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Resummed Memory Kernels in Generalized System-Bath Master Equations

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Generalized master equations provide a concise formalism for studying reduced population dynamics. Usually, these master equations require a perturbative expansion of the memory kernels governing the dynamics; in order to prevent divergences, these expansions must be resummed. Resummation techniques of perturbation series are ubiquitous in physics, but they have not been readily studied for the time-dependent memory kernels used in generalized master equations. In this paper we present a comparison of different resummation techniques for such memory kernels up to fourth order. We study specifically the spin-boson Hamiltonian as a model system bath Hamiltonian, treating the diabatic coupling between the two states as a perturbation. A novel derivation of the fourth-order memory kernel for the spin-boson problem is presented; then, the second- and fourth-order kernels are evaluated numerically for a variety of spin-boson parameter regimes. We find that resumming the kernels through fourth order using a Padé approximant results in divergent populations in the strong electronic coupling regime due to a singularity introduced by the nature of the resummation, and thus recommend a non-divergent exponential resummation (the "Landau-Zener resummation" of previous work). The inclusion of fourth-order effects in a Landau-Zener-resummed kernel is shown to improve both the dephasing rate and the obedience of detailed balance over simpler prescriptions like the non-interacting blip approximation (NIBA), showing a relatively quick convergence on the exact answer. The results suggest that including higher-order contributions to the memory kernel of a generalized master equation and performing an appropriate resummation can provide a numerically-exact solution to system-bath dynamics for a general spectral density, opening the way to a new class of methods for treating system-bath dynamics.

I. INTRODUCTION

Generalized master equations are useful constructs in chemical physics for solving problems that involve a few "system" degrees of freedom interacting with a large number of "bath" degrees of freedom, like when considering electron transfer in solution. When used to monitor time evolution of system populations, these equations generally have the form

$$\dot{\mathbf{P}}(t) = \int_0^t \mathbf{K}(t-s)\mathbf{P}(s)ds \qquad (1)$$

where $\mathbf{P}$ is a vector containing the populations of the various system states and $\mathbf{K}$ is a matrix controlling the (non-Markovian) flow of populations among states *without explicitly referencing the bath degrees of freedom*; this time-nonlocal matrix $\mathbf{K}$ is often referred to as the *memory kernel*. Such equations allow us to solve explicitly for system observables while only taking into account aspects of the bath that directly influence the system. Formally equivalent to generalized Langevin equations and path integral methods, generalized master equations allow for a somewhat phenomenological description of the bath and are thus useful when detailed statistical information about the bath is not known *a priori*.

Many different methods have been proposed that solve the system-bath dynamics problem to varying extents; unfortunately, none are both robust and general. Due to the existence of the influence functional for harmonic baths [1], path-integral-based numerical methods have been quite successful for this problem [2, 3]. Additionally, there are also formulations of this problem that are not fully quantum-mechanical. The simplest formulation is a mixed quantum-classical set-up where the system (and perhaps a few important bath degrees of freedom) are treated quantum-mechanically and (the rest of) the bath is treated classically. There are several detailed reviews of these methods including their successes and shortcomings in the literature [4–6].

In recent years, several alternative methods not based on generalized master equations have been proposed that successfully solve the quantum dynamics problem for certain classes of system-bath Hamiltonians. One method of particular merit is the multi-configuration time-dependent Hartree approach [7–9], which in and of itself is limited to treating only a few degrees of freedom exactly but can be quite powerful when coupled with other degrees of freedom semiclassically [10, 11]. Even more recently, hierarchical equation of motion (HEOM) approachs to this problem have been proposed which in principle give numerically exact results [12, 13]. Unfortunately, these state-of-the-art numerical methods are not general in that they require very specific assumptions about the nature of the bath. They can also often be extremely slow to converge, especially at low temperatures [14].

In the general case of a generalized master equation of the form of equation 1, $\mathbf{K}(t)$ cannot be obtained; often, we must resort to using perturbation theory to gain information about $\mathbf{K}(t)$. In cases when the system-bath coupling is weak, one can expand the Hamiltonian perturbatively in the system-bath coupling and utilize the tools of Redfield theory to obtain a solution [15, 16]. In the opposite regime, when the strength of the system-bath coupling is much stronger than the strength of the intrasystem electronic couplings, one can first apply a *polaron transform* and then expand the kernels perturbatively in the system-bath coupling. The original polaron transform was proposed for application in solid state physics [17, 18], but can be particularly effective for system-bath dynamics problems in the special case of a harmonic bath [19–23]. Recently, for particular classes of harmonic bath models, polaron transformations have been used effectively to solve the quantum dynamics problem in an effectively nonperturbative fashion [24, 25].

In other treatments, the memory kernel is expanded in a power series in the electronic coupling V. A truncation of this series at second order results in the famous non-interacting blip approximation (NIBA) [19, 26, 27], which gives a second-order approximation of the dynamics and Fermi's Golden Rule rate constants.

Additionally, many groups have worked with this expansion out to fourth order in certain limits. The Cao group has worked extensively with fourth order rate constants (given by $\mathbf{k} = \mathbf{K}(\omega = 0)$)[28, 29, 35], inspired by the analytical work of Mukamel [30]

and Silbey [31]. Reichman, working with Silbey and Neu, derived analytical results for dynamics in the low-temperature limit for certain classes of baths [32–34]. Finally, a fourth-order correction to Redfield theory that is guaranteed to obey detailed balance has been derived [36]; however, it requires making additional assumptions about the system-bath coupling. Despite this work, no one has studied detailed short-time two-state *dynamics* for a system-bath Hamiltonian governed by a generalized master equation.

In this work, we examine for the first time the dynamics generated by a resummed memory kernel correct to fourth-order. We consider in detail the spin-boson Hamiltonian [26], for which it is possible to derive analytical expressions for $K^{(2)}$, $K^{(4)}$, and (in principle) all higher-order coefficients. We present what we believe to be a novel derivation of $K^{(4)}$ for this problem that can be easily generalized to derive both higher-order terms and non-Condon versions of $K^{(2)}$, $K^{(4)}$, etc. with electronic coupling linear in the bath coordinate. We then present numerical results where we evaluate our analytical memory kernels using a model spectral density. In our numerical results, we compare several methods to resum $K^{(2)}$ and $K^{(4)}$ into a kernel K containing **all** orders of the electronic coupling—a necessary procedure to prevent long-time divergence of the populations. Finally, we show how we can almost trivially force our resummed kernels to obey detailed balance, giving the correct infinite-time equilibrium populations. Our aim is to build towards a general, robust, systematically-improvable system-bath approximation for molecular systems in condensed phases.

II. THEORY

A. Generalized Master Equation Formalism

Despite its simplicity, the brute-force numerical propagation of a density matrix under the influence of a system-bath Hamiltonian is not possible, as the computational cost of such a propagation scales exponentially with the number of bath modes represented; hence, generalized master equation approaches become useful. Unfortunately, the memory kernels of equation 1 are as computationally intractable as the propagator.

To approach this problem, we can use time-dependent perturbation theory. For simplicity, we shall restrict our discussion to the special case where our system contains only two (diabatically-coupled) states; however, all of the results in this section can be generalized to the general problem of many interacting system states. For any two-level system, we can suggestively write the Hamiltonian as

$$\hat{H} = \begin{pmatrix} \hat{h}_1 & 0 \\ 0 & \hat{h}_2 \end{pmatrix} + \lambda \begin{pmatrix} 0 & \hat{V} \\ \hat{V} & 0 \end{pmatrix} \equiv \hat{H}_0 + \hat{H}_1 \qquad (2)$$

where $\hat{h}_1$ and $\hat{h}_2$ represent all diagonal elements of the Hamiltonian related to both system and bath, $\hat{V}$ represents all off-diagonal

elements of the Hamiltonian related to both system and bath, and we have introduced an ordering parameter λ. The physical Hamiltonian is recovered for $\lambda = 1$.

To study the quantum dynamics generated by memory kernel resummations, we adopt the generalized master equation for the populations of a two-level system interacting with a general bath first derived by Sparpaglione and Mukamel [30] using projection operator methods [37–39]

$$\dot{p}_1(t) = -\int_0^t K_{11}(t-s)p_1(s)ds + \int_0^t K_{22}(t-s)p_2(s)ds$$

$$\dot{p}_2(t) = \int_0^t K_{11}(t-s)p_1(s)ds - \int_0^t K_{22}(t-s)p_2(s)ds \qquad (3)$$

where $p_1(t)$ and $p_2(t)$ are the populations of the two states as functions of time, and K_{11} and K_{22} are the time-dependent memory kernels for the forward $(1 \to 2)$ and backward $(2 \to 1)$ transitions. We use this formalism primarily because it can be trivially generalized to include many states.

We will work explicitly with populations *differences*. It can be shown using the normalization condition $p_1(t) + p_2(t) = 1$ that equation 3 can be rewritten in terms of $P(t) \equiv p_1(t) - p_2(t)$ as

$$\dot{P}(t) = -\int_0^t K_+(t-s)P(s)ds - \int_0^t K_-(s)ds \qquad (4)$$

where $K_{\pm}(t) \equiv K_{11}(t) \pm K_{22}(t)$. Note that equation 4 has the form of a generalized Langevin equation, with K_+ acting as a friction kernel and the integral of K_- acting as a random noise term.

Using this formalism allows us to expand the memory kernels perturbatively, using λ to collect terms of similar order:

$$K_{11/22}(t) = \lambda^2 K^{(2)}_{11/22}(t) + \lambda^4 K^{(4)}_{11/22}(t) + \cdots \qquad (5)$$

where $K^{(2n)}_{11/22}(t)$ is the $2n$th-order contribution to the memory kernel. Note that in the special case where $\hat{V}$ is a constant, V, this is equivalent to expanding the memory kernels in a power series in V. For the remainder of this paper and in order to simplify our discussion, we shall assume that $\hat{V}$ is a constant.

B. The Spin-Boson Model

In order to examine the dynamics generated by these memory kernels in detail, we restrict ourselves to specifically to the spin-boson Hamiltonian. This form of system-bath Hamiltonian is used widely in elementary studies of chemical dynamics because of its moderate assumptions and overall simplicity. The spin-boson Hamiltonian (also known as the Caldeira-Leggett model) [26] can be written as

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

$$= \begin{pmatrix} \frac{\varepsilon}{2} & \hat{V} \\ \hat{V} & -\frac{\varepsilon}{2} \end{pmatrix} + \sum_j \begin{pmatrix} \frac{p_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2 x_j^2 & 0 \\ 0 & \frac{p_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2 x_j^2 \end{pmatrix} + \sum_j \begin{pmatrix} c_j x_j & 0 \\ 0 & -c_j x_j \end{pmatrix} \qquad (6)$$

where the p_j and x_j describe normal mode harmonic bath coordinates and momenta described by mass m_j and frequency ω_j, and the c_j are coefficients determining the strength that each harmonic bath mode couples to the system. The spin-boson model thus describes a two-level system coupled to a bath of harmonic oscillators, where the system-bath coupling is linear in the bath coordinate.

In practice, knowing the minute details of the bath modes is irrelevant: by invoking system-bath models, we are implicitly only interested in the detailed dynamics of the system, so we only need to know about the bath insomuch as it affects system dynamics. For a harmonic bath, population dynamics are completely characterized by the bath *spectral density*, [27, 40, 41]

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{c_j^2}{m_j \omega_j} \delta(\omega - \omega_j) \tag{7}$$

In principle, a particular spectral density can generally be obtained by Fourier transforming a corresponding bath time corre-

lation function [41]; these time correlation functions can, in turn, be obtained from experiment or from molecular dynamics simulations. In practice, an analytical form is usually assumed for the spectral density.

C.   Derivation of $K^{(4)}$ for the Spin-Boson Model

Because the spin-boson Hamiltonian comprises a two-level system linearly coupled to a bath of harmonic oscillators, it should come as no surprise that analytical expressions can be derived for $K^{(2)}(t)$, $K^{(4)}(t)$, and all $K^{(2n)}(t)$. We present here the main analytical result of this paper: a novel, generalizable derivation of $K^{(4)}(t)$ that does not invoke Liouville space. For the spin-boson problem, the memory kernels can be written as

$$K^{(2)}_{11/22}(t) = 2\mathrm{Re}\left[f_2^\pm(t)\right] \tag{8}$$

$$
\begin{aligned}
K^{(4)}_{11/22}(t) &= \int_0^t ds_1 \int_0^{s_1} ds_2 K^{(2)}_+(t-s_1) K^{(2)}_{11/22}(s_2) - 2 \int_0^t ds_1 \int_0^{t-s_1} ds_2 \mathrm{Re}\left[f_4^\pm(t-s_1-s_2,s_1,s_2)\right] \\
&\quad + 2 \int_0^t ds_1 \int_0^{-t} ds_2 \mathrm{Re}\left[f_4^\pm(-t-s_2,t-s_1,s_1)\right] - 2 \int_0^t ds_1 \int_0^{t-s_1} ds_2 \mathrm{Re}\left[f_4^\pm(-t,t-s_1-s_2,s_1)\right]
\end{aligned}
\tag{9}
$$

where $K^{(2)}_+(t) = K^{(2)}_{11}(t) + K^{(2)}_{22}(t)$ and the top sign is for K_{11} / the bottom sign is for K_{22}. The ubiquitous functions $f_2^\pm$ and $f_4^\pm$ can be represented analytically as

$$f_2^\pm(t) = V^2 \exp\left[-i\varepsilon t - \left(Q'(t) \pm iQ''(t)\right)\right] \tag{10}$$

$$f_4^\pm(s_1, s_2, s_3) = V^4 \exp\left[-i\varepsilon(s_1+s_3) - \left(S'(s_1,s_2,s_3) \pm iS''(s_1,s_2,s_3)\right)\right] \tag{11}$$

where

$$
\begin{aligned}
S'(s_1,s_2,s_3) &= Q'(s_1) + Q'(s_2) + Q'(s_3) - Q'(s_1+s_2) - Q'(s_2+s_3) + Q'(s_1+s_2+s_3) \\
S''(s_1,s_2,s_3) &= Q''(s_1) + Q''(s_2) + Q''(s_3) - Q''(s_1+s_2) - Q''(s_2+s_3) + Q''(s_1+s_2+s_3)
\end{aligned}
\tag{12}
$$

and

$$
\begin{aligned}
Q'(t) &= \frac{4}{\pi} \int_0^\infty \frac{J(\omega)}{\omega^2} (1 - \cos(\omega t)) \coth\left(\frac{\beta\omega}{2}\right) \tag{13} \\
Q''(t) &= \frac{4}{\pi} \int_0^\infty \frac{J(\omega)}{\omega^2} \sin(\omega t) \tag{14}
\end{aligned}
$$

A detailed derivation of equations 8 through 13 can be found in the Supporting Information [42].

D.   Resummation Schemes

It is well-known that series generated from perturbation theory are not always convergent, especially when truncated [43]. Re-

summation techniques are ubiquitous in many areas of physics, including quantum electrodynamics [44, 45], renormalization group theory [46, 47], and quantum chemistry [48]. Resummations have also been used in the context of system-bath models to compute rate constants [29–31], but to our knowledge have never been applied to time-dependent rate kernels in order to study dynamics.

We will focus our attention in particular to resummations of memory kernels for generalized master equations. Resumming at the level of the memory kernels is preferable to resumming at the level of the populations for many reasons, summarized concisely in References [49] and [50]. These resummations are historically performed in the frequency domain, defined through the Fourier transform

$$K(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} K(t) dt$$

As such, we will be focusing in particular on ways to resum $K^{(2)}(\omega)$ and $K^{(4)}(\omega)$ into a $K(\omega)$ containing all orders of the electronic coupling V.

For the particular problem at hand, two resummation schemes have been proposed [30], dubbed the "Padé resummation" and the "Landau-Zener resummation." The Padé resummation is a rational resummation based off of Padé approximants [51], which have been very successful in several areas of physics related to the present problem. Particularly relevant is the result of Cho and Silbey, who showed [31] that the in the subspace comprised of N perturbatively-expanded states, the Fourier transform of the memory kernel $K(\omega)$ can best be represented by an $[N/N-1]$-Padé approximant. The authors proved that this particular resummation choice obeys Schwinger's stationary variational principle for scattering processes [52]. The consequence of this result is that rates obtained from these memory kernels will obey detailed balance as best as possible, a desirable feature that suggests that Padé resummation is the optimal resummation choice for this problem.

For the case $N = 1$ (our present scenario), the Padé approximant, to fourth order, is

$$K_{Pad\acute{e}}(\omega) = \frac{V^2 \left[K^{(2)}(\omega)\right]^2}{K^{(2)}(\omega) - V^2 K^{(4)}(\omega)} \quad (15)$$

This form of resummation has been recently employed by Wu and Cao [29] to study kinetics (the $t \to \infty$ limit of equation 1). Using the $\omega \to 0$ limit of equation 15, the authors showed that the Padé resummation gives very good agreement with numerically-exact results for a model problem. The authors also pointed out that part of this agreement can be attributed to the fact that the Padé resummation recovers the Zusman result [53] in the limit of weak system-bath and weak electronic coupling.

The Padé resummation scheme has been previously investigated in the context of certain classes generalized master equations [54, 55], with the conclusion that a Padé-resummed memory kernel leads to dynamics that converge for all times. Later work by Shi *et al* [49] pointed out that the quality of the dynamics generated by a Padé-resummed memory kernel for arbitrary regimes of Hamiltonian parameter space is still unknown. The general applicability of the Padé resummation for dynamics is one of the central questions this work sets out to answer.

An alternative resummation scheme proposed [56] has been dubbed the Landau-Zener resummation due to its similarity in form to the famous Landau-Zener equation. To fourth order, the Landau-Zener resummation is given by

$$K_{LZ}(\omega) = -\frac{\left[K^{(2)}(\omega)\right]^2}{2K^{(4)}(\omega)} \left[1 - \exp\left(\frac{2V^2 K^{(4)}(\omega)}{K^{(2)}(\omega)}\right)\right] \quad (16)$$

It has been shown [30] that this resummation scheme agrees with the Padé scheme in the nonadiabatic limit, but differs from the Padé scheme by a factor of 2 in the adiabatic limit. This flaw prevents the Landau-Zener scheme from being applicable to study dynamics in the adiabatic regime. Fortunately, mixed quantum-classical and semiclassical schemes have great success when the dynamics evolve strictly on one adiabat, so we shall focus our attention on the nonadiabatic regime.

E. Populations at Equilibrium

For the case of a system with electronic bias, resummation is rather arbitrary: Do we resum the forward rate kernel K_{11} and the backward rate kernel K_{22} and then add and subtract them to form $K_\pm$? Or do we resum $K_\pm$ directly? Stating this another way, we can define a resummation function that takes a second-order kernel and a fourth-order kernel and returns a resummed kernel (through, for instance, a Padé resummation):

$$K = R\left[K^{(2)}, K^{(4)}\right] \quad (17)$$

we can then imagine that we can form $K_\pm$ through a number of different schemes; for instance,

$$K_\pm = R\left[K_{11}^{(2)}, K_{11}^{(4)}\right] \pm R\left[K_{22}^{(2)}, K_{22}^{(4)}\right] \quad (18)$$

or

$$K_\pm = R\left[K_{11}^{(2)} \pm K_{22}^{(2)}, K_{11}^{(4)} \pm K_{11}^{(4)}\right] \quad (19)$$

Both of these schemes give the exact perturbation series to fourth order, but differ at higher orders. Selecting one over the other is an arbitrary choice.

We can reduce this arbitrariness by introducing a parameter α that interpolates smoothly between these two limits:

$$\begin{aligned} K_\pm = \ &R\left[(1-\alpha)K_{11}^{(2)} \pm \alpha K_{22}^{(2)}, (1-\alpha)K_{11}^{(4)} \pm \alpha K_{22}^{(4)}\right] \\ &+R\left[\alpha K_{11}^{(2)} \pm (1-\alpha)K_{22}^{(2)}, \alpha K_{11}^{(4)} \pm (1-\alpha)K_{22}^{(4)}\right] \end{aligned} \quad (20)$$

As long as the resummation is first-order homogeneous (as is the case for both the Padé scheme and the Landau-Zener scheme), we can recover equation 18 if $\alpha = 0$ and equation 19 if $\alpha = \frac{1}{2}$.

Adding in this additional degree of freedom allows us to ensure that the dynamics created by the resummed memory kernel will obey detailed balance. It is well-known that using master equations with second-order kernels does not guarantee that the dynamics settle on the correct equilibrium populations in the case of a system with electronic bias [11, 57]. Introducing α allows us to choose from an infinitely large number of arbitrary choices the optimal manner of resummation that gets equilibrium populations correct. Namely, if the equilibrium populations are known (e.g.,

from a path integral Monte Carlo simulation [58, 59]), we can tune α by enforcing the detailed balance condition

$$\frac{k_{11}(\alpha)}{k_{22}(\alpha)} = \frac{p_2^{eq}}{p_1^{eq}} \qquad (21)$$

by tuning α over the interval $\left[0, \frac{1}{2}\right]$, where $k_{11} \equiv K_{11}(\omega = 0)$ and $k_{22} \equiv K_{22}(\omega = 0)$ are the forward and backward rate constants, and p_1^{eq} and p_2^{eq} are the equilibrium populations.

III.   RESULTS AND DISCUSSION

A.   Implementation Details

For each set of spin-boson parameters studied, $K_{11}^{(2)}$ and $K_{11}^{(4)}$ (and, in cases where an electronic bias is present, $K_{22}^{(2)}$ and $K_{22}^{(4)}$) were calculated using a FORTRAN95 implementation of equations 8 and 9. All integrals were computed using an adaptive Gauss-Legendre quadrature until an integral tolerance of 10^{-6} was reached. The frequency integrals over the spectral density were computed with a hard upper frequency cutoff of $\omega = 30$, which was found to be enough to give stable and convergent results for the short propagation time ranges studied.

Once the kernels were computed, they were resummed according to equation 15 (Padé resummation) and equation 16 (Landau-Zener resummation). Then, a standard algorithm for solving Volterra integrodifferential equations of the second kind [60] was used to solve equation 4 for $P(t) \equiv p_1(t) - p_2(t)$, the difference in population between states 1 and 2 as a function of time. Propagating population dynamics using only $K_{11}^{(2)}$ and $K_{22}^{(2)}$, i.e. applying the non-interacting blip approximation or NIBA, is also considered for comparison.

In order to benchmark our fourth-order resummations, we use an Ohmic spectral density with a Drude-Lorentz cutoff, often referred to as a Debye spectral density

$$J(\omega) = \frac{\eta \omega \omega_c}{\omega_c^2 + \omega^2} \qquad (22)$$

where η and ω_c are parameters that control the strength of the system-bath coupling the the upper cutoff frequency of the bath, respectively. A benefit of using this spectral density is that numerical results for this problem have been presented in the past [11, 57] using various approximate methods.

Additionally, a hierarchical equation of motion (HEOM) technique has recently been presented [12, 13] that obtains (in principle) numerically-exact results for the spin-boson problem. The HEOM technique is a path-integral-based technique which replaces the Vernon-Feynman influence functional with a set of time-nonlocal auxilliary density matrices which account for non-Markovian system-bath coherences. These density matrices are related to one another via hierarchical equations; truncating this hierarchy at order M is equivalent to order $2M$ in perturbation theory in the system-bath coupling [61]. As such, the hierarchy is often very quickly convergent, provided the system-bath coupling is not strong. If changing the depth of the hierarchy does not change the resulting population dynamics, the approximation is equivalent to infinite-order perturbation theory and is thus exact.

While the HEOM has the potential to give numerically-exact results, it has some shortcomings. The most glaring is that it can only be used for spectral densities of the form given in equation

22. Additionally, the HEOM requires evaluation of many depths of a hierarchy of increasing computational complexity; a deeper hierarchy is needed for strong system-bath coupling or low temperature. However, despite the breakdown of the standard HEOM technique in the strong system-bath coupling regime and the low-temperature regime (the latter problem which can been solved using a stochastic HEOM [14]), for many parameter regimes of the Debye spectral density, the HEOM gives extremely accurate results. In this work, we consider results from a sufficiently deep HEOM truncation (a hierarchy depth of 11 with a maximum Matsubara frequency of 6) to be numerically exact for this problem. For all calculations, the cutoff frequency ω_c was normalized to 1, and other parameters adjusted with relation to ω_c.

B.   Stability with Increasing Electronic Coupling

As noted previously, NIBA fails with increasing electronic coupling. The reason is quite obvious: we are doing a perturbative expansion in the electronic coupling, so a second-order truncation won't capture any quantum events that involve more than two hops between energy surfaces [57]. Figure 1 shows clearly that this is indeed the case. For the case of small electronic coupling (panel (a)), NIBA is good enough to reproduce the HEOM result, and, as higher-order terms in the perturbation series are small, any fourth-order resummation does not significantly change this result.

Going to higher and higher values of the electronic coupling (panels (b) through (d)), NIBA breaks down: two-hop events are no longer sufficient to accurately describe the short-time quantum dynamics of the spin-boson model. Specifically, oscillations in population die out much too fast. Comparing the two fourth-order resummation schemes presented in this work with the HEOM result, however, shows that there is hope: higher-order terms recover these oscillations with nearly the correct frequency and a relatively correct damping rate.

In the case of very strong electronic coupling, it is interesting to note that recovering qualitatively correct dynamics depends on the nature of the fourth-order resummation. In particular, using a Padé approximant to resum the second- and fourth-order memory kernels gives a memory kernel which leads to populations that oscillate wildly in time and at the incorrect frequency; by contrast, the Landau-Zener-resummed kernel produces populations which are well-behaved for all times.

This is a notable result, as the Padé approximant is the resummation method of choice for rate constants, the zero-frequency limit of the frequency-dependent memory kernel [29, 31]. It can easily be shown that in the small electronic, slow bath limit, the Padé-resummed rate is exactly the rate derived by Zusman connecting the nonadiabatic regime to the adiabatic regime [31, 53].

For short-time dynamics in the large electronic coupling limit, however, the dynamics generated by a Padé resummation are qualitatively incorrect. The reason why this approximate resummation is good for rate constants but bad for dynamics can be seen by examining equation 15: When $K^{(2)}(\omega) \approx V^2 K^{(4)}(\omega)$, the Padé-resummed kernel diverges. It is very unlikely that this equality will occur at $\omega = 0$; however, as V grows, the chance that this divergence will occur for some larger value of ω also grows. This introduces a spurious high-frequency component to the memory kernel in the time domain, which translates into populations that oscillate indefinitely, rather than settling down to equilibrium at the desired rate.
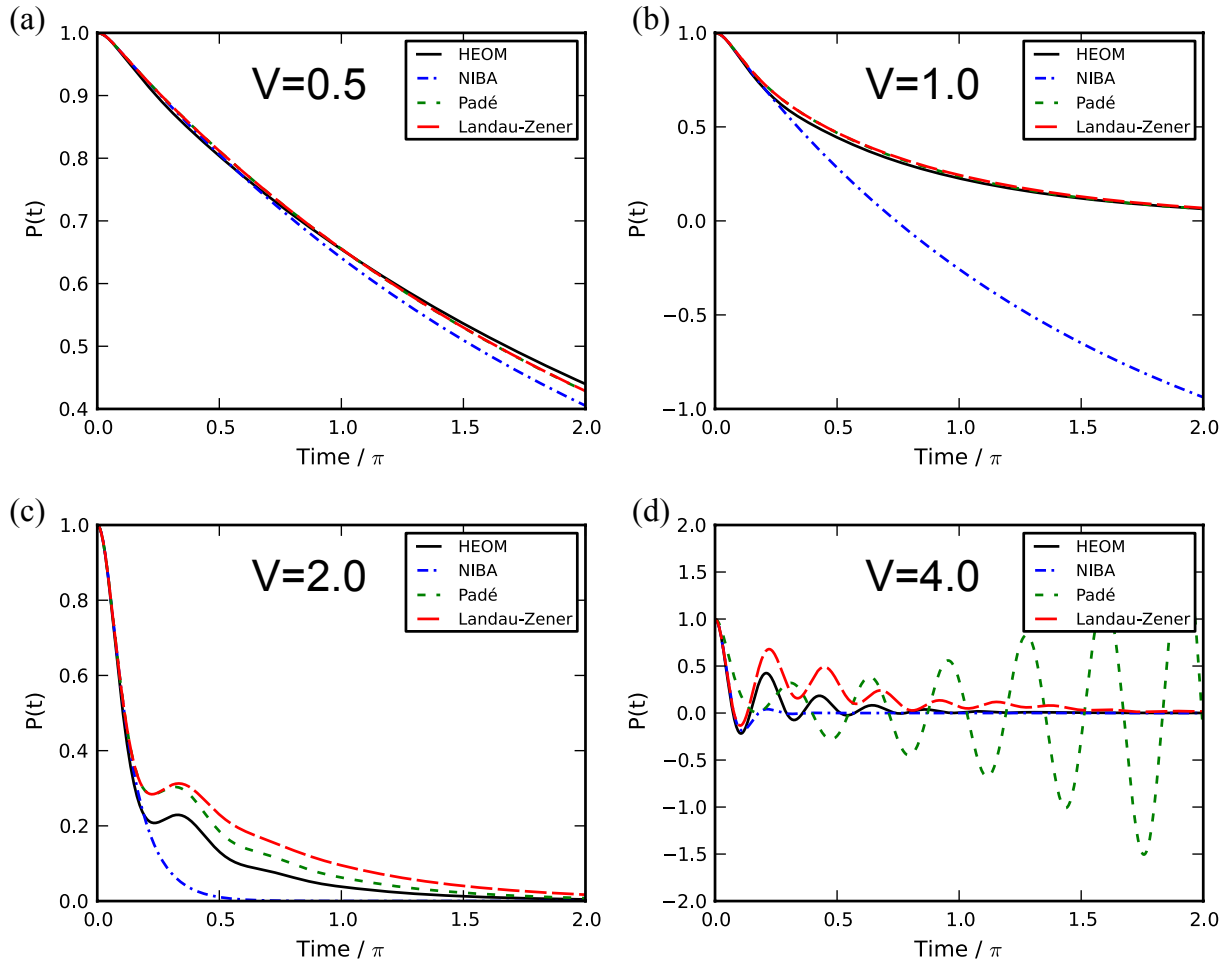
Figure 1: Population dynamics of the spin-boson Hamiltonian for various strengths of the electronic coupling. The HEOM (exact) result and the NIBA result are plotted to compare with the two different fourth-order resummations presented in this work: the Padé resummation (equation 15) and the Landau-Zener resummation (equation 16). Values of the Hamiltonian parameters are $\omega_c = 1.0$, $\eta = 2.0$, $\beta = 0.125$, and (a) $V = 0.5$, (b) $V = 1.0$, (c) $V = 2.0$, and (d) $V = 4.0$.

C.   Temperature Dependence

The low-temperature regime has often proved problematic for quantum dynamics studies, as many systems are "very quantum" at extremely low temperatures. This problem was studied (and to some extent solved for Ohmic baths) in detail by Reichman [33], but the general case remains an open problem in quantum dynamics. Even the HEOM approach to solving the spin-boson problem breaks down as the temperature approaches 0: while still in principle exact, computation of the exact answer requires inclusion of many Matsubara frequencies and a very deep hierarchy, which very quickly becomes computationally intractable. Other formulations of the HEOM have been designed to fix this problem [14], but a solution still does not exist for general spectral densities.

While our approach is robust in the strong electronic coupling regime, the same cannot be said for the low-temperature regime. Short-time dynamics of the spin-boson Hamiltonian to fourth order in V are shown in figure 2 for moderate values of the system-bath coupling and the electronic coupling. As can be seen in the figure, for high temperature (small values of $\beta \equiv 1/k_B T$), even NIBA gets qualitatively correct dynamics. This makes sense, as the Marcus rate for electron transfer can be formulated as the high-temperature, slow-bath, long-time limit of NIBA [30, 41], and the

Marcus rate is a quite good description of the kinetics of many experimental systems [62].

At low temperatures, both NIBA and any fourth-order resummations give qualitatively incorrect description of the dynamics: NIBA dephases too quickly, and the fourth-order resummations do not decay to equilibrium quickly enough. Both the lack of low-frequency oscillations and the incorrect zero-frequency component of the population dynamics can be traced to the presence of a large number of low-frequency bath modes at low temperatures, which have a large contribution to the memory kernels. The fourth-order resummations studied in this work assume a "small" $V^4 K^{(4)}$, which may not necessarily be the case at low temperatures; this observation may lend to the development of alternative resummation schemes for fourth-order perturbation series and beyond.

We note in passing that for regimes where NIBA does not give good dynamics, adding in fourth-order effects tends to *overcorrect*. This result has been observed for rates [29], and is seen very clearly in figure 2 to also be the case for dynamics.
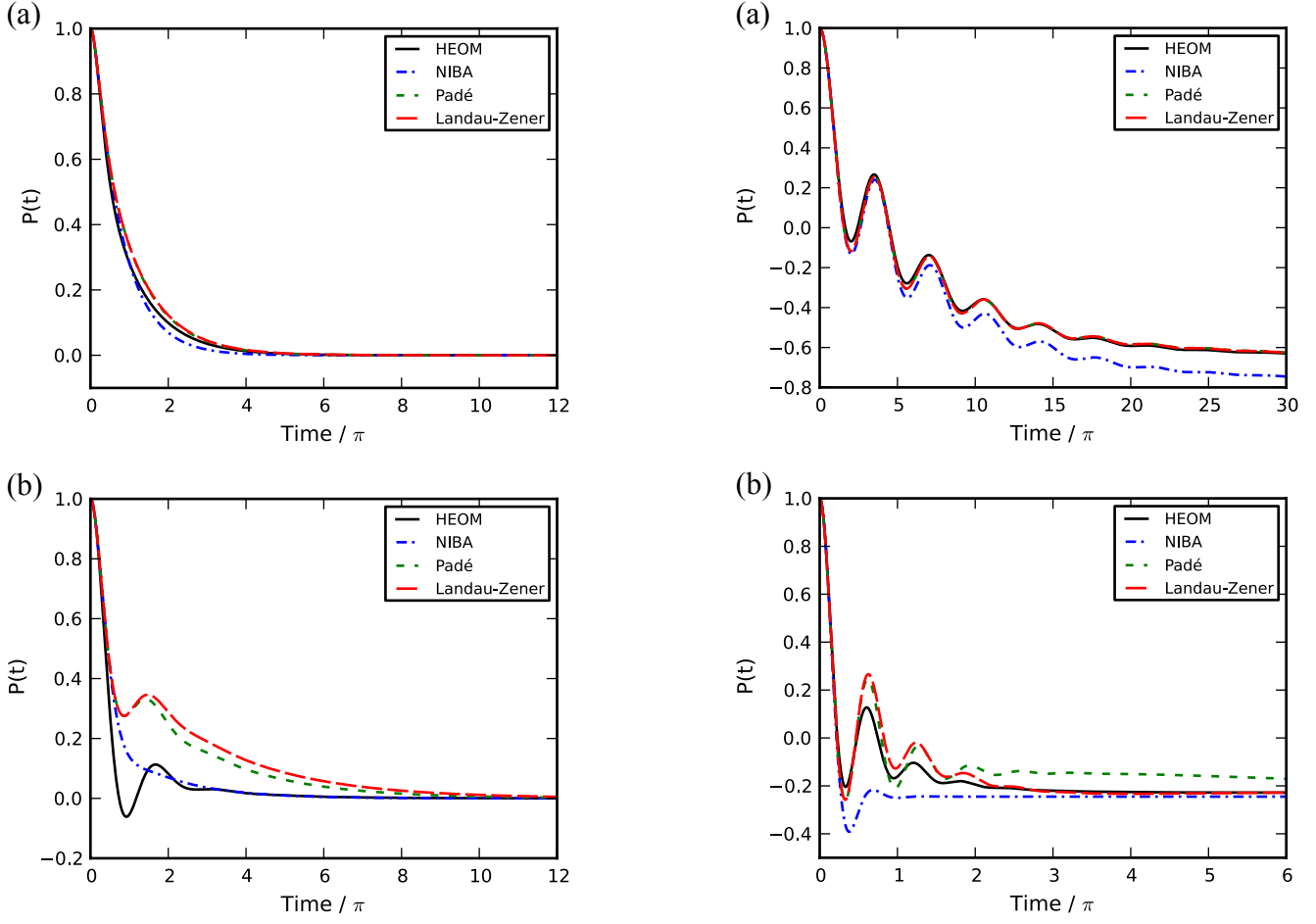
(a)

(b)

Figure 2: Population dynamics of the spin-boson Hamiltonian for various temperatures at moderate electronic coupling. Values of the Hamiltonian parameters are $\omega_c = 1.0$, $\eta = 1.0$, $V = 0.5$ and (a) $\beta = 0.5$ (high temperature); or (b) $\beta = 10.0$ (low temperature).

D.   Systems with Electronic Bias

A systematic problem with NIBA arises in systems with an electronic bias: NIBA memory kernels generate population dynamics that do not decay to the correct equilibrium, meaning these memory kernels disobey detailed balance. Disobedience of detailed balance implies a fictitious breaking of time-reversal symmetry, which may cause systemic problems with short-time dynamics. This issue should be addressed, at least to some extent, by including higher-order contributions to the memory kernel; indeed, it has previously been shown that fourth-order corrections to Redfield theory obey detailed balance exactly [36]. We now turn our attention to the dynamics of a system with an electronic bias, particularly to the question of how including fourth-order effects in the memory kernels affects the obedience of detailed balance.

Figure 3 shows our main result for the biased case: going to fourth order helps, but does not guarantee, the satisfaction of the detailed balance condition (and, in some cases, conservation of probability!). As expected, for small values of the electronic coupling (when effects fourth-order in the coupling are small), the equilibrium populations are more-or-less exactly correct; for larger values, the equilibrium populations deviate more from their correct values. For reasons discussed in cases without bias, using a Padé resummation can exacerbate this problem; as such, a
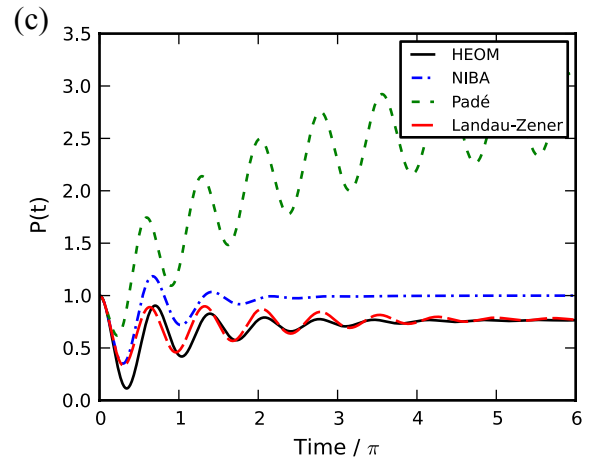
(a)

(b)

(c)

Figure 3: Population dynamics of the spin-boson Hamiltonian for various strengths of the electronic bias. All resummations were conducted using equation 20 for the reasons discussed in section II E; the value of the parameter α was fixed by enforcing detailed balance, equation 21. Values of the Hamiltonian parameters are (a) $\omega_c = 1.0$, $\eta = 0.1$, $\beta = 5.0$, $V = 0.2$, and $\varepsilon = 0.4$ ($\alpha = 0.19$ for both resummations; note the different scale on the time axis); (b) $\omega_c = 1.0$, $\eta = 0.665$, $\beta = 0.376$, $V = 1.33$, and $\varepsilon = 1.33$ ($\alpha = 0.37$ for both resummations); and (c) $\omega_c = 1.0$, $\eta = 0.5$, $\beta = 5.0$, $V = 1.0$, and $\varepsilon = -2.0$ ($\alpha = 0.16$ for Padé, $\alpha = 0.5$ for Landau-Zener).

Landau-Zener resummation is again recommended for cases with bias.

Including memory effects up to infinite order in V is one way
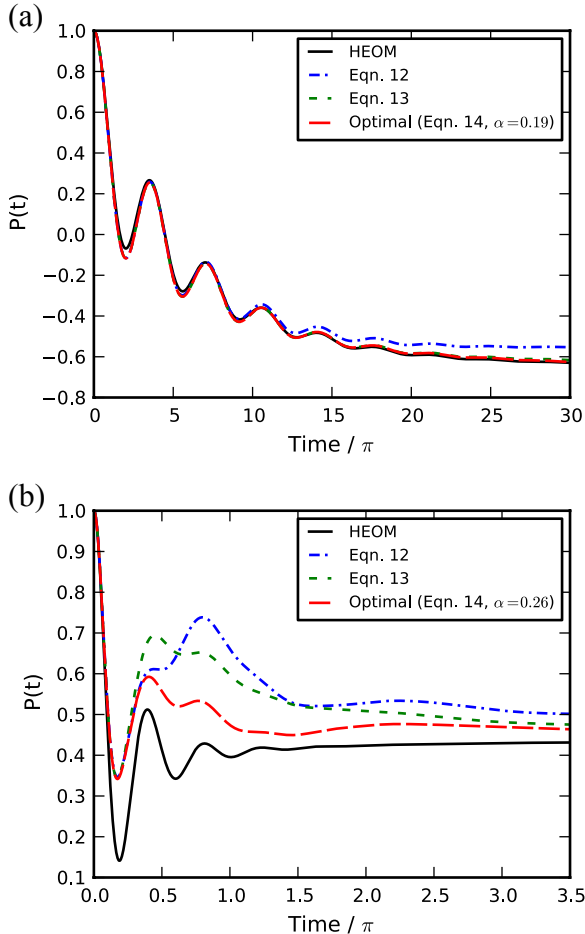
(a)

(b)

Figure 4: As stated in the text, there is an arbitrary choice of which memory kernels to resum: the forward and backwards rate kernels K_{11} and K_{22}, or some linear combination of these kernels. Plotted here are three specific choices of which memory kernels to resum in a Landau-Zener fashion (i.e. according to equation 16): resummation according to equation 18, equation 19, and equation 20. (a) For most choices of Hamiltonian parameters, it is possible to satisfy the detailed balance condition exactly using an intermediate value of α. For the set of Hamiltonian parameters in figure 3(a) ($\omega_c = 1.0$, $\eta = 0.1$, $\beta = 5.0$, $V = 0.2$, and $\varepsilon = 0.4$), using $\alpha = 0.19$ causes detailed balance to be satisfied. (b) For other sets of Hamiltonian parameters, it is only possible to satisfy detailed balance in a least-squares sense. For example, with $\omega_c = 1.0$, $\eta = 1.0$, $\beta = 0.25$, $V = 2.0$, and $\varepsilon = -4.0$, using $\alpha = 0.26$ will give dynamics with the "best" long-time asymptotics allowed. Note that the time axes on the two panels have different ranges.

to guarantee the obedience of detailed balance. Since this is not computationally feasible, we present an alternative approach that guarantees that any kernel resummed to fourth order (or higher) will generate dynamics that decay to the correct equilibrium populations.

Following the discussion in section II E, we have tried resummations of the form of equation 20, enforcing the detailed balance relation in equation 21 to optimize a parameter α. This scheme exploits a choice we have when deciding how to perform a resummation in order to guarantee the correct equilibrium. We will note that in general, it is also possible to know *a priori* the correct equilibrium populations, either by knowing the long-time limit of a numerically exact solution (as is the case in this present work), or, more generally, by doing path integral Monte Carlo or molecu-

lar dynamics simulations in order to explore the energy landscape of the two states as they interact with a bath [58, 59].

Figure 4 shows the dynamics generated by a Hamiltonian in the moderate electronic coupling, moderate system-bath coupling, moderate temperature regime with strong electronic bias. In each panel, four dynamics runs are plotted: the HEOM run, and runs generated by resumming the memory kernels in a Landau-Zener fashion according to equations 18, 19, and 20. For most sets of Hamiltonian parameters, like those in figure 4(a), the detailed balance condition can be met exactly with some $0 \leq \alpha \leq \frac{1}{2}$. For some sets of Hamiltonian parameters, like those in figure 4(b), the detailed balance condition can only be satisfied in a least-squares sense.

As can be seen in the figure, the different choices for how to resum the forward and backward memory kernels can give very different trajectories. The different trajectories are entirely artifactual: were we to know all of the $K^{(2n)}$ out to infinite order, we wouldn't need to perform an approximate resummation and the discrepancy in how we choose to resum kernels disappears. Nevertheless, if we wish to compute memory kernels to finite order, we must make an arbitrary choice. Figure 4 shows that the best value for this choice is the particular interpolation between equations 18 and 19 that satisfies equation 21 (either exactly or in a least-square manner)—i.e., the particular resummation where the long-time limit of the resummed kernels best obeys detailed balance.

It is worth noting that for some parameter regimes, one of the two resummations in equations 18 and 19 diverges. A set of parameters where this occurs is the set of parameters used in figure 3(c): the kernel resummed according to equation 18 diverges but the kernel resummed according to equation 19 does not. Using equation 20 to resum and optimizing α gives a value $\alpha = 0.5$. For this value of α, equation 20 reduces exactly to equation 19. Thus, using equation 20 and optimizing α to enforce detailed balance not only gives qualitatively better dynamics for some parameter regimes, but prevents divergences in other parameter regimes. Doing the resummation in this manner is not just a bonus; it is imperative.

IV.   CONCLUSIONS

In this manuscript, we have shown for the first time numerical results for a generalized system-bath master equation that uses rate kernels resummed from a fourth-order perturbation series in the electronic coupling. We have shown that for the case of a two-level system interacting with a harmonic bath that an exponential resummation (the "Landau-Zener form") is recommended for computing short-time dynamics, as the previously-recommended Padé resummation diverges for even moderate values of the electronic coupling. The current resummation techniques robustly describe the dynamics for a wide range of Hamiltonian parameters, including cases with an electronic bias—cases which have historically troubled system-bath methods. The low-temperature regime, a regime which has plagued system-bath models for decades, remains problematic. We have lastly shown that by using a fourth-order resummation, one can always guarantee that the dynamics reach the correct equilibrium by exploiting a freedom inherent in the structure of the problem.

One of our goals when beginning this work was to develop a general, systematically improvable scheme to study system-bath dynamics. We have noted that the scheme that we have presented

gets close to the exact answer for a model spectral density in most parameter regimes, but does not recover the exact result for regimes of very strong electronic coupling or low temperature.

To address the former issue, we need to include higher orders in the perturbation series. The simplest approach is to generalize our derivation in section II C to arrive at an expression for $K^{(6)}$; unfortunately, the computational scaling becomes limiting when going out to such high orders of perturbation theory. Perhaps a more promising approach is to enforce both good short-time behavior *and* good strong-coupling behavior. The Landau-Zener resummation scheme succeeds at the former, but disagrees with the adiabatic ($V \to \infty$) limit by a factor of two [30]. Correct behavior in the adiabatic limit can be built into a more sophisticated resummation scheme. To improve even more on behavior in the strong-coupling (but not adiabatic) regime, we can derive expressions for the lowest-order non-adiabatic correction to adiabatic behavior and incorporate it into our resummed memory kernels.

To address the latter issue, new resummation schemes are required that correctly capture the low-temperature limit. Other resummation schemes, such as a generalized high-order resummation [30], the noncrossing cumulant scheme [34], and convolution resummation with auxillary kernels [49, 63] have the potential to capture this limit. Exploration into the numerical results of kernels generated by these resummation schemes to fourth order is ongoing.

Finally, and perhaps most excitingly, we have limited the discussion in this work to one particular form of the spectral density $J(\omega)$—namely, the Debye spectral density. Our method makes no assumptions as to the form of the spectral density; as such, we should be able to investigate system-bath dynamics using arbitrary spectral densities. Many procedures have been suggested in the literature for sampling numerical spectral densities from classical molecular dynamics trajectories and applying a post-hoc quantum-mechanical correction to the classical trajectories to extract a semiclassical spectral density [2, 62, 64–66]. We are currently investigating the fourth-order dynamics for the case of a general spectral density, with the hope that approximate dynamics for a large number of chemically-relevant problems may become accessible in the near future.

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A. Derivation of general expressions for $K_{11}^{(2)}$ and $K_{11}^{(4)}$ from time-dependent perturbation theory

Our starting point is time-dependent perturbation theory for the density matrix, $\rho(t)$. We're interested in deriving an expression for $K_{11}^{(2n)}$ and $K_{22}^{(2n)}$—quantities related to $\dot{p}_1$ and $\dot{p}_2$, the time derivatives of the populations of the two states. We shall examine $K_{11}^{(2n)}$ and p_1 in particular, but the steps in this derivation can easily be repeated with p_2 as the starting point to arrive at an expression for $K_{22}^{(2n)}$. Additionally, we will specifically derive the expressions for $K_{11}^{(2)}$ and $K_{11}^{(4)}$, but the result can easily be generalized to derive higher-order rate kernels.

In the interaction representation, we can write the population in state 1 as

$$p_1(t) = Tr_b\left[U(t)\rho(0)U^\dagger(t)|1\rangle\langle 1|\right] \tag{1}$$

where $U(t)$ is the time evolution operator $U(t) \equiv \exp\left[-i\hat{H}t\right]$, and the subscript "b" on the trace indicated a trace over all bath coordinates. To 4th order,

$$
\begin{aligned}
p_1(t) &= 1 + Tr_b\left[2\text{Re}\left[U^{(2)}(t)\rho(0)\right]|1\rangle\langle 1|\right] \\
&\quad + Tr_b\left[2\text{Re}\left[U^{(4)}(t)\rho(0)\right]|1\rangle\langle 1| \right.\\
&\quad \left. + U^{(2)}(t)\rho(0)U^{\dagger(2)}(t)|1\rangle\langle 1|\right] + \dots \\
&\equiv 1 + V^2 p_1^{(2)}(t) + V^4 p_1^{(4)}(t) + \dots
\end{aligned}
$$

where we have defined $p_1^{(2n)}$ in the last line and used the operator identity $\hat{O} + \hat{O}^\dagger = 2\text{Re}\left[\hat{O}\right]$. Taking a time derivative and working through some algebra, one can show that

$$\dot{p}_1^{(2)}(t) = -2\int_0^t \text{Re}\left[f_2^+(s_1)\right]ds_1 \tag{2}$$

$$
\begin{aligned}
\dot{p}_1^{(4)}(t) = 2\int_0^t ds_1 \int_0^{t-s_1} ds_2 \\
\left[\int_0^{t-s_1-s_2} ds_3 \text{Re}\left[f_4^+(s_1,s_2,s_3)\right]\right. \\
\left. + \int_{-s_1-s_2}^{t-s_1-s_2} dt_3 \text{Re}\left[f_4^+(-s_1-s_2-s_3,s_1,s_2)\right]\right]
\end{aligned}
\tag{3}
$$

where we have introduced two functions $f_2^+(s_1)$ and $f_4^+(s_1,s_2,s_3)$ defined as

$$f_2^+(s_1) \equiv V^2 Tr_b\left[\hat{O}(s_1)\rho(0)\right] \tag{4}$$

$$f_4^+(s_1,s_2,s_3) \equiv V^4 Tr_b\left[\hat{O}(s_1)\hat{O}^\dagger(s_2)\hat{O}(s_3)\rho(0)\right] \tag{5}$$

where we have defined $\hat{O}(t) \equiv e^{i\hat{h}_1 t} e^{-i\hat{h}_2 t}$, and $\hat{h}_1$ and $\hat{h}_2$ are defined through equation 2 in the main text.

We can perform a similar expansion on equation 3 in the main text (using $p_1^{(0)} = 1 - p_2^{(0)} = 1$) to show that

$$\dot{p}_1^{(2)}(t) = -\int_0^t K_{11}^{(2)}(t-s)ds \tag{6}$$

$$
\begin{aligned}
\dot{p}_1^{(4)}(t) = -\int_0^t \left(K_{11}^{(2)}(t-s)p_1^{(2)}(s) \right. \\
\left. + K_{11}^{(4)}(t-s) + K_{22}^{(2)}(t-s)p_1^{(2)}(s)\right)ds
\end{aligned}
\tag{7}
$$

Comparing equations 2 to 6 and equations 3 to 7 (doing some algebra in the latter case) allows us to arrive at the equations for $K^{(2)}$ and $K^{(4)}$ in terms of equations f_2^+ and f_4^+; all that remains is to work out the functional forms of these traces. This result is general for any two-level system coupled to a bath, so long as the electronic coupling is constant; we have not yet specified the bath to be harmonic.

B. Derivation of the bath correlation functions f_2 and f_4 for the spin-boson problem using Gaussian coherent states

We now compute the traces in equations 4 and 5 for the special case of a harmonic bath. In order to make computation simple, we shall assume that the reduced density matrix describing the system initially contains no populations in state 2 and no coherences (i.e. its (1,1) element is unity, and all other elements are zero). We shall additionally assume that the bath is in equilibrium with a thermal heat reservoir of inverse temperature $\beta \equiv 1/k_B T$. This brings our list of assumptions up to 3:

1. The electronic coupling is constant;

2. The bath is harmonic and coupled to the system linearly to the system; and

3. The full density matrix at time t=0 can be represented as $\rho(0) = e^{-\beta \hat{h}_1} / \operatorname{Tr}\left[e^{-\beta \hat{h}_1}\right]$

Of particular importance is that *we have not assumed anything about the bath other than its harmonicity*, which should manifest in the form of our equations depending on a *general* spectral density function $J(\omega)$. In passing, we will also note that it should be possible to repeat this derivation relaxing assumption 1, though we shall leave this to future work.

In the position representation, a Gaussian coherent state $|p,q;\phi\rangle$ parameterized by average position q and average momentum p with phase ϕ can be written

$$\langle x|p,q;\phi\rangle = \left(\frac{\omega}{\pi}\right)^{1/4} \exp\left[-\frac{\omega}{2}(x-q)^2 + ip(x-q) + i\phi\right] \tag{8}$$

Note that for a harmonic oscillator, the phase $\phi(t)$ does not depend explicitly on t, only on $p(t)$ and $q(t)$ [1]; thus, phase space integration over p and q will eliminate ϕ as well. Nevertheless, we include it in the definition of our Gaussian coherent state for clarity, as will be made evident over the next few steps in the derivation.

Using these Gaussian coherent states as a basis, we can work out the traces. For brevity, we shall work out the fourth-order trace (equation 5), as it is more related to the general case and the second-order trace has been previously computed elsewhere. The trace can be written as

$$f_4^+(s_1,s_2,s_3) = \frac{V^4}{Z} \int \langle p,q;\phi|\hat{O}(s_1)\hat{O}^\dagger(s_2)\hat{O}(s_3)e^{-\beta \hat{h}_1}|p,q;\phi\rangle dp_0 dq_0$$

where $Z \equiv \int \langle p,q;\phi|e^{-\beta \hat{h}_1}|p,q;\phi\rangle dp dq$ is the partition function, and the phase space integral is over all initial positions and momenta.

In order to compute this integral, we can utilize the property of Gaussian coherent states that their average position, momentum, and phase evolve classically in time. We can also exploit the fact that $\hat{h}_1$ and $\hat{h}_2$ are related by symmetry: since the bath is (by assumption) significantly larger than the system, the bath Hamiltonians contain identical spectra, and only differ by some displacement δ along one coordinate. These two facts allow us to compute the action of the operator $e^{i\hat{h}_1 t}e^{-i\hat{h}_2 t}$ on the state $|p,q;\phi\rangle$ mode-by-mode. We shall perform this deconstruction, and then "reassemble" the complete bath in the final step. The two states of the system see a bath mode of frequency ω as the same one-dimensional harmonic well displaced horizontally by a distance δ and vertically by a distance ε, the energy bias between the states. The time evolution due to the (constant) energy bias ε can be factored out; the rest of the time evolution can be evaluated analytically according to the classical equations of motion for a harmonic oscillator [2]

$$\begin{aligned}
e^{i\hat{h}_1 t}e^{-i\hat{h}_2 t}|p,q;\phi\rangle &= e^{i\varepsilon t}|p(t),q(t);\phi(t)\rangle \\
q(t) &= q_0 - \delta\omega(\cos(\omega t) - 1) \\
p(t) &= p_0 - \delta\omega\sin(\omega t) \\
\phi(t) &= \frac{\delta^2\omega}{2}(\cos(\omega t) - 1)\sin(\omega t) - \delta\omega q_0\sin(\omega t)
\end{aligned}$$

Acting the real time evolution operators to the left, and the imaginary time evolution operator to the right, we obtain

$$f_4^+(s_1,s_2,s_3) = \frac{V^4}{Z}\int\langle -p(s_1)+p(s_2)-p(s_3), -q(s_1)+q(s_2)-q(s_3); -\phi(s_1)+\phi(s_2)-\phi(s_3)|p(-i\beta),q(-i\beta);\phi(-i\beta)\rangle dp_0 dq_0$$

which is just the integral of the overlap of two Gaussians over all possible initial values of position and momentum. This can be computed analytically (inserting a resolution of the identity and using equation 8) to derive an explicit form for $f_4(s_1,s_2,s_3)$ for a single bath mode. We were able to verify that our expression for $K^{(4)}$ together with equation 7 gives the correct fourth-order population for the one mode problem by solving the for the populations of this problem numerically-exactly through brute-force time propagation of the full density matrix.

A spectral density can be incorporated noting that a spectral density is just a way of specifying exactly what the harmonic displacement δ that each state "sees" at each frequency of the bath ω:

$$J(\omega) = \frac{\pi}{2}\sum_j \omega_j^3 \delta_j^2 \delta(\omega - \omega_j)$$

Putting all of this together, one arrives at equation 11 in the main text. A similar (simpler) derivation can be used to arrive at equation 10 in the main text, and the extension to calculate bath correlation functions involving five-time events, seven-time events, and higher is straightforward.

C. A note on the backwards rate kernel, K_{22}

All of the results in the previous two sections can be applied as well to compute K_{22}. Only two things change:

1. We must compute the trace over the equilibrium configuration of state 2, which effectively means $\hat{h}_1 \leftrightarrow \hat{h}_2$ (and thus, by symmetry, $\delta/2 \leftrightarrow -\delta/2$) everywhere

2. The initial condition changes to $p_1(0) = 1 - p_2(0) = 0$, changing $K_{11}^{(2)}(s_2) \to K_{22}^{(2)}(s_2)$ in equation 9 in the main text.

Otherwise, the derivation proceeds virtually identically.

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