1. Therefore, we plot only the phonon excitation on the electronic state $|\varphi_{2e}\rangle$. The EET dynamics is simulated for various dephasing times, γ_{vib} , in Fig. 3. Figure 3(a) presents the time evolution of the electronic donor population affected by only intramolecular vibrations of pigment 2 in the case of $\gamma_{\text{vib}}^{-1} = 2 \text{ ps}$. Calculations in Fig. 3 were performed using the same parameters as in Fig. 2 (except γ_{vib}). Figure 3(b) shows the phonon excitation on the electronic state $|\varphi_{2e}\rangle$ corresponding to the electronic donor population dynamics in Fig. 3(a) and behaves in a similar way as the case of two vibrational modes in Fig. 2(b). In the case of $\gamma_{\text{vib}}^{-1} = 1 \text{ ps}$, the oscillatory behavior

FIG. 3. Time evolution of donor population dynamics in the molecular dimer with intramolecular vibration of pigment 2 in the case of (a) $\gamma_{\text{vib}}^{-1} = 2 \text{ ps}$, (c) $\gamma_{\text{vib}}^{-1} = 1 \text{ ps}$, and (e) $\gamma_{\text{vib}}^{-1} = 500 \text{ fs}$. The dashed line indicates the benchmark result by RCME. Panels (b), (d), and (f) present phonon energy of intramolecular vibration of pigment 2 in the case of $\gamma_{\text{vib}}^{-1} = 2 \text{ ps}$, $\gamma_{\text{vib}}^{-1} = 1 \text{ ps}$, and $\gamma_{\text{vib}}^{-1} = 500 \text{ fs}$, respectively. The spectral density is discretized into 50 equally spaced modes in the interval $[120:220] \text{ cm}^{-1}$. The calculations were performed using the same parameters except γ_{vib} as in Fig. 2.

of donor population dynamics in Fig. 3(c) quickly vanishes compared with Fig. 3(a). The peak of lower frequency ($\omega_k \approx 170 \text{ cm}^{-1}$) in $\chi_{2e,k}(t)$ in the case of $\gamma_{\text{vib}}^{-1} = 1 \text{ ps}$ disappears after 3 ps, suggesting that the fast thermal fluctuations eradicate the electronic-vibrational mixture. This tendency becomes more pronounced with increasing dephasing rate, γ_{vib} , as shown in Figs. 3(e) and 3(f).

In order to explore impacts of the phonon frequency on polaron formation, we calculate the time evolution of electronic donor population dynamics for the values of $\omega_{\text{vib}} = 140 \text{ cm}^{-1}$ and 160 cm^{-1} with results shown in Figs. 4(a) and 4(c), respectively. The calculations are performed using the same parameters as in Fig. 2 (except ω_{vib}). The phonon frequency in Fig. 4 is far from the resonance condition, and the population dynamics shows no oscillatory component due to the vibronic mixing between the vibronic transitions shown in the red arrows of Fig. 1, and these off-resonant vibrations do not promote EET dynamics compared with the resonant case in Fig. 3(a). The discrete modes around ω_{vib} are excited after the photoexcitation, as shown in Figs. 4(b) and 4(d). The excitation

FIG. 4. Time evolution of donor population in a molecular dimer with intramolecular vibration of the pigment 2 in the case of (a) $\omega_{\text{vib}} = 140 \text{ cm}^{-1}$ and (c) $\omega_{\text{vib}} = 160 \text{ cm}^{-1}$. The dashed line indicates the benchmark result by RCME. Panels (b) and (d) present the time evolution of $\chi_{2e,k}(t)$ in the case of $\omega_{\text{vib}} = 140 \text{ cm}^{-1}$ and $\omega_{\text{vib}} = 160 \text{ cm}^{-1}$, respectively. The spectral densities in the panels (a) and (c) are discretized into 50 equally spaced modes in the interval (a) [100:200] and (c) [120:220] cm^{-1} , respectively. The calculations were performed using the same parameters except ω_{vib} as in Fig. 2.

of the discrete modes on the state $|\varphi_{2e}\rangle$ diffuses over a wide range of phonon frequencies and does not clearly show electronic-vibrational mixture unlike Fig. 3(b). Recent analyses of beating amplitude in 2D electronic spectra^{12,17,22} have demonstrated that at the cryogenic temperature, the polaronic states are robust over a wide phonon frequency range around the vibronic resonance even under the influence of environmentally induced fluctuations. Our results suggest that the electronic-vibrational mixing is sensitive to the frequency of the intramolecular vibration, contrary to speculations based on 2D electronic spectra.

B. Singlet fission

In this subsection, we apply our boson dynamics approach to singlet fission processes. In this study, we adopt a model dimer for the singlet fission process based on the four-electron four-orbital picture.^{35,67,75–85} A simple scheme of the singlet fission process is considered as $g \rightarrow S_1 \rightarrow TT$, which involves the electronic ground state (g), the photoexcited singlet excited state ($S_1, |1\rangle$), and the triplet pair state ($TT, |2\rangle$). The Hamiltonian of the singlet fission process consisting of two electronic states is expressed as^{35,85}

$$\hat{H} = \frac{\epsilon}{2} \sigma_z + \Delta \sigma_x + \sum_m |m\rangle \langle m| \sum_k g_{m,k} (b_k^\dagger + b_k) + \sum_k \omega_k b_k^\dagger b_k, \quad (3.2)$$

where b_k ($b_k^\dagger$) represents the annihilation (creation) operator of the k th phonon mode with frequency ω_k . The functional

form of spectral density $J_m(\omega)$ is the same as in Eq. (3.1) in Subsection III A. The multi-D₂ Ansatz is adopted,

$$|D_2^M(t)\rangle = \sum_i^M \sum_n^2 c_{i,n}(t) |n\rangle e^{\sum_k (f_{i,k}(t) b_k^\dagger - f_{i,k}^*(t) b_k)} |0\rangle_b, \quad (3.3)$$

where $f_{i,k}(t)$ represents the phonon displacement with i and k denoting the i th coherent state and the k th boson mode. The expectation values of the phonon number and the phonon displacement for time t can be evaluated as follows:

$$\begin{aligned} \chi_{gk}(t) &= \langle D_2^M(t) | b_k^\dagger b_k | D_2^M(t) \rangle \\ &= \sum_{i,j}^M \sum_n^2 c_{i,n}^*(t) c_{j,n}(t) f_{i,k}^*(t) f_{j,k}(t) S_{ij}(t), \end{aligned} \quad (3.4)$$

$$\begin{aligned} \chi_{ek}(t) &= \langle D_2^M(t) | g_{m,k} (b_k^\dagger + b_k) | D_2^M(t) \rangle \\ &= \sum_{i,j}^M c_{i,m}^*(t) c_{j,m}(t) [g_{m,k} (f_{i,k}^*(t) + f_{j,k}(t))] S_{ij}(t), \end{aligned} \quad (3.5)$$

where

$$S_{ij}(t) = e^{\sum_k (f_{i,k}^*(t) f_{j,k}(t) - |f_{i,k}(t)|^2/2 - |f_{j,k}(t)|^2/2)}. \quad (3.6)$$

In the Hamiltonian of singlet fission in our study, it is assumed that the fluctuations of the electronic state induced by phonons are correlated. Both the phonon number and the phonon displacement display the same information, and thus we present only the time evolution of the phonon displacement in this subsection.

Figure 5(a) presents the time evolution of the singlet state population in the case of $\gamma_{\text{vib}}^{-1} = 500 \text{ fs}$. The population dynamics calculated by RCME^{26,66} is also plotted in Fig. 5(a) in order to demonstrate the validity of the results by the multi-D₂ Ansatz. The population dynamics by the multi-D₂ Ansatz is quantitatively consistent with the numerically exact result from the RCME. An overall population dynamics exhibits an exponential decay with small-amplitude oscillations. The oscillatory component in the singlet population is attributed to the presence of the underdamped vibrational mode. The intramolecular vibrations generate a resonance between the singlet and the correlated triplet pair states by matching their energy difference and play an essential role in enhancement of fission dynamics, as shown in Fig. 5(a).

To explore the interplay between electronic and vibrational states, boson dynamics as a function of ω_k in the case of $\gamma_{\text{vib}}^{-1} = 250 \text{ fs}$, $\gamma_{\text{vib}}^{-1} = 500 \text{ fs}$, and $\gamma_{\text{vib}}^{-1} = 1 \text{ ps}$ is shown in Figs. 5(b)–5(d), respectively. In the case of $\gamma_{\text{vib}}^{-1} = 1 \text{ ps}$, a few discrete boson modes around $\omega_{\text{vib}} = 80 \text{ meV}$ are excited after the photoexcitation, as shown in Fig. 5(d). Given the parameters of our model, the energy difference, ϵ , is much larger than the interstate coupling strength, Δ , and the energy splitting between eigenstates is on the order of 3–5 meV.³⁵ Thus, the time evolution of the phonon displacement in Fig. 5 does not show clear peak splitting, unlike Figs. 2, 3, and 4 in Subsection III A. The states of these discrete modes are robust under the fluctuations due to a slow vibrational dephasing time $\gamma_{\text{vib}}^{-1} = 1 \text{ ps}$. The excited levels of the discrete modes around

FIG. 5. (a) Time evolution of singlet population in the case of (a) $\gamma_{\text{vib}}^{-1} = 500$ fs. The dashed line indicates the benchmark result by RCME. Panels (b)–(d) show time evolution of the phonon displacement $\chi_k(t)$ in the case of $\gamma_{\text{vib}}^{-1} = 250$ fs, $\gamma_{\text{vib}}^{-1} = 500$ fs, and $\gamma_{\text{vib}}^{-1} = 1$ ps, respectively. Parameters: $\epsilon = 100$ meV, $\Delta = 20$ meV, $S_1 = 0.7$, $S_2 = 1.4$, $\omega_{\text{vib}} = 80$ meV, and $T = 0$ K. The multiplicities in the panels (b)–(d) are set to (b) $M = 19$, (c) $M = 7$, and (d) $M = 3$, respectively. The spectral density in (b)–(d) is discretized into 50 equally spaced modes in the interval (b) [30:110], (c) [50:90], and (d) [50:90] meV, respectively. These parameters were used in Ref. 35.

ω_{vib} behave as stiff vibrational levels, which create a resonance between the singlet and the correlated triplet pair states by matching their energy difference. These results show that the discrete modes except those around ω_{vib} are not important for population dynamics of S_1 and TT states, and these vibrational levels do not drive fission dynamics when the vibrational mode does not satisfy the energy matching condition. As shown in Fig. 5(c), at $\gamma_{\text{vib}}^{-1} = 500$ fs, the width of the excited levels of the discrete modes broadens around ω_{vib} , but the excited levels are still distributed mainly in the vicinity of ω_{vib} . If one continues decreasing the vibrational relaxation rate to $\gamma_{\text{vib}}^{-1} = 250$ fs, the boson dynamics shows the excitation of the discrete modes in the broad range of ω_k as displayed in Fig. 5(b). The discrete modes away from ω_{vib} affect the superposition of S_1 and TT, and thus the quantum mixture created by the resonance between the vibronic transitions is quickly eroded.

In this subsection, we considered the singlet fission dynamics with single intramolecular vibration. Previous theoretical study in singlet fission dynamics demonstrated that several vibrational modes with relatively small Huang-Rhys factors may not enhance the fission process by themselves but can dramatically affect the interplay between fission dynamics and other dominant vibrational modes.³⁵ The fitting of the measured absorption spectra of tetracene derivatives in cyclohexane with the spectroscopic model based on quantum chemical calculations reveals that several intramolecular vibrational modes in tetracene derivatives have Huang-Rhys

factors beyond 0.1.⁸⁶ Investigation of the boson dynamics based on the realistic spectral density model extracted from spectroscopies or molecular dynamics simulations may identify functional vibrational modes for promoting singlet fission dynamics, and better understandings of the interplay between electronic and vibrational states provide insights into how to control dynamics and help design promising new organic solar materials.

C. Circuit QED

In this subsection, the multi- D_2 Ansatz is employed to investigate interactions between a qubit and an EM field with focus on explicit boson dynamics. Figure 6 is the schematics of a circuit with a Josephson junction coupled with an EM field supplied by a coplanar transmission line resonator, in which the QED is investigated.^{87,88} Figure 6(a) shows an experimental setup of a system that is equivalent to a qubit implemented by a real atom placed in a cavity of the EM wave. The corresponding circuit of Fig. 6(a) is plotted in Fig. 6(b). The energy of the qubit can be tuned by changing the external magnetic field, which controls over the interaction between the qubit and the EM field. The energy separation of the qubit can be set through appropriate circuit design easily.⁸⁸ These properties makes the circuit a powerful tool to investigate a quantum system interacting with the EM field. For qubits interacting with a transmission line, the whole system can be modeled as spins coupled to the one-dimensional EM field.^{42,89–94} The system Hamiltonian can be formulated as

$$H = \frac{1}{2} \epsilon \sigma_x + \sum_k \omega_k b_k^\dagger b_k + \frac{\sigma_z}{2} \sum_k (g_k^* b_k + g_k b_k^\dagger), \quad (3.7)$$

FIG. 6. (a) Schematic diagram of a superconducting qubit coupled to a coplanar transmission line resonator. The control line supplies an external magnetic flux to tune the energy level separation of the qubit (yellow). The length of the transmission line resonator shown in green is L , and the dashed pink lines illustrate the EM field. (b) The schematic circuit diagram corresponding to (a). The inductance per unit length is l_0 , and the capacitance per unit length is c_0 . The control line supplies the magnetic flux Φ_x threading the qubit. The semi-infinite transmission lines couple to the resonator via the capacitance C_0 .

where g_k is the strength of qubit-EM coupling and $b_k^\dagger$ (b_k) is the creation (annihilation) operator of the quantized EM field with frequency ω_k . The emitter is modeled as a two-level atom, also referred to as the qubit or the spin, and ϵ is the splitting of the two-level system typically set by the Josephson energy associated with the superconducting qubit. A detailed derivation of the system Hamiltonian is given in [Appendix A](#). The transmission line of length L is discretized into N parts equally, and the length of each part is $\delta x = L/N$. The coupling strength (see [Appendix A](#)) is

$$g_k = \begin{cases} ig\sqrt{\frac{2\omega_k}{Ll_0}} e^{in\delta xk} \cos\left(\frac{\delta xk}{2}\right) & k > 0 \\ -ig\sqrt{\frac{2\omega_k}{Ll_0}} e^{in\delta xk} \cos\left(\frac{\delta xk}{2}\right) & k < 0 \end{cases}, \quad (3.8)$$

in which g is determined by the parameters of the qubit-line system, and l_0 is the inductance per unit length. g_k is a complex number and can be expressed as $g_k = |g_k|e^{i\theta_k}$. The phase θ_k can be seen as an arbitrary extra phase of the EM field and does not change the value of observables such as $\langle\sigma_z\rangle$ and $\langle b_k^\dagger b_k\rangle$. The factor $\cos(\delta xk/2)$ is approximately 1 for low frequencies. Letting $\delta x \rightarrow 0$, for the modes with sufficiently low frequencies, Eq. (3.8) yields the Ohmic spectral density

$$J(\omega) = \sum_k |g_k|^2 \delta(\omega - \omega_k) = 2\alpha\omega, \quad (3.9)$$

in which

$$\alpha = \frac{g^2}{\pi v_{\text{EM}}}, \quad (3.10)$$

and v_{EM} is the speed of the EM field. In the literature, an exponential decay is usually employed as the cutoff of the spectral density,⁴²

$$J(\omega) = 2\alpha\omega e^{-\omega/\omega_c}. \quad (3.11)$$

In the weak coupling limit, it is customary to invoke the RWA,^{90–92} where the Hamiltonian in Eq. (3.7) is truncated such that only qubit levels dressed by adjacent Fock states are included. However, this approximation breaks down for large coupling cases, and so for our purposes, the model must be addressed in its full complexity. A particular defect of the RWA is the lack of many-body renormalization, that is, the strong reduction of the bare tunneling energy ϵ to a smaller value.⁴² This renormalization effect is, however, well described by the multiple Davydov trial states, where the dressing of the qubit levels occurs via coherent states.^{93,94} The multi- D_2 Ansatz and the phonon displacement $\chi_k(t)$ given by Eqs. (3.4) and (3.6) are used here, respectively.

From the discussion above, the coupling g_k can be obtained in two procedures. One is from a continuous spectral density in Eq. (3.11) and the other one is from a discrete form of the coupling in Eq. (3.8). The continuous one includes the conditions that $\delta x \rightarrow 0$ and the frequencies are sufficiently low. It is necessary to know whether the two procedures would lead to the same dynamics of the qubit. As shown in Fig. 7, the dynamics of the population difference $P_z(t) = \langle D_2^M(t) | \sigma_z | D_2^M(t) \rangle$ from the two procedures is compared for various coupling

FIG. 7. Comparison between dynamics of g_k from the Ohmic spectral in Eq. (3.11) (solid line in red) and the discrete form of the coupling in Eq. (3.8) (dashed line in green). $\alpha = 0.05$ and 0.2 are employed in panels (a) and (b), respectively. To benchmark our calculations, the comparison between $P_z(t)$ from the multi- D_2 Ansatz and that from the QUAPI method at $\alpha = 0.02, 0.2$, and 0.5 is plotted in (c)–(e), respectively. ω_c is the unit of the frequency, v/ω_c is the unit of length and the length transmission is $L = Nv/\omega_c$. Other parameters: the bias $\epsilon = 0.1\omega_c$, the number of modes $N = 180$, and the inductance per unit length $l_0 = 1$.

strengths α . At weak coupling ($\alpha = 0.05$), the two procedures produce quite similar dynamics (both in amplitude and phase). At strong coupling ($\alpha = 0.2$), however, the two procedures generate different dynamics, which shows that the conditions under which the Ohmic spectral density is valid are met only for weak coupling. High frequency modes of the EM field are not excited at weak coupling, and therefore the two procedures lead to similar dynamical behaviors, while the same is not true at strong coupling with the excitation of those modes. It is inferred that for strong coupling, excitation of the high frequency modes must be avoided if the Ohmic spectral density can be employed to model the EM field. Finally, to demonstrate the reliability of our simulations, the QUAPI approach is employed to provide benchmark calculations. As shown in Figs. 7(c)–7(e), the two methods are in quantitative agreement from the very weak coupling $\alpha = 0.02$ to the strong

coupling $\alpha = 0.5$. The deviation is observed at $\alpha = 0.7$. At strong coupling, the QUAPI method needs a larger memory time $\tau_{mem} = K\delta t$ to achieve convergence, where K is the memory parameter and δt is the time step size. The memory size for QUAPI convergence is found to increase exponentially with K .⁴⁷

Recently, in Ref. 42, the photon number $\langle b_k^\dagger b_k \rangle$ at stationary state is investigated as a function of the coupling strength α and the frequency of the modes ω_k . It is found that a peak in the distribution exists around the renormalized qubit frequency, while how the distribution approaches to the stationary state is still unknown. Thus, simulations are performed to clarify the evolution of the EM field coupling with the qubit. Figure 8(a) presents $P_z(t)$ for the various values of α . The multi- D_2 Ansatz reveals incoherent dynamics for $\alpha > 0.5$, whereas the dynamics is coherent for $\alpha = 0.2$. This result is consistent with that of the non-interacting blip approximation method, which showed that a coherent-incoherent crossover takes place at $\alpha = 0.5$.⁹⁵ In order to investigate the interplay between the spin and the photon, Figs. 8(b)–8(d) show the time evolution of the photon number $\chi_k(t)$ for the cases of $\alpha = 0.2, 0.5$, and 0.7 , respectively. After electronic excitation

at $t = 0$, the peak of the photon number is located in the vicinity of the cutoff frequency ω_c and the frequency decreases over time. In the case of $\alpha = 0.2$, the peak position finally converges to $\omega_k = 0.1$, which is comparable to ϵ and resonates the energy gap between two spin states. In the case of the incoherent phase, the oscillation amplitude of photon modes becomes large due to increase of α and the peak position converges to $\omega_k = 0$.

To further investigate the evolution of the EM field, we also extract the peak of the photon number at each time from Figs. 8(b)–8(d) and plot the evolution of the peak in the same figure with a log-log scale. As shown in Fig. 8(e), the three curves coincide before reaching their stationary states. α only changes the steady-state frequency, as shown in the case of $\alpha = 0.2$. Thus, the evolution of the peak is insensitive with the coupling strength. Interestingly, the decrease of the curves satisfies a power law with a slope of roughly 1. To the best of our knowledge, the power law behavior of the peak is found for the first time and further study is needed to elucidate its underlying mechanism. The peak position in the cases of $\alpha = 0.5$ and $\alpha = 0.7$ shows that the oscillation of the photon number survives even at very long times. This long-lived oscillation is due to a finite value of $P_z(t)$ at long times, as discussed using an analytical formula by Schoröder and Chin.⁹⁶

To probe the relation between the peak of the photon distribution and the number of modes N_b (i.e., the system size), simulations are performed for the system with the Ohmic bath of $N_b = 120$ modes. The power-law behavior is still found to exist, and the slopes of the curves in a log-log plot are approximately 1. Results show that the power-law behavior does not depend on the system size. Simulations are also carried out for the peak of the photon distribution using a discrete form of coupling g_k . The coupling strengths $\alpha = 0.2, 0.5$, and 0.7 are chosen, similar to the case of the Ohmic spectral density. The number of modes is $N_b = 180$. While the three curves decrease in time with similar rates as the ones in the Ohmic spectral density case, the power-law behavior is absent in the plot, which is likely attributed to the Ohmic spectral density.

This peak behavior in the steady state can be understood in the framework of polaron unitary transformation.⁴² In the polaron transformed frame, the transition frequency ϵ is renormalized due to fluctuations induced by the displaced photon modes. For large coupling strengths, the renormalized transition frequency is reduced to zero. Therefore, the frequency of the photon modes that resonate with the energy gap between two spin states decrease with increasing coupling strength α , and the peak position finally reaches zero in the limit of strong coupling.

The multi- D_2 Ansatz is an efficient method for dynamics simulations of open quantum systems. Here we discuss the performance of the multi- D_2 Ansatz using the circuit QED as an example. The trial wave function of the multi- D_2 Ansatz for the spin-boson model is

$$|D_2^M\rangle = \sum_n [A_n(t) |1\rangle + B_n(t) |2\rangle] e^{\sum_i f_{ni}(t) b_i - f_{ni}^*(t) b_i^\dagger} |0\rangle_b, \quad (3.12)$$

FIG. 8. (a) Time evolution of the population difference for the various values of α . [(b)–(d)] Time evolution of the photon number $\chi_k(t)$ in the case of $\alpha = 0.2, 0.5$, and 0.7 , respectively. (e) The time evolution of the peak of the photon distribution in the case of $\alpha = 0.2, 0.5$, and 0.7 , respectively. The dashed line is a power-law fit for $\alpha = 0.5$. Parameters: $\Delta = 0.1$, $\omega_c = 1$, and $T = 0$.

where $|1\rangle$ and $|2\rangle$ represent the up and down states, respectively. The variational parameters A_n and B_n are the amplitudes of the up and down states, respectively.

To estimate the memory size needed, the equations of motion are expressed in the matrix form (see Appendix B for details)

$$G\dot{\mathbf{x}}^T = \mathbf{b}. \quad (3.13)$$

It follows that the memory size used by the multi- D_2 *Ansatz* is approximately proportional to $N_b^2 \cdot M^2$ as estimated below. The expression of the vector $\dot{\mathbf{x}}$ includes time derivatives of the variational parameters, $A_n(t)$, $B_n(t)$, and $f_{nl}(t)$, and their complex conjugates. There are M elements for $\dot{A}_n$ and $\dot{B}_n$ and $M \cdot N_b$ elements for $\dot{f}_{nl}$. Thus, the number of elements of $\dot{\mathbf{x}}$ is $2M \cdot (N_b + 2)$. Because G is a full rank square matrix, G has $4M^2 \cdot (N_b + 2)^2$ elements. Thus, the memory needed for the multi- D_2 *Ansatz* with the multiplicity M and the number of modes N_b is roughly $kM^2 \cdot N_b^2$ and $k \approx 4$.

We can also estimate how the computational time grows with the increase of the number of modes. Since N_b is usually much larger than M and is the main factor that determines the computational time, the multiplicity is fixed at $M = 6$. For $N_b = 180, 230$, and 300 , the computational time needed is 120 h, 236 h, and 355 h, respectively. The computational time is found to increase linearly with the number of modes. One may be under the impression that the computational time would grow rapidly with the increase of the size of G . However, as G is a block matrix, it is found that the computation time increases only linearly. The parameters employed above are for the cases of moderate to strong coupling. For the ultra-strong coupling, one can use the single Davydov *Ansatz* and computation is much faster. For the QUAPI method, however, a sufficiently large memory time $\tau_{\text{mem}} = K \cdot \delta t$ is needed to obtain convergence. Memory needed for the QUAPI method to reach convergence is proportional to D^{2K+2} , where D is the dimension of the system Hilbert space, and $D = 2$ for the spin-boson model.⁴⁷ The needed memory time is long when the coupling is strong or the long-lasting bath memory effect exists. For these cases, it is difficult or even impossible to achieve QUAPI convergence because of the exponential increase of the memory size with K . The situation worsens as the dimension D increases. Thus, for cases with strong memory effects, the multi- D_2 *Ansatz* is an efficient approach in comparison with the QUAPI method. Meanwhile, with larger D , the memory size needed increases slower for the multi- D_2 *Ansatz* than for the QUAPI method.

In this subsection, we focus on the interplay between the qubit and the photon modes in a circuit QED system. There is much recent interest in hybrid light-matter systems on the delocalization-localization transition of polaritons in a coupled-cavity array.^{97,98} In addition, beyond the picture of an ideal cavity-QED system, coupling to phonons has been shown to play a crucial role. A non-Markovian description of bath phonon dissipation in the phonon is essential to explain various phenomena involving phonons in these systems. For strong qubit-phonon coupling, phonon dynamics may destroy the delocalized polariton states despite phonon assisted transfer between the polariton states. Our boson dynamics analysis based on the multiple Davydov *Ansatz* is expected to

capture the dynamical transition of the polariton in the QED coupled to phonon, which will be investigated in future study.

IV. CONCLUDING REMARKS

In this work, we have presented the methodology of exploring boson dynamics of coupled electron-boson systems by using a finite-temperature method of wave function propagation with the multiple Davydov *Ansatz*, going beyond what state-of-the-art density matrix approaches are capable to offer. In the finite-temperature time-dependent variational approach, a large number of boson modes are treated explicitly, and individual trajectories of the excitations with an initial thermal equilibrium state of the boson modes can be traced at a given temperature. Thus, the effect of thermal fluctuations on the electronic-boson dynamics can be probed with great detail. The Dirac-Frenkel time-dependent variational principle is employed to derive the equations of motion of the variational parameters. Our method is non-perturbative, which allows for exploration of boson dynamics of realistic systems where the electronic resonant coupling and the boson reorganization are of the similar strength, without having to consider one of them as a small perturbation. Also, due to the explicit treatment of boson modes, an arbitrary form of spectral density function can be assumed, including both continuous spectral density functions and specific prominent molecular vibrations.

In order to demonstrate the applicability of the boson dynamics analysis, we have deployed our method to the boson dynamics in three scenarios, i.e., the photosynthetic EET, the singlet fission process, and the circuit QED. In these physical systems, the exciton often couples strongly to the boson DOFs, and treatments of the boson bath based on traditional reduced density matrix approaches wipe out a wealth of information on coupled electron-boson dynamics. Our analysis of the boson dynamics revealed the peak position of the boson excitation in the excited state manifold splitting into two peaks in photosynthetic EET. This peak splitting indicates the creation of polaronic states by the resonance between two vibronic transitions on the different pigments. This is a novel feature from explicit calculations of boson dynamics as the reduced density matrix approach cannot unveil the formation of polaronic states directly. Our analysis of the boson dynamics also revealed the role of bosons in the ground state manifold on the photosynthetic EET dynamics. Meanwhile, for the singlet fission processes, it is shown in the analysis of the boson dynamics that a large vibrational relaxation rate γ_{vib}^{-1} induces excitation of the discrete modes for a broad range of the phonon frequency, which leads to quick erosion of quantum mixture created by the resonance between the vibronic transitions. Finally, our analysis also uncovers new information on the circuit QED systems whose environment is composed of photons. As the Davydov *Ansätze* can treat different forms of the bath spectral density function, one can compare in great detail boson dynamics from a discrete form of the coupling g_k with that from the Ohmic spectral density, leading to the conclusion that the Ohmic spectral density is a good approximation in the presence of weak

coupling. More interestingly, a power law behavior of the photon-distribution peak is discovered for the first time, opening up a new venue for further study of its underlying mechanism. Successful application to the photosynthetic EET, the singlet fission, and the QED demonstrates the versatility of our approach to boson dynamics. It has been convincingly shown that the analysis of boson dynamics based on the wave function propagation technique leads to a clear revelation of boson modes strongly coupled to electronic states, as well as in-depth description of polaron creation and destruction in the presence of thermal fluctuations.

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APPENDIX A: DERIVATION OF HAMILTONIAN IN CIRCUIT QED SYSTEM

The transmission line can be seen as inductors connecting in series whose inductance is l_0 per unit length, as shown in Fig. 6. Meanwhile, the capacitance per unit length is c_0 . The artificial atom can be implemented with various circuits, such as the Cooper-pair box,⁸⁷ persistent current qubit, and radio frequency superconducting quantum interference device (RF SQUID).⁸⁸ In this section, the RF SQUID is employed as an example. The flux qubit is a two-level system at low temperature, and the Hamiltonian is

$$H_q = \frac{1}{2}(-\varepsilon_0\sigma_z - \delta\sigma_x), \quad (\text{A1})$$

where $\varepsilon_0 = (2I_p)(\Phi_x - \Phi_0/2)$ is the bias and δ is the level repulsion. I_p is the persistent current and is roughly equal to half the critical current I_c of the Josephson junction. If the qubit works at or near $\Phi_x = \Phi_0/2$, the Hamiltonian can be written in a simpler form

$$H_q = \frac{\varepsilon}{2}(|0\rangle\langle 0| - |1\rangle\langle 1|) = \frac{\varepsilon}{2}\sigma_z, \quad (\text{A2})$$

where $\varepsilon = \sqrt{\varepsilon_0^2 + \delta^2}$. $|0\rangle$ and $|1\rangle$ are the symmetric and anti-symmetric superpositions of clockwise and anti-clockwise persistent currents, respectively.

The time dependent current density $j(x, t)$ and charge density $q(x, t)$ in the transmission line generate the EM field. The Lagrangian of the 1D EM⁹⁹ field is

$$L_{\text{EM}} = \int_0^L d\xi \left[\frac{1}{2c_0} q^2(\xi, t) - \frac{l_0}{2} j^2(\xi, t) \right]. \quad (\text{A3})$$

With the flux,

$$\Phi(x, t) = \int_{-\infty}^t d\tau V(x, \tau), \quad (\text{A4})$$

the Lagrangian is expressed as

$$L_{\text{EM}} = \int_0^L d\xi \left\{ \frac{c_0}{2} \dot{\Phi}^2(\xi, t) - \frac{1}{2l_0} \left[\frac{d\Phi(\xi, t)}{d\xi} \right]^2 \right\}, \quad (\text{A5})$$

where $V(x, t)$ is the local voltage on the transmission line. To simulate the system with the variational method, we discretize the transmission line with the length of L into N parts equally, and the length of each part is $\delta x = L/N$. The discretized Lagrangian is

$$L_{\text{EM}} = \sum_n \left[\frac{c_0 \delta x}{2} \dot{\Phi}_n^2 - \frac{1}{2l_0 \delta x} (\Phi_{n+1} - \Phi_n)^2 \right]. \quad (\text{A6})$$

With the creation and annihilation operators $b_k^\dagger$ and b_k satisfying

$$\begin{aligned} b_k &= \sqrt{\frac{c_0 \delta x \omega_k}{2}} \left(Q_k + \frac{i}{c_0 \delta x \omega_k} P_{-k} \right), \\ b_k^\dagger &= \sqrt{\frac{c_0 \delta x \omega_k}{2}} \left(Q_{-k} - \frac{i}{c_0 \delta x \omega_k} P_k \right), \end{aligned} \quad (\text{A7})$$

and

$$b_k^\dagger = b_{-k}, k = \frac{2\pi}{L} m (m = 0, \pm 1, \pm 2, \dots, \pm N/2), \quad (\text{A8})$$

the Hamiltonian of the EM field can be expressed as

$$H_{\text{EM}} = \sum_k \omega_k (b_k^\dagger b_k + \frac{1}{2}). \quad (\text{A9})$$

Here Q_k is the norm mode of Φ_n , satisfying $\Phi_n = 1/\sqrt{N} \sum_k Q_k e^{-in\delta x k}$, P_k is the conjugate momentum of Q_k , and

$$\omega_k = \omega_c \sqrt{2 - 2 \cos(\delta x k)}, \quad (\text{A10})$$

is the frequency of the k th mode. In Eq. (A10), $\omega_c = v_{\text{EM}}/\delta x$ is the cutoff frequency and $v_{\text{EM}} = 1/\sqrt{l_0 c_0}$ is the speed of the EM field.

Then the interaction between the EM field and the qubit can be estimated as follows. The circuit of the qubit is a closed loop and has a magnetic dipole moment μ . The transmission line excites oscillating magnetic field B , and the interaction energy between the qubit and the EM field is $H = -\mu \cdot B$. When the frequency of the EM field is not sufficiently low, $B = \mu_0 \sigma_z j_n / (2\pi r)$, in which j_n is the local current on the n th segment of the transmission line, μ_0 is the permeability of vacuum, r is the distance between the qubit and the transmission line. With Eq. (A4),

$$\begin{aligned} j_n &= -\frac{\Phi_{n+1} - \Phi_{n-1}}{2l_0 \delta x} \\ &= -\sum_{k < 0} \sqrt{\frac{\omega_k}{2Ll_0}} (ie^{-in\delta x k} b_k - ie^{in\delta x k} b_k^\dagger) \cos\left(\frac{\delta x k}{2}\right) \\ &\quad + \sum_{k > 0} \sqrt{\frac{\omega_k}{2Ll_0}} (ie^{-in\delta x k} b_k - ie^{in\delta x k} b_k^\dagger) \cos\left(\frac{\delta x k}{2}\right). \end{aligned} \quad (\text{A11})$$

Thus, the interaction Hamiltonian is

$$\begin{aligned}
H_i &= \frac{I_b A \mu_0}{2\pi r} \sigma_z j_n \\
&= -\sigma_z g \sum_{k<0} \sqrt{\frac{\omega_k}{2Ll_0}} \left(i e^{-i n \delta x k} b_k - i e^{i n \delta x k} b_k^\dagger \right) \cos\left(\frac{\delta x k}{2}\right) \\
&\quad + \sigma_z g \sum_{k>0} \sqrt{\frac{\omega_k}{2Ll_0}} \left(i e^{-i n \delta x k} b_k - i e^{i n \delta x k} b_k^\dagger \right) \cos\left(\frac{\delta x k}{2}\right) \\
&= \sum_k \sigma_z (g_k^* b_k + g_k b_k^\dagger),
\end{aligned} \tag{A12}$$

in which

$$g_k = \begin{cases} i g \sqrt{\frac{2\omega_k}{Ll_0}} e^{i n \delta x k} \cos\left(\frac{\delta x k}{2}\right) & k > 0 \\ -i g \sqrt{\frac{2\omega_k}{Ll_0}} e^{i n \delta x k} \cos\left(\frac{\delta x k}{2}\right) & k < 0 \end{cases} \tag{A13}$$

and

$$g = \frac{I_b A \mu_0}{\pi r}. \tag{A14}$$

The advantage of the circuit system of the transmission line is that the zero-point energy distributes over a very small effective volume which yields much stronger interaction between the EM field and the qubit.⁹⁹ The spectral density function

$$J(\omega) = \sum_k |g_k|^2 \delta(\omega - \omega_k) \tag{A15}$$

fully determines the influence of the bath on the qubit. Letting $\delta x \rightarrow 0$, for the modes with sufficiently low frequencies, the spectral density is Ohmic,

$$J(\omega) = 2\alpha\omega, \tag{A16}$$

where the coupling strength $\alpha = |g|^2/(\pi l_0 v_{EM})$ is the dimensionless coupling strength.

APPENDIX B: THE MULTIPLE DAVYDOV ANSATZ FOR THE SPIN-BOSON MODEL

To apply the Dirac-Frenkel time-dependent variational principle, the Lagrangian L is defined as

$$\begin{aligned}
L &= \frac{i}{2} \left\langle D_2^M(t) \left| \frac{\partial}{\partial t} \right| D_2^M(t) \right\rangle - \frac{i}{2} \left\langle D_2^M(t) \left| \frac{\partial}{\partial t} \right| D_2^M(t) \right\rangle \\
&\quad - \langle D_2^M(t) | \hat{H} | D_2^M(t) \rangle.
\end{aligned} \tag{B1}$$

The explicit form of the Lagrangian is

$$\begin{aligned}
L &= \frac{i}{2} \sum_n \sum_u \left[A_n^* \dot{A}_u - \dot{A}_n^* A_u + \frac{1}{2} A_n^* A_u \sum_k (\dot{f}_{nk} f_{nk}^* + f_{nk} \dot{f}_{nk}^* - \dot{f}_{uk} f_{uk}^* - f_{uk} \dot{f}_{uk}^* + 2f_{nk}^* \dot{f}_{uk} - 2\dot{f}_{nk}^* f_{uk}) \right] R(f_n^*, f_u) \\
&\quad + \frac{i}{2} \sum_n \sum_u \left[B_n^* \dot{B}_u - \dot{B}_n^* B_u + \frac{1}{2} B_n^* B_u \sum_k (\dot{f}_{nk} f_{nk}^* + f_{nk} \dot{f}_{nk}^* - \dot{f}_{uk} f_{uk}^* - f_{uk} \dot{f}_{uk}^* + 2f_{nk}^* \dot{f}_{uk} - 2\dot{f}_{nk}^* f_{uk}) \right] R(f_n^*, f_u) - \langle D_2^M(t) | \hat{H} | D_2^M(t) \rangle,
\end{aligned} \tag{B2}$$

in which

$$\begin{aligned}
\langle D_2^M(t) | \hat{H} | D_2^M(t) \rangle &= \sum_n \sum_u \left\{ A_n^* A_u \left[\sum_l \omega_l f_{nl}^* f_{ul} + \sum_l \frac{1}{2} (g_l f_{nl}^* + g_l^* f_{ul}) \right] R(f_n^*, f_u) \right. \\
&\quad \left. + B_n^* B_u \left[\sum_l \omega_l f_{nl}^* f_{ul} - \sum_l \frac{1}{2} (g_l f_{nl}^* + g_l^* f_{ul}) \right] R(f_n^*, f_u) - \frac{\varepsilon}{2} (A_n^* B_u + B_n^* A_u) R(f_n^*, f_u) \right\}.
\end{aligned} \tag{B3}$$

$R(f_n^*, f_u) \equiv \exp \left[\sum_l i f_{nl}^* f_{ul} - \frac{1}{2} (|f_{nl}|^2 + |f_{ul}|^2) \right]$ denotes the Debye-Waller factor. Adopting the Lagrangian formalism of the Dirac-Frenkel time-dependent variational principle, the derived equations of motion for the variational parameters can be calculated with

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{u}_n^*} \right) - \frac{\partial L}{\partial u_n^*} = 0, \tag{B4}$$

where u_n^* denotes the complex conjugate of the variational parameters u_n , which can be A_n , B_n , or f_{nl} . And the equations of motion are

$$\begin{aligned}
&\sum_n \left[-i \dot{A}_n + \frac{i}{2} A_n \sum_k (\dot{f}_{nk} f_{nk}^* + f_{nk} \dot{f}_{nk}^* - 2f_{mk}^* \dot{f}_{nk}) \right] R(f_m^*, f_n) \\
&= \sum_n A_n \left[-\sum_k \omega_k f_{mk}^* f_{nk} - \sum_k \frac{1}{2} (g_k f_{mk}^* + g_k^* f_{nk}) \right] \\
&\quad \times R(f_m^*, f_n) + \frac{\varepsilon}{2} \sum_n B_n R(f_m^*, f_n),
\end{aligned} \tag{B5}$$

and

$$\begin{aligned}
&\sum_n \left[-i \dot{B}_n + \frac{i}{2} B_n \sum_k (\dot{f}_{nk} f_{nk}^* + f_{nk} \dot{f}_{nk}^* - 2f_{mk}^* \dot{f}_{nk}) \right] R(f_m^*, f_n) \\
&= \sum_n B_n \left[-\sum_k \omega_k f_{mk}^* f_{nk} + \sum_k \frac{1}{2} (g_k f_{mk}^* + g_k^* f_{nk}) \right] \\
&\quad \times R(f_m^*, f_n) + \frac{\varepsilon}{2} \sum_n A_n R(f_m^*, f_n),
\end{aligned} \tag{B6}$$

and

$$\begin{aligned}
& \frac{i}{2} \sum_n^N \left[-2A_m^* \dot{A}_n f_{nl} - 2A_m^* A_n \dot{f}_{nl} + A_m^* A_n f_{nl} \sum_k \sum_i \left(\dot{f}_{nk}^* f_{nk} + f_{nk}^* \dot{f}_{nk} - 2f_{mk}^* \dot{f}_{nk} \right) \right] R(f_m^*, f_n) \\
& + \frac{i}{2} \sum_n^N \left[-2B_m^* \dot{B}_n f_{nl} - 2B_m^* B_n \dot{f}_{nl} + B_m^* B_n f_{nl} \sum_k \sum_i \left(\dot{f}_{nk}^* f_{nk} + f_{nk}^* \dot{f}_{nk} - 2f_{mk}^* \dot{f}_{nk} \right) \right] R(f_m^*, f_n) \\
& = \sum_n f_{nl} A_m^* A_n \left[-\sum_k \sum_i \omega_k f_{mk}^* f_{nk} - \sum_k \frac{1}{2} (g_k f_{mk}^* + g_k^* f_{nk}) \right] R(f_m^*, f_n) \\
& + \sum_n f_{nl} B_m^* B_n \left[-\sum_k \sum_i \omega_k f_{mk}^* f_{nk} + \sum_k \frac{1}{2} (g_k f_{mk}^* + g_k^* f_{nk}) \right] R(f_m^*, f_n) \\
& + \sum_n A_m^* A_n \left(-\omega_l f_{nl} - \frac{g_l}{2} \right) R(f_m^*, f_n) + \sum_n B_m^* B_n \left(-\omega_l f_{nl} + \frac{g_l}{2} \right) R(f_m^*, f_n) \\
& + \sum_n \frac{\epsilon}{2} f_{nl} (A_m^* B_n + B_m^* A_n) R(f_m^*, f_n).
\end{aligned} \tag{B7}$$

Form the complex conjugate of the above equations, one can simply get the equations of motions of A_n^* , B_n^* , and f_{nl}^* . The left-hand side of each equation is a linear combination of $\dot{A}_n$, $\dot{B}_n$, $\dot{f}_{nl}$, and their complex conjugates. And the right-hand side of each equation is a function whose arguments are the variational parameters. Thus, the equations can be expressed in a matrix form

$$G\dot{\mathbf{x}}^T = \mathbf{b}, \tag{B8}$$

in which $\mathbf{x}$ is comprised with the variational parameters A_n , B_n , f_{nl} , and their complex conjugates.

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