

Efficient memory equation algorithm for reduced dynamics in spin-boson models

Andrei A. Golosov, Richard A. Friesner, and Philip Pechukas
Department of Chemistry, Columbia University, New York, New York 10027

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The dynamics of a one-dimensional quantum system coupled to a harmonic bath can be expressed through Feynman's path integral expression for the reduced density matrix. In this expression the influence of the environment is seen in correlations between positions of the system that are nonlocal in time. Makri and Makarov [J. Chem. Phys. **102**, 4600 (1995)] showed that for many practical problems correlations over only a few time steps, Δk_{\max} , need to be taken into account, which led to an efficient iterative scheme. However, this algorithm scales as the size of the system to the power of $2(\Delta k_{\max} + 1)$, which restricts the size of the system that can be studied with this method. In this work we present an efficient algorithm which scales linearly with Δk_{\max} . In our method the reduced density matrix is written as a convolution of its past values with an integral equation kernel. The calculation of that kernel is based on a perturbative expansion of the discretized quasiadiabatic path integral expression for the reduced density matrix. The expansion ignores certain types of correlations. © 1999 American Institute of Physics.
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I. INTRODUCTION

The dynamical simulation of quantum dissipative systems is a challenging problem in condensed matter physics and chemistry.¹ Such systems consist of a few relevant degrees of freedom coupled to a huge environment, the "bath," and serve as a model to describe condensed phase dynamical processes such as charge-transfer reactions,² vibrational relaxation,³ macroscopic tunneling,⁴ etc.

The most commonly used microscopic model of dissipative systems is of the spin-boson type,⁴ i.e., a few-level system bilinearly coupled to an infinite set of harmonic oscillators. Within the path integral approach,⁵ the harmonic bath can be integrated out giving rise to an influence functional⁶ with time correlations between different path segments. This is the basis of quantum Monte Carlo (QMC),⁷⁻⁹ the only feasible exact method available so far. Since the number of paths to be included in QMC increases exponentially with the number of time slices, this approach becomes problematic for long propagation times.

This difficulty prompted the development of approximate methods. Classical path methods,¹⁰⁻¹³ surface-hopping techniques¹⁴⁻¹⁷ and the recent mixed semiclassical-classical approach¹⁸ all assume that the system is described quantum mechanically, while the bath is described classically. This kind of approximation is valid when the temperature of the bath is higher than its characteristic frequency. By sampling initial positions and momenta of the bath particles from the Wigner instead of the Maxwell-Boltzmann distribution function, Stock¹⁹ showed using the example of the spin-boson system that mixed quantum-classical method (a particular version derived using a semiclassical self-consistent field approach) may give qualitatively correct results even at low temperatures. These mixed techniques have problems in the

nonadiabatic regime, where the bath dynamics is much faster than that of the system.

In that regime, theories of a perturbative type work very well. These include Redfield theory,²⁰ the noninteracting cluster approximation (NICA)²¹ and its specific case for a two-level system, the celebrated noninteracting blip approximation (NIBA).^{4,22} For example, Redfield theory has been successfully applied to a variety of problems including ESR and NMR,²⁰ vibrational relaxation^{3,23} and electron transfer.²⁴ Such theories fail in the adiabatic to intermediate region, where the bath dynamics is slower than or as fast as that of the system.

Several recent methods such as centroid molecular dynamics,²⁵ the discretized integral equation approach²⁶ and techniques based on the semiclassical approximation¹⁸ look very promising. However, further tests are necessary to reveal all of the benefits of these methods.

Several years ago Makarov and Makri^{27,28} developed a method based on an approximation which is the truncation of time correlations in the influence functional. They observed that the broad spectrum of the environment to which the system is coupled leads to a finite range of correlations between different path segments. They showed that for many practical purposes correlations over only a few time steps, Δk_{\max} , need to be taken into account. This led to a reasonably efficient iterative procedure which scales as $O(n^{2(\Delta k_{\max} + 1)})$ for an n -level system. However, the exponential scaling limits the size of the system that can be studied to very few levels. In this paper we present an efficient numerical scheme which overcomes this bottleneck without substantial loss of accuracy. It has linear scaling with Δk_{\max} .

The rest of the paper is organized in the following way. In Sec. II, a model system coupled to a harmonic bath is discussed. For this model, the quasiadiabatic path integral

expression and the tensor multiplication algorithm are briefly reviewed in Secs. III and IV, respectively. These sections introduce the main notations and equations which will be used in Sec. V, which describes the memory equation algorithm, the essential result of this paper. Numerical results are presented in Secs. VI, and Sec. VII contains concluding remarks and sketches some directions for a possible improvement of the method.

II. MODEL

A commonly used model for quantum dissipation is a one-dimensional (1D) system bilinearly coupled to an infinite set of harmonic oscillators that mimic the environment (bath) within the regime of validity of linear response theory. Its Hamiltonian can be written as

$$H = \frac{P^2}{2M} + V(Q) + \frac{1}{2} \sum_j^{M_{\text{modes}}} \left(p_j^2 + \omega_j^2 \left(q_j - \frac{g_j Q}{\omega_j} \right)^2 \right), \quad (1)$$

where Q is the system coordinate with conjugate momentum P , and q_j is the position of the j th bath mode with conjugate momentum p_j , frequency ω_j and coupling strength g_j . All information about the bath that is essential for the dynamics of the system can be captured in the compact form of the spectral density function

$$J(\omega) = \frac{\pi}{2} \sum_j \frac{g_j^2}{\omega} \delta(\omega - \omega_j). \quad (2)$$

III. DISCRETIZED QUASI-ADIABATIC PATH INTEGRAL

The quantity of interest is the reduced density matrix σ , the trace of the total system-bath density matrix over bath coordinates,

$$\sigma(t) = \text{Tr}_B \rho(t) = \text{Tr}_B (e^{-iHt} \rho(0) e^{iHt}), \quad (3)$$

where \hbar is assumed to be 1 throughout the paper. It fully describes the dynamics of the system.

Introducing a reference Hamiltonian

$$H_{\text{ref}} = \frac{P^2}{2M} + V(Q) + \frac{1}{2} \sum_j^{M_{\text{modes}}} \frac{g_j^2}{\omega_j^2} Q^2, \quad (4)$$

the system-bath Hamiltonian can be split into two parts

$$H = H_{\text{ref}} + H_{\text{env}}, \quad (5)$$

where

$$H_{\text{env}} = \frac{1}{2} \sum_j^{M_{\text{modes}}} (p_j^2 + \omega_j^2 q_j^2) + \sum_j^{M_{\text{modes}}} g_j q_j Q. \quad (6)$$

Rewriting e^{iHt} as $(e^{iH_{\text{ref}} \Delta t})^N$, inserting the identity

$$\int dQ |Q\rangle \langle Q| \prod_{j=1}^{M_{\text{modes}}} \int dq_j |q_j\rangle \langle q_j| = 1 \quad (7)$$

between each pair of $e^{iH_{\text{ref}} \Delta t}$, utilizing an adiabatic partitioning of each exponential operator

$$e^{iH \Delta t} \approx e^{iH_{\text{env}} \Delta t/2} e^{iH_{\text{ref}} \Delta t} e^{iH_{\text{env}} \Delta t/2} \quad (8)$$

and integrating over the bath coordinates, Makri obtained the quasi-adiabatic propagator path integral (QUAPI) expression for the reduced density matrix. For a factorized initial density matrix

$$\rho(0) = \rho_s(0) \otimes \frac{e^{-\beta H_{\text{bath}}}}{Z}, \quad (9)$$

which corresponds to switching on interactions between a system and a bath which is in equilibrium at the initial time (here H_{bath} is the bath Hamiltonian and Z is its partition function), the reduced density matrix can be written as²⁷

$$\begin{aligned} \sigma(Q'', Q'; t = N\Delta t) = & \int dQ_0^+ Q_1^+ \dots Q_{N-1}^+ \\ & \times \int dQ_0^- Q_1^- \dots Q_{N-1}^- \\ & \times \langle Q'' | e^{-iH_{\text{ref}} \Delta t} | Q_{N-1}^+ \rangle \dots \\ & \times \langle Q_1^+ | e^{-iH_{\text{ref}} \Delta t} | Q_0^+ \rangle \\ & \times \langle Q_0^+ | \rho_s(0) | Q_0^- \rangle \\ & \times \langle Q_0^- | e^{iH_{\text{ref}} \Delta t} | Q_1^- \rangle \dots \\ & \times \langle Q_{N-1}^- | e^{iH_{\text{ref}} \Delta t} | Q' \rangle \\ & \times I(\{Q_i^+, Q_i^-\}_{i=0}^N; \Delta t), \end{aligned} \quad (10)$$

where the influence functional $I(\{Q_i^+, Q_i^-\}_{i=0}^N; \Delta t)$ captures the effect of the environment on the system by the introduction of nonlocal correlations between positions of the system at different times. It can be written as

$$I = \exp \left[- \sum_{k=0}^N \sum_{k'=0}^k (Q_k^+ - Q_k^-) (\eta_{kk'} Q_{k'}^+ - \eta_{kk'}^* Q_{k'}^-) \right], \quad (11)$$

where $\eta_{kk'}$ is an integral expression which depends only on the spectral function $J(\omega)$, temperature T , and discretization time step Δt ($\eta_{kk'}$ depends only on $|k-k'|$ for $0 < k, k' < N$). This expression for the influence functional is just a discretized version of that of Feynman and Vernon⁶ for the continuous forward $Q^+(t)$ and backward $Q^-(t)$ paths of the system

$$\begin{aligned} I = \exp \left[- \int_0^t dt' \int_0^{t'} dt'' (Q^+(t') - Q^-(t')) \right. \\ \left. \times (\alpha(t' - t'') Q^+(t'') - \alpha^*(t' - t'') Q^-(t'')) \right], \end{aligned} \quad (12)$$

with

$$\alpha(t) = \frac{1}{\pi} \int_0^\infty d\omega J(\omega) \left(\coth \left(\frac{\beta \omega_j}{2} \right) \cos(\omega t) - i \sin(\omega t) \right), \quad (13)$$

which gives meaning to Q_k^+ and Q_k^- as forward and backward constant path segments at $\max(0, k - \frac{1}{2})\Delta t \leq t \leq \min(k + \frac{1}{2}, N)\Delta t$, respectively. Here $\alpha(t)$, a so-called memory kernel, is a measure of nonlocality of the influence functional. In the memoryless, or Markovian, limit $\text{Re}[\alpha(t)]$ is propor-

tional to a delta functional and $\text{Im}[\alpha(t)]$ is proportional to its derivative, and therefore $\eta_{kk'} = 0, |k - k'| > 1$. In the opposite, or adiabatic, limit $\alpha(t)$ is a constant, indicating infinite time range correlations between positions of the system at different time steps. In many practical situations the width of the memory kernel (the memory length) is between those two extreme limits, i.e., it is finite. Employing a cutoff t_{\max} on the memory length [$\eta_{kk'}$ in Eq. (11) is set to zero for $|k - k'| > \Delta k_{\max}, \Delta k_{\max} \Delta t = t_{\max}$], Makri and Makarov implemented an efficient tensor multiplication algorithm.^{27,28}

IV. TENSOR MULTIPLICATION ALGORITHM

Since our algorithm is closely related to the tensor multiplication scheme, this section is essential for understanding further material. However, it should be considered as a brief introduction; details can be found in the original papers by Makarov and Makri.^{27,28} We have changed some of their notation and order of summation for convenience.

In the discrete variable representation, i.e., in the basis set formed by eigenvalues (labeled s) of a system position operator

$$\langle s_\alpha | Q | s_\beta \rangle = \tilde{Q}_\alpha \delta_{\alpha\beta}, \quad (14)$$

expression (10) for the reduced density matrix can be rewritten as

$$\begin{aligned} \sigma(s'', s'; t = N\Delta t) &= \sum_{s_0^+, s_1^+, \dots, s_{N-1}^+} \sum_{s_0^-, s_1^-, \dots, s_{N-1}^-} \langle s'' | e^{-iH_{\text{ref}}\Delta t} | s_{N-1}^+ \rangle \dots \\ &\times \langle s_1^+ | e^{-iH_{\text{ref}}\Delta t} | s_0^+ \rangle \langle s_0^+ | \rho_s(0) | s_0^- \rangle \\ &\times \langle s_0^- | e^{iH_{\text{ref}}\Delta t} | s_1^- \rangle \dots \langle s_{N-1}^- | e^{iH_{\text{ref}}\Delta t} | s' \rangle \\ &\times I(\{s_i^+, s_i^-\}_{i=1}^N; \Delta t), \end{aligned} \quad (15)$$

where

$$\begin{aligned} I(\{s_i^+, s_i^-\}_{i=1}^N; \Delta t) &= \exp\left(-\sum_{k=0}^N \sum_{k'=0}^k (\tilde{Q}_k^+ - \tilde{Q}_k^-)(\eta_{kk'} \tilde{Q}_{k'}^+ - \eta_{kk'}^* \tilde{Q}_{k'}^-)\right) \end{aligned} \quad (16)$$

with \tilde{Q}_k^\pm being eigenvalues corresponding to eigenstates $|s_k^\pm\rangle$. Labeling pairs of indices (s_k^+, s_k^-) as s_k , (s'', s') as s_N and introducing short-hand notations for a free system propagator

$$\langle s_i^+ | e^{-iH_{\text{ref}}\Delta t} | s_j^+ \rangle \langle s_j^- | e^{iH_{\text{ref}}\Delta t} | s_i^- \rangle = A_0(s_i, s_j), \quad (17)$$

and for the density matrix of the system at the initial moment

$$\langle s_0^+ | \rho_s(0) | s_0^- \rangle = \sigma_0(s_0) \quad (18)$$

the above expression for the reduced density matrix can be written as

$$\begin{aligned} \sigma(s_N; t = N\Delta t) &= \sum_{s_0, s_1, \dots, s_{N-1}} A_0(s_N, s_{N-1}) \\ &\times A_0(s_{N-1}, s_{N-2}) \dots \\ &\times A_0(s_1, s_0) \sigma_0(s_0) \times I(\{s_i\}_{i=1}^N; \Delta t). \end{aligned} \quad (19)$$

The influence functional can be decomposed into pairwise products

$$I(\{s_i\}_{i=1}^N; \Delta t) = \prod_{k=0}^N \prod_{\Delta k=0}^k I_{\Delta k}(s_k, s_{k-\Delta k}), \quad (20)$$

where

$$I_{|k-k'|}(s_k, s_{k'}) = \exp[-(\tilde{Q}_k^+ - \tilde{Q}_k^-)(\eta_{kk'} \tilde{Q}_{k'}^+ - \eta_{kk'}^* \tilde{Q}_{k'}^-)]. \quad (21)$$

After defining

$$A_1(s_k, s_{k-1}) = A_0(s_k, s_{k-1}) I_0(s_k, s_k) I_1(s_k, s_{k-1}), \quad (22)$$

$\sigma(t)$ can be expressed as

$$\begin{aligned} \sigma(s_N; t = N\Delta t) &= \sum_{s_0, s_1, \dots, s_{N-1}} A_1(s_N, s_{N-1}) \prod_{\Delta k=2}^N I_{\Delta k}(s_N, s_{N-\Delta k}) \\ &\times A_1(s_{N-1}, s_{N-2}) \prod_{\Delta k=2}^{N-1} I_{\Delta k}(s_{N-1}, s_{N-1-\Delta k}) \\ &\dots \\ &\times I_0(s_0, s_0) \sigma_0(s_0). \end{aligned} \quad (23)$$

The first, the second and following lines of the right side expression contain correlations between, respectively, s_N , s_{N-1} , \dots configurations and all configurations at the previous time steps up to the initial moment s_0 .

Expression (23) is the basis of Makri and Makarov's algorithm. Consider the simplest case, in which $\Delta k_{\max} = 2$. The result after rearrangement of the summation indices is

$$\begin{aligned} \sigma(s_N; t = N\Delta t) &= \sum_{s_{N-1}} A_1(s_N, s_{N-1}) \sum_{s_{N-2}} I_2(s_N, s_{N-2}) \\ &\times A_1(s_{N-1}, s_{N-2}) \sum_{s_{N-3}} I_2(s_{N-1}, s_{N-3}) \\ &\dots \\ &\times A_1(s_2, s_1) \sum_{s_0} I_2(s_2, s_0) \\ &\times A_1(s_1, s_0) I_0(s_0, s_0) \sigma_0(s_0). \end{aligned} \quad (24)$$

From here we can see that summation in each successive line performed in the direction from the bottom to the top line of Eq. (24) gives the expression which depends only on two indices which can be used in the calculation of the above lines. In other words, if we denote the result of the first line (from the bottom) as

$$\rho(s_1, s_0) = A_1(s_1, s_0) I_0(s_0, s_0) \sigma_0(s_0), \quad (25)$$

then the second line gives

$$\rho(s_2, s_1) = A_1(s_2, s_1) \sum_{s_0} I_2(s_2, s_0) \rho(s_1, s_0), \quad (26)$$

and so on until the last line where

$$\sigma(s_N; t = N\Delta t) = \sum_{s_{N-1}} \rho(s_N, s_{N-1}). \quad (27)$$

In the actual calculation it was taken into account that $I_{\Delta k}(s_k, s_{k-\Delta k})$ depends only on $|k-k'|$ for $k \neq N, \Delta k$. In this calculation ρ , a so-called augmented density tensor, depends only on its value from the previous time step, thereby the nonMarkovian dynamics for the reduced density matrix is mapped into the Markovian dynamics of an augmented reduced density tensor.

In general, for a given Δk_{\max} , the augmented reduced density tensor depends on Δk_{\max} indices. The cost of its propagation is $O(n^{2(\Delta k_{\max}+1)})$ in CPU and $O(n^{2\Delta k_{\max}})$ in storage. Here n is the number of DVR states. In the next section we will introduce a method with propagation cost of $O(n^4 \Delta k_{\max})$.

V. MEMORY EQUATION ALGORITHM

Our ansatz is to present the reduced density matrix as a convolution of its previous values in time with an operator K

$$\sigma(t = N\Delta t) = \sum_{\Delta k=1}^{\min(\Delta k_{\max}, N)} K_{\Delta k}(\Delta t) \sigma(t - \Delta k \Delta t), \quad (28)$$

where σ is represented as a vector of length n^2 , $K_{\Delta k}$ is a matrix of size $n^2 \times n^2$, and n is the number of DVR states (which for a discrete system is the total number of states). This expression is just a discretized version of a generalized master equation.²⁹ In this section, we will develop an approximate scheme of the construction of the kernels in Eq. (28), the heart of the *memory equation algorithm*.

Suppose we know $K_{\Delta k}$, then the CPU cost of propagation by this convolution expression scales as $O(n^4 \Delta k_{\max})$ in comparison to that of the tensor multiplication algorithm which scales as $O(n^{2(\Delta k_{\max}+1)})$. Since for most of the cases studied in the literature, Δk_{\max} is at least of order of 10, this would mean enormous savings both in CPU time and storage, especially for $n > 2$ [although even for $n = 2$ and $\Delta k = 10$ the saving is of order $2^{22}/(2^4 10) \approx 2.6 \times 10^4$]. In fact for $n = 3$ and $\Delta k_{\max} > 6$, Sim and Makri³⁰ first had to select important paths by performing a random walk in $n^{2\Delta k_{\max}}$ dimensional space in order to use their tensor multiplication algorithm.

The question remains how to calculate $K_{\Delta k}$? Let us look at the dynamics for the first two time steps. Using Eq. (24), the reduced density matrix after the first time step is

$$\sigma(s_1; t = \Delta t) = \sum_{s_0} A_1(s_1, s_0) \sigma(s_0; 0), \quad (29)$$

where we denote $I_0(s_0, s_0) \sigma_0(s_0)$ as $\sigma(s_0; 0)$ and $\sigma(s_N; t = N\Delta t)$ is the reduced density matrix for all t except 0. After the second time step, σ becomes

$$\begin{aligned} \sigma(s_2; t = 2\Delta t) &= \sum_{s_1} A_1(s_2, s_1) \\ &\times \sum_{s_0} I_2(s_2, s_0) A_1(s_1, s_0) \sigma(s_0; 0). \end{aligned} \quad (30)$$

This can be rewritten as

$$\begin{aligned} \sigma(s_2; t = 2\Delta t) &= \sum_{s_1} A_1(s_2, s_1) \sum_{s_0} (I_2(s_2, s_0) - 1 + 1) \\ &\times A_1(s_1, s_0) \sigma(s_0; 0) \\ &= \sum_{s_1} \underbrace{A_1(s_2, s_1)}_{K_1(s_2, s_1)} \sum_{s_0} \underbrace{A_1(s_1, s_0) \sigma(s_0; 0)}_{\sigma(s_1; t = \Delta t)} \\ &+ \sum_{s_0} \underbrace{\sum_{s_1} A_1(s_2, s_1) A_1(s_1, s_0) (I_2(s_2, s_0) - 1)}_{K_2(s_2, s_0)} \sigma(s_0; 0) \\ &= \sum_{s_1} K_1(s_2, s_1) \sigma(s_1; t = \Delta t) + \sum_{s_0} K_2(s_2, s_0) \sigma(s_0; 0), \end{aligned} \quad (31)$$

where $K_1 = A_1$ and $K_2 = A_1^2 * (I_2 - 1s)$. Here “*” stands for the element-by-element product and $1s$ is a $n^2 \times n^2$ matrix with all elements equal to one. Thus we obtain

$$\sigma(2\Delta t) = K_1 \sigma(\Delta t) + K_2 \sigma(0), \quad (32)$$

which is an exact expression. If $\Delta k_{\max} = 2$, we truncate the memory equation (28) to the first two terms:

$$\sigma(N\Delta t) \approx K_1 \sigma((N-1)\Delta t) + K_2 \sigma((N-2)\Delta t), \quad N > 2. \quad (33)$$

In a moment we will show that this approximation is of a perturbative type, but right now let us consider the generalization of Eq. (33) to $\Delta k_{\max} > 2$. We introduce two approximate propagators of the reduced density matrix from the initial moment $t = 0$ to $t = N\Delta t$. The first, $A_N(s_N, s_0)$, and the second, $\bar{A}_N(s_N, s_0)$, include correlations up to $\Delta k_{\max} = \max(N-1, 1)$ and $\Delta k_{\max} = N$, respectively. We would like to build these propagators recursively, i.e., to express A_N and \bar{A}_N in terms of $A_{N'}$ and $\bar{A}_{N'}$, where $N' < N$.

From Eq. (29) it is obvious that $A_1 = \bar{A}_1$. To find A_2 and \bar{A}_2 we rewrite Eq. (31) as

$$\begin{aligned} \sigma(s_2; t = 2\Delta t) &= \sum_{s_0} \left(\sum_{s_1} K_1(s_2, s_1) \bar{A}_1(s_1, s_0) \right) I_2(s_2, s_0) \sigma(s_0; 0) \\ &= \sum_{s_0} \bar{A}_2(s_2, s_0) \sigma(s_0; 0). \end{aligned} \quad (34)$$

If $\Delta k = 2$ correlation were not included in this expression, $I_2(s_2, s_0)$ would be omitted, and therefore $A_2 = K_1 \bar{A}_1$. The inclusion of that correlation gives

$$\bar{A}_2 = A_2 \cdot * I_2,$$

$$K_2 = \bar{A}_2 - A_2 = A_2 \cdot *(I_2 - 1s). \quad (35)$$

The propagator A_3 includes correlations only up to $\Delta k_{\max} = 2$. Thus it can be calculated directly from Eq. (33) or, more strictly, its expanded form Eq. (31)

$$\begin{aligned} & \sum_{s_0} A_3(s_3, s_0) \sigma(s_0; 0) \\ &= \sum_{s_2} K_1(s_3, s_2) \sigma(s_2; t=2\Delta t) \\ &+ \sum_{s_1} K_2(s_3, s_1) \sigma(s_1; t=\Delta t) \\ &= \sum_{s_0} \left\{ \sum_{s_2} K_1(s_3, s_2) \bar{A}_2(s_2, s_0) \right. \\ &\quad \left. + \sum_{s_1} K_2(s_3, s_1) \bar{A}_1(s_1, s_0) \right\} \sigma(s_0; 0). \quad (36) \end{aligned}$$

From the above expression it follows that

$$A_3 = K_1 \bar{A}_2 + K_2 \bar{A}_1. \quad (37)$$

The inclusion of the correlation with $\Delta k=3$ gives $\bar{A}_3 = A_3 \cdot * I_3$. Furthermore, the expression for the reduced density matrix after the third time step,

$$\sigma(3\Delta t) = \sum_{s_3} \bar{A}_3(s_3, s_0) \sigma(s_0; 0), \quad (38)$$

can be split into two parts

$$\begin{aligned} \sigma(3\Delta t) &= \sum_{s_3} A_3(s_3, s_0) \sigma(s_0; 0) + \sum_{s_3} A_3(s_3, s_0) \\ &\quad \times (I_3(s_3, s_0) - 1) \sigma(s_0; 0). \quad (39) \end{aligned}$$

The first term contains all correlations except $\Delta k=3$, and therefore according to Eq. (33), is equal to $K_1 \sigma(2\Delta t) + K_2 \sigma(\Delta t)$. Thus in order to get the above expression in the form of (28), we assign the second term as $K_3 \sigma(0)$, where $K_3 = \bar{A}_3 - A_3 = A_3 \cdot *(I_3 - 1s)$. Similarly, we can calculate the kernels K_N of the integral equation (28) by the recurrence relations

$$\begin{aligned} K_N &= A_N \cdot *(I_N - 1s), \\ \bar{A}_N &= A_N \cdot * I_N, \\ A_N &= K_1 \bar{A}_{N-1} + K_2 \bar{A}_{N-2} + \dots + K_{N-1} \bar{A}_1, \quad N > 1, \\ K_1 &= A_1, \quad \bar{A}_1 = A_1. \end{aligned} \quad (40)$$

These kernels are then used to calculate the reduced density matrix

$$\begin{aligned} \sigma(N\Delta t) &= K_1 \sigma((N-1)\Delta t) + K_2 \sigma((N-2)\Delta t) + \dots \\ &\quad + K_N \sigma(0). \quad (41) \end{aligned}$$

Equations (40) and (41) constitute the *memory equation algorithm*.

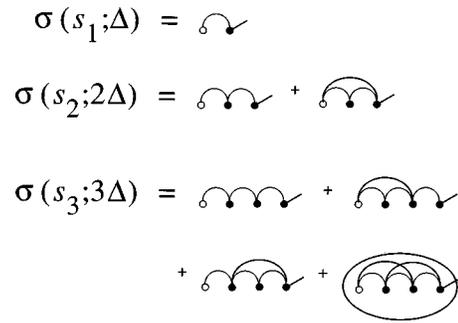


FIG. 1. A diagrammatic expansion of the reduced density matrix for $\Delta k_{\max}=2$.

Now let us consider what the approximation given by Eq. (40) means. We will use a diagrammatic representation. Let A_1 be a bond (also referred to as local bond) connecting adjacent time steps. Further, in our graph formalism, $(I_N - 1s)$, $N > 1$, is a bond connecting points N time steps apart; an open circle is an opened (unsummed) index; a closed circle is a closed (summed) index; a straight line segment is $\sigma(s_0; 0)$. Using this notation, the reduced density matrix of the first several steps for $\Delta k_{\max}=2$ is shown in Fig. 1. Here, circled terms in corresponding expressions for σ are those which are *not* generated by (40) and (41). It is not hard to see that the only diagrams which will be left out by the memory equation algorithm are those containing overlaps of bonds. The largest error will be due to terms containing only two overlapping bonds, like the circled term for $\sigma(3\Delta t)$.

In cases where of $\Delta k_{\max} > 2$, the situation is even more complicated, since more diagrams are ignored, and therefore the error will increase as Δk_{\max} increases. However, our goal for a given spectral density function $J(\omega)$, and therefore for a given memory kernel, is to find the dynamics of the system. $\alpha(t)$ usually has a finite width, say t_{\max} . Therefore, for a given Δt , we have $\Delta k_{\max} = [t_{\max}/\Delta t] + 1$, where square brackets stand for an integer part of an inside expression. The bigger the time step Δt , the smaller the number of correlations Δk_{\max} that need to be taken into account, and therefore the smaller the error by Eqs. (41) and (40). On the other hand, the error due to the adiabatic partitioning (8) will be larger. Therefore, there must be an optimal time step to minimize the two types of errors simultaneously. To find it we have used “a principle of minimal sensitivity” which was successfully applied to recent calculations of energy levels by the semiclassical quantization method.³¹ Utilizing this principle to determine this optimal time step, we find $\sigma(t)$ for a different Δt (but so that $\Delta k_{\max} \Delta t = t_{\max} = \text{const}$) and choose Δt at which $\sigma(t)$ is the least sensitive to the change in Δt .

The knowledge of an optimal time step is also important for an efficient evaluation of the QUAPI expression by either the QMC or tensor multiplication techniques or their combination, although the optimal time step in this context is the largest one which still gives “reasonable” results (say within 10% error). This makes Δk_{\max} as small as possible, which cuts the computational cost $O(n^{2(\Delta k_{\max}+1)})$ substantially. Hopefully, both of the above-mentioned optimal time steps

are close to each other. In the next section we will try to estimate them from the properties of the memory kernel.

VI. NUMERICAL RESULTS

The memory equation algorithm was tested on two dissipative spin-boson models, a two-state system (TSS) and a three-state system bilinearly coupled to harmonic heat baths. The two-state model has been extensively¹ used to describe chemical reactions at very low temperatures when tunneling between products and reactants is the major contribution to the rate of the reaction. Its Hamiltonian, introduced by Caldeira and Leggett,⁴ is

$$H = \epsilon \sigma_z + K \sigma_x + \frac{1}{2} \sum_j^{M_{\text{modes}}} (p_j^2 + \omega_j^2 q_j^2) + \sigma_z \sum_j^{M_{\text{modes}}} g_j q_j, \quad (42)$$

where σ_z and σ_x are Pauli matrices of the TSS, ϵ is a bias, K is a tunneling element between two sites, and q_j is the position of the j th bath mode with conjugate momentum p_j , frequency ω_j and coupling strength g_j . The spectral density function was chosen to be ohmic

$$J(\omega) = \frac{\pi}{2} \alpha \omega \exp(-\omega/\omega_c), \quad (43)$$

where α is a Kondo parameter and ω_c is a cutoff frequency. This type of $J(\omega)$ has been used most frequently in the literature, because a compact analytical solution given by NIBA can be obtained, and in addition, the spin-boson system with this type of the spectral density shows a set of interesting phenomena,⁴ which include a transition from coherent to incoherent dynamics, and symmetry breaking at zero temperature. As for the last property, it has been shown that unbiased ($\epsilon=0$) TSS coupled to a harmonic heat bath with the ohmic spectral density exhibits the localization of a tunneling particle on one of the sites for $\alpha \geq 1$.

For the two-state system we have calculated the population dynamics, $\langle \sigma_z(t) \rangle = \text{Tr}(\sigma(t) \sigma_z)$, which is of most in-

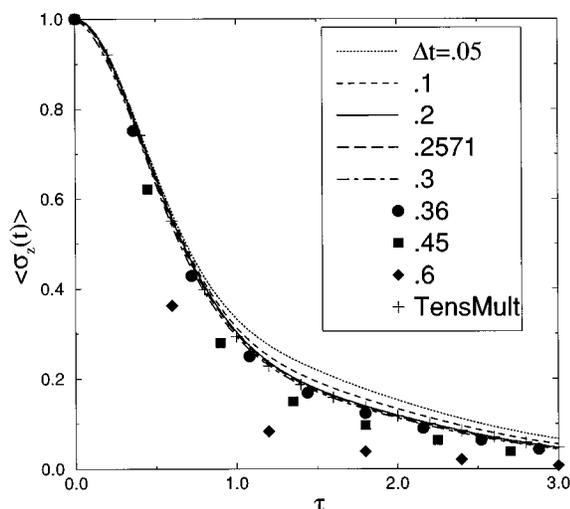


FIG. 2. The population dynamics calculated from the memory equation as a function of a discretization time step. The parameters are $\alpha=0.64$, $T=2.5$, $\omega_c=2.5$, $K=1$.

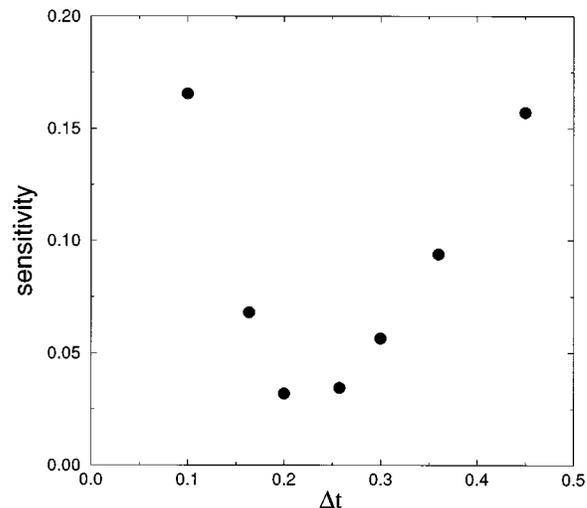


FIG. 3. The sensitivity as a function of time step. The parameters are the same as for Fig. 2.

terest for the study of chemical reaction dynamics. For each of the cases studied, we determined an optimal time step Δt_{opt} for the memory equation. It was obtained by looking at the dependence of the populations of each site $P_i(t)$ on Δt (so that $\Delta k_{\text{max}} \Delta t = t_{\text{max}}$, which was kept constant). At an optimal step we expect $P_i(t)$ to be the least sensitive to a change in Δt . The sensitivity is estimated as the root of the sum of the mean-square displacement of $P_i(t)$ over i between two successive values of Δt , say Δt_1 and Δt_2 , divided by $|\Delta t_1 - \Delta t_2|$. This is illustrated by Figs. 2 and 3, where $\tau = Kt$. The time step was incremented by 0.05 starting from 0.05 and rounded to the nearest value giving integer Δk_{max} . Note, at Δt near 0.2 $\langle \sigma_z(t) \rangle$ depends the least on the time step and practically coincides with the calculation by tensor multiplication scheme done for the same memory length cutoff. The width of the memory kernel was chosen large enough to make sure that Δt_{opt} does not depend on it. For example, in the case presented on Figs. 2 and 3, $\Delta k_{\text{max}} \Delta t$ was set to 1.8. In this way we have determined the optimal time step for all but one examples given here. (The exception was the case presented on Fig. 7.) Here the time step was incremented by 0.005 starting from 0.005. We also estimated whether at this optimal time step the tensor multiplication scheme, whenever it was used for a comparison, still gives reasonable results. To do this we compared the calculation at the current time step with that of $\Delta t/2$ and $2\Delta k_{\text{max}}$ (i.e., keeping the memory length constant). Unfortunately, this is only an estimate, because we could make a comparison only at a smaller memory length; $\Delta k_{\text{max}} \geq 9$ would take enormous numerical effort.

We have tested our method for several sets of parameters: the transition from a coherent (damped oscillations) to an incoherent (a simple exponential decay) regime at low and high temperatures (Figs. 4 and 5); $T=0$ and $\alpha = \frac{1}{2}$ (the parameter at which NIBA predictions are exact for $\omega_c/K \geq 1$) (Figs. 6 and 7); strong system-bath coupling ($\alpha = 2$) at low and high temperatures and at different values of the tunneling element K (Figs. 8 and 9); an adiabatic (sluggish) bath (Fig. 10).

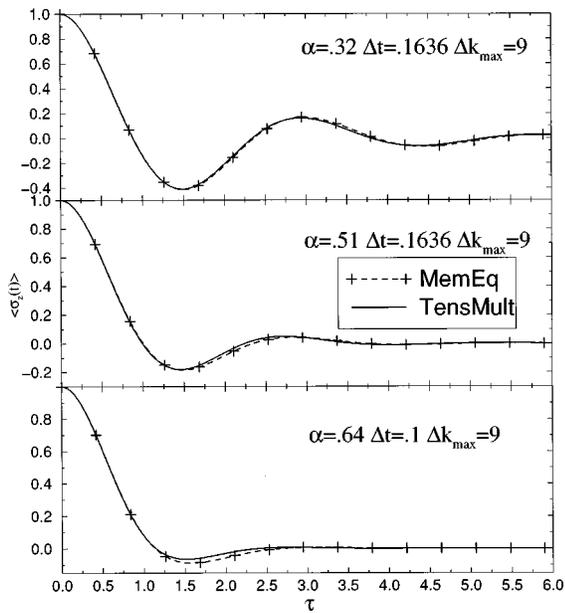


FIG. 4. The transition from the coherent to the incoherent regime at $T=0.625$, $w_c=2.5$, $K=1$ (parameters from Ref. 7).

First of all, we notice that the high temperature dynamics is reproduced more accurately than the low temperature one. Obviously, the method cannot handle accurately enough the dynamics with distinct nonmonoexponential decay and it becomes unreliable when $\Delta k_{\max} \gg 10$ (the top of Fig. 8). For the rest of the plots, $\Delta k_{\max}=9$ was large enough to reach convergence. It can be also noticed that for $\Delta k_{\max} < 10$ the method worked reasonably well in all cases (including the top of Fig. 8) studied here. Such Δk_{\max} means that the width of the memory kernel is not too large. It can be seen from the examples studied that this is the case in a range including both the intermediate and nonadiabatic regimes. The hardest

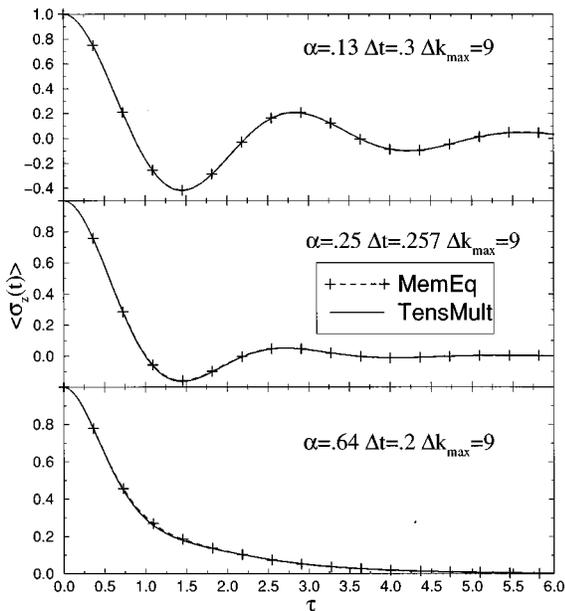


FIG. 5. The transition from the coherent to the incoherent regime at $T=2.5$, $w_c=2.5$, $K=1$ (parameters from Ref. 7).

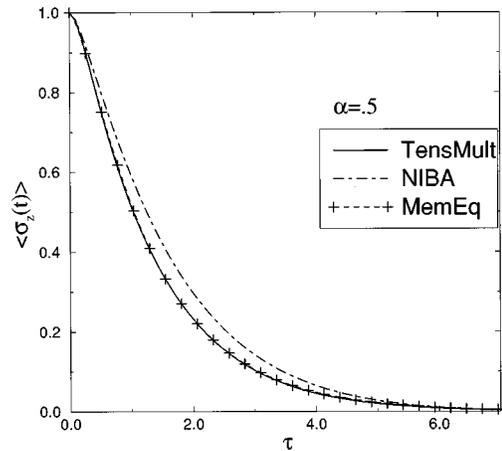


FIG. 6. Zero temperature dynamics compared to NIBA predictions for $\alpha=\frac{1}{2}$, $K=1.0$, $w_c=10.0$; $\Delta t=0.1636$, $\Delta k_{\max}=9$.

test is in the adiabatic regime. This is a regime where the mixed quantum-classical method¹⁹ is a good approximation. As expected, the result of our method substantially deviates from the calculation done by that technique. In that calculation the integration time step was 0.05. The bath was discretized by $M_{\text{modes}}=400$ harmonic modes with uniformly distributed frequencies between 0 and $10\omega_c$. The couplings g_j were obtained from integration of both sides of Eq. (2) by the trapezoidal rule and the assignment of g_j to the term containing $J(\omega_j)$. We ran 2500 trajectories in order to obtain a converged result.

And finally, the result (Fig. 11) for a three-state system coupled to the ohmic bath with parameter from Ref. 30 is in very good agreement with the recent calculations by the filtered propagator technique. This was the most time consuming calculation which took less than a second of CPU time on PowerPC (604e/200MHz) under AIX 4.1

And now let us address the question of the estimate of the optimal time step; in other words, where we should look for it. If A_1 is a bare propagator (i.e., $\Delta k_{\max}=1$ for the reduced density matrix), then the inverse of the fastest rate obtained for A_1 would be the shortest time scale $\tau_{A_1}^{\text{low}}$ (one of

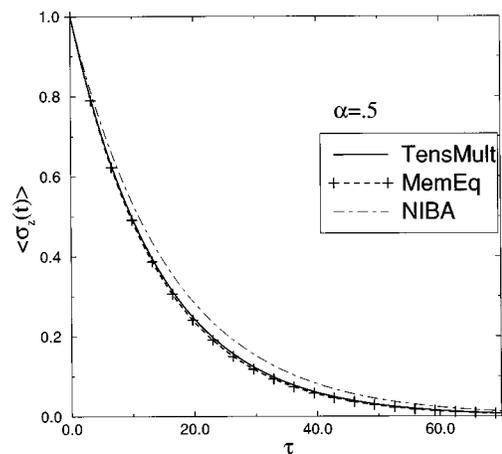


FIG. 7. Zero temperature dynamics compared to NIBA predictions for $\alpha=\frac{1}{2}$, $K=1.0$, $w_c=100.0$; $\Delta t=0.01636$, $\Delta k_{\max}=9$.

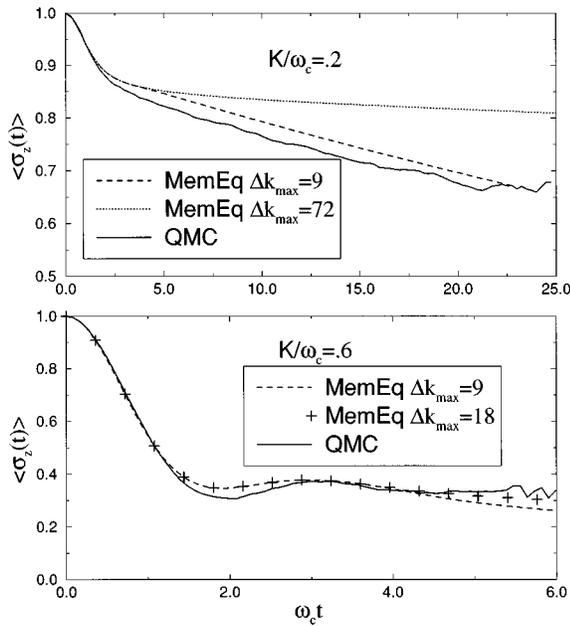


FIG. 8. Simulations for strong system-bath coupling, where $\alpha=2$, $T/\omega_c=0.4$, $\Delta t=0.36$. QMC calculations are from Ref. 9.

the eigenvalues of A_1 will be 1; the others can be written in the form $\exp(-\Gamma_i \Delta t + i\Omega_i \Delta t)$, where Γ_i and Ω_i are real, and Γ_i stands for the decay rate of either diagonal or off-diagonal elements). Since we are expanding correlations of the influence functional in a perturbative series and taking longer and longer range correlations less and less accurately, at an optimal time step, A_1 determines the time scales for the evolution of the system. Therefore, we can expect that Δt at which $|\Delta t - \tau_{A_1}^{\text{low}}(\Delta t)|$ has a minimum is close to an optimal time step (if there are several crossings we choose the smallest Δt). According to Table I this is, indeed, the case.

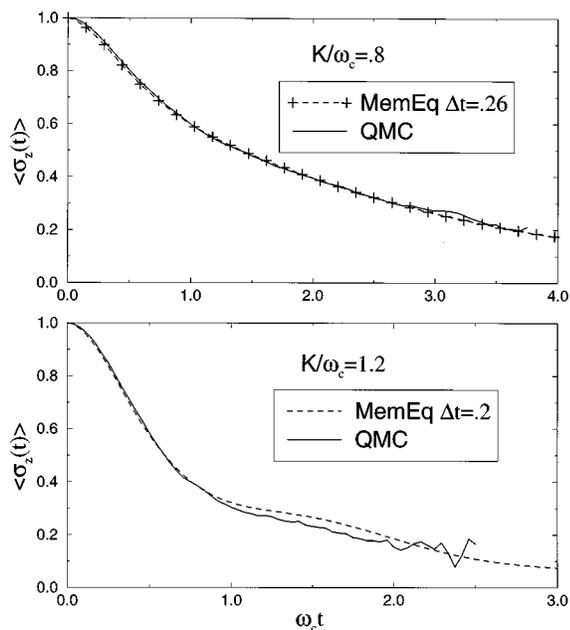


FIG. 9. Simulations for strong system-bath coupling $\alpha=2$, $T/\omega_c=4.0$, $\Delta k_{\max}=9$. QMC calculations are from Ref. 9.

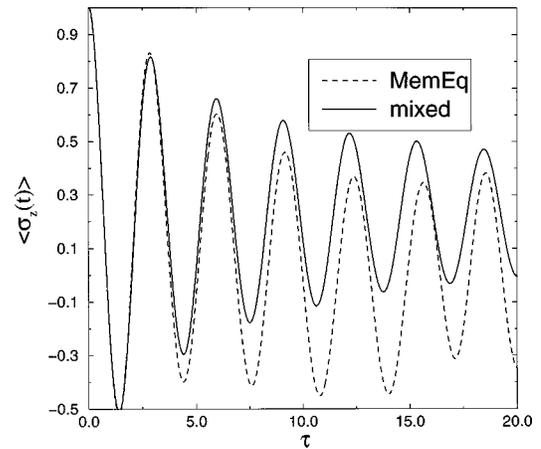


FIG. 10. Memory equation result ($\Delta t=0.2$ and $\Delta k_{\max}=80$) compared to the mixed quantum-classical calculation in the near adiabatic regime ($\alpha=200$, $T=0.2$, $K=1$, $\omega_c=0.01$).

VII. CONCLUSION

We have developed an efficient algorithm for the calculation of the quantum dynamics of a one-dimensional system bilinearly coupled to a harmonic bath. The algorithm is based on an approximation of Makri and Makarov's tensor multiplication scheme which, in its turn, is based on their observation that the broad spectrum of the environment to which the system is coupled leads to a finite range of correlations among positions of the system at different times (i.e., the finite width of the memory kernel in the influence functional which is equal to $\Delta k_{\max} \Delta t$). Our method presents the reduced density matrix as the convolution of its past values with an integral equation kernel, which is constructed approximately. Thus the propagation cost of the reduced density matrix scales as $O(n^4 \Delta k_{\max})$ in CPU and storage. The cost of the operator construction scales as $O(n^6 \Delta k_{\max})$. Since for the most interesting cases studied in the literature $\Delta k_{\max} \sim 10$, this means huge savings in computer resources compared to Makri and Makarov's tensor multiplication

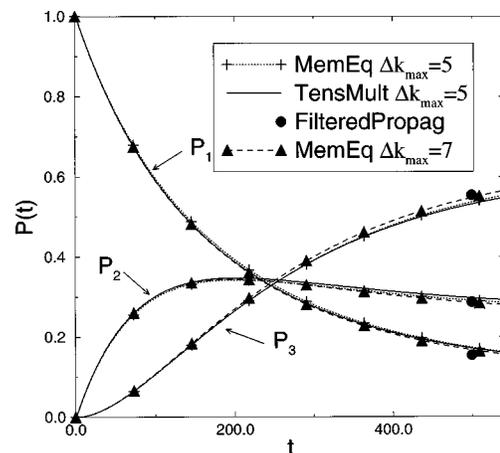


FIG. 11. The site population dynamics for the three-state system coupled to an ohmic bath with parameters from Ref. 30. The time step for memory equation calculations and tensor multiplication scheme was chosen to be 0.72. The circles are the final converged result ($\Delta t=0.3$, $\Delta k_{\max}=16$) obtained by the filtered propagator technique (see Table 5 of the Ref. 30).

TABLE I. Estimates, $\tau_{A_1}^{\text{low}}$, of the optimal steps Δt_{opt} for different parameters of both spin-boson models.

α	T	w_c	K	Δt_{opt}	$\tau_{A_1}^{\text{low}}$
0.32	0.625	2.5	1.0	0.16	0.5
0.51	0.625	2.5	1.0	0.16	0.5
0.64	0.625	2.5	1.0	0.1	0.45
0.13	2.5	2.5	1.0	0.3	0.5
0.25	2.5	2.5	1.0	0.26	0.8
0.64	2.5	2.5	1.0	0.2	0.25
0.5	0	10.	1.0	0.16	0.55
0.5	0	100.	1.0	0.016	0.015
2.0	0.4	1.0	0.2	0.36	0.4
2.0	0.4	1.0	0.6	0.36	0.45
2.0	4.0	1.0	0.8	0.26	0.15
2.0	4.0	1.0	1.2	0.2	0.15
200	0.2	.01	1.0	0.2	0.5
three-state system				0.72	0.25

scheme which has a CPU cost which scales as $O(n^{2(\Delta k_{\text{max}}+1)})$, especially for $n > 2$. Although the tensor multiplication algorithm was substantially improved³⁰ by the important path selection technique, the configuration space for the QMC used in it grows exponentially with Δk_{max} imposing limits on its efficiency. In most of the cases studied our results are in good agreement with those of QMC and tensor multiplication schemes.

Our method can be viewed as an extension of NIBA and Redfield theory from the nonadiabatic to intermediate regime where the time scales of the bath and system dynamics are of the same order and other approximate methods break down.

Some issues remain unresolved. Most importantly, we need to find a consistent, yet an efficient, way of finding the integral equation kernel, which will allow us to avoid searching for the optimal time step, and to improve results at lower temperatures.

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