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A variational master equation approach to quantum dynamics with off-diagonal coupling in a sub-Ohmic environment

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A master equation approach based on an optimized polaron transformation is adopted for dynamics simulation with simultaneous diagonal and off-diagonal spin-boson coupling. Two types of bath spectral density functions are considered, the Ohmic and the sub-Ohmic. The off-diagonal coupling leads asymptotically to a thermal equilibrium with a nonzero population difference $P_z(t \rightarrow \infty) \neq 0$, which implies localization of the system, and it also plays a role in restraining coherent dynamics for the sub-Ohmic case. Since the new method can extend to the stronger coupling regime, we can investigate the coherent-incoherent transition in the sub-Ohmic environment. Relevant phase diagrams are obtained for different temperatures. It is found that the sub-Ohmic environment allows coherent dynamics at a higher temperature than the Ohmic environment. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4950888>]

I. INTRODUCTION

The dissipative two-level system (TLS) has been studied in a variety of disciplines including condensed phase physics, chemistry, and biology,^{1–4} with applications to topics ranging from quantum computation,⁵ quantum dots (QDs) in contact with a harmonic environment,^{6–8} to electronic excitation transfer in photosynthetic light harvesting systems.^{9–12} Traditionally, the effect of a bath of harmonic oscillators is characterized by a spectral density $J_s(\omega) = 2\alpha\omega_s^{1-s}\omega^s \exp(-\omega/\omega_c)$ with the dimensionless coupling strength α , the upper cutoff frequency ω_c , and an additional energy scale ω_s . The index $s = 1$ ($s > 1$) represents the Ohmic (super-Ohmic) bath, whereas $0 < s < 1$ represents the sub-Ohmic bath.^{13,14} For example, electromagnetic noise can generate frequency-independent damping, which can be described by an Ohmic environment,¹⁵ and a dominant noise source in solid state devices such as superconducting qubits,¹⁶ quantum dots,¹⁷ and the $1/f$ noise experiments^{13,14} can be characterized by a bath of the sub-Ohmic one.

The influence of the environment has to be correctly accounted for in order to determine tunneling and phase coherence in the TLS system with a variety of complex behaviors.^{1,18} The dynamics of the TLS with the bath is usually described in one of two perturbative limits. In the limit of weak system-bath coupling, the system-bath coupling can be treated perturbatively to derive a quantum master equation (QME). The most commonly used theory in this limit is the Redfield theory,¹⁹ which has been applied in areas of condensed phase chemical dynamics.^{20–31,40} In the opposite limit, it is possible to treat the coupling between electronic states perturbatively. This treatment leads to the Förster theory, which is used to describe purely incoherent

dynamics in a molecular dimer.^{32,33} However, a key quantity in electronic energy transfer is the relation between two time scales: the characteristic time scale of the environment reorganization and the inverse of the electronic coupling.^{10,34} In the typical photosynthetic light harvesting system, the two coupling magnitudes and/or the two time scales are of similar magnitude. Therefore, the description of these regimes is challenging because the absence of vanishingly small parameters rules out standard perturbative and Markovian approaches such as the Förster and the Redfield theories. To go beyond the traditional Förster and Redfield theories, one must adopt exact numerical methods, such as the quasiadiabatic propagator path integral (QUAPI),^{35,36} the hierarchical equation of motion method,^{10,34,37–39} and the path-integral-based linearized density matrix approach.^{40,41}

On the other hand, the aforementioned studies mainly focused only on the system-bath coupling in the diagonal form. Off-diagonal coupling is often introduced in the description of the charge transport in organic crystal.^{42,43} The charge-transfer state in organic materials, for example, is of particular interest due to its simultaneous coupling to intramolecular (diagonal) and intermolecular (off-diagonal) phonons.⁴³ The diagonal and off-diagonal forms of the spin-boson coupling can also sit side by side in an extended spin-boson model, denoting bath-induced modulation of the spin bias and the tunneling, respectively.^{44,45} In addition, the interplay between the diagonal and the off-diagonal coupling is known to give rise to a much richer phase diagram. The analysis of the two-bath spin-boson model with simultaneous diagonal and off-diagonal coupling by a density-matrix renormalization group approach⁴³ demonstrated that diagonal exciton-phonon coupling is responsible for localization, whereas off-diagonal coupling may lead to simultaneous localization and delocalization. It has also been revealed that the off-diagonal coupling lifts the degeneracy in the localized

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phase.^{46–48} To account for the range of frequencies over which the bath can influence the system, the renormalization energy is often given as $\int_0^\infty d\omega J_s(\omega)/\omega$. The renormalization energy in the sub-Ohmic regime is larger than that in the Ohmic regime, and thus much more time is needed for a sub-Ohmic bath to return to thermal equilibrium.⁴⁹ It is also found that the coherent phase still exists even in the strong coupling regime for a sub-Ohmic environment at zero temperature.¹⁴

However, difficulties in achieving an accurate theoretical treatment of the sub-Ohmic bath remain as one explores real-time quantum dynamics at finite temperatures. Therefore, an efficient, reliable approach based on approximations is typically required. The QME method based on a full polaron transformation^{45,50–54} works for stronger coupling and is less computationally expensive in the super-Ohmic regime. However, due to the well-known infra-red divergence in the Ohmic and sub-Ohmic regimes,⁵⁵ only incoherent dynamics can be captured when the QME with a full polaron transformation is used in conjunction with a time-local master equation approach. Recently, a new master equation technique with a variationally optimized polaron transformation was shown to be valid over a wide range of parameters for the super-Ohmic and Ohmic regimes.^{8,55–58} Here the optimized variational parameter was determined by minimizing the value of the upper bound of the free energy based on the Bogoliubov inequality. This new technique not only reproduces the results of both the Redfield theory and the polaron equations in the appropriate limits but also gives qualitatively reliable results beyond these parameter regimes. Therefore, the variational master equation (VME) can be used to explore quantum dynamics for a range of system-bath coupling forms, strengths, and environmental temperatures.⁵⁵

In this work, we aim to evaluate the accuracy of the VME in the simultaneous presence of diagonal and off-diagonal coupling at finite temperatures in a sub-Ohmic environment. This analysis will be useful for a comprehensive investigation on the quantum dynamics in the sub-Ohmic case at finite temperature and will provide a deeper insight into the effects of competition between the two forms of spin-boson coupling. The rest of the paper is organized as follows: Section II presents the model and the methodology employed in this paper. In Section III, we compare the numerically exact results calculated by the QUAPI technique to verify the accuracy of the VME. Furthermore, the numerical results and some discussions of the dynamics in the sub-Ohmic environment are presented. Finally, conclusions are drawn in Section IV.

II. HAMILTONIAN AND VARIATIONAL TRANSFORMATION

A. Variational transformation

We consider a model describing a single TLS in a dissipative environment, and the total Hamiltonian can be written as (we set $\hbar = 1$)

$$H = \Omega\sigma_x + \epsilon\sigma_z + H_B - \sum_k g_k(\sigma_z + \gamma\sigma_x)(b_k^\dagger + b_k), \quad (1)$$

where σ_x and σ_z are the usual Pauli spin matrices, 2Ω is the tunneling splitting, 2ϵ describes the bias of the system, and $b_k^\dagger(b_k)$ is the creation (annihilation) operator of the k th mode of the bath. $H_B = \sum_k \omega_k(b_k^\dagger b_k + 1/2)$ is the bath Hamiltonian, and g_k denotes the coupling strength of the TLS to the k th oscillator with the spectral density given by $J_s(\omega) = \sum_k |g_k|^2 \delta(\omega - \omega_k) = 2\alpha\omega_s^{1-s}\omega^s \exp(-\omega/\omega_c)$, where ω_s is a typical bath frequency (~ 100 cm⁻¹) that is set to unity and used as the energy scale, ω_c is the cutoff frequency. We adopt $s \leq 1$ in all calculations of this paper. γ is the adjustable off-diagonal coupling parameter.

According to the polaron transformation method,^{8,55,56,59,60} the generator of the transformation is defined by

$$V = \sum_k \frac{f_k}{2\omega_k} \sigma_z(b_k^\dagger - b_k). \quad (2)$$

Note that the set $\{f_k\}$ are variational parameters which are determined by the free-energy minimization arguments. If f_k is fixed equal to $-2g_k$ (for all modes), the transformation is changed into the known full polaron displacement.

The transformed Hamiltonian is given by $H_V = e^V H e^{-V} = H_S + H_B + H_I$. The dressed system Hamiltonian is

$$H_S = \epsilon\sigma_z + \Omega\Theta\sigma_x + \sum_k \left(\frac{f_k^2}{4\omega_k} + \frac{g_k f_k}{\omega_k} \right), \quad (3)$$

where the third term of H_S is the energy shifted by the bath displacement dependent upon the variational parameters, which in the limit of the full polaron displacement becomes

$$\begin{aligned} -\lambda_s &= -\sum_k \frac{g_k^2}{\omega_k} \\ &= -\int_0^\infty \frac{J_s(\omega)}{\omega} d\omega \\ &= -2\alpha\omega_s^{1-s}\omega_c^s \Gamma(s). \end{aligned} \quad (4)$$

Here, $\Gamma(s)$ is the Gamma function. λ_s not only reflects the interaction between the system and the bath but also accounts for the range of frequencies over which the bath can influence the system. The interaction Hamiltonian becomes

$$\begin{aligned} H_I &= \sigma_x \left[-\sum_k \gamma g_k \cosh B(b_k^\dagger + b_k) - \sum_k \gamma g_k \frac{f_k}{\omega_k} \sinh B \right. \\ &\quad \left. + \Omega(\cosh B - \Theta) \right] + \sigma_y \left\{ -i \sum_k \gamma g_k \frac{f_k}{\omega_k} (\cosh B - \Theta) \right. \\ &\quad \left. - i \sum_k \gamma g_k \left[\sinh B(b_k^\dagger + b_k) + \frac{f_k}{\omega_k} \Theta \right] + i\Omega \sinh B \right\} \\ &\quad - \sum_k \left(\frac{f_k}{2} + g_k \right) \sigma_z(b_k^\dagger + b_k), \end{aligned} \quad (5)$$

where the parameters read

$$B = \sum_k \frac{f_k}{\omega_k} (b_k^\dagger - b_k),$$

$$\Theta = \langle \cosh B \rangle_{H_B} \quad (6)$$

$$= \exp \left[-\frac{1}{2} \sum_k \frac{f_k^2}{\omega_k^2} \coth \left(\frac{\beta \omega_k}{2} \right) \right],$$

where the thermal average has been introduced, $\langle \cdots \rangle_{H_B} = \text{Tr}_B \{ \cdots \rho_B \}$ with the thermal equilibrium state $\rho_B = e^{-\beta H_B} / \text{Tr}_B \{ e^{-\beta H_B} \}$. Here, $\beta = 1/k_B T$ is the inverse temperature of the bath. By construction, $\langle H_I \rangle_{H_B} = 0$. Now we can separate the transformed Hamiltonian into a zeroth-order part $H_0 = H_S + H_B$ and a perturbation part H_I . This perturbation treatment is valid even in the presence of strong system-bath coupling due to a weak residual interaction H_I .

In the interaction picture, one has

$$\tilde{B}(t) = \sum_k \frac{f_k}{\omega_k} (b_k^\dagger e^{i\omega_k t} - b_k e^{-i\omega_k t}) \quad (7)$$

and

$$\begin{aligned} \tilde{H}_I(t) &= e^{iH_0 t} H_I e^{-iH_0 t} \\ &= \sum_{i=1}^5 \chi_i(t) \otimes X_i(t), \end{aligned} \quad (8)$$

where the system operators $\chi_i(t)$ and the bath operators $X_i(t)$ can be written as

$$\begin{aligned} \chi_1(t) &= \Omega \tilde{\sigma}_x(t) - i \sum_k \gamma g_k \frac{f_k}{\omega_k} \tilde{\sigma}_y(t), \\ \chi_2(t) &= - \sum_k \gamma g_k \frac{f_k}{\omega_k} \tilde{\sigma}_x(t) + i \Omega \tilde{\sigma}_y(t), \\ \chi_3(t) &= -\tilde{\sigma}_x(t), \\ \chi_4(t) &= -i \tilde{\sigma}_y(t), \\ \chi_5(t) &= -\tilde{\sigma}_z(t), \\ X_1(t) &= \cosh \tilde{B}(t) - \Theta, \\ X_2(t) &= \sinh \tilde{B}(t), \\ X_3(t) &= \sum_k \gamma g_k \cosh \tilde{B}(t) (b_k^\dagger e^{i\omega_k t} + b_k e^{-i\omega_k t}), \\ X_4(t) &= \sum_k \gamma g_k \\ &\quad \times \left[\sinh \tilde{B}(t) (b_k^\dagger e^{i\omega_k t} + b_k e^{-i\omega_k t}) + \frac{f_k}{\omega_k} \Theta \right], \\ X_5(t) &= \sum_k \left(\frac{f_k}{2} + g_k \right) (b_k^\dagger e^{i\omega_k t} + b_k e^{-i\omega_k t}). \end{aligned} \quad (9)$$

Here, $\tilde{\sigma}_{x,y,z}(t)$ are the operators in the interaction picture. In the eigenstate representation of the operator H_S , they are given by

$$\begin{aligned} \tilde{\sigma}_x(t) &= \sin \theta (|+\rangle\langle+| - |-\rangle\langle-|) \\ &\quad + \cos \theta (|+\rangle\langle-| e^{iE_{\text{dif}} t} + \text{h.c.}), \\ \tilde{\sigma}_y(t) &= -i(|+\rangle\langle-| e^{iE_{\text{dif}} t} - \text{h.c.}), \\ \tilde{\sigma}_z(t) &= \cos \theta (|+\rangle\langle+| + |-\rangle\langle-|) \\ &\quad - \sin \theta (|+\rangle\langle-| e^{iE_{\text{dif}} t} + \text{h.c.}), \end{aligned} \quad (10)$$

where $|\pm\rangle$ denote the two eigenstates of H_S , $E_{\text{dif}} = 2\sqrt{\Omega^2 \Theta^2 + \epsilon^2}$ is the energy difference between the two eigenstates, $\theta = \arctan(\frac{\Omega \Theta}{\epsilon})$, and h.c. stands for Hermitian

conjugate. Thus we can easily handle the QME within the interaction picture.

B. Determination of the variational parameters

The parameters $\{f_k\}$ appearing in our transformed Hamiltonian need to be determined by minimizing the free energy. The upper bound on the free energy is given by the Feynman-Bogoliubov inequality^{8,59,60}

$$A \leq A_B = -\frac{1}{\beta} \ln(\text{Tr} \{ e^{-\beta H_0} \}) + \langle H_I \rangle_{H_0} + O(\langle H_I^2 \rangle_{H_0}), \quad (11)$$

where the second term on the right side of Eq. (11) vanishes, and the higher-order terms are neglected in the calculations to follow. The minimization condition with respect to f_k leads to $f_k = F(\omega_k) g_k$, with

$$F(\omega_k) = -\frac{1}{\frac{1}{2} + \Omega^2 \Theta^2 \coth(\beta \omega_k / 2) \tanh(\beta \eta) / (\eta \omega_k)}. \quad (12)$$

In the continuum limit, we can use the integral form to describe the momentum summation by introducing the spectral density $J_s(\omega)$, i.e.,

$$\Theta = \exp \left[-\frac{1}{2} \int_0^\infty J_s(\omega) \frac{F(\omega)^2}{\omega^2} \coth \left(\frac{\beta \omega}{2} \right) d\omega \right]. \quad (13)$$

Thus the variational parameters f_k are determined self-consistently, and in the continuum limit $F(\omega_k)$ is written as $F(\omega)$. Setting $F(\omega) = -2$ corresponds to the full polaron transformation. To better understand the relation between the variational transformation and the full polaron transformation, we plot in Fig. 1 the function $F(\omega)$ for $\alpha = 0.025$ and 0.075 , and various values of the spectral power exponent s and the temperature T . Other parameters adopted are $\epsilon = 100 \text{ cm}^{-1}$, $\Omega = 100 \text{ cm}^{-1}$, and $\omega_c = 750 \text{ cm}^{-1}$. For $\alpha = 0.025$, the temperature as a major factor affects the function $F(\omega)$. And a higher temperature yields a lower value of $F(\omega)$, which means weakened coherent dynamics. For a stronger coupling strength $\alpha = 0.075$, the value of $F(\omega)$ is obviously lower than that in Fig. 1(a). Therefore, we can also speculate

FIG. 1. $F(\omega)$ plotted for several values of the exponent s and two temperatures, 77 K and 300 K. The parameters used are $s = 1$ and $T = 77$ K (black and solid), $s = 1$ and $T = 300$ K (red and solid), $s = 0.5$ and $T = 77$ K (blue and dashed), and $s = 0.5$ and $T = 300$ K (purple and dashed). (a) For $\alpha = 0.025$. (b) For $\alpha = 0.075$.

weakened coherent dynamics in this case. It is interesting that the full-polaron-transformation results for $\alpha = 0.075$, $s = 1$, and $T = 300$ K are recovered. Due to the known infrared divergence, only incoherent dynamics can be captured for the case. To overcome this defect, other variational procedures⁵⁶ or some more suitable variational parameters should be considered. Besides, it is observed that a smaller exponent s can increase the function $F(\omega)$ in Fig. 1(b). From that, we can speculate that a smaller exponent s tends to better maintain coherent dynamics, especially for a stronger coupling strength. It is worth to mention that the off-diagonal coupling parameter γ does not appear in Eq. (12). However, the parameter γ will affect system coherent dynamics due to its occurrence in the bath correlation functions as indicated by Eq. (A1). These issues will be discussed in Sec. III.

C. Quantum master equation

In order to describe the dynamics of the system, we employ a homogeneous QME method which can be derived by the time-convolutionless (TCL) projection operator technique. This technique uses a projection super-operator, $\mathcal{P}$, defined by $\mathcal{P}(\cdot) \equiv \text{Tr}_B\{\cdot\} \otimes \rho_B$, and the complementary super-operator $\mathcal{Q}$ is also defined through $\mathcal{Q} \equiv 1 - \mathcal{P}$. The total density operator of the system and the bath at time t is denoted as $\rho_T(t)$. The TCL equation for the variationally transformed density operator, $\rho_T^V(t) = e^V \rho_T(t) e^{-V}$, up to the second order in the interaction picture is known as^{4,61,62}

$$\begin{aligned} \frac{d\mathcal{P}\tilde{\rho}_T^V(t)}{dt} = & \mathcal{P}\tilde{\mathcal{L}}_I(t)\mathcal{Q}\tilde{\rho}_T^V(0) + \int_0^t ds \mathcal{P}\tilde{\mathcal{L}}_I(t)\tilde{\mathcal{L}}_I(s)\mathcal{Q}\tilde{\rho}_T^V(0) \\ & + \int_0^t ds \mathcal{P}\tilde{\mathcal{L}}_I(t)\tilde{\mathcal{L}}_I(s)\mathcal{P}\tilde{\rho}_T^V(t), \end{aligned} \quad (14)$$

where $\tilde{\mathcal{L}}_I(t)(\cdot) = -i[\tilde{H}_I(t), \cdot]$ and the interaction picture representation of $\rho_T^V(t)$ is $\tilde{\rho}_T^V(t) = e^{iH_0 t} \rho_T^V(t) e^{-iH_0 t}$. The first two terms in the right hand side (r.h.s.) of Eq. (14) are inhomogeneous terms. They are non-zero only when the initial bath state differs from the reference state ρ_B chosen to be the thermal equilibrium state. In this paper, the cutoff frequency is set to be such that $\Omega \ll \omega_c$, and the bath relaxation is much faster than the population dynamics. In this case, the inhomogeneous terms can be omitted because the bath immediately reaches thermal equilibrium. In this work, the initial-state-dependent inhomogeneous terms are approximately neglected, i.e., ρ_B is chosen as the reference state in the polaron frame. Thus we can write the homogeneous interaction picture master equation as⁸

$$\frac{d\tilde{\rho}^V(t)}{dt} = - \int_0^t ds \text{Tr}_B\{[\tilde{H}_I(t), [\tilde{H}_I(s), \tilde{\rho}^V(t) \rho_B]]\}, \quad (15)$$

where $\tilde{\rho}^V(t) = \text{Tr}_B\{\tilde{\rho}_T^V(t)\}$ represents the reduced density operator in the variationally transformed frame. In the calculation of Eq. (15), one needs to use the bath correlation functions which are defined as $C_{ij}(\tau) = \text{Tr}_B[X_i(0)X_j(\tau)\rho_B]$. The nonzero two-time bath correlation functions can be found in the Appendix. Using Eq. (8) and returning to the Schrödinger picture, we then obtain

$$\begin{aligned} \frac{d\rho^V(t)}{dt} = & -i[H_S, \rho^V(t)] \\ & - \int_0^t ds \left\{ \sum_{i,i'=1}^5 [\chi_i(0), \chi_{i'}(s-t)\rho^V(t)] C_{ii'}(s-t) + \text{h.c.} \right\}. \end{aligned} \quad (16)$$

In our calculation, the factorized initial state in the original representation is assumed to be

$$\rho_T(0) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}_S \otimes \rho_B. \quad (17)$$

III. RESULTS AND DISCUSSION

A. Validity of the variational master equation

To evaluate the dynamics of the system in a sub-Ohmic environment, we compare the predictions of the VME approach with numerically accurate results calculated using the well-known QUAPI method. Since $e^V \sigma_z e^{-V} = \sigma_z$, the population as a function of time can be written as

$$\begin{aligned} \langle \sigma_z(t) \rangle = & \text{Tr}_{S+B}[\sigma_z \rho_T(t)] \\ = & \text{Tr}_{S+B}[\sigma_z e^{-V} \rho^V(t) \rho_B e^V] \\ = & \text{Tr}_S[\sigma_z \rho^V(t)]. \end{aligned} \quad (18)$$

Here $\langle \sigma_z(t) \rangle = P_z(t)$ describes the population difference. To ensure the reliability of our method, we carry out dynamics comparisons with the path integral approach for the Ohmic and the sub-Ohmic environment, as shown in Figs. 2 and 3. For the low temperatures and a sub-Ohmic spectral density, the correlation time of the whole system increases greatly. Therefore, a larger maximal correlated step length $\Delta k_{\max}$ and a smaller time step may be needed in the QUAPI calculation. Limited by the cost of computation, we adopt $\alpha = 0.025$ which is a small coupling strength. In addition, the energy unit is set as 100 cm^{-1} in this paper. Thus the unit time corresponds to 333.3 fs.

In Figs. 2 and 3, we plot the time evolution of the population difference $P_z(t)$ calculated from the VME and the QUAPI method for the Ohmic bath ($s = 1$) and the sub-Ohmic bath ($s = 0.75$). Good agreement is achieved between the two approaches, which is impossible for the method of full polaron transformation due to the infra-red divergence. As the off-diagonal coupling parameter γ increases, it is found that the VME approach gradually deviates from the QUAPI results. This deviation mainly arises from the oscillation enhancement in the interaction Hamiltonian Eq. (5). However, from Figs. 2(d) and 3(d), it is observed that our results are still reliable even for $\gamma = 0.3$. In addition, we find that stronger off-diagonal coupling between the system and the bath can help sustain a greater value of $P_z(t)$.

B. Dynamics in a sub-Ohmic environment

In this subsection, we use the VME approach to describe the dynamics of a two-level system in contact with a sub-Ohmic environment, which allows for the exploration of certain parameter regimes (for example, a stronger coupling

FIG. 2. Time evolution of $P_z(t)$ plotted for several values of the off-diagonal coupling strength γ in the Ohmic environment ($s = 1$). For the QUAPI, perfectly converged results are obtained with the maximal correlated step length $\Delta k_{\max} = 7$ and the time step $\Delta t = 0.15$. And the reorganization energy is $\lambda_s = 37.5 \text{ cm}^{-1}$. (a) $\gamma = 0$. (b) $\gamma = 0.1$. (c) $\gamma = 0.2$. (d) $\gamma = 0.3$. The other parameters are set as $\epsilon = 100 \text{ cm}^{-1}$, $\Omega = 100 \text{ cm}^{-1}$, $T = 77 \text{ K}$, and $\omega_c = 750 \text{ cm}^{-1}$. The unit time represents 333.3 fs.

strength and a lower temperature) so that the QUAPI can be very computationally expensive. We note that the validity of the VME approach has yet to be established in the strong coupling regime, such as in the cases considered in Figs. 5

and 7. More theoretical efforts are in need to resolve the issue.

The effect of the off-diagonal coupling on $P_z(t)$ with zero detuning ($\epsilon = 0$) is also investigated by the VME method

FIG. 3. Time evolution of $P_z(t)$ plotted for several values of the off-diagonal coupling γ in the sub-Ohmic environment ($s = 0.75$). For the QUAPI, the converged results are obtained with the maximal correlated step length $\Delta k_{\max} = 7$ and the time step $\Delta t = 0.15$. We fix $\lambda_s = 27.8 \text{ cm}^{-1}$. (a) $\gamma = 0$. (b) $\gamma = 0.1$. (c) $\gamma = 0.2$. (d) $\gamma = 0.3$. The rest of the parameters are the same as in Fig. 2. The unit time represents 333.3 fs.

FIG. 4. Time evolution of $P_z(t)$ plotted for several values of the off-diagonal coupling γ in the sub-Ohmic environment ($s = 0.75$). $\epsilon = 0$ (zero detuning) and $\alpha = 0.05$ are assumed. The reorganization energy is $\lambda_s = 55.6 \text{ cm}^{-1}$. The rest of the parameters are the same as in Fig. 2. The unit time represents 333.3 fs. The inset shows the QUAPI results. The relevant parameters are $\Delta k_{\max} = 7$ and $\Delta t = 0.15$.

and the QUAPI method, as shown in Fig. 4. Similar results are obtained. The equilibrium value $P_z(t \rightarrow \infty)$ without the off-diagonal coupling is zero. As γ increases, the equilibrium value shows a downward tendency and moves gradually away from zero. At a given temperature, the off-diagonal coupling will destroy the global symmetry of the system, which eventually leads to the localization, i.e., $P_z(t \rightarrow \infty) \neq 0$. In addition, the oscillation width of $P_z(t)$ decreases with the increase of γ , which means that the off-diagonal coupling restrains the coherent dynamics for the sub-Ohmic case.

The coherent and incoherent dynamics for a sub-Ohmic environment ($s = 0.4$) at a finite temperature are also studied. It is known that only coherent dynamics occur for $0 < s < 0.5$ at zero temperature under the polarized bath initial conditions.^{14,36} However, for the factorizing initial condition Eq. (17), a coherent-incoherent changeover always

FIG. 5. Time evolution of $P_z(t)$ plotted for several values of the coupling strength α in the sub-Ohmic environment ($s = 0.4$). $\epsilon = 0$ (zero detuning) and $\gamma = 0$ (without off-diagonal coupling) are adopted. The rest of the parameters are the same as in Fig. 2. The unit time represents 333.3 fs.

FIG. 6. Time evolution of $P_z(t)$ plotted for two values of the exponent s . $\alpha = 0.05$, $\epsilon = 0$, and $\gamma = 0$ are adopted. The rest of the parameters are the same as in Fig. 2. The unit time represents 333.3 fs. The inset shows the QUAPI results. The relevant parameters are $\Delta k_{\max} = 7$ and $\Delta t = 0.15$.

occurs even at zero temperature.⁴⁹ In Fig. 5, we can observe that the coherent-incoherent changeover occurs at $\alpha_c \sim 0.2$ for $T = 77 \text{ K}$. For a higher temperature, a lower changeover α_c is expected.

From Fig. 1(b), we have obtained that a smaller exponent s leads to a larger $F(\omega)$, which suggests that a smaller exponent s may better protect the coherent dynamics. For $\omega_c = 750 \text{ cm}^{-1}$, λ_s in the sub-Ohmic regime (e.g., $s = 0.5$) is smaller than in the Ohmic case, which hints that the coherent dynamics is easier to be maintained. In order to obtain the definite evidence, we plot the dynamics of $P_z(t)$ with different exponent s in Fig. 6. For $\alpha = 0.05$, the behaviors of coherent dynamics for $s = 0.5$ are more obvious than that for $s = 1$. It is worth mentioning that similar results are also obtained by the QUAPI method.

Finally, to obtain the full dynamics information, we plot the phase diagrams of coherent and incoherent dynamics for two different temperatures, as shown in Fig. 7. It is known that

FIG. 7. Phase diagram of coherent and incoherent dynamics of our model for $0.2 \leq s \leq 1$ with $T = 77 \text{ K}$. The inset is for $T = 300 \text{ K}$. The rest of the parameters are $\epsilon = 0$, $\Omega = 100 \text{ cm}^{-1}$, $\omega_c = 750 \text{ cm}^{-1}$, and $\gamma = 0$.

the population expectation $P_z(t) \sim e^{-\gamma_c t} \cos(\Omega' t)$ ¹⁴ on certain time scales in the spin-boson model. The oscillation $\cos(\Omega' t)$ represents the quantum coherence. The decay exponent γ_c represents the classical friction effect that is induced by the bath. The coherent phase is defined if $\Omega' \neq 0$, otherwise it is the incoherent phase. For fixed s , with the increasing coupling strength α there exists a changeover from coherent to incoherent transition, i.e., from damped oscillations to overdamped decay. This transition will always occur for the sub-Ohmic environment at zero temperature due to the choice of the factorized bath initial conditions.⁴⁹ As s decreases, the critical coupling α_c increases with a nearly linear trend. For a higher temperature, the critical coupling α_c is lower due to the suppression of coherent dynamics.

IV. CONCLUSIONS

In this paper, a variationally optimized polaron transformation has been adopted in a master-equation approach to study the spin-boson dynamics in the Ohmic or the sub-Ohmic regimes. For both bath types, the well-known infra-red divergence has been circumvented in our VME calculations. The numerically exact QUAPI method is used to confirm the validity of the VME approach. Good agreement is achieved for weak and moderate off-diagonal coupling strengths. By minimizing the free-energy upper limit based on the Bogoliubov inequality, optimized variational parameters $F(\omega_k)$ are obtained. From the function $F(\omega)$, we can identify the incoherent-coherent transition in various parameter regimes. In addition, the effects of the off-diagonal coupling on the dynamics have been discussed in the work. It is found that the off-diagonal coupling leads to the localization, i.e., the equilibrium value $P_z(t \rightarrow \infty) \neq 0$. An increase in the off-diagonal coupling strength inhibits the overall coherent dynamics.

We also investigate the effects of the spin-bath coupling strength and the exponent s on the dynamics. For a given temperature, the coherent-incoherent transition is described by a line in the phase diagram. As the exponent s decreases, the coherent-incoherent changeover α_c gradually increases, which shows that the sub-Ohmic environment is more capable to maintain the coherent dynamics for the system.

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APPENDIX: THE TWO-TIME CORRELATION FUNCTIONS

The nonzero two-time bath correlation functions are given by

$$\begin{aligned}
 C_{11}(\tau) &= \frac{1}{2} \Theta^2 [e^{-\phi(\tau)} + e^{\phi(\tau)} - 2], \\
 C_{41}(\tau) &= \frac{1}{2} \Theta^2 \phi_1(\tau) [e^{\phi(\tau)} - e^{-\phi(\tau)}] \\
 &\quad - \frac{1}{2} \xi \Theta^2 [e^{-\phi(\tau)} + e^{\phi(\tau)} - 2], \\
 C_{22}(\tau) &= \frac{1}{2} \Theta^2 [e^{\phi(\tau)} - e^{-\phi(\tau)}], \\
 C_{32}(\tau) &= \frac{1}{2} \Theta^2 \phi_1(\tau) [e^{\phi(\tau)} + e^{-\phi(\tau)}] \\
 &\quad - \frac{1}{2} \xi \Theta^2 [e^{\phi(\tau)} - e^{-\phi(\tau)}], \\
 C_{52}(\tau) &= \Theta \phi_2(\tau), \\
 C_{23}(\tau) &= -\frac{1}{2} \Theta^2 \phi_1(\tau) [e^{\phi(\tau)} + e^{-\phi(\tau)}] \\
 &\quad - \frac{1}{2} \xi \Theta^2 [e^{\phi(\tau)} - e^{-\phi(\tau)}], \\
 C_{33}(\tau) &= \frac{1}{2} \Theta^2 [\xi^2 - \phi_1^2(\tau)] [e^{\phi(\tau)} - e^{-\phi(\tau)}] \\
 &\quad + \frac{1}{2} \Theta^2 \phi_3(\tau) [e^{\phi(\tau)} + e^{-\phi(\tau)}], \\
 C_{53}(\tau) &= -\Theta \xi \phi_2(\tau) + \Theta \phi_4(\tau), \\
 C_{14}(\tau) &= -\frac{1}{2} \Theta^2 \phi_1(\tau) [e^{\phi(\tau)} - e^{-\phi(\tau)}] \\
 &\quad - \frac{1}{2} \Theta^2 \xi [e^{\phi(\tau)} + e^{-\phi(\tau)}] + \xi \Theta^2, \\
 C_{44}(\tau) &= \frac{1}{2} \Theta^2 [\xi^2 - \phi_1^2(\tau)] [e^{\phi(\tau)} + e^{-\phi(\tau)}] \\
 &\quad + \frac{1}{2} \Theta^2 \phi_3(\tau) [e^{\phi(\tau)} - e^{-\phi(\tau)}], \\
 C_{25}(\tau) &= -\Theta \phi_2(\tau), \\
 C_{35}(\tau) &= \Theta \xi \phi_2(\tau) + \Theta \phi_4(\tau), \\
 C_{55}(\tau) &= \phi_5(\tau),
 \end{aligned} \tag{A1}$$

where

$$\begin{aligned}
 \phi(t) &= -\sum_k \frac{f_k^2}{\omega_k^2} \left[\cos(\omega_k t) \coth\left(\frac{\beta \omega_k}{2}\right) + i \sin(\omega_k t) \right], \\
 \phi_1(t) &= \sum_k \gamma g_k \frac{f_k}{\omega_k} \left[\cos(\omega_k t) + i \sin(\omega_k t) \coth\left(\frac{\beta \omega_k}{2}\right) \right], \\
 \phi_2(t) &= \sum_k \left(g_k + \frac{f_k}{2} \right) \frac{f_k}{\omega_k} \\
 &\quad \times \left[\cos(\omega_k t) + i \sin(\omega_k t) \coth\left(\frac{\beta \omega_k}{2}\right) \right], \\
 \phi_3(t) &= \sum_k \gamma^2 g_k^2 \left[\cos(\omega_k t) \coth\left(\frac{\beta \omega_k}{2}\right) + i \sin(\omega_k t) \right], \\
 \phi_4(t) &= \sum_k \gamma g_k \left(g_k + \frac{f_k}{2} \right) \\
 &\quad \times \left[\cos(\omega_k t) \coth\left(\frac{\beta \omega_k}{2}\right) + i \sin(\omega_k t) \right], \\
 \phi_5(t) &= \sum_k \left(g_k + \frac{f_k}{2} \right)^2 \left[\cos(\omega_k t) \coth\left(\frac{\beta \omega_k}{2}\right) + i \sin(\omega_k t) \right], \\
 \xi &= \sum_k \gamma g_k \frac{f_k}{\omega_k}.
 \end{aligned} \tag{A2}$$

Substituting the above Eqs. (A1) and (A2) into Eq. (15), we can solve the equation of motion for the reduced density operator.

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