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Non-Markovian reduced dynamics based upon a hierarchical effective-mode representation

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A reduced dynamics representation is introduced which is tailored to a hierarchical, Mori-chain type representation of a bath of harmonic oscillators which are linearly coupled to a subsystem. We consider a spin-boson system where a single effective mode is constructed so as to absorb all system-environment interactions, while the residual bath modes are coupled bilinearly to the primary mode and among each other. Using a cumulant expansion of the memory kernel, correlation functions for the primary mode are obtained, which can be suitably approximated by truncated chains representing the primary-residual mode interactions. A series of reduced-dimensional bath correlation functions is thus obtained, which can be expressed as Fourier-Laplace transforms of spectral densities that are given in truncated continued-fraction form. For a master equation which is second order in the system-bath coupling, the memory kernel is re-expressed in terms of local-in-time equations involving auxiliary densities and auxiliary operators. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4752078]

I. INTRODUCTION

Harmonic oscillator models play a central role in the modeling of dissipative effects on quantum systems. Among the vast number of applications are the spin-boson model,[1,2] explicit models for (generalized) Langevin dynamics,[3–7] models for the decay of a metastable state,[8] and multidimensional transition state theory.[9–11] These models provide microscopic realizations of system-bath dynamics from which different reduced dynamics formulations can be derived, e.g., master equations like the Caldeira-Leggett form[12] and its non-Markovian generalizations,[13] influence functionals,[2,14,15] stochastic algorithms,[16,17] and hierarchical approaches to non-Markovian dynamics,[18–21] to provide a non-exhaustive list.

A variant of these highly versatile models are Brownian-oscillator representations which can be derived from the conventional harmonic-oscillator bath models by re-casting the system-bath interaction in terms of collective environmental modes.[19,22–27] These models have been used, e.g., to describe reaction coordinates defined by the environment, i.e., generalized "solvent coordinates." Such environmental coordinates provide a simple and intuitively appealing realization of non-Markovian dynamics, where the environment's intrinsic time scale can be similar to the system time scale and the limit of fast fluctuations does not apply. Analogs of these models can be found in various fields, notably in solid-state physics where so-called cluster modes or interaction modes[28,29] have

been used to describe dynamical Jahn-Teller effects. In a similar context, such models have recently been employed to describe collective environmental effects on the dynamics at conical intersections.[30–32] Furthermore, the Brownian oscillator model with its characteristic Lorentzian spectral density[25] has recently been applied to describe structured environments in the context of quantum computation.[33–38]

In this paper, we address generalizations of the Brownian oscillator model, involving the construction of chains of effective modes which result from orthogonal transformations within the harmonic bath subspace. This construction closely resembles the chains of observables that are used in Mori theory.[39–41] Further, analogies exist with respect to the transformation techniques of the numerical renormalization group approach which has recently been applied to bosonic baths.[42] Furthermore, the time-dependent form of the density matrix renormalization group (DMRG) method,[43] involving a mapping of the system-bath Hamiltonian to a 1D harmonic chain, was recently combined with the properties of orthogonal polynomials.[44,45]

The present approach is particularly suitable to describe short-time dynamical effects in high-dimensional systems. A paradigm example is photoinduced dynamics in extended molecular systems, which often falls into a short-time regime where inertial, coherent effects dominate, and the many-particle dissipative dynamics has not yet set in. This generally precludes the use of standard system-bath approaches and necessitates a non-Markovian treatment, or alternatively, an explicit dynamical treatment of the combined subsystem-plus-environment supermolecular system. The effective-mode approach presented here provides a systematic reduction scheme in such situations and has already been

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successfully applied, e.g., to elementary charge and energy transfer processes in organic materials.[46–48]

The hierarchical chain representation naturally leads to truncation schemes based on including a limited number of effective modes. In Refs. [49–53], we have employed such truncation schemes to construct a series of approximate spectral densities from an arbitrary given distribution of bath modes. It was shown in Ref. [52] that for an arbitrary spectral density of typical complex multi-peaked form, a simple one-term recurrence relation can be derived that defines a sequence of residual spectral densities that converge to a quasi-Ohmic form. That is, the spectral density associated with the final member of the chain coupled to the residual bath will be quasi-Ohmic (i.e., of Rubin form[2,51–53]) provided a sufficient number of effective modes are included. Furthermore, it was shown in Ref. [53] that truncated chains with Ohmic closure for the nth effective mode reproduce the memory kernel exactly to $4n$th order in time.

In the following, we use the same transformation techniques in order to construct a non-Markovian master equation representation that is specifically adapted to the hierarchy of modes as described in Refs. [49] and [50]. To this end, a cumulant expansion of the memory kernel is employed in conjunction with a truncated chain representation for the residual bath.[54–57] A series of reduced-dimensional bath correlation functions are thus obtained. The cumulant expansion described here corresponds either to a time non-local (TNL) form, according to the so-called chronological ordering prescription (COP),[55,56] or to a local-in-time (TL) master equation[54–56,58,59] obtained by a suitable resummation. For both the TNL and TL forms, a local-in-time formulation in terms of auxiliary density matrices (or operators) can be obtained at the second order of the cumulant expansion, similar to Refs. [58,60–62]. The present work generalizes related approaches[27] where second-order cumulant master equations were formulated using a Brownian oscillator representation of the bath.

The remainder of the paper is organized as follows. We first describe the relevant transformation of the system-bath Hamiltonian (Sec. II) and then formulate a non-Markovian master equation using this transformed Hamiltonian in conjunction with cumulant expansion techniques (Sec. III). Section IV addresses a second-order master equation using an auxiliary density/operator formulation. In Sec. V, we present results for pure dephasing and population transfer dynamics for a spin-boson model. Finally, Sec. VI concludes.

II. SYSTEM-BATH HAMILTONIAN

This section introduces the spin-boson Hamiltonian in a transformed, chain type representation (Sec. II A) and presents the concept of truncated chain models (Sec. II B) which are useful as reduced-dimensional representations of the system.

A. Spin-boson Hamiltonian and effective-mode transformation

Our starting point is a spin-boson Hamiltonian,

$$\hat{H} = \hat{H}_S + \hat{H}_{SB} + \hat{H}_B \qquad (1)$$

with the usual definitions for the two-level system (spin) Hamiltonian $\hat{H}_S$, the system-bath (spin-boson) coupling $\hat{H}_{SB}$, and the bath (boson) Hamiltonian $\hat{H}_B$,

$$\hat{H}_S = \Delta\,\hat{\sigma}_z + \lambda\hat{\sigma}_x$$

$$\hat{H}_{SB} = \sum_{i=1}^{N_B} c_i \hat{x}_{Bi} \hat{\sigma}_z \qquad (2)$$

$$\hat{H}_B = \sum_{i=1}^{N_B} \frac{\omega_{Bi}}{2}\big(\hat{p}_{Bi}^2 + \hat{x}_{Bi}^2\big)\hat{1},$$

where $\hat{H}_B$ is defined in mass and frequency weighted coordinates with frequencies $\{\omega_{Bi}\}$.

The spin-boson Hamiltonian under consideration has been extensively studied over recent years using path integral methods,[1,2,14,63–66] numerically exact wavepacket methods like the multi-configuration time-dependent Hartree (MCTDH) method[67–72] and its multi-layer variant (ML-MCTDH),[73,74] semiclassical methods,[75–78] time-dependent coherent-state basis set methods,[79] various mixed quantum-classical techniques,[80,81] Markovian reduced dynamics methods like Redfield theory[82] and semigroup approaches, non-Markovian approaches like those referred to above, renormalization group approaches,[42] and various other explicit or reduced dynamical schemes. In this paper, we apply the above-mentioned effective-mode approach which relies on coordinate transformations that allow one to re-formulate the Hamiltonian in such a way that a series of reduced-dimensional models and associated spectral densities are generated.

The Hamiltonian Eq. (1) is transformed by an orthogonal coordinate transformation, i.e., $\hat{X} = T\hat{x}$, in such a way that the system-bath coupling is entirely absorbed into a single effective mode $\hat{X}_{B1}$:

$$\hat{H}_{SB} = \sum_{i=1}^{N_B} c_i \hat{x}_{Bi} \hat{\sigma}_z = D\hat{X}_{B1}\hat{\sigma}_z \qquad (3)$$

and the resulting residual bath Hamiltonian has the following structure:

$$\hat{H}_B = \sum_{i=1}^{N_B} \frac{\Omega_{Bi}}{2}\big(\hat{P}_{Bi}^2 + \hat{X}_{Bi}^2\big)\hat{1}$$

$$+ \sum_{i,j=1,i\neq j}^{N_B} d_{ij}(\hat{P}_{Bi}\hat{P}_{Bj} + \hat{X}_{Bi}\hat{X}_{Bj})\hat{1}. \qquad (4)$$

The new frequencies $\{\Omega_{Bi}\}$ and couplings $\{d_{ij}\}$ result from the coordinate transformation introduced above, such that $\Omega_{Bi} = \sum_{j=1}^{N_B} \omega_{Bj} t_{ji}^2$ and $d_{ij} = \sum_{k=1}^{N_B} \omega_{Bk} t_{ki} t_{kj}$, where t_{ji} are the elements of the transformation matrix T. The residual modes are thus seen to be coupled bilinearly to the effective mode $\hat{X}_{B1}$ and among each other, but do not couple directly to the spin subsystem.

Given the above, general form of the transformed bath Hamiltonian $\hat{H}_B$, several realizations can be envisaged. A particularly appealing transformation that has been detailed in Refs. [49] and [50], and which we now outline, casts the

bilinear coupling matrix into a band diagonal form, similar to a Mori chain type construction.[39–41,83]

B. Mori-type chain with Ohmic closure

For the Mori-type construction, the residual bath is transformed to a band-diagonal representation exhibiting nearest-neighbor couplings. We have referred to this variant as a hierarchical electron-phonon (HEP) model.[47,84,85] The chain is terminated at a chosen order k by coupling the kth chain member to a dissipative bath. The bilinear interaction Hamiltonian therefore takes the form

$$\hat{H}_B^{(k)} = \sum_{i=1}^{N_B} \frac{\Omega_{Bi}}{2} \left(\hat{P}_{Bi}^2 + \hat{X}_{Bi}^2 \right) \hat{1}$$
$$+ \sum_{i=1}^{k-1} d_{i\,i+1}(\hat{P}_{Bi}\hat{P}_{Bi+1} + \hat{X}_{Bi}\hat{X}_{Bi+1})\hat{1} + \hat{H}_{\text{diss}}^{(k)}, \quad (5)$$

where $\hat{H}_{\text{diss}}^{(k)}$ corresponds to a dissipative bath composed of modes $\{k+1, \ldots, N_B\}$ which are all coupled to the kth mode of the chain,

$$\hat{H}_{\text{diss}}^{(k)} = \sum_{i=k+1}^{N_B} d_{ki}(\hat{P}_{Bk}\hat{P}_{Bi} + \hat{X}_{Bk}\hat{X}_{Bi})\hat{1}. \quad (6)$$

The Brownian oscillator model[19,22–25] represents a special case of this construction with $k = 1$. The distribution of dissipative bath modes is usually approximated in terms of an Ohmic spectral density, in which case the picture of a Mori-type chain with Ohmic truncation at the kth order arises. As demonstrated in Ref. 52, the model in fact provides a rigorous description of non-Markovian dynamics, since the residual bath can be shown to converge toward a (quasi-)Ohmic form under very general conditions.

We will assume throughout separable initial conditions. This applies to both the pre-transformed and all of the transformed versions of the system. At $T = 0$ K, the orthogonal coordinate transformations in question leave the initial density operator separable if mass- and frequency weighted coordinates are referred to.[32]

III. NON-MARKOVIAN MASTER EQUATION

The above, transformed spin-boson Hamiltonian will be analyzed using a master equation that is derived via cumulant expansion techniques.[55–57] In view of our previous analysis of the Hamiltonian moments (cumulants) characterizing the evolution under a truncated effective mode Hamiltonian,[32,47,86] we will be particularly interested in such truncated expansions in a reduced-dynamics setting. This could lead to a significant simplification of the dynamical problem at least on short time scales where few effective modes determine the dynamics. To start with, the general form of the master equation will be outlined.

A. Master equation in cumulant expansion form

The relevant non-Markovian master equation is the following standard integro-differential equation for the reduced density operator, here in TNL form,

$$\frac{\partial \hat{\rho}_S}{\partial t} = -i\hat{\hat{L}}_S(t)\hat{\rho}_S(t) + \int_{t_0}^t dt' \, \hat{\hat{G}}(t, t')\hat{\rho}_S(t'), \quad (7)$$

where $\hat{\rho}_S = \text{Tr}_B \hat{\rho}$ is the subsystem density operator. The double hat symbol denotes Liouvillian superoperators, and $\hbar = 1$ is used throughout. Equation (7) corresponds to the conventional master equation obtained, e.g., by projection operator techniques.[87] We disregard here the so-called inhomogeneous term[87] which accounts for system-bath correlations at the initial time t_0, and we thus assume that the system and bath are initially uncorrelated, $\hat{\rho}(t_0) = \hat{\rho}_S(t_0) \otimes \hat{\rho}_B^{\text{ref}}$, with the reference bath state $\hat{\rho}_B^{\text{ref}}$. A special case corresponds to $\hat{\rho}_B^{\text{ref}} = \hat{\rho}_B^{\text{eq}}$, i.e., the equilibrium state of the isolated bath (as used in Sec. III D. below). Initial correlations can be accounted for as described in Refs. 57 and 90.

The master equation (7) can alternatively be derived using cumulant expansion techniques.[54–57,88,89] This entails a cumulant expansion of the memory kernel,

$$\hat{\hat{G}}^I(t, t') = -\hat{\hat{\theta}}_2(t, t') + \sum_{m=1}^{\infty} (-i)^{m+2}$$
$$\times \int_{t'}^t d\tau_1 \ldots \int_{t'}^{\tau_{m-1}} d\tau_m \hat{\hat{\theta}}_{m+2}(t, \tau_1, \ldots, \tau_m, t'),$$
$$(8)$$

where the superscript "I" in $\hat{\hat{G}}^I(t, t')$ refers to the interaction frame, i.e., $\hat{\hat{G}}^I(t, t') = \hat{\hat{U}}_S^\dagger(t, t_0)\hat{\hat{G}}(t, t')\hat{\hat{U}}_S(t', t_0)$. Noting that $\hat{\hat{G}}^I(t, t')$ is a superoperator acting on the system subspace, the interaction frame transformation relating to the complete system-plus-bath space reduces to the Liouvillian propagator $\hat{\hat{U}}_S$ that is associated with the system Liouvillian $\hat{\hat{L}}_S$.

The cumulants or connected averages $\hat{\hat{\theta}}_n$ are related as follows to the moments $\hat{\hat{m}}_n$:

$$\hat{\hat{\theta}}_1(\tau_1) = \hat{\hat{m}}_1(\tau_1)$$
$$\hat{\hat{\theta}}_2(\tau_1, \tau_2) = \hat{\hat{m}}_2(\tau_1, \tau_2) - \hat{\hat{m}}_1(\tau_1)\hat{\hat{m}}_1(\tau_2),$$
$$(9)$$

which are in turn defined as

$$\hat{\hat{m}}_n(\tau_1 \ldots \tau_n) = \text{Tr}_B\left\{ \hat{\hat{L}}_{SB}(\tau_1) \ldots \hat{\hat{L}}_{SB}(\tau_n) \hat{\rho}_B^{\text{ref}} \right\}, \quad (10)$$

where the Liouvillian $\hat{\hat{L}}_{SB}$ derives from the Hamiltonian $\hat{H}_{SB}$ of Eq. (2) and is given as follows in the interaction frame:

$$\hat{\hat{L}}_{SB}(t) = \hat{\hat{U}}_0^\dagger(t, t_0)\hat{\hat{L}}_{SB}\hat{\hat{U}}_0(t, t_0). \quad (11)$$

Here, $\hat{\hat{U}}_0(t, t_0)$ is the Liouvillian zeroth-order propagator

$$\hat{\hat{U}}_0(t, t_0) = \exp(-i\hat{\hat{L}}_0(t - t_0))$$
$$= \exp(-i\hat{\hat{L}}_S(t - t_0)) \exp(-i\hat{\hat{L}}_B(t - t_0)), \quad (12)$$

which is associated with the corresponding Hamiltonian zeroth-order propagator $\hat{U}_0(t, t_0) = \hat{U}_0^S(t, t_0)\hat{U}_0^B(t, t_0)$ $= \exp(-i\hat{H}_0(t - t_0))$ where $\hat{H}_0 = \hat{H}_S + \hat{H}_B$.

Assuming separable initial conditions, the master equation (7) with the kernel (8) provides an exact representation

of the system's reduced dynamics. The form Eq. (8) of the kernel corresponds to a COP series which is also known as the time non-local (TNL), or time convolution approach as mentioned above. The COP series of Eq. (8) can be equivalently obtained by projection techniques and a subsequent time-ordered perturbation expansion.[55,57]

Alternatively, the "partial ordering prescription" (POP, involving partial time ordering) is often used in cumulant expansions[55,56,88–90] which is also known as the TL, or time convolutionless approach. The POP series represents a resummation of Eq. (8) and leads to dynamical equations for the reduced density operator that are local-in-time;[56,88–90] in this case, the memory effects are entirely contained in the cumulants. The TL form can be formally obtained from the TNL form by making the substitution $\hat{\rho}_S(t') = \hat{U}_S^\dagger(t, t')\hat{\rho}_S(t)$.[58] In the TL form the equation of motion corresponding to Eq. (7) is given by

$$\frac{\partial \hat{\rho}_S}{\partial t} = -i\hat{L}_S(t)\hat{\rho}_S(t) + \int_{t_0}^{t} dt' \,\hat{\mathcal{K}}(t, t')\hat{\rho}_S(t). \quad (13)$$

The following development, which combines the cumulant expansion technique with the transformed Hamiltonian of Sec. II can be carried out for the TNL (COP) approach as well as the TL (POP) scheme. In Secs. IV and V, we will compare results obtained from the respective second-order master equations.

B. Application to effective-mode Hamiltonian

The distinguishing feature of the transformed Hamiltonian described in Sec. II is that the system-bath coupling is restricted to the primary effective bath mode $\hat{X}_{B1}$, i.e., $\hat{H}_{SB} = D\hat{\sigma}_z\hat{X}_{B1}$, see Eq. (3). Following the above development, we thus obtain for the moment superoperators of Eq. (10),

$$\hat{m}_n(\tau_1, \ldots, \tau_n)\,\hat{\rho}_S(t_0)$$
$$= \text{Tr}_B\{\hat{L}_{SB}(\tau_1)\ldots\hat{L}_{SB}(\tau_n)\hat{\rho}_B^{\text{ref}}\}\hat{\rho}_S(t_0)$$
$$= \text{Tr}_B\{[D\hat{\sigma}_z(\tau_1)\hat{X}_{B1}(\tau_1), [\ldots$$
$$\ldots[D\hat{\sigma}_z(\tau_n)\hat{X}_{B1}(\tau_n), \hat{\rho}_B^{\text{ref}} \otimes \hat{\rho}_S(t_0)]]]\}, \quad (14)$$

where $\hat{\sigma}_z(\tau_1) = \hat{U}_0^{S\dagger}(\tau_1, t_0)\hat{\sigma}_z\hat{U}_0^S(\tau_1, t_0)$. For example, the second-order contribution leads to

$$\hat{m}_2(\tau_1, \tau_2)\,\hat{\rho}_S(t_0)$$
$$= D^2\,[\hat{\sigma}_z(\tau_1), \hat{\sigma}_z(\tau_2)\hat{\rho}_S(t_0)]\,\text{Tr}\{\hat{X}_{B1}(\tau_1)\hat{X}_{B1}(\tau_2)\hat{\rho}_B^{\text{ref}}\}$$
$$- D^2\,[\hat{\sigma}_z(\tau_1), \hat{\rho}_S(t_0)\hat{\sigma}_z(\tau_2)]\,\text{Tr}\{\hat{X}_{B1}(\tau_2)\hat{X}_{B1}(\tau_1)\hat{\rho}_B^{\text{ref}}\}$$
$$(15)$$

with the two-point bath correlation function

$$\mathcal{C}_B^{(2)}(\tau_1, \tau_2) = D^2\,\text{Tr}\{\hat{X}_{B1}(\tau_1)\hat{X}_{B1}(\tau_2)\hat{\rho}_B^{\text{ref}}\}$$
$$\equiv D^2\langle\hat{X}_{B1}(\tau_1)\hat{X}_{B1}(\tau_2)\rangle. \quad (16)$$

It should be noted that the "coupling-weighted" mode $D\hat{X}_{B1}(t)$ corresponds exactly (apart from a change in sign) to the random force $\hat{\xi}(t)$ in the Langevin equation,[52] provided that the dynamics of interest is that determined by the free evolution of the bath,

$$D^2\langle\hat{X}_{B1}(\tau_1)\hat{X}_{B1}(\tau_2)\rangle = \langle\hat{\xi}(\tau_1)\hat{\xi}(\tau_2)\rangle. \quad (17)$$

More generally, n-point bath correlation functions $\mathcal{C}_B^{(n)}$ appear that are the following—scalar—quantities derived from the bath operators:

$$\mathcal{C}_B^{(n)}(\tau_1, \ldots, \tau_n) = D^n\,\text{Tr}\{\hat{X}_{B1}(\tau_1)\ldots\hat{X}_{B1}(\tau_n)\hat{\rho}_B^{\text{ref}}\}$$
$$= D^n\langle\hat{X}_{B1}(\tau_1)\ldots\hat{X}_{B1}(\tau_n)\rangle. \quad (18)$$

These expressions have a simple appearance since they only involve Heisenberg operators of the primary bath mode $\hat{X}_{B1}$. However, all complications of the many-body bath dynamics are contained in the time evolution of these operators,

$$\hat{X}_{B1}(t) = \hat{U}_B^\dagger(t, t_0)\hat{X}_{B1}\hat{U}_B(t, t_0), \quad (19)$$

where

$$\hat{U}_B(t, t_0) = \exp(-i\hat{H}_B(t - t_0))$$
$$= \exp(-i(\hat{H}_B^0 + \hat{H}_B^{\text{int}})(t - t_0)), \quad (20)$$

where the bath Hamiltonian is as defined in Eqs. (4) and (5) and contains the bilinear couplings between the bath modes according to the transformations discussed in Sec. II B. By these couplings, the primary mode $\hat{X}_{B1}$ is coupled to the residual bath.

The simplest level of approximation would obviously consist in ignoring $\hat{H}_B^{\text{int}}$, and thus the residual bath modes $\hat{X}_{B2}, \ldots, \hat{X}_{BN_B}$ altogether, in which case a purely coherent dynamics of the effective mode results with $\mathcal{C}_B^{(2)}(\tau_1, \tau_2) = D^2\exp(-i\Omega_{B1}(\tau_1 - \tau_2))$. Even though this crude approximation would reproduce the shortest-time dynamics accurately,[32] all dissipative effects are then disregarded. In the following, we discuss a strategy to go beyond this simplest approximation, which makes use of the chain model described in Sec. II B.

C. Mori chain development for the secondary bath

The Mori chain model of Sec. II B is now used to derive a hierarchical sequence of approximations for the secondary bath. A truncated kth-order chain Hamiltonian corresponds to an approximate propagator

$$\hat{U}_B^{(k)}(t, t_0) = \exp(-i\hat{H}_B^{(k)}(t - t_0)) \quad (21)$$

and likewise for the corresponding Liouvillian propagator $\hat{U}_B^{(k)}(t, t_0) = \exp(-i\hat{L}_B^{(k)}(t - t_0))$.

When considering the zero-temperature cumulant (moment) expansion of the kth order propagator $\text{Tr}\{\hat{U}_B^{(k)}\hat{\rho}_B^{T=0}\}$ where $\hat{\rho}_B^{T=0} = |0_B\rangle\langle0_B|$ (with $|0_B\rangle$ the bath ground state), it has been shown that this cumulant expansion agrees with the

corresponding cumulant expansion of the exact propagator up to the $(2k + 1)$th order.[32,47,49,53,86] This implies that the dynamics is exactly reproduced by the approximate propagator over a certain time scale, up to a point where the cumulant expansions diverge. Even though the cumulant analysis does not rigorously carry over to the case where the bath exhibits initial excitations, the kth-order chain propagators can therefore be considered suitable approximants, involving a limited number of bath modes.

With a kth-order approximate propagator, the two-point correlation function of Eq. (16) now reads as follows:

$$\mathcal{C}_B^{(2,k)}(\tau_1, \tau_2)$$
$$= D^2 \, \mathrm{Tr}\big\{\hat{X}_{B1}(\tau_1)\hat{X}_{B1}(\tau_2)\hat{\rho}_B^{\mathrm{ref}}\big\}$$
$$= D^2 \, \mathrm{Tr}\big\{\hat{U}_B^{(k)\dagger}(\tau_1, t_0)\hat{X}_{B1}\hat{U}_B^{(k)}(\tau_1, \tau_2)\hat{X}_{B1}\hat{U}_B^{(k)}(\tau_2, t_0)\hat{\rho}_B^{\mathrm{ref}}\big\},$$
$$(22)$$

where $\mathcal{C}_B^{(2,k)}$ carries a double index which denotes the (n = 2)-point correlation function (i.e., second order in $\hat{H}_{SB}$), approximated at the kth order in the chain expansion of $\hat{H}_B$.

D. Correlation functions from spectral densities

The most convenient way to calculate the relevant two-point correlation functions for the equilibrium reference bath state $\hat{\rho}_B^{\mathrm{ref}} = \hat{\rho}_B^{\mathrm{eq}}$, involves the Fourier-Laplace transform relation to the corresponding spectral density $J(\omega)$,[24,25,91]

$$\mathcal{C}_B^{(2)}(t) = \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega J(\omega) n_B(\omega)e^{i\omega t}$$
$$= \frac{1}{\pi}\int_0^{\infty} d\omega J(\omega)[\coth(\beta\omega/2)\cos(\omega t) - i\sin(\omega t)],$$
$$(23)$$

where $n_B(\omega) = 1/(e^{\beta\omega} - 1)$ is the Bose-Einstein distribution, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann's constant, and T is the temperature. The correlation function is taken to be independent of the choice of the time origin, $\mathcal{C}_B^{(2)}(\tau, \tau + t) \equiv \mathcal{C}_B^{(2)}(t)$, due to the invariance of the reference (equilibrium) bath state under the zeroth-order propagator. Further, Eq. (23) is invariant with respect to the coordinate representation—pretransformed versus post-transformed—that is chosen, and is

most conveniently derived in the pre-transformed representation.

The above correlation functions are often expressed in terms of a summation over Matsubara frequencies $\nu_l = 2\pi l/\beta$[15,24] using the series expansion

$$\coth(\beta\omega/2) = \frac{2}{\beta}\left(\frac{1}{\omega} + 2\sum_{l=1}^{l=\infty}\frac{\omega}{\omega^2 + \nu_l^2}\right),\qquad(24)$$

which converges rapidly for finite temperatures (but requires an infinite number of terms in the $T = 0$ limit).

In order to apply Eq. (23) to the Mori chain form of the bath Hamiltonian, the relevant spectral density has to be expressed in terms of the transformed representation. As demonstrated in Appendix A and in Refs. 49, 50, and 92, the spectral density associated with the original, pre-transformed Hamiltonian of Eqs. (1) and (2), $J(\omega) = \pi/2\sum_n c_n^2\delta(\omega - \omega_n)$, can be re-written analytically in the form of a continued fraction. Truncation and Markovian closure of this continued fraction at the kth order yields the form of Eqs. (A10) and (A11) of the approximate spectral density $J_{\mathrm{eff}}^{(k)}(\omega)$.

Following the strategy of Sec. II B, we will thus calculate successive kth order spectral densities $J_{\mathrm{eff}}^{(k)}(\omega)$ for truncated Mori chains with Ohmic closure. From these spectral densities, the corresponding correlation functions (22) are obtained from the relation (23),

$$\mathcal{C}_B^{(2,k)}(t) = \frac{1}{\pi}\int_0^{\infty} d\omega J_{\mathrm{eff}}^{(k)}(\omega)[\coth(\beta\omega/2)\cos(\omega t) - i\sin(\omega t)].$$
$$(25)$$

For the lowest-order case where only the primary effective mode is accounted for ($k = 1$), we have following Eqs. (A10) and (A11) for the spectral density,

$$J_{\mathrm{eff}}^{(1)}(\omega) = J_{+,\mathrm{eff}}^{(1)}(\omega) + J_{-,\mathrm{eff}}^{(1)}(\omega)$$
$$(26)$$
$$J_{\pm,\mathrm{eff}}^{(1)}(\omega) = \frac{2\eta\omega D'^2}{(\Omega_{B1} \mp \omega)^2 + (2\eta\omega)^2}$$

i.e., a Lorentzian form, with the antisymmetric property $J_{\mathrm{eff}}^{(1)}(-\omega) = -J_{\mathrm{eff}}^{(1)}(\omega)$ and the definition $D' = D/\sqrt{2}$ which is introduced in Appendix A.

The corresponding correlation function is obtained from Eqs. (23)–(26), with the following real part:

$$\mathrm{Re}\,\mathcal{C}_B^{(2,1)}(t) = D'^2\left(\frac{1}{\beta\Omega_{B1}} + 2\sum_{l=1}^{l=\infty}\frac{\Omega_{B1}\big[\Omega_{B1}^2 + \nu_l^2(1 - 4\eta^2 - i4\eta)\big]}{\beta\big[(\Omega_{B1}^2 + \nu_l^2(1 - 4\eta^2))^2 + 16\eta^2\nu_l^4\big]}\right)\exp(-i\alpha(1 - i2\eta)t)$$

$$+ D'^2\left(\frac{1}{\beta\Omega_{B1}} + 2\sum_{l=1}^{l=\infty}\frac{\Omega_{B1}\big[\Omega_{B1}^2 + \nu_l^2(1 - 4\eta^2 + i4\eta)\big]}{\beta\big[(\Omega_{B1}^2 + \nu_l^2(1 - 4\eta^2))^2 + 16\eta^2\nu_l^4\big]}\right)\exp(i\alpha(1 + i2\eta)t)$$

$$- \sum_{l=1}^{l=\infty}\frac{8D'^2\eta\nu_l\big[\Omega_1^2 - (1 + (2\eta)^2)\nu_l^2\big]}{\beta\big[(\Omega_{B1}^2 - (1 + (2\eta)^2)\nu_l^2)^2 + (2\Omega_{B1}\nu_l)^2\big]}\exp(-\nu_l t),\qquad(27)$$

where $\alpha = \Omega_{B1}/(1 + 4\eta^2)$. The imaginary part $\mathrm{Im}\, \mathcal{C}_B^{(2,1)}(t)$ is given by

$$- \mathrm{Im}\, \mathcal{C}_B^{(2,1)}(t) = i\frac{D'^2}{2}\left(\frac{1 - i2\eta}{1 + 4\eta^2}\exp(-i\alpha(1 - i2\eta)t)\right.$$

$$\left. - \frac{1 + i2\eta}{1 + 4\eta^2}\exp(i\alpha(1 + i2\eta)t)\right)$$

$$= \frac{D'^2 \exp(-2\eta\alpha t)}{[1 + 4\eta^2]}(2\eta\cos\alpha t + \sin\alpha t). \quad (28)$$

One should point out that the real and imaginary parts of the correlation function are directly related through the relation (23), and can be derived from each other.[24, 106]

The above case again corresponds to the simplest Brownian oscillator model. The higher order, $k = 2$, result $\mathcal{C}_B^{(2,2)}$ is given by Eq. (A14) of Appendix A.

Since the correlation functions as defined above consist of complex exponentials that result from the poles of the spectral densities they take the general form

$$\mathcal{C}_B^{(2,k)}(t) = \sum_{l=1}^{n_M + 2k} f_{l,k}\exp(p_{l,k}t), \quad (29)$$

where $\{f_{l,k}, p_{l,k}\}$ are complex parameters. There are n_M poles resulting from the Matsubara summation which lie along the imaginary axis and $2k$ terms from the k effective modes. The exponential property is an important ingredient in the development that is described in Sec. IV, by which the non-Markovian memory kernel is replaced by a set of coupled local-in-time equations. It will also be convenient to separate $\mathcal{C}_B^{(2,k)}(t)$ into its real and imaginary parts

$$\mathcal{C}_B^{(2,k)}(t) = \sum_{l=1}^{n_M + 2k} a_{l,k}\exp(p_{l,k}t) - i\sum_{l=n_M + 1}^{n_M + 2k} b_{l,k}\exp(p_{l,k}t), \quad (30)$$

where the $\{p_{l,k}, a_{l,k}, b_{l,k}\}$ are complex parameters. The relation between the coefficients $a_{l,k}$ and $b_{l,k}$ again follows from the relation between the real and imaginary parts of the correlation functions, see Ref. 106.

IV. SECOND-ORDER MASTER EQUATION USING AUXILIARY DENSITY FORMULATION

Using the above construction of the relevant correlation functions, we now return to the master equations (7) and (13) and focus on the second order form as a special case. As will be shown below, the complex exponential form Eq. (30) of the correlation functions leads to a useful formulation of the reduced dynamics problem, allowing one to convert the convolution form of the master equation to a set of coupled local-in-time equations. The approach bears some similarity to the scheme introduced by Meier and Tannor[60] where the relevant spectral densities were fitted to a sum of complex Lorentzian functions; this scheme has meanwhile been successfully applied to various problems.[58, 61, 62] The present approach, by comparison, does not necessitate any fitting procedure since the relevant spectral densities and the associated correlation

functions are determined by the transformations described in Sec. II.

We will address both the time non-local (TNL) and the time local (TL) form of Eqs. (7) and (13), respectively.

A. Time non-local approach

The weak-coupling non-Markovian master equation resulting from truncation of the cumulant expansion of Eq. (7) at the second order in $\hat{H}_{SB}$, and taken to the kth order in the interaction with the residual bath, reads as follows:

$$\frac{\partial\hat{\rho}_S}{\partial t} = -i\hat{\hat{L}}_S(t)\hat{\rho}_S(t) - \int_{t_0}^{t} dt'\,\hat{U}_S(t, t_0)\hat{\hat{\theta}}_2(t, t')\hat{U}_S^{\dagger}(t', t_0)\hat{\rho}_S(t')$$

$$= -i\hat{\hat{L}}_S(t)\hat{\rho}_S(t)$$

$$- \left[\hat{\sigma}_z, \int_{t_0}^{t} dt'\,\mathcal{C}_B^{(2,k)}(t, t')\hat{U}_S(t, t')\hat{\sigma}_z\hat{\rho}_S(t')\right]$$

$$+ \left[\hat{\sigma}_z, \int_{t_0}^{t} dt'\,\hat{U}_S(t, t')\hat{\rho}_S(t')\hat{\sigma}_z\mathcal{C}_B^{*(2,k)}(t, t')\right]$$

$$= -i\hat{\hat{L}}_S(t)\hat{\rho}_S(t)$$

$$- \left[\hat{\sigma}_z, \int_{t_0}^{t} dt'\,\mathrm{Re}\,\mathcal{C}_B^{(2,k)}(t, t')\hat{U}_S(t, t')[\hat{\sigma}_z, \hat{\rho}_S(t')]\right]$$

$$- i\left[\hat{\sigma}_z, \int_{t_0}^{t} dt'\,\mathrm{Im}\,\mathcal{C}_B^{(2,k)}(t, t')\hat{U}_S(t, t')[\hat{\rho}_S(t'), \hat{\sigma}_z]_+\right], \quad (31)$$

where Eqs. (15) and (16) were used, and it was assumed that the first moments $\hat{m}_1(t)$ which appear in the second-order cumulant according to Eq. (9) vanish. In the above equation, $[\,,\,]_+$ denotes the anticommutator. Equation (31) can be formally re-written as follows:

$$\frac{\partial\hat{\rho}_S}{\partial t} = -i\hat{\hat{L}}_S(t)\hat{\rho}_S(t) - \left[\hat{\sigma}_z, \sum_{l=1}^{n_M + 2k}\hat{\rho}_R^{(l,k)}(t)\right]$$

$$+ i\left[\hat{\sigma}_z, \sum_{l=n_M + 1}^{n_M + 2k}\hat{\rho}_I^{(l,k)}(t)\right], \quad (32)$$

where the auxiliary density matrices $\hat{\rho}_R^{(l,k)}$ and $\hat{\rho}_I^{(l,k)}$ were introduced,

$$\hat{\rho}_R^{(l,k)}(t) = \int_{t_0}^{t} dt'\,a_{l,k}\exp(p_{l,k}(t - t'))$$

$$\times \exp(-i\hat{\hat{L}}_S(t - t'))[\hat{\sigma}_z, \hat{\rho}_S(t')] \quad (33)$$

$$\hat{\rho}_I^{(l,k)}(t) = \int_{t_0}^{t} dt'\,b_{l,k}\exp(p_{l,k}(t - t'))$$

$$\times \exp(-i\hat{\hat{L}}_S(t - t'))[\hat{\sigma}_z, \hat{\rho}_S(t')]_+.$$

From this definition, the equations of motion of these quantities are given as

$$\frac{\partial \hat{\rho}_R^{(l,k)}}{\partial t} = (p_{l,k} - i\hat{L}_S)\hat{\rho}_R^{(l,k)}(t) + a_{l,k}[\hat{\sigma}_z, \hat{\rho}_S(t)]$$

$$\frac{\partial \hat{\rho}_I^{(l,k)}}{\partial t} = (p_{l,k} - i\hat{L}_S)\hat{\rho}_I^{(l,k)}(t) + b_{l,k}[\hat{\sigma}_z, \hat{\rho}_S(t)]_+, \tag{34}$$

where we used the general form Eq. (30) of the correlation functions. Furthermore,[60] expressing Eq. (31) in terms of the real and imaginary parts of the correlation functions reduces the number of auxiliary density matrices from $2(n_M + 2k)$ to $(n_M + 4k)$.

The coupled equations for the subsystem operator $\hat{\rho}_S$ and auxiliary operators $\{\hat{\rho}_R^{(l,k)}, \hat{\rho}_I^{(l,k)}\}$, Eqs. (32) and (34), replace the convolution form of the master equation (31). The kth order auxiliary densities are generated from the corresponding correlation functions $\mathcal{C}_B^{(2,k)}(t, t')$.

B. Time local approach

As explained in Sec. III A, the TL master equation is obtained from the TNL form of Eq. (31) by resummation. In the TL form the equation of motion corresponding to Eq. (31) is given by

$$\frac{\partial \hat{\rho}_S}{\partial t} = -i\hat{L}_S(t)\hat{\rho}_S(t)$$

$$- \left[\hat{\sigma}_z, \int_{t_0}^t dt' \, \mathcal{C}_B^{(2,k)}(t,t')\hat{U}_S(t,t')\hat{\sigma}_z\hat{U}_S^\dagger(t,t')\hat{\rho}_S(t)\right]$$

$$+ \left[\hat{\sigma}_z, \hat{\rho}_S(t)\int_{t_0}^t dt' \, \hat{U}_S(t,t')\hat{\sigma}_z\mathcal{C}_B^{*(2,k)}(t,t')\right]$$

$$= -i\hat{L}_S(t)\hat{\rho}_S(t)$$

$$- \left[\hat{\sigma}_z, \int_{t_0}^t dt' \, \mathrm{Re}\,\mathcal{C}_B^{(2,k)}(t,t')\hat{U}_S(t,t')[\hat{\sigma}_z, \hat{\rho}_S(t)]\right]$$

$$- i\left[\hat{\sigma}_z, \int_{t_0}^t dt' \, \mathrm{Im}\,\mathcal{C}_B^{(2,k)}(t,t')\hat{U}_S(t,t')[\hat{\rho}_S(t), \hat{\sigma}_z]_+\right]$$

$$= -i\hat{L}_S(t)\hat{\rho}_S(t) - \left[\hat{\sigma}_z, \left[\sum_{l=1}^{n_M+2k} \hat{\Upsilon}_R^{(l,k)}(t), \hat{\rho}_S(t)\right]\right]$$

$$+ i\left[\hat{\sigma}_z, \left[\sum_{l=n_M+1}^{n_M+2k} \hat{\Upsilon}_I^{(l,k)}(t), \hat{\rho}_S(t)\right]_+\right], \tag{35}$$

where the auxiliary operators $\hat{\Upsilon}_R^{(l,k)}$ and $\hat{\Upsilon}_I^{(l,k)}$ were introduced,

$$\hat{\Upsilon}_R^{(l,k)}(t) = \int_{t_0}^t dt' a_{l,k} \exp(p_{l,k}(t-t')) \exp(-i\hat{L}_S(t-t'))\hat{\sigma}_z \tag{36}$$

$$\hat{\Upsilon}_I^{(l,k)}(t) = \int_{t_0}^t dt' b_{l,k} \exp(p_{l,k}(t-t')) \exp(-i\hat{L}_S(t-t'))\hat{\sigma}_z.$$

From this definition, the equations of motion of these quantities are given as

$$\frac{\partial \hat{\Upsilon}_R^{(l,k)}}{\partial t} = (p_{l,k} - i\hat{L}_S)\hat{\Upsilon}_R^{(l,k)}(t) + a_{l,k}\hat{\sigma}_z$$

$$\frac{\partial \hat{\Upsilon}_I^{(l,k)}}{\partial t} = (p_{l,k} - i\hat{L}_S)\hat{\Upsilon}_I^{(l,k)}(t) + b_{l,k}\hat{\sigma}_z. \tag{37}$$

As mentioned above, the advantage of the present scheme as compared with the related approaches of Refs. 58, 60, and 61 lies in the fact that the decomposition Eq. (29) of the spectral density in terms of complex exponential terms does not result from a fitting procedure, but is a unique result of the effective-mode transformations described in Sec. II.

V. RESULTS AND DISCUSSION

The results presented here refer to the TNL and TL master equations, Eq. (7) and Eq. (13), using either analytical solutions (Sec. V B) or else the auxiliary density/operator approach (Sec. V C) as detailed in Sec. IV. We begin this section by analyzing the two-point bath correlation function $\mathcal{C}_B^{(2)}(t, t')$, in accordance with the discussion of Sec. III D. In Sec. V B, we focus on a pure dephasing example, which is interesting because the TL equations are exact for the case under consideration, as also demonstrated in Ref. 93. In Sec. V C, results are shown for the more general spin-boson example of Eq. (2). For comparing the TL and TNL form, comparison is made with explicit system-bath multi-dimensional wavepacket calculations carried out using the MCTDH method[70–72,98] as further detailed in the supplementary material.[108]

A. Bath correlation functions

We focus here on the low-order correlation functions $\mathcal{C}_B^{(2,k)}(t, t')$ for $k = 1, 2$, which determine the short-time dynamics within the Mori chain model. The parameters of the relevant correlation functions are obtained from the effective mode transformation described in Sec. II. For each order k the hierarchy is terminated by approximating the coupling of the final member of the chain to the bath by an Ohmic spectral density. The correlation functions are analytically determined from the corresponding spectral densities, as described in Sec. III D.

In Fig. 1, the correlation function $\mathcal{C}_B^{(2,k)}$ is depicted for $k = 1$ and 2. At the $k = 1$ level that involves the primary effective mode coupled ohmically to the bath, $\mathcal{C}_B^{(2,1)}$ as defined in Eqs. (27) and (28) consists of (1) an expansion in exponentially decaying terms determined by the Matsubara frequencies and (2) it also possesses an exponential term that has a single carrier oscillation of frequency $\Omega_{B1}/(1 + 4\eta^2)$ with an exponentially decaying envelope—as depicted in Fig. 1. The rate of decay is determined by both the friction parameter η and Ω_{B1}.

At high temperatures, Eqs. (27) and (28) yield

$$\mathcal{C}_B^{(2,1)}(t) \sim \mathrm{Re}\, \mathcal{C}_B^{(2,1)}(t)$$

$$= \frac{2D'^2 k_B T}{\Omega_{B1}} \exp(-2\alpha\eta t)\cos(\alpha t) + \mathcal{C}_M^{(1)}(t), \tag{38}$$
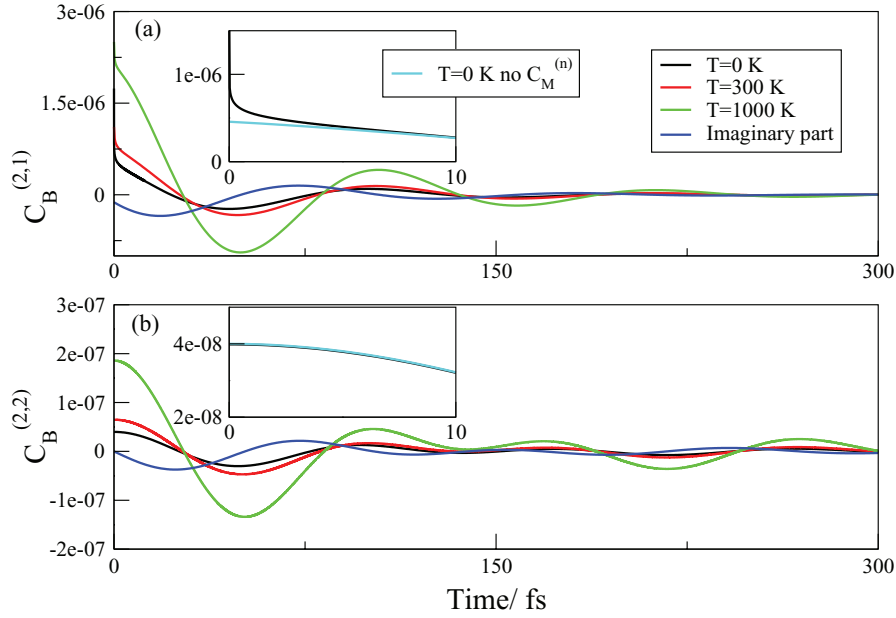
FIG. 1. Bath correlation functions $\mathcal{C}_B^{(2,k)}$ for the imaginary part (blue) and at various temperatures for the temperature dependent real part. (a) depicts the lowest $k = 1$ order correlation function with parameters $D' = 0.0007$, $\Omega_{B1} = 0.0015$, and $\eta = 2/15$; (b) depicts the $k = 2$ order correlation function with parameters $D' = 0.0004 = d_{12}$, $\Omega_{B1} = 0.0015$, $\Omega_{B2} = 0.0014$, and $\eta = 1/7$. The inset figures in both part (a) and (b) depict Re $\mathcal{C}_B^{(2,k)}(t, T = 0)$ evaluated with (black) and without (cyan) $\mathcal{C}_M^{(k)}$.

where the contribution of Re $\mathcal{C}_B^{(2,1)}$ overwhelms that of Im $\mathcal{C}_B^{(2,1)}$ and the Matsubara sum gives the term $\mathcal{C}_M^{(1)}(t)$ $= -(D'^2/\pi)(4\eta/(1 + 4\eta^2) \ln(1 - \exp(-2\pi t/\beta))$ which is only important at short times.

As the temperature is lowered the Matsubara frequencies get denser and the summation may be replaced by an integral over the Matsubara frequencies $\nu_l \to x$:

$$\lim_{T \to 0} \frac{2}{\beta} \sum_{l=1}^{\infty} \to \frac{1}{\pi} \int_0^{\infty} dx. \qquad (39)$$

Evaluating this integral for Eq. (27) gives

$$\text{Re } \mathcal{C}_B^{(2,1)}(t, T = 0) = \frac{iD'^2}{2} \left(\frac{-i + 2\eta}{1 + 4\eta^2} \exp(i\alpha(1 + i2\eta)t) \right.$$
$$\left. - \frac{i + 2\eta}{1 + 4\eta^2} \exp(-i\alpha(1 - i2\eta)t) \right) + \mathcal{C}_M^{(1)}. \qquad (40)$$

The first two exponential terms on the right-hand side arise from the complex exponential components of Eq. (27), and for $t > 0$

$$\mathcal{C}_M^{(1)} = \frac{D'^2}{2\pi} \left\{ \frac{i + 2\eta}{1 + 4\eta^2}(\exp(-i\alpha(1 - i2\eta)t)\Gamma[0, -i\alpha(1 - i2\eta)t] \right.$$

$$+ \exp(i\alpha(1 - i2\eta)t)\Gamma[0, i\alpha(1 - i2\eta)t])$$

$$+ \frac{-i + 2\eta}{1 + 4\eta^2}(\exp(i\alpha(1 + i2\eta)t)\Gamma[0, i\alpha(1 + i2\eta)t]$$

$$\left. + \exp(-i\alpha(1 + i2\eta)t)\Gamma[0, -i\alpha(1 + i2\eta)t]) \right\} \qquad (41)$$

arises from the $\exp(-\nu_l t)$ part of Eq. (27). The term $\Gamma[a, b]$ is the incomplete gamma function. At short times, $\mathcal{C}_M^{(1)}$ diverges but stays integrable, $\mathcal{C}_M^{(1)}(t \to 0)$ $\sim -(D'^2/\pi)(4\eta/(1 + 4\eta^2) \ln t$; the same holds, at all temperatures, for the last term on the r.h.s. of Eq. (37) and Eq. (38). At long times $\mathcal{C}_M^{(1)}$ decays algebraically to zero, $\mathcal{C}_M^{(1)}(t \to \infty) = (4\eta D'^2/\pi \Omega^2)(1/t^2)$. If $\mathcal{C}_M^{(1)}$ is neglected the correlation function $\mathcal{C}_B^{(2,1)}(t, T = 0)$ then consists of only a single complex exponential term $-iD'^2(i + 2\eta)\exp(-i\alpha(1 - i2\eta)t)/(1 + 4\eta^2)$.[107]

For the $k = 2$ case of the primary effective mode coupled to the secondary effective mode which is ohmically coupled to a bath, the explicit form of $\mathcal{C}_B^{(2,2)}$ is given by Eq. (A14) in Appendix A. The temperature dependency of $\mathcal{C}_B^{(2,2)}$ is quite similar to the $k = 1$ case. However, as illustrated in the inset of Fig. 1(b), at $T = 0$ K the short-time influence of $\mathcal{C}_M^{(2)}$ is not very noticeable for the $k = 2$ case. $\mathcal{C}_B^{(2,2)}$ is then very well approximated as

$$\mathcal{C}_B^{(2,2)}(t) = -\frac{i4D'^2 d_{12}^2 \eta}{1 + 4\eta^2} \sum_{r=1}^{2} \frac{p_r \exp(-ip_r t)}{\Pi_{j \neq r}^4 (p_r - p_j)} \qquad (42)$$

where the term p_r is defined in Eq. (A15) of Appendix A.

B. Pure dephasing

A pure dephasing situation is obtained when $\hat{H}_S = \Delta \hat{\sigma}_z$ in Eq. (2). For this model $\hat{\sigma}_z$ is a conserved quantity and the same holds for any function of it. The resulting equations of motion for the reduced density matrix elements are uncoupled

and only the coherences are time-dependent,

$$\frac{\partial \rho_{11}}{\partial t} = 0 = \frac{\partial \rho_{22}}{\partial t}$$

(43)

$$\frac{\partial \rho_{12}}{\partial t} = -i2\Delta\rho_{12}(t) - 4\int_{t_0}^{t} dt' \, \mathrm{Re}\, \mathcal{C}_B^{(2,k)}(t,t')\rho_{12}(\tau) = \frac{\partial \rho_{21}^*}{\partial t},$$

where $\tau = t$ for the TL approach and $\tau = t'$ for the TNL approach. The equation of motion for the coherence in TL form is easily solved to give

$$\rho_{12}^{TL}(t) = \rho_{12}(t_0) \exp\left(-2i\Delta t - \frac{4}{\pi}\int_0^{\infty} d\omega J^{(k)}(\omega)\right.$$

$$\left. \times \coth(\beta\omega/2)\frac{1-\cos\omega t}{\omega^2}\right).$$

(44)

In Appendix B, it is shown that the TL form defined in Eq. (44) for pure dephasing is exact for the harmonic oscillator thermal bath. It was also shown in Ref. 93 that the TL form is exact if the bath modes are Gaussian. Exact solutions for the TL form have further been discussed in Refs. 88, 89, 94, and 95.

To investigate more clearly the influence of the bath on the system dynamics we set $\Delta = 0$. The system dephasing dynamics is then completely determined by the influence of the bath on the system.

1. k = 1 case

At $T = 0$ K the exact TL expression for the coherence is given by

$$\rho_{12}^{TL}(t, T = 0) = \rho_{12}(t_0) \exp\left(-\frac{4D'^2}{\Omega_{B1}^2}[1 - \exp(-2\alpha\eta t)\right.$$

$$\left. \times (\cos\alpha t + 2\eta\sin\alpha t) + \mathcal{M}^{(1)}]\right), \quad (45)$$

where $\mathcal{M}^{(1)}$ is the term that arises from $\mathcal{C}_M^{(1)}$ of Eq. (41) and for $t > 0$ is given by

$$\mathcal{M}^{(1)} = \frac{4\eta}{\pi}\left\{\gamma_E + \ln\frac{\Omega_{B1}t}{\sqrt{1+4\eta^2}}\right.$$

$$+ \frac{1}{8\eta}\left[2\left(\cos^{-1}\frac{2\eta}{\sqrt{1+4\eta^2}} - \cos^{-1}\frac{-2\eta}{\sqrt{1+4\eta^2}}\right)\right.$$

$$+ (-i+2\eta)\left(\exp\left(\frac{\Omega_{B1}t}{i-2\eta}\right)\Gamma\left[0,\frac{\Omega_{B1}t}{i-2\eta}\right]\right.$$

$$+ \exp\left(\frac{\Omega_{B1}t}{-i+2\eta}\right)\Gamma\left[0,\frac{\Omega_{B1}t}{-i+2\eta}\right]\right)$$

$$+ (i+2\eta)\left(\exp\left(\frac{-\Omega_{B1}t}{i+2\eta}\right)\Gamma\left[0,\frac{-\Omega_{B1}t}{i+2\eta}\right]\right.$$

$$\left.\left.\left. + \exp\left(\frac{\Omega_{B1}t}{i+2\eta}\right)\Gamma\left[0,\frac{\Omega_{B1}t}{i+2\eta}\right]\right)\right]\right\}.$$

(46)

The term $\gamma_E \simeq 0.577216$ is Euler's constant. Figure 2 depicts $\rho_{12}^{TL}(t, T = 0)$ and for the TNL case $\rho_{12}^{TNL}(t, T = 0)$, evaluated using the parameters defined in Table I along with $\eta = 1/15$, and initial condition $\rho_{12}(t_0) = -i/2$. The TL and TNL form differ significantly. The TL case has a damped oscillation of frequency α followed by a long time decay of the coherence. The TNL coherence oscillation is shifted to a higher frequency of

$$\alpha' = \frac{\sqrt{4D'^2(1+4\eta^2)+\Omega_{B1}^2}}{1+4\eta^2}.$$

(47)

In Fig. 2(a), $\rho_{12}^{TNL}(t, T = 0)$ evaluated with and without the inclusion of $\mathcal{C}_M^{(1)}$ is depicted. By excluding $\mathcal{C}_M^{(1)}$, $\rho_{12}^{TNL}(t, T = 0)$ is evaluated relatively straightforwardly by Laplace transform
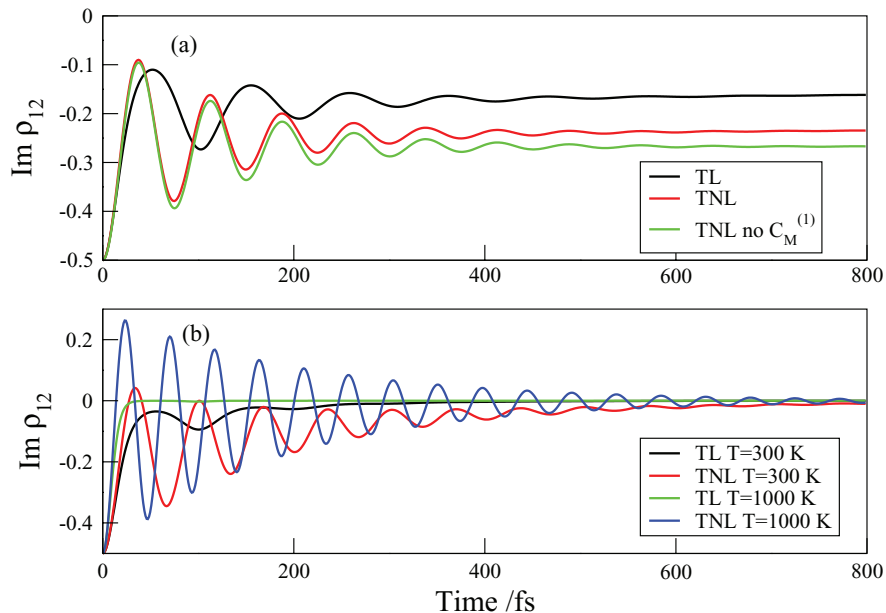

FIG. 2. Pure dephasing dynamics at the $k = 1$ level using the parameters defined in Table I along with $\eta = 1/15$, and initial condition $\rho_{12}(t_0) = -i/2$ for the TL and TNL approach. (a) depicts the T = 0 K case for $\rho_{12}^{TL}(t, T = 0)$ (black), and $\rho_{12}^{TNL}(t, T = 0)$ evaluated with (red), and without (green) inclusion of $\mathcal{C}_M^{(1)}$ of Eq. (41). In (b) $\rho_{12}^{TL}(t)$ and $\rho_{12}^{TNL}(t)$ are depicted at T = 300 K and T = 1000 K.

TABLE I. Parameters, quoted in atomic units.

	Ω_{B1}	Ω_{B2}	D'	d_{12}
Dephasing	0.0015	0.0014	0.0007	0.0004
Spin-boson	0.0015	0.0014	0.00025	0.0004

to give

$$\rho_{12}^{\text{TNL}}(t, T = 0)$$

$$= \rho_{12}(t_0)\left\{\frac{\Omega_{B1}^2}{4D'^2 + \Omega_{B1}^2} + \frac{4D'^2 \exp(-2\alpha\eta t)}{4D'^2 + \Omega_{B1}^2}\left[\cos\alpha't\right.\right.$$

$$\left.\left. + \frac{2\eta\Omega_{B1}\sin\alpha't}{\sqrt{4D'^2(1 + 4\eta^2) + \Omega_{B1}^2}}\right]\right\}. \quad (48)$$

From the definition of α' it is clear that $\rho_{12}^{\text{TNL}}(t, T = 0)$ becomes more accurate for high frequency (large Ω_{B1}) weakly coupled (small D value) baths where α gets closer to α'.

As the temperature increases the coherence decays more rapidly to zero for both the exact $\rho_{12}^{\text{TL}}(t)$ and $\rho_{12}^{\text{TNL}}(t)$. In the high temperature limit and excluding the contribution of $\mathcal{C}_M^{(1)}$ in Eq. (38)

$$\rho_{12}^{\text{TL}}(t) = \rho_{12}(t_0)\exp\left(-\frac{8D'^2}{\beta\Omega_{B1}^2}\left[2\eta t\right.\right.$$

$$+ \alpha^{-1}(1 - \exp(-2\alpha\eta t)\cos\alpha t)$$

$$\left.\left. - \frac{4\eta}{\Omega_{B1}}\exp(-2\alpha\eta t)\sin\alpha t\right]\right). \quad (49)$$

In Fig. 2(b), $\rho_{12}^{\text{TL}}(t)$ is depicted at T = 1000 K along with $\rho_{12}^{\text{TNL}}(t)$ which becomes more oscillatory and is shifted to even higher frequency. For $\rho_{12}^{\text{TNL}}(t)$ the high temperature expression is quite complicated and its explicit form is not very instructive.

2. k = 2 case

The explicit analytical expression for $\rho_{12}^{\text{TL}}(t)$ is more complicated than the corresponding $k = 1$ expression, and although its evaluation is straightforward its analytical expression is not very instructive. Due to the dependency of $\rho_{12}(t)$ on the primary and secondary effective mode frequencies, the coupling between the modes and the friction term, the coherence dynamics will be more complicated than the $k = 1$ case. Figure 3 depicts $\rho_{12}^{\text{TL}}(t)$ and $\rho_{12}^{\text{TNL}}(t)$ at (a) T = 0 K, (b) T = 300 K, and (c) T = 1000 K. Figure 3(a) also depicts $\rho_{12}(t)$ evaluated with and without $\mathcal{M}^{(2)}$; however, the coherences are virtually indistinguishable because $\mathcal{C}_M^{(2,2)}$ contributes little to Re $\mathcal{C}_B^{(2,2)}(t, T = 0)$, as clearly illustrated in Fig. 1(b). As in the $k = 1$ case the TL and TNL coherences differ significantly, especially at high temperature, as illustrated in Fig. 3(c). At high temperature $\rho_{12}^{\text{TNL}}(t)$ oscillates at a higher frequency and possesses a relatively large amplitude which takes over 40 ps to decay, compared to around 500 fs for $\rho_{12}^{\text{TL}}(t)$.

C. Spin-boson model

This section focusses on the more general spin-boson Hamiltonian $\hat{H}_S = \Delta\hat{\sigma}_z + \lambda\hat{\sigma}_x$ where neither the second order TNL or TL form are exact. The dynamics of $\rho^{\text{TNL}}(t)$ and $\rho^{\text{TL}}(t)$ are evaluated using the auxiliary approaches of Eq. (34) or Eq. (37), respectively. The accuracy of the two approaches is assessed at $T = 0$ K by comparing the dynamics of $\rho^{\text{TNL}}(t)$ and $\rho^{\text{TL}}(t)$ with multi-dimensional wavepacket calculations using the MCTDH method[70–72] (Heidelberg MCTDH package[98]).

For the wavepacket calculations, a procedure similar to the one described in Refs. 49–51 was employed. An explicit discretized representation using 30 modes sampled from the kth-order spectral density $J_{\text{eff}}^{(k)}(\omega)$ (see Eq. (A10)) with equally
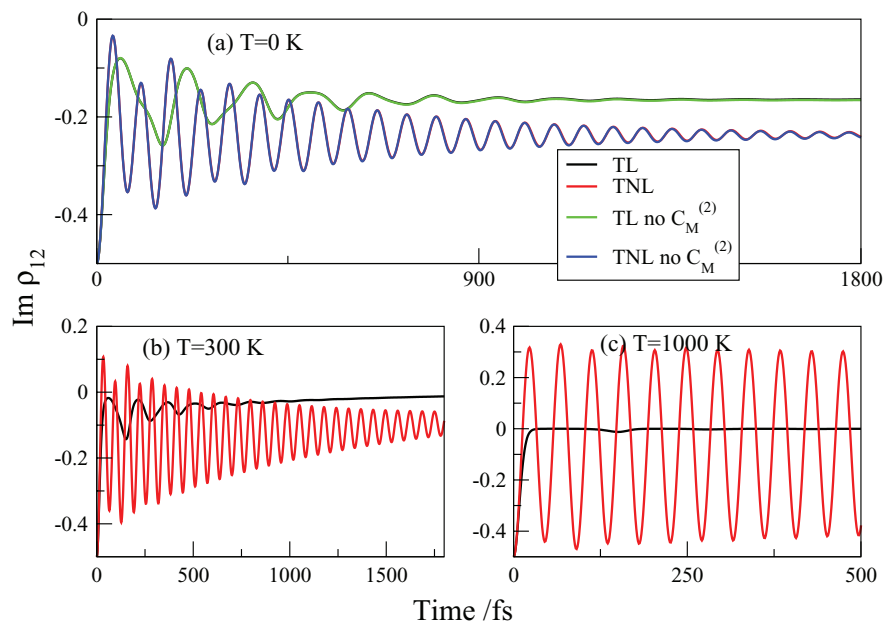

FIG. 3. Pure dephasing dynamics at the $k = 2$ level using the parameters defined in Table I along with $\eta = 1/14$, and initial condition $\rho_{12}(t_0) = -i/2$ for the TL (black) and TNL (red) approach. (a) depicts the T = 0 K case for $\rho_{12}^{\text{TL}}(t, T = 0)$ (black), and $\rho_{12}^{\text{TNL}}(t, T = 0)$ evaluated with (red), and without (green for TL and blue for TNL) inclusion of $\mathcal{C}_M^{(2)}$. In (b) $\rho_{12}^{\text{TL}}(t)$ and $\rho_{12}^{\text{TNL}}(t)$ are depicted at T = 300 K, and (c) at T = 1000 K.
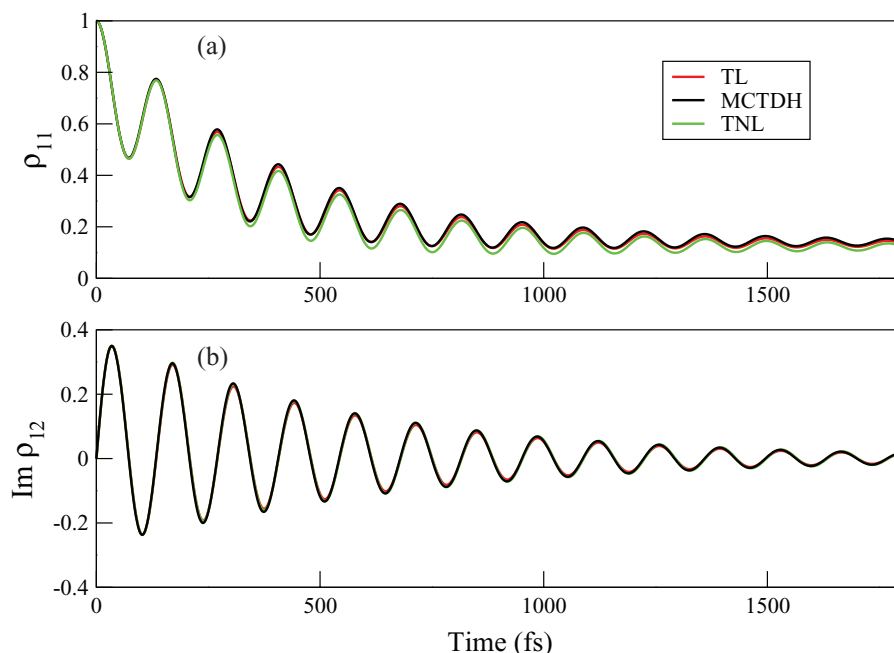
FIG. 4. (a) Population and (b) coherence dynamics at the $k = 1$ level and temperature T = 0 K for the TL, TNL, and wavepacket MCTDH approach. The parameters are defined in Table I along with $\eta = 4/15$ and initial condition $\rho_{11}(t_0) = 1$.

spaced frequencies was employed to simulate the system-bath dynamics at $T = 0$ K, where all the bath modes are in the ground state. The system-bath coupling coefficients c_n (here, in the pre-transformed representation) are related to the spectral density by[51]

$$c_n = \sqrt{\frac{2}{\pi} J_{\text{eff}}^{(k)}(\omega) \Delta \omega}. \tag{50}$$

Further details are provided in the supplementary material.[108]

Results are presented for the lowest order $k = 1$ case of the primary effective mode Ω_{B1} coupled directly to the Ohmic bath, and for the $k = 2$ case which consists of the primary effective mode coupled to a secondary effective mode Ω_{B2} which is directly coupled to the bath. Initial conditions $\rho_{11}(t_0) = 1$, $\rho_{12}(t_0) = \rho_{21}(t_0) = \rho_{22}(t_0) = 0$ were used for both the $k = 1$ and $k = 2$ case.

1. k = 1 case

Figure 4 depicts the population and coherence dynamics at $T = 0$ K using the system parameters $\Delta = 0.0004 = \lambda$ and bath parameters defined in Table I along with $\eta = 4/15$ and initial condition $\rho_{11}(t_0) = 1$. All three calculations are in good agreement with each other. The TL approach is in closer agreement with the MCTDH results than the TNL approach. This is in stark contrast to the dephasing results of Sec. V B where the TNL results differed significantly from the exact TL results. However, in this case the system parameters were set to zero and so the system dynamics was completely due to the interaction with the bath. In this spin-boson case the system dynamics masks some of the influence of the bath and so the discrepancy between the TL and TNL form is not as pronounced. Furthermore, a large D coupling parameter was

chosen for the dephasing results which amplifies the differences between the two approaches.

The population dynamics of Fig. 4(a) displays a decaying almost Rabi oscillatory profile of frequency $\sim \sqrt{\lambda^2 + \Delta^2}$. The imaginary part of the coherence ρ_{12} is depicted in Fig. 4(b).

In Fig. 5, the population and coherence dynamics is depicted for various temperatures. For the populations the amplitude of the Rabi oscillation diminishes as temperature increases and the populations relax almost to a Boltzmann distribution. The coherence decays more rapidly as temperature increases.

2. k = 2 case

Figure 6 depicts the population and coherence dynamics at $T = 0$ K using the system parameters $\Delta = 0.0004 = \lambda$ and bath parameters defined in Table I along with $\eta = 2/14$, and initial condition $\rho_{11}(t_0) = 1$. All three calculations are in good agreement with each other. The TL approach is in closer agreement with the MCTDH results than the TNL approach, as was the case for $k = 1$.

Both the population and coherence dynamics of Fig. 6 is very similar to the corresponding dynamics illustrated in Fig. 4 for the $k = 1$ case. This is not surprising because we expect a low order truncation of the effective mode chain to accurately reproduce the short-time dynamics of the system.[49–53] The accuracy of the dynamics persists as the temperature is varied, as illustrated in Fig. 7, which should be compared with the $k = 1$ model of Fig. 5.

D. Discussion

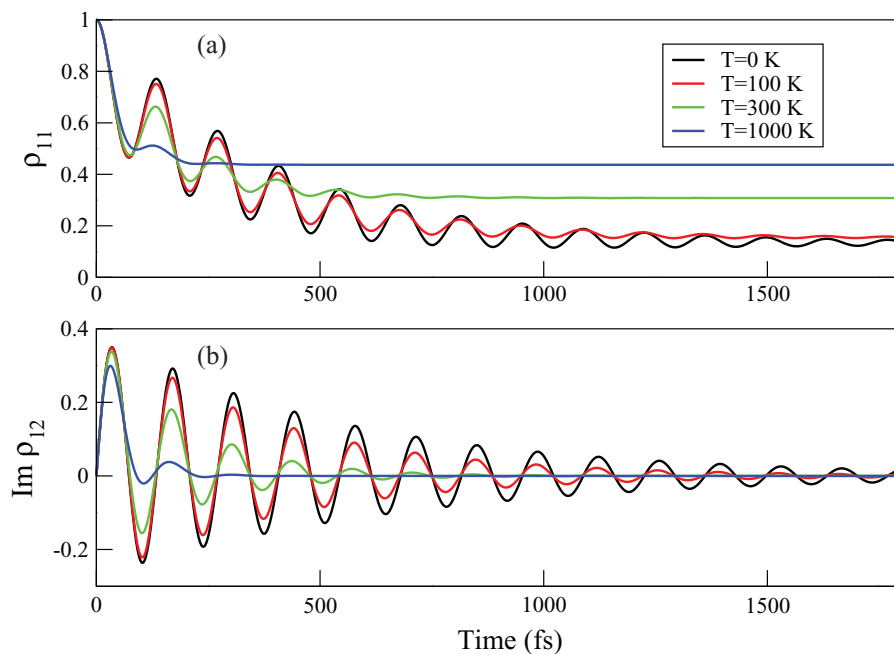The above examples have focused on the analytically solvable pure dephasing case (Sec. V B) and a more general

FIG. 5. (a) Population and (b) coherence dynamics at the $k = 1$ level at temperatures T = 0, 100, 300, and 1000 K for the TL approach using the initial condition $\rho_{11}^{\mathrm{TL}}(t_0) = 1$ and parameters defined in Table I along with $\eta = 4/15$.

spin-boson dynamics where the second-order master equation result was in very good agreement with numerically exact, non-perturbative MCTDH results (Sec. V C). The $C_B^{(2,k)}$, $k = 1, 2$, correlation functions were calculated from the analytical expressions of Sec. III D (see Fig. 1), and the resulting dynamics were compared. The results of Figs. 4 versus 6 and Figs. 5 versus 7 illustrate the similarity of the $k = 1, 2$ calculations for a broad range of temperatures. These results, even

though restricted to low orders in k, are useful by themselves, and could capture the dominant non-Markovian behavior in a class of systems where the Brownian oscillator picture provides a good zeroth-order model.

Some focus was placed upon the comparison between the TL and TNL dynamics. In particular, it was shown that for the pure dephasing model the TL form is exact for thermal harmonic baths, see also Refs. 88, 89, 94, and 95. The TNL
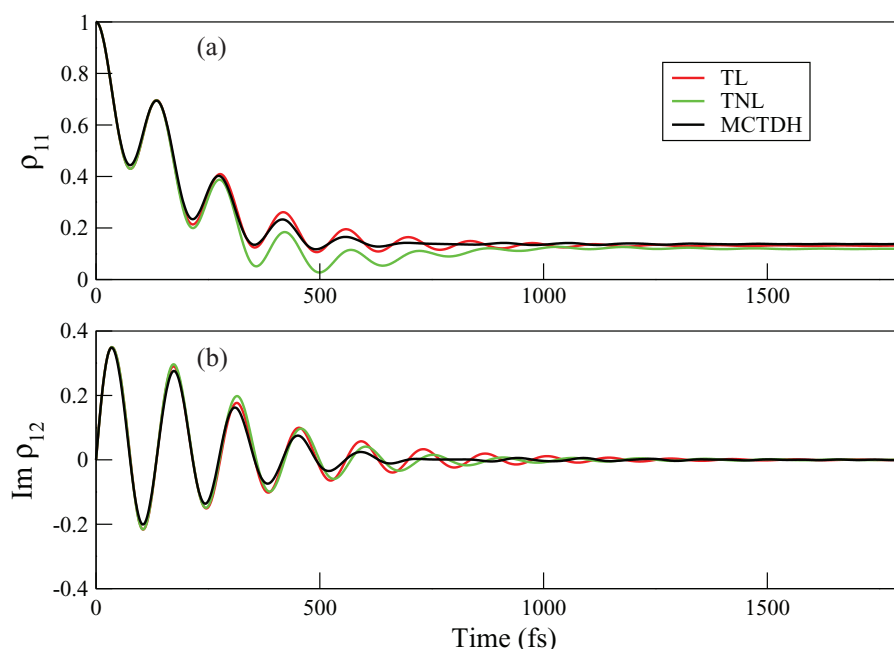

FIG. 6. (a) Population and (b) coherence dynamics at the $k = 2$ level and temperature T = 0 K for the TL, TNL, and wavepacket MCTDH approach. The parameters are defined in Table I along with $\eta = 2/14$ and initial condition $\rho_{11}(t_0) = 1$.
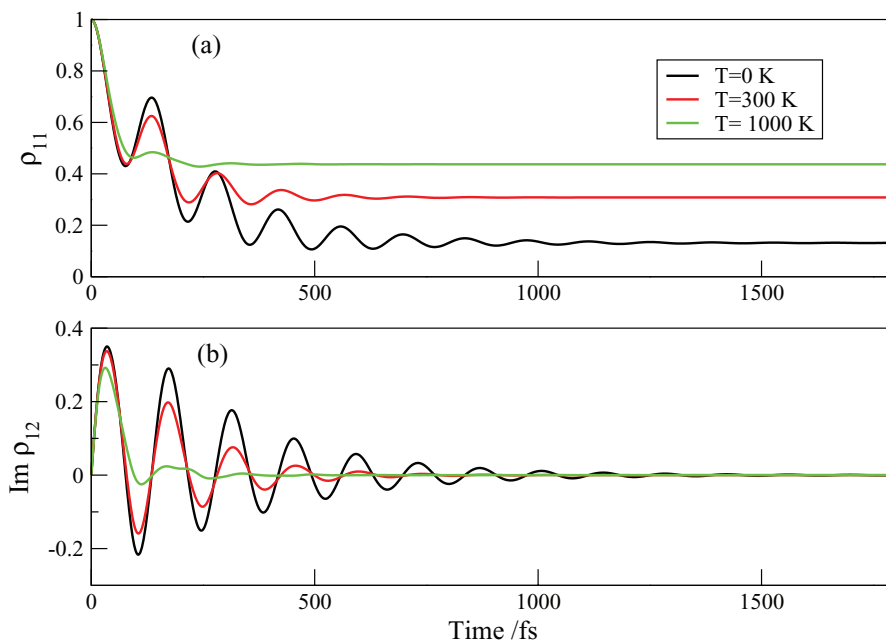
FIG. 7. (a) Population and (b) coherence dynamics at the $k = 2$ level at temperatures T = 0, 300, and 1000 K for the TL approach using the initial condition $\rho_{11}^{TL}(t_0) = 1$ and parameters defined in Table I along with $\eta = 2/14$.

form only showed good agreement with the exact result for weak coupling and high frequency baths. This observation has also been noted in Refs. 101 and 102 in the study of optical line shape widths of excitonic molecular aggregates.

For the spin-boson case neither the TL or TNL form is exact, but in the results presented here the TL form was more accurate than the TNL form and this was generally the case for other caclulations that we performed (but did not highlight in this paper) using different parameters for the spin-boson model. However, one should not assume that the TL form is globally superior to the TNL form; as noted in Refs. 94, 96, 97, and 101 the accuracy of the TL versus TNL forms is dependent on the system under study.

Future work will address higher-order correlation functions, and their approximation by lower order $\mathcal{C}_B^{(2,k)}$'s. While the analytical correlation function expressions become increasingly demanding, and are in practice difficult to obtain beyond $k = 2$, the numerical calculation of the correlation functions is straightforward. Also, it is feasible to numerically obtain the complex poles that are required for the representation Eq. (29), as a prerequisite for the auxiliary density matrix/operator approach.

VI. CONCLUSIONS AND OUTLOOK

The hierarchical approach developed here can be viewed as a Liouville-space analog of the Mori-chain representation[39–41,83] which is generally applied in the Heisenberg picture. This chain representation of the environment provides a natural approach to non-Markovian dynamics, as is manifest already for its simplest realization, i.e., the Brownian oscillator model. By the coupling of the primary oscillator to the residual chain of bath modes, the dynamics of the former becomes more complicated and eventually re-

veals all details of the many-body environment and its coupling to the quantum subsystem. Note that the approach is distinct from multi-mode Brownian oscillator models.[24]

While the transformation techniques addressed here have been explored in our recent work[30–32,46,47] and the usefulness of the method has been demonstrated, e.g., to describe the photophysics of extended systems,[46–48] the interest of the present work is to systematically construct a reduced dynamics approach that builds upon the effective mode picture. Cumulant expansion techniques are the method of choice since they connect to our previous analysis in terms of moments (cumulants) of the Hamiltonian propagator,[32,47] as well as the analysis of Ref. 86 in terms of moments of the Liouvillian propagator.

In keeping with earlier works,[25–27,99,100] we have used the fact that the central quantities appearing in the analysis are correlation functions of the primary effective mode, which is the only bath mode that is directly involved in the system-bath coupling $\hat{H}_{SB}$. The residual bath appears in terms of the coupling to the primary mode, and can be accounted for using various levels of approximation. In particular, the intra-bath couplings are cast into a band-diagonal form resulting in a chain of residual modes. In accordance with the Mori chain picture, an Ohmic closure is introduced at the kth-order truncation point within the chain.

The present analysis is parallel to our recent development of Refs. 49 and 50 where we proposed to generate a hierarchical series of approximate spectral densities $J_{\text{eff}}^{(k)}(\omega)$, using the same effective mode description with successive kth order truncations. The two-point correlation functions $\mathcal{C}_B^{(2,k)}$ which are the central quantities of interest in the present study—at the level of a second-order master equation description—are obtained as the Fourier-Laplace transforms of these spectral densities.

Using the complex exponential property of the correlation functions, we have further introduced a time-local form of the second-order master equation which employs a formulation in terms of auxiliary densities for the TNL form or auxiliary operators for the TL form, similar to Refs. 58, 60, and 61. Importantly, no fitting procedure to a sum of complex exponentials is necessary in the present approach.

This procedure, which would be able to capture important aspects of the dynamics even at the level of the weak-coupling (second-order) non-Markovian master equation, has been illustrated for the first few orders in the chain expansion. Analytical results have been obtained for the two-point correlation functions $C_B^{(2,k)}$, $k = 1, 2$, which are 2nd order in $\hat{H}_{SB}$ and kth order in the chain expansion. In view of our recent study of the convergence properties of the hierarchical effective-mode approach of Ref. 53, we expect convergence with respect to k to be rapid. Specifically, it has been shown in the latter reference that the random force correlation functions of the Langevin equation (which are essentially the same correlation functions as those described in this work) are rapidly convergent and accurately reproduce the memory kernel to $4k$th order in time.

Although powerful numerical techniques are available to explicitly provide exact solutions for the spin-boson problem in many dimensions,[64–67,73] the present transformation techniques can be useful for more general system-bath problems, as exemplified by our recent applications.[49,50] An approximate, reduced-dimensional treatment of the residual bath can thus bring significant advantages for ultrafast system-bath dynamics in markedly non-Markovian regimes.

Various extensions and applications of the present approach can be envisaged. First and foremost, the proposed approximation schemes need to be carefully assessed and compared with the approximations made in reduced dynamics descriptions of the original Hamiltonian (prior to the effective mode transformation). *A priori*, the present approach is not limited to weak coupling, provided that higher orders in the cumulant expansion are included. This can in principle be done, based on the observation that the bath in the chain representation represents a Gaussian process – as is the case in the pre-transformed representation. Further, relevant extensions involve the generalization to more complicated quantum subsystems like conical intersections, where several effective modes appear at each order of the Mori chain hierarchy.[30–32] Finally, interesting connections exist to numerical renormalization group techniques, which have recently been extended to bosonic baths, using very similar chain constructions as the one employed here.[42] Overall, we hope that the present approach could provide a useful alternative to other hierarchical schemes that have recently been developed in order to make non-Markovian reduced dynamics feasible in practice.[18,20,58,60,103,104]

ACKNOWLEDGMENTS

APPENDIX A: CONTINUED-FRACTION SOLUTION OF MORI CHAIN EQUATIONS WITH MARKOVIAN CLOSURE

In this appendix, we derive a general form of the spectral density for a truncated Mori chain with Ohmic closure, which yields by Fourier transformation the correlation functions of Sec. III D. The resulting spectral densities are the analog, in mass and frequency weighted coordinates, of the spectral densities obtained in Refs. 49 and 50. Similarly to these references, the spectral density pertaining to the chain representation Eq. (5) is obtained in terms of the imaginary part of a Laplace-domain propagator $\hat{K}_B(z)$ which describes the effect of the bath on the subsystem.

For a two-level system, we consider the Heisenberg operators $\{\hat{\sigma}_x, \hat{\sigma}_y, \hat{\sigma}_z\}$. For convenience, we employ the operators $\hat{\sigma}_\pm = 1/2(\hat{\sigma}_x \pm i\hat{\sigma}_y)$ which are found to evolve independently under the coupling to the bath,

$$(z \pm 2\Delta)\hat{\sigma}_\pm(z) \mp \lambda\hat{\sigma}_z(z) - i\hat{\sigma}_{\pm,0} = \hat{K}_B^{(\pm)}(z)\hat{\sigma}_\pm(z). \quad (A1)$$

The operator $\hat{\sigma}_z$ is independent of the bath, and its evolution follows from the relation $\dot{\hat{\sigma}}_z = -i2\lambda(\hat{\sigma}_+ - \hat{\sigma}_-)$.

From the propagator $\hat{K}_B^{(\pm)}(z)$, the spectral density is obtained as follows:[25,49,50]

$$J(\omega) = \lim_{\epsilon \to 0^+} \text{Im}\hat{K}_B(\omega - i\epsilon), \quad (A2)$$

i.e., the spectral density is given as the imaginary part of the dynamic susceptibility.[25]

As in Refs. 25, 49, and 50, we now employ a mixed quantum-classical representation and replace the bosonic creation and annihilation operators $\hat{A}_{Bn} = 1/\sqrt{2}(\hat{X}_{Bn} + i\hat{P}_{Bn})$ and $\hat{A}_{Bn}^\dagger = 1/\sqrt{2}(\hat{X}_{Bn} - i\hat{P}_{Bn})$ by their c-number analogs,

$$\alpha_{Bn} = \frac{1}{2^{1/2}}(X_{Bn} + iP_{Bn}); \quad \alpha_{Bn}^* = \frac{1}{2^{1/2}}(X_{Bn} - iP_{Bn}), \quad (A3)$$

noting that α_n is the eigenvalue of the annihilation operator when acting on the corresponding coherent state, $\hat{A}_n|\alpha_n\rangle = \alpha_n|\alpha_n\rangle$, and likewise, $\langle\alpha_n|\hat{A}_n^\dagger = \langle\alpha_n|\alpha_n^*$. We emphasize that the classical approximation for the bath degrees of freedom only concerns the construction of the spectral densities, and does not impose any approximation regarding the dynamical treatment of the bath. (See also the discussion of Ref. 92 where a full quantum treatment of the bath is addressed.)

As a result of the Fourier/Laplace transform, we obtain for the Heisenberg operators of the two-level system,

$$-iz\hat{\sigma}_\pm(z) - \hat{\sigma}_{\pm,0} = \pm i2\Delta\hat{\sigma}_\pm(z) \mp i\lambda\hat{\sigma}_z(z) \pm iD'(\alpha_1(z)$$
$$+ \alpha_1^*(z)) * \hat{\sigma}_\pm(z)$$

$$-iz\hat{\sigma}_z(z) - \hat{\sigma}_{z,0} = -i2\lambda(\hat{\sigma}_+(z) - \hat{\sigma}_-(z)), \quad (A4)$$

where the * symbol denotes the frequency domain convolution and $\hat{\sigma}_{\pm,0}$ and $\hat{\sigma}_{z,0}$ correspond to the operator initial

conditions. For the bath variables, we obtain

$$-iz\alpha_1(z) = -i\Omega_{B1}\alpha_1(z) - iD'\hat{\sigma}_z(z) - id_{1,2}\alpha_2(z)$$

$$-iz\alpha_2(z) = -i\Omega_{B2}\alpha_2(z) - id_{1,2}\alpha_1(z) - id_{2,3}\alpha_3(z)$$

$$\vdots \quad \vdots$$

$$-iz\alpha_k(z) = -i\Omega_{Bk}\alpha_k(z) - id_{k-1,k}\alpha_{k-1}(z) - i\sum_{n=k+1}^{N} d_{k,n}\alpha_n(z)$$

$$-iz\alpha_{k+1}(z) = -i\Omega_{Bk+1}\alpha_{k+1}(z) - id_{k,k+1}\alpha_k(z)$$

$$\vdots \quad \vdots$$

$$-iz\alpha_{N_B}(z) = -i\Omega_{BN}\alpha_N(z) - id_{k,N}\alpha_k(z) \tag{A5}$$

and a corresponding set of equations for the α_n^* quantities.

From the first equation of Eq. (A5), an expression for $\alpha_1(z)$ is obtained, which is to be inserted into Eq. (A4):

$$\alpha_1(z) = \frac{D'\hat{\sigma}_z(z)}{z - \Omega_{B1} - d_{1,2}\frac{\alpha_2(z)}{\alpha_1(z)}}. \tag{A6}$$

With an analogous equation for $\alpha_1^*(z)$, and referring back to Eq. (A1), we have

$$\hat{K}_B^{(\pm)}(z)\hat{\sigma}_\pm(z)$$

$$= \pm D'^2\left(\frac{1}{z - \Omega_{B1} - d_{1,2}\frac{\alpha_2(z)}{\alpha_1(z)}} + \frac{1}{z + \Omega_{B1} + d_{1,2}\frac{\alpha_2^*(z)}{\alpha_1^*(z)}}\right)\hat{\sigma}_\pm(z),$$

$$\tag{A7}$$

where we used $\hat{\sigma}_z\hat{\sigma}_\pm = \pm\hat{\sigma}_\pm$ and the convolution form on the rhs of Eq. (A4) was approximated by assuming $\hat{\sigma}_\pm(z - z') \sim \hat{\sigma}_{\pm,0}\delta(z - z')$ in the interaction frame.[92] To continue, an equation for $\alpha_2(z)/\alpha_1(z)$ is obtained from the third equation of Eq. (A5), and similarly for the following orders. A continued fraction pattern thus develops.[49,50]

When the kth member is reached, the hierarchy terminates as follows:

$$\frac{\alpha_k(z)}{\alpha_{k-1}(z)} = \frac{d_{k-1,k}}{z - \Omega_{Bk} - \sum_{n=k+1}^{N_B}\frac{d_{k,n}^2}{z-\Omega_n}}, \tag{A8}$$

where we used $\alpha_n(z) = d_{k,n}\alpha_k(z)/(z - \Omega_{Bn})$ from the last $N - k$ equations of Eq. (A5).

In the limit where the last $N - k$ modes conform to an Ohmic bath, one can replace

$$\sum_{n=k+1}^{N_B}\frac{d_{k,n}^2}{z - \Omega_{Bn}} \to i2\eta z, \tag{A9}$$

where η is the friction coefficient from a Langevin treatment. Analogous expressions can again be obtained for the α_n^* variables.

With an Ohmic closure at the kth order, we thus obtain the kth order spectral density as follows according to Eq. (A2):[49]

$$J_{\text{eff}}^{(k)}(\omega) = \lim_{\epsilon\to 0^+}\text{Im}\hat{K}_B^{(k)}(\omega - i\epsilon) \tag{A10}$$

with $\hat{K}_B^{(k)}$ given as a continued fraction of order k,

$$\hat{K}_B^{(k)}(z) = \hat{K}_{B,+}^{(k)}(z) + \hat{K}_{B,-}^{(k)}(z)$$

$$\hat{K}_{B,\pm}^{(k)}(z) = -\cfrac{D'^2}{\Omega_{B1}\mp z - \cfrac{d_{1,2}^2}{\Omega_{B2}\mp z - \cdots \cfrac{d_{k-2,k-1}^2}{\Omega_{Bk-1}\mp z - \cfrac{d_{k-1,k}^2}{\Omega_{Bk}\mp z + i2\eta z}}}}$$

$$\equiv -\frac{D'^2|}{|\Omega_{B1}\mp z} - \frac{d_{1,2}^2|}{|\Omega_{B2}\mp z} - \cdots \frac{d_{k-2,k-1}^2|}{|\Omega_{Bk-1}\mp z} - \frac{d_{k-1,k}^2|}{|\Omega_{Bk}\mp z + i2\eta z}, \tag{A11}$$

where the continued-fraction notation of Pringsheim[105] was used.

At the first order of the hierarchy, $k = 1$, the relation (A10) results in the Lorentzian spectral density of Eq. (26). The corresponding correlation function is obtained by Fourier transformation and is given by Eq. (27).

At the second order, $k = 2$, we obtain the spectral density

$$J_{\text{eff}}^{(2)}(\omega) = J_{+,\text{eff}}^{(2)}(\omega) + J_{-,\text{eff}}^{(2)}(\omega) \tag{A12}$$

with

$$J_{\pm,\text{eff}}^{(2)}(\omega) = \frac{2D'^2 d_{12}^2\eta\omega}{\{(\Omega_{B1}\mp\omega)[\Omega_{B2}\mp\omega(1 - i2\eta)] - d_{12}^2\}\{(\Omega_{B1}\mp\omega)[\Omega_{B2}\mp\omega(1 + i2\eta)] - d_{12}^2\}} \tag{A13}$$

and the corresponding correlation function is given as

$$C_B^{(2,2)}(t) = -\frac{i2D'^2 d_{12}^2 \eta}{1 + 4\eta^2}$$

$$\times \sum_{r=1}^{4} \frac{\exp(-i p_r t)}{\Pi_{j\neq r}^4 (p_r - p_j)} \left(p_r + \frac{2}{\beta} \left\{ 1 + \sum_{n=1}^{n=\infty} \frac{2p_r^2}{p_r^2 + v_n^2} \right\} \right)$$

$$- \frac{2}{\beta} D'^2 d_{12}^2 \eta \sum_{n=1}^{\infty} v_n \exp(-v_n t)$$

$$\times \left(\frac{1}{\{(\Omega_{B1} + i v_n)[\Omega_{B2} + i v_n(1 - i2\eta)] - d_{12}^2\}\{(\Omega_{B1} + i v_n)[\Omega_{B2} + i v_n(1 + i2\eta)] - d_{12}^2\}} \right.$$

$$\left. + \frac{1}{\{(\Omega_{B1} - i v_n)[\Omega_{B2} - i v_n(1 - i2\eta)] - d_{12}^2\}\{(\Omega_{B1} - i v_n)[\Omega_{B2} - i v_n(1 + i2\eta)] - d_{12}^2\}} \right), \quad \text{(A14)}$$

where

$$p_{1(2)} = \frac{\Omega_{B2} + \Omega_{B1}[1 + i2\eta]}{2[1 + i2\eta]}$$

$$+ (-) \frac{\sqrt{(\Omega_{B2} - \Omega_{B1}[1 + i2\eta])^2 + 4d_{12}^2[1 + i2\eta]}}{2[1 + i2\eta]}, \quad \text{(A15)}$$

$$p_{3(4)} = -\frac{\Omega_{B2} + \Omega_{B1}[1 - i2\eta]}{2[1 - i2\eta]}$$

$$+ (-) \frac{\sqrt{(\Omega_{B2} - \Omega_{B1}[1 - i2\eta])^2 + 4d_{12}^2[1 - i2\eta]}}{2[1 - i2\eta]}. \quad \text{(A16)}$$

APPENDIX B: ANALYTICAL SOLUTION FOR THE PURE DEPHASING CASE

For the dephasing example,

$$\hat{H} = \hat{H}_S + \hat{H}_{SB} + \hat{H}_B$$

$$= \Delta \hat{\sigma}_z + \hat{\sigma}_z \sum_n c_n x_n + \sum_n \frac{\omega_n}{2} (\hat{x}_n^2 + \hat{p}_n^2) \hat{1}. \quad \text{(B1)}$$

We assume factorised initial conditions $\hat{\rho}_S \otimes \hat{\rho}_B$. The harmonic oscillator bath is in thermal equilibrium with a density matrix given by[2]

$$\rho_B(x, x', \beta) = \frac{1}{\sqrt{2\pi \sinh \beta\omega}} \exp\left(-\frac{(x + x')^2}{4} \tanh \frac{\beta\omega}{2} \right.$$

$$\left. - \frac{(x - x')^2}{4} \coth \frac{\beta\omega}{2} \right), \quad \text{(B2)}$$

where x represents the collective bath coordinates $\{\hat{x}_n\}_1^{N_B}$. The presence of the interaction $\hat{\sigma}_z \sum_n c_n x_n$ shifts the harmonic potential along the bath coordinate for state 1 to $x_{0,n} = -c_n/\omega_n$ and the other is shifted to $-x_{0,n} = c_n/\omega_n$. Furthermore, $\hat{H}_S$ raises state 1 by Δ and lowers state 2 by an equal amount. The total system plus bath density matrix for the off-diagonal dephasing part is then given by a thermal coherent state,

$$\rho_{12}(x, x', \beta) = \frac{1}{\sqrt{2\pi \sinh \beta\omega}} \exp\left(-\frac{[x + x_0(1 - \cos \omega t) + x' - x_0(1 - \cos \omega t)]^2}{4} \tanh \frac{\beta\omega}{2} \right)$$

$$\times \exp\left(-\frac{[x + x_0(1 - \cos \omega t) - x' + x_0(1 - \cos \omega t)]^2}{4} \coth \frac{\beta\omega}{2} \right)$$

$$\times \exp(i x_0(x + x') \sin \omega t - i2\Delta t)$$

$$= \frac{1}{\sqrt{2\pi \sinh \beta\omega}} \exp\left(-\frac{[x + x']^2}{4} \tanh \frac{\beta\omega}{2} \right)$$

$$\times \exp\left(-\frac{[x - x' + 2x_0(1 - \cos \omega t)]^2}{4} \coth \frac{\beta\omega}{2} \right)$$

$$\times \exp(i x_0(x + x') \sin \omega t - i2\Delta t). \quad \text{(B3)}$$

Taking the trace gives

$$
\begin{aligned}
\rho_{12} &= \frac{1}{\sqrt{2\pi \sinh \beta\omega}} \exp\left(-i2\Delta t - x_0^2(1-\cos\omega t)^2 \coth\frac{\beta\omega}{2}\right) \\
&\quad \times \int dx \exp\left(-x^2 \tanh\frac{\beta\omega}{2} + i2x_0 x \sin\omega t\right) \\
&= \sqrt{\frac{\pi}{2\pi \sinh \beta\omega \tanh\frac{\beta\omega}{2}}} \exp\left(-i2\Delta t - x_0^2(1-\cos\omega t)^2 \coth\frac{\beta\omega}{2}\right) \\
&\quad \times \exp\left(-\frac{4x_0^2 \sin^2 \omega t}{4\tanh\frac{\beta\omega}{2}}\right) \\
&= \sqrt{\frac{1}{2 \sinh \beta\omega \tanh\frac{\beta\omega}{2}}} \exp\left(-i2\Delta t - x_0^2(1-\cos\omega t)^2 \coth\frac{\beta\omega}{2}\right) \\
&\quad \times \exp\left(-x_0^2 \sin^2 \omega t \coth\frac{\beta\omega}{2}\right) \\
&= \frac{1}{2\sinh\frac{\beta\omega}{2}} \exp\left(-i2\Delta t - 2x_0^2(1-\cos\omega t)\coth\frac{\beta\omega}{2}\right). \quad \text{(B4)}
\end{aligned}
$$

For $N \to \infty$

$$
\begin{aligned}
2\sum_n^N &\frac{c_n^2}{\omega_n^2}(1-\cos\omega_n t) \\
&= \frac{4}{\pi}\int_0^\infty d\omega \frac{c_n^2}{\omega_n^2}(1-\cos\omega_n t)\delta(\omega-\omega_n) \\
&= \frac{4}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega^2}(1-\cos\omega t) \quad \text{(B5)}
\end{aligned}
$$

and so we have

$$
\begin{aligned}
\rho_{12}(t) = \frac{1}{2\sinh\frac{\beta\omega}{2}} \exp\Bigg(&-i2\Delta t - \frac{4}{\pi}\int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \\
&\times \coth\frac{\beta\omega}{2}(1-\cos\omega t)\Bigg), \quad \text{(B6)}
\end{aligned}
$$

which is essentially what we have for the time-local form $\rho_{12}^{\mathrm{TL}}(t)$.

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[106] From Eq. (23), the real and imaginary parts of the correlation functions $\mathcal{C}_B^{(2,k)}$ are related, as can be seen most easily from the following relation for the Fourier transform $\tilde{\mathcal{C}}_B^{(2,k)}(\omega) = \int_{-\infty}^{\infty} dt \exp(i\omega t)\mathcal{C}_B^{(2,k)}(t)$,

$$\mathrm{Re}\,\tilde{\mathcal{C}}_B^{(2,k)}(\omega) = \coth(\beta\omega/2)\mathrm{Im}\,\tilde{\mathcal{C}}_B^{(2,k)}(\omega),$$

where the real and imaginary parts are given as $\mathrm{Re}\,\tilde{\mathcal{C}}_B^{(2,k)}(\omega) = 2\int_0^{\infty} dt\,\cos\omega t\,\mathrm{Re}\,\tilde{\mathcal{C}}_B^{(2,k)}(t)$ and $\mathrm{Im}\,\tilde{\mathcal{C}}_B^{(2,k)}(\omega) = 2\int_0^{\infty} dt\,\sin\omega t\,\mathrm{Im}\,\tilde{\mathcal{C}}_B^{(2,k)}(t)$, see Ref. 24.

[107] If $\mathcal{C}_M^{(k)}$ is neglected, then $\mathcal{C}_B^{(2,k)}(t, T = 0) = -\frac{1}{\pi}\int_0^{\infty} d\omega J_{+,\mathrm{eff}}^{(k)}(\omega)\sin(\omega t)$.

[108] See supplementary material at http://dx.doi.org/10.1063/1.4752078 for further comments on the application of the MCTDH method in the present context.