Parsing the Influence Functional: Harmonic Bath Mapping and Anharmonic Small Matrix Path Integral

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Abstract

The influence functional (IF) encodes all the information required for calculating dynamical properties of a system in contact with its environment. A direct and simple procedure is introduced for extracting from a few numerical evaluations of the IF, without computing time correlation functions or evaluating integrals, the parameters required for path integral calculations, either within or beyond the harmonic mapping, and for assessing the accuracy of the harmonic bath approximation. Further, the small matrix decomposition of the path integral (SMatPI) is extended to anharmonic environments and the required matrices are constructed directly from the IF.

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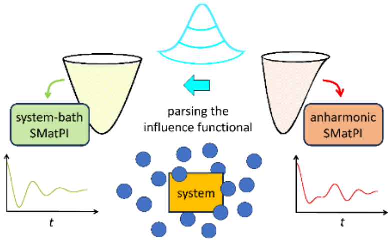

Theoretical studies of quantum mechanical processes in systems with many degrees of freedom often employ the system-bath simplification, where the observed degree(s) of freedom constitute the "system" while all other variables that comprise the system's "environment" are described in terms of independent harmonic oscillators that couple to the system coordinate. Besides offering an excellent starting point for incorporating the generic dissipative effects of condensed phase environments,[1-3] the system-bath decomposition leads to insightful and often near-quantitative descriptions of chemical transformations along a reaction path,[4-5] the impact of intramolecular and lattice vibrations on tunneling dynamics,[6] vibronic effects in spectroscopy,[7-8] charge and energy transfer in solution or biomolecules,[9] and a plethora of other phenomena. From a practical perspective, numerically exact and efficient real-time path integral methods for simulating the dynamical processes described by system-bath Hamiltonians have been available since the 1990s[10-11] and developments in this direction continue at a vigorous pace.

Expressing the Hamiltonian for a process in a fluid or biological environment in system-bath form requires calculating a time correlation function for the environment and performing a Fourier-type transformation to construct a spectral density.[12-13] The time-discretized Gaussian influence functional (IF), which contains all the effects from the effective harmonic bath on the dynamics of the system, can then be constructed in terms of coefficients given by integrals of the spectral density.[10] The conventional procedure is in principle straightforward but involves several steps and may encounter numerical difficulties, as time correlation functions can be noisy and may not decay sufficiently rapidly for accurate transformation to the frequency domain. A more direct approach that avoids the transformation to the frequency domain but requires the evaluation of two-dimensional integrals has been described in recent work.[14] Both procedures require availability of the correlation function on a dense time grid. To date, no methods are available for assessing the accuracy of the harmonic bath mapping. Adding to the IF terms beyond second order would necessitate the calculation of higher-order correlation functions, an impractical task. Rigorous methods for computing the system's reduced density matrix (RDM) beyond the harmonic bath approximation are rather limited in scope and performance.

To address these challenges, the present Letter introduces a direct procedure for (i) obtaining the IF coefficients for the system-bath mapping of a process, (ii) checking the validity of the harmonic bath approximation, and (iii) constructing the required IF components for propagation through a small matrix path integral (SMatPI) decomposition that is not limited to harmonic baths. The procedure involves parsing the IF, is rigorous, and requires minimal effort. Applications on systems of coupled two-level systems (TLS) are presented, which illustrate the quantitative nature as well as the failure of the Gaussian IF assumption under a variety of conditions.

The Hamiltonian is expressed in the general form

$$\hat{H} = \hat{H}_0 + \hat{H}_{\text{sb}} \tag{1}$$

where H_0 is the Hamiltonian of the system and H_{sb} describes the general environment or bath and its interaction with the system coordinate $s = \sum_i \kappa_i \left| \varphi_i \right\rangle \left\langle \varphi_i \right|$. The discretized path integral expression for the RDM at the time $N\Delta t$ (where Δt is the path integral time step) has the form

$$\tilde{\rho}^{(N0)}_{s_N^\pm s_0^\pm} = \sum_{s_{N-1}^\pm}^{\sigma_n} \cdots \sum_{s_1^\pm=1}^{\sigma_n} G_{s_N^\pm s_{N-1}^\pm} \cdots G_{s_1^\pm s_0^\pm} F^{(N0)}_{s_N^\pm \cdots s_0^\pm} \tag{2}$$

Here $G_{s_{k+1}^\pm s_k^\pm}$ is the product of forward and backward short-time system propagators and $F^{(N0)}_{s_N^\pm \cdots s_0^\pm}$ is the influence functional. If the isolated bath with Hamiltonian H_b is initially at a temperature $T = 1/k_\mathrm{B}\beta$, i.e. $\rho_\mathrm{b}(0) = Z_\mathrm{b}^{-1} \exp\left(-\beta H_\mathrm{b}\right)$, and the system is in the state $\left|s_0^+\right\rangle\left\langle s_0^-\right|$, the IF is given by the expression

$$\begin{aligned} F^{(N0)}_{s_N^\pm \cdots s_0^\pm} = Z_\mathrm{b}^{-1} \operatorname{Tr}_\mathrm{b} \Big[& e^{-i\hat{H}_\mathrm{sb}\left(s_N^+\right)/\Delta t/2\hbar} e^{-i\hat{H}_\mathrm{sb}\left(s_{N-1}^+\right)/\Delta t/\hbar} \cdots e^{-i\hat{H}_\mathrm{sb}\left(s_0^+\right)/\Delta t/2\hbar} \\ & e^{-\beta\hat{H}_\mathrm{b}} e^{i\hat{H}_\mathrm{sb}\left(s_0^-\right)/\Delta t/2\hbar} e^{i\hat{H}_\mathrm{sb}\left(s_1^-\right)/\Delta t/\hbar} \cdots e^{i\hat{H}_\mathrm{sb}\left(s_N^-\right)/\Delta t/2\hbar} \Big] \end{aligned} \tag{3}$$

where H_b is the Hamiltonian of the isolated bath. Without losing generality, suppose that the system-bath coupling vanishes at the value $s = 0$, i.e. $H_\mathrm{sb}(0) = H_\mathrm{b}(0)$ at the origin. Setting all $s_k^\pm = 0$ except s_k^+ and $s_{k+\Delta k}^+$ with $k, k+\Delta k \neq 0, N$, it is easy to see that Eq. (3) becomes

$$F^{(N0)}_{s_N^\pm \cdots s_0^\pm} = \operatorname{Tr}\left[e^{-i\hat{H}_\mathrm{sb}\left(s_{k+\Delta k}^+\right)/\Delta t/\hbar} e^{-i(\Delta k-1)\hat{H}_\mathrm{b}\Delta t/\hbar} e^{-i\hat{H}_\mathrm{sb}\left(s_k^+\right)/\Delta t/\hbar} \hat{\rho}_\mathrm{b}(0)\, e^{i(\Delta k+1)\hat{H}_\mathrm{b}\Delta t/\hbar} \right] \tag{4}$$

showing that the influence functional depends only on the difference Δk. Similar expressions can be obtained by giving three or more variables nonzero values. Such expressions demonstrate that the influence functional is translationally invariant away from the endpoints, regardless of the form of the Hamiltonian.

Earlier work[13] showed that the IF from a general anharmonic environment is the exponential of a power series in the coordinates of the forward and backward system paths,

$$F^{(N0)}_{s_N^\pm \cdots s_1^\pm s_0^\pm} = e^{-\sum\limits_{k=1}^{N}\left(\alpha_k^+ s_k^+ + \alpha_k^- s_k^-\right) - \sum\limits_{k=1}^{N}\sum\limits_{k'=1}^{k}\left(\beta_{kk'}^{++} s_k^+ s_{k'}^+ + \beta_{kk'}^{+-} s_k^+ s_{k'}^- + \cdots\right) - \sum\limits_{k=1}^{N}\sum\limits_{k'=1}^{k}\sum\limits_{k''=1}^{k'} \left(\gamma_{kk'k''}^{+++} s_k^+ s_{k'}^+ s_{k''}^+ + \gamma_{kk'k''}^{++-} s_k^+ s_{k'}^+ s_{k''}^- + \cdots\right) - \cdots} \tag{5}$$

where the coefficients of the linear terms are given by bath averages, while the coefficients of the quadratic, cubic, etc. terms are discretized forms of two-, three-, etc. time correlation functions of the environment. In the special case where the interaction between the system and the environment is diluted over a large number of degrees of freedom, all terms beyond quadratic order vanish. The resulting Gaussian influence functional defines an effective harmonic bath, whose two-time correlation function equals that of the anharmonic medium and which produces the same system dynamics as the actual environment. This equivalence, which has been widely used in classical statistical mechanics,[12] can be employed to map a complex (e.g. biological) environment on a simple harmonic bath, inviting the use of simulation methods suitable for system-bath Hamiltonians.

The cumulant expansion of the influence functional also shows that (as long as the environment is large) the temporal correlations induced by the bath, which render the dynamics non-Markovian, have a finite span. Exploiting the finite memory length has led to a general iterative decomposition of the path integral[15] that is based on the numerical evaluation of the influence functional. The resulting algorithm[15] is the generalization of the iterative quasi-adiabatic propagator path integral (QuAPI) algorithm[16-17] to anharmonic environments, for which the influence functional is not available analytically. Its main drawback is the storage and manipulation of tensors, which when combined with the computationally intensive evaluation of the IF at each sequence of system coordinates, can be impractical.

To overcome these difficulties, this Letter proceeds to parse the IF from general, anharmonic environments, assuming that the latter may be computed using available algorithms (e.g. see [18] or [19]). The starting point is the cumulant expression, Eq. (5). Note that the IF coefficients satisfy certain symmetry relations, e.g. $\beta_{kk'}^{-+} = -\left(\beta_{kk'}^{+-}\right)^*$ and that the linear terms may be eliminated by shifting the system coordinate. Setting $s_{k'}^{\pm} = 0$ for all k' except $s_k^+ = x$, where x can be given arbitrary values, gives

$$F^{(N0)}_{s_k^+ = x} = e^{-\alpha_k^+ x - \beta_{kk}^{++} x^2 - \gamma_{kkk}^{+++} x^3 - \cdots} \tag{6}$$

where the subscript in the IF labels only the path integral variables that are not equal to zero. Since it is assumed that the IF can be computed for any sequence of system coordinates, it is straightforward to evaluate Eq. (6) at several values of x. One can then easily check whether the exponent is a quadratic function, and if so, determine the diagonal (single-time) influence functional coefficients. If the linear term is equal to zero, one obtains

$$\beta_{kk}^{++} = -\frac{\ln F^{(N0)}_{s_k^+ = x}}{x^2} = -\frac{\ln F^{(20)}_{s_1^+ = x}}{x^2}, \quad 0 < k < N \ . \tag{7}$$

On the other hand, if the linear term does not vanish, evaluation of Eq. (6) at two values x_1 and x_2 uniquely determines the coefficients α_k^+ and β_{kk}^{++} as

$$\beta_{kk}^{++} = \frac{x_1 \ln F^{(N0)}_{s_k^+ = x_2} - x_2 \ln F^{(N0)}_{s_k^+ = x_1}}{x_1 x_2 \left(x_1 - x_2\right)}, \quad \alpha_k^+ = -\frac{x_1^2 \ln F^{(N0)}_{s_k^+ = x_2} - x_2^2 \ln F^{(N0)}_{s_k^+ = x_1}}{x_1 x_2 \left(x_1 - x_2\right)} \ . \tag{8}$$

Proceeding similarly, one can obtain the values of α_k^-, β_{kk}^{+-}, etc., although these coefficients can also be determined from the symmetry relations mentioned above.

It is also easy to obtain the two-time (off-diagonal) influence functional coefficients for the effective harmonic bath by setting $s_{k'}^{\pm} = 0$ for all k' except k and $k + \Delta k$, with $s_k^+ = s_{k+\Delta k}^+ = x$. Since the coefficients of the linear and diagonal quadratic terms have already been determined, this step leads to

$$\beta_{k+\Delta k, k}^{++} = -\frac{\ln F^{(k+\Delta k, k)}_{s_{k+\Delta k}^+ = x, s_k^+ = x}}{x^2} - \frac{\alpha_{k+\Delta k}^+ + \alpha_k^+}{x} - \left(\beta_{k+\Delta k, k+\Delta k}^{++} + \beta_{kk}^{++}\right). \tag{9}$$

Equations (7)-(9) completely specify the IF coefficients for the effective harmonic bath from a small number of simple and efficient calculations. They avoid altogether the computation of the two-time correlation function of the environment on a dense time grid and the evaluation of integrals of the latter. Using the determined IF coefficients, one can compute the system's RDM (or any other property) using any of the available methods for system-bath dynamics. It is also possible to calculate the cubic and quartic IF coefficients through a similar procedure.

If the above procedure determines that the influence functional deviates significantly from the Gaussian form, one must proceed differently. Recent work[20] outlined the generalization of the small matrix decomposition of the path integral[21-22] (SMatPI) for system-bath dynamics to situations where the IF does not have the Gaussian form. The main idea was described in the context of the modular path integral (MPI) algorithm[23-24] with a SMatPI decomposition of path amplitudes,[25] and is developed below for the most general situation.

Regrouping the components in Eq. (5) according to the number of path integral variables they contain and combining one- and two-variable factors, the influence functional from a general environment can be written in the form

$$F^{(N0)}_{s_N^\pm \cdots s_0^\pm} = \prod_{k=1}^{N} \prod_{k'<k} f^{(kk')}_{s_k^\pm s_{k'}^\pm} \prod_{k=1}^{N} \prod_{k'<k} \prod_{k''<k'} f^{(kk'k'')}_{s_k^\pm s_{k'}^\pm s_{k''}^\pm} \cdots \tag{10}$$

where, with ordinary values of the time step required for convergence, all factors are of order unity. The SMatPI decomposition employs the auxiliary propagation matrices $\mathbf{R}^{(rr')}$, which are RDMs with appropriate IF boundary conditions[22] (for propagation if $r < N$ or termination if $r = N$). Defining

$$M^{(10)}_{s_1^\pm s_0^\pm} \equiv R^{(10)}_{s_1^\pm s_0^\pm} = G_{s_1^\pm s_0^\pm} f^{(10)}_{s_1^\pm s_0^\pm}, \quad M^{(21)}_{s_2^\pm s_1^\pm} = G_{s_2^\pm s_1^\pm} f^{(21)}_{s_2^\pm s_1^\pm}, \tag{11}$$

the propagation RDM at the second time point is expressed as

$$R^{(20)}_{s_2^\pm s_0^\pm} = \sum_{s_1^\pm=\kappa_1}^{\kappa_n} M^{(21)}_{s_2^\pm s_1^\pm} R^{(10)}_{s_1^\pm s_0^\pm} + M^{(20)}_{s_2^\pm s_0^\pm} \tag{12}$$

where

$$M^{(20)}_{s_2^\pm s_0^\pm} \equiv \sum_{s_1^\pm=\kappa_1}^{\kappa_n} G_{s_2^\pm s_1^\pm} G_{s_1^\pm s_0^\pm} f^{(21)}_{s_2^\pm s_1^\pm} f^{(10)}_{s_1^\pm s_0^\pm} \left(f^{(20)}_{s_2^\pm s_0^\pm} f^{(210)}_{s_2^\pm s_1^\pm s_0^\pm} - 1 \right). \tag{13}$$

is the residual. Eq. (13) is the first step in the SMatPI decomposition and is analogous to the corresponding matrix for a harmonic bath, although in the present case the factors do not generally have a Gaussian form and the term in the parenthesis is a function of three variables. Just as in the harmonic bath case, the presence of the small factor $f^{(210)}_{s_2^\pm s_1^\pm s_0^\pm} - 1$ implies that the elements of the residual matrix $\mathbf{M}^{(20)}$ have small values compared to those of $\mathbf{M}^{(10)}$.

Proceeding to the next time point, the SMatPI decomposition of the propagation RDM becomes

$$R^{(30)}_{s_3^\pm s_0^\pm} = \sum_{s_2^\pm=\kappa_1}^{\kappa_n} M^{(32)}_{s_3^\pm s_2^\pm} R^{(20)}_{s_2^\pm s_0^\pm} + \sum_{s_1^\pm=\kappa_1}^{\kappa_n} M^{(31)}_{s_3^\pm s_1^\pm} R^{(10)}_{s_1^\pm s_0^\pm} + M^{(30)}_{s_3^\pm s_0^\pm}, \tag{14}$$

and straightforward algebra shows that the residual is given by

$$M^{(30)}_{s_3^\pm s_0^\pm} \equiv \sum_{s_2^\pm=\kappa_1}^{\kappa_n} \sum_{s_1^\pm=\kappa_1}^{\kappa_n} G_{s_3^\pm s_2^\pm} G_{s_2^\pm s_1^\pm} G_{s_1^\pm s_0^\pm} f^{(32)}_{s_3^\pm s_2^\pm} f^{(21)}_{s_2^\pm s_1^\pm} f^{(10)}_{s_1^\pm s_0^\pm} \\ \times \left[f^{(31)}_{s_3^\pm s_1^\pm} f^{(321)}_{s_3^\pm s_2^\pm s_1^\pm} \left(f^{(20)}_{s_2^\pm s_0^\pm} f^{(30)}_{s_3^\pm s_0^\pm} f^{(210)}_{s_2^\pm s_1^\pm s_0^\pm} f^{(320)}_{s_3^\pm s_2^\pm s_0^\pm} f^{(310)}_{s_3^\pm s_1^\pm s_0^\pm} f^{(3210)}_{s_3^\pm s_2^\pm s_1^\pm s_0^\pm} - 1 \right) - \left(f^{(20)}_{s_2^\pm s_0^\pm} f^{(210)}_{s_2^\pm s_1^\pm s_0^\pm} - 1 \right) \right] \tag{15}$$

Analogous expressions can be obtained for higher order residuals.

In the case of a harmonic bath, if the environment is sufficiently large, the two-time correlation function decays to zero within a finite interval known as the memory length $L\Delta t$. This behavior is observed in anharmonic baths as well, where all time correlation functions decay to zero when the difference of any two variables exceeds the memory interval. It follows that the IF factors rapidly approach unity when the memory length is exceeded. Just as in the case of a Gaussian IF, the SMatPI residuals are dominated by the memory (not by the entanglement of variables they contain).[21-22] For example, if $L = 2$ Eq. (15) simplifies to

$$M^{(30)}_{s_3^\pm s_0^\pm} \equiv \sum_{s_2^\pm=\kappa_1}^{\kappa_n} \sum_{s_1^\pm=\kappa_1}^{\kappa_n} G_{s_3^\pm s_2^\pm} G_{s_2^\pm s_1^\pm} G_{s_1^\pm s_0^\pm} f^{(32)}_{s_3^\pm s_2^\pm} f^{(21)}_{s_2^\pm s_1^\pm} f^{(10)}_{s_1^\pm s_0^\pm} \left(f^{(31)}_{s_3^\pm s_1^\pm} f^{(321)}_{s_3^\pm s_2^\pm s_1^\pm} - 1 \right) \left(f^{(20)}_{s_2^\pm s_0^\pm} f^{(210)}_{s_2^\pm s_1^\pm s_0^\pm} - 1 \right). \tag{16}$$

This expression shows that the elements of $\mathbf{M}^{(30)}$ are smaller than those of $\mathbf{M}^{(20)}$. This trend continues, with the elements of $\mathbf{M}^{(r0)}$ decreasing rapidly with $r > L$. Eventually, the residuals $\mathbf{M}^{(kk')}$ become negligible when the time separation $(k - k')\Delta t$ exceeds the entanglement time $r_{\max}\Delta t$, and thus may be omitted in subsequent steps, leading to the SMatPI decomposition

$$\mathbf{R}^{(k0)} = \sum_{k'=1}^{k-1} \mathbf{M}^{(kk')} \cdot \mathbf{R}^{(k'0)}, \; k > r_{\max}. \tag{17}$$

An analogous expression (with endpoint IF factors[21-22]) gives the RDM at the desired time.

Since the influence functional components are translationally invariant away from endpoints, the propagation SMatPI matrices depend only on the time separation, i.e. $\mathbf{M}^{(k+\Delta k,k)} = \mathbf{M}^{(1+\Delta k,1)}$ for $k \neq 0$ (but $\mathbf{M}^{(1+\Delta k,1)} \neq \mathbf{M}^{(\Delta k,0)}$). Re-labeling $\mathbf{M}^{(kk')}$ as $\mathbf{M}^{(\Delta k)}$ in Eq. (17), one sees that the SMatPI decomposition of the auxiliary propagation matrix $\mathbf{R}^{(rr')}$ has the structure of the Nakajima-Zwanzig generalized quantum master equation[26-27] (GQME), and the SMatPI matrices become the discretized elements of the GQME kernel. The SMatPI decomposition of the actual RDM differs slightly because of IF endpoint effects, which are the consequence of a symmetric partitioning of the short-time propagator. If, instead, the path integral is discretized using an asymmetric partitioning, the SMatPI decomposition takes the GQME form where all kernel matrices depend only on time separation.[22] Since the Trotter error vanishes in the limit $\Delta t \to 0$, the GQME is recovered from a SMatPI decomposition.

The SMatPI matrices $\mathbf{M}^{(1+\Delta k,1)}$ are given by the residuals and are obtained recursively if $\mathbf{M}^{(21)}$ is provided. The starting matrix $\mathbf{M}^{(21)}$ can be achieved by following a procedure similar to that described for the harmonic bath mapping. Evaluating the IF with $s_k^\pm = 0$ for all k except $s_1^+ = x,\ s_2^+ = y$ and removing the component that depends only on $s_1^+ = x$, one obtains the value of $f^{(21)}_{s_2^+=x, s_1^+=y}$, which determines $\mathbf{M}^{(21)}$.

To illustrate these ideas, consider a TLS with right and left states labeled R and L, described by the Hamiltonian

$$\hat{H}_0 = -\hbar\Omega\hat{\sigma}_x^0 = -\hbar\Omega\left(|\mathrm{R}\rangle\langle\mathrm{L}| + |\mathrm{L}\rangle\langle\mathrm{R}|\right) \tag{18}$$

where the level splitting is $2\hbar\Omega$, and suppose that the TLS is coupled to d "bath TLSs" according to the Hamiltonian

$$\hat{H}_\mathrm{b} = -\sum_{i=1}^{d}\left(\frac{1}{2}\hbar\omega_i\hat{\sigma}_x^i + c_i\hat{s}\,\hat{q}_i\right), \quad \hat{s} = \gamma\hat{\sigma}_z^0, \quad \hat{q}_i = \sqrt{\frac{\hbar}{2\omega_i}}\hat{\sigma}_z^i \tag{19}$$

where σ_x^0, σ_z^0 and σ_x^i, σ_z^i are the Pauli spin matrices for the system and bath, respectively, and $\gamma = 1$. The parameter γ is introduced to allow the scaling of the system TLS "coordinate" σ_z^0. Coupled TLSs (where the two states represent the ground and excited electronic states of a molecule) are often employed in studies of excitation energy transfer in molecular aggregates. Further, the TLS Hamiltonian describes a spin-½ interacting with other spins, a situation of much current interest because of its relevance to quantum information science. Besides its physical relevance, the TLS bath offers an excellent testbed for demonstrating the theoretical ideas described in this Letter: A single TLS is a highly nonlinear system, inducing dynamical effects that can be differ vastly from those of a harmonic oscillator. In addition, the correlation function of a TLS is available analytically, simplifying the harmonic bath mapping in the $d \to \infty$ limit.[28-29]

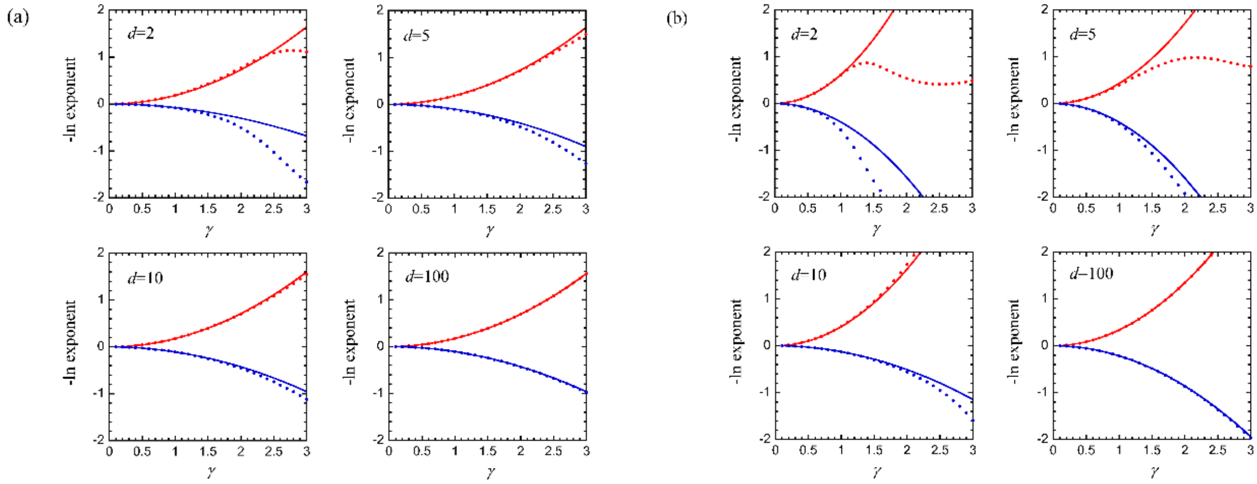

Fig. 1. Natural logarithm of the influence functional as a function of the coordinate scaling parameter γ for the TLS bath with $\xi = 1, \omega_\mathrm{c} = 10\Omega$ at a temperature $\hbar\Omega\beta = 1$ for $d = 2,5,10$ and 100. The path integral time step is $\Delta t = 0.1\Omega^{-1}$. (a) $s_1^+ = \gamma$, (b) $s_1^+ = s_6^+ = \gamma$.

In the limit of $d \to \infty$ the bath frequencies ω_i and coupling parameters c_i are assumed to be related through the spectral density function $J(\omega) = \frac{1}{2}\pi\xi\hbar\omega e^{-\omega/\omega_\mathrm{c}}$, which peaks at ω_c and ξ is a measure of the overall coupling strength. With finite values of *d*, the frequencies ω_i are obtained by applying the logarithmic discretization,[13-14] which in the case of a harmonic bath partitions the spectral density into regions of equal reorganization energies. The TLS is initially placed in the R state, while the bath TLSs are at thermal equilibrium at the reciprocal temperature $\beta = 1/k_{\mathrm{B}}T$. The IF from the TLS bath is calculated numerically using matrix operations.[18]

Figure 1 shows the logarithm of the influence functional for $\xi = 1$, $\omega_{\mathrm{c}} = 10\Omega$ at a temperature $\hbar\Omega\beta = 1$ with (a) $s_1^+ = \gamma$ and (b) $s_1^+ = s_6^+ = \gamma$ (and all other path variables set to zero), for several values of *d*. The values of the single- and two-time IF coefficients are also determined within the Gaussian approximation according to Equations (6)-(8), respectively, using a small value of γ. When the number of bath TLSs is small, the departure from the Gaussian form is visibly obvious. The anharmonicity effects decrease with increasing *d* and become very small for $d > 1000$. In this case, the IF coefficient obtained is independent of the chosen value of γ, indicating that the Gaussian response limit has been reached and the collective effect of the bath TLSs is the same as that of a bath of harmonic oscillators whose parameters can (depending on the temperature) differ significantly from those of the TLSs).

Figure 2 shows the time evolution of the population $P_{\mathrm{R}}(t)$ (i.e. the diagonal RDM element) of the system TLS, with bath TLS parameters $\xi = 0.5$ and $\omega_{\mathrm{c}} = 10\Omega$, for $d = 5, 10$ and 50. The TLS bath is initially at the temperature $\hbar\Omega\beta = 5$, while the system TLS is in the R state. The path integral time step set is set to $\Omega\Delta t = 0.2$. The panels compare the results calculated with the anharmonic SMatPI algorithm to those under the effective harmonic bath approximation, obtained with the SMatPI module of the PATHSUM package[30] using IF coefficients from Equations (8) and (9). For $d = 5$ and 10, exact results obtained by full diagonalization of the Hamiltonian are also presented.

Time correlation functions in a finite-dimensional bath exhibit prominent recurrences of varying amplitude, which reflect the many time scales that characterize the dynamics and which induce infinite memory. As the number *d* of bath degrees of freedom is increased, such recurrences become weaker and the population curves become smoother. This behavior implies that the iterative evaluation of the RDM (either with full anharmonicity or under the Gaussian mapping) cannot converge with small values of *d*, but for a fixed value of $r_{\max} = L$ convergence over longer time intervals is attained as the number of bath TLSs increases. For $d = 5$ and 10 the SMatPI results are converged up to $\Omega t \simeq 4$, while for $d = 50$ they are converged over much longer times and practically reach equilibrium.

In both cases where diagonalization of the full Hamiltonian is possible, the anharmonic SMatPI results are in close agreement with the exact calculations. Very small deviations are the consequence of Trotter error in the QuAPI splitting[10] of the system-bath Hamiltonian. The results obtained with the effective harmonic bath approximation differ significantly from the exact results for $d = 5$ and 10 and the discrepancies grow with time, suggesting that anharmonic corrections are important with the chosen parameters. When the number of bath spins is increased to 50, the effective harmonic approximation becomes nearly quantitative, although small differences from the results obtained with the anharmonic SMatPI algorithm are seen even in this case. Upon further increasing the number of bath spins, the effective harmonic bath results approach and eventually become identical to the exact path integral results.

In the $d \to \infty$ limit the influence functional from the TLS bath becomes Gaussian, i.e. the TLS bath becomes equivalent to a bath of harmonic oscillators with a modified, temperature-dependent spectral density.[13] Since the two-time correlation function of a two-level system can be obtained analytically, the spectral density of the effective harmonic bath can be calculated exactly.[28-29] With a large number of bath spins ($d \simeq 10^3$) the IF coefficients obtained using Equations (8) and (9) are identical through several significant figures to those calculated with the harmonic bath spectral density from the analytical correlation function, and the population results are identical as well.

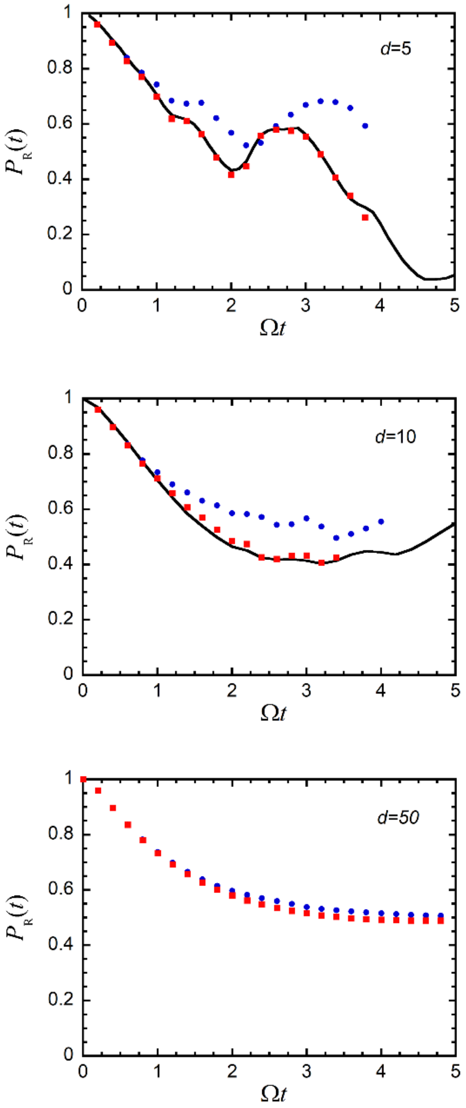

Fig. 2. Population of the R state as a function of time for a TLS coupled to a bath of d TLSs given in Equations (18) and (19). Red squares: results obtained with the fully anharmonic SMatPI algorithm. Blue circles: results obtained with the effective harmonic bath from the Gaussian IF approximation using IF coefficients from Equations (8) and (9). Black line: exact results from diagonalization of the full Hamiltonian.

As a last example, the system TLS is coupled to another identical TLS through the term $-J\hat{\sigma}_z^0\hat{\sigma}_z^1$ with $J = 0.5\hbar\Omega$ and also (weakly) to a continuous harmonic bath with $\xi = 0.1$ and $\omega_{\mathrm{c}} = 10\Omega$ at an intermediate temperature $\beta^{-1} = \hbar\Omega$. The bath TLS is initially placed in an eigenstate of its own Hamiltonian. The inclusion of a dissipative environment leads to smoother dynamics, but the coupled single-TLS bath gives rise to infinite memory. However, accurate and well-converged results over long times are obtained by processing the RDM for the two-spin system coupled to a harmonic bath, which was computing with the standard SMatPI algorithm.

Figure 3 compares the time evolution of P_{R} for the system TLS in the presence of the composite bath, obtained using the anharmonic SMatPI algorithm, the effective harmonic approximation with coefficients obtained through the IF parsing procedure, and the fully converged harmonic SMatPI results for the pair. In all cases the SMatPI results with $L = r_{\max} = 16$ are converged up to approximately $\Omega t \simeq 4$. In order to decipher the roles of the two separate bath components, results are also presented for the system TLS with the environment composed of either just the bath TLS ($J = 0.5\hbar\Omega$, $\xi = 0$) or only the harmonic bath ($J = 0$, $\xi = 0.1$).

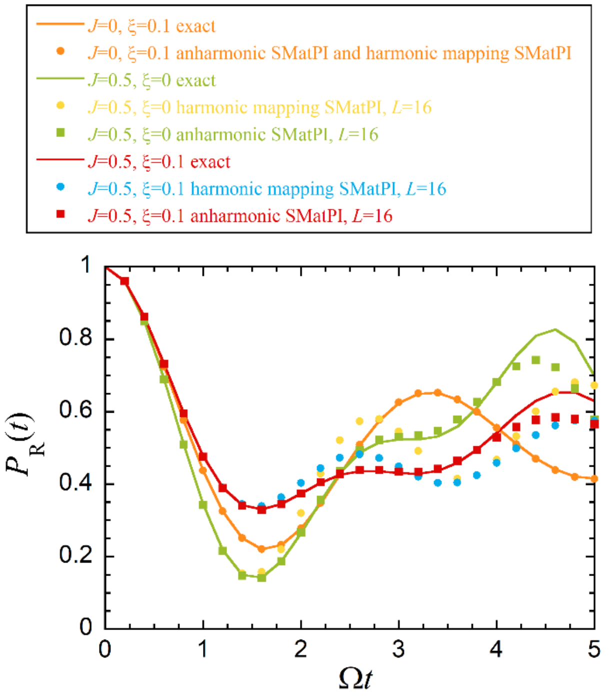

Fig. 3. Population of the R state as a function of time for a TLS coupled to a composite environment consisting of a TLS and a harmonic bath. The lines show numerically exact results obtained with the harmonic SMatPI algorithm for the two TLSs coupled to a harmonic bath. Squares show results obtained with the anharmonic SMatPI algorithm with $L = r_{\max} = 16$, while circles show the results of the harmonic mapping. Lime green and yellow: $J = 0.5\hbar\Omega$, $\xi = 0$. Orange: $J = 0$, $\xi = 0.1$. Red and blue: $J = 0.5$, $\xi = 0.1$.

Even though the overall damping effects of these two environments are comparable in magnitude, the TLS population dynamics differ significantly. In the presence of a weakly dissipative harmonic bath, the system population exhibits underdamped oscillatory dynamics. The IF is Gaussian in this case and the SMatPI calculation with IF coefficients from the parsing procedure yields exact results. The generalized anharmonic SMatPI algorithm also produces identical results. In contrast, coupling to a single-TLS bath modulates the system dynamics but does not lead to equilibration. Even with this single-TLS bath, the effective harmonic approximation is seen to capture the correct dynamics up to the first local minimum of the population, but subsequently deviates significantly from the exact results.

The dynamics of the TLS interacting with the composite environment exhibits the signatures of the strongly coupled bath TLS, in addition to the damping induced by the harmonic bath. During very early times, the effects from the two bath components are nearly additive, leading to a shallower population minimum compared to those observed when the system is coupled to either the harmonic bath or the other spin. The results of the anharmonic SMatPI algorithm match well the exact results over the converged range. (Again, some very small differences arise because of different Trotter factorization in the two methods.) The effective harmonic approximation is seen to be accurate up to the first local population minimum in this case as well, deviating at longer times, although it continues to qualitatively track the exact results because of the appreciable quadratic component in the bath Hamiltonian.

In summary, the ideas described in this Letter offer new possibilities for simulating the quantum dynamics of systems in environments that are not restricted to common quadratic Hamiltonians. By parsing the IF, it was shown that the coefficients of the time-discretized Gaussian IF under the effective harmonic bath mapping can be obtained through a very simple and efficient procedure that avoids the calculation of the environment's time correlation function, along with its double integration, or (equivalently) its conversion to a spectral density and subsequent integration. Further, the same procedure can be used to examine any deviations of the IF from the Gaussian form, in order to assess whether the harmonic mapping should offer an adequate approximation. Last, it was shown that the parsing ideas can be adapted to the calculation of SMatPI matrices without resorting to the harmonic bath form, thus generalizing the SMatPI decomposition to anharmonic environments. The resulting SMatPI expressions have the GQME structure away from endpoints, and from this perspective the SMatPI form of the RDM does not come as a surprise. However, the calculation of the GQME kernel from the Hamiltonian presents an extremely demanding task. Further, the SMatPI matrices developed from the discretized path integral do not have the translationally invariant GQME form at endpoints, and these differences are important for the exact nature of the propagation algorithm.

Application of these ideas hinge on the ability to numerically evaluate the influence functional for anharmonic environments. In the most general situation, this task entails performing fully quantum mechanical calculations over the relatively short memory interval. At present, influence functionals from anharmonic environments can be generated fully quantum mechanically in the case of separable baths,[18] and through the forward-backward semiclassical approximation[19] (FBSD) for general many-body environments. Further, the MPI algorithm[23-24] can be used to calculate the IF of multi-component systems with a one-dimensional topology. More work is needed to devise methods for calculating the IF of more complicated environments without introducing approximations. Nevertheless, the developments described in this Letter are encouraging toward the long-standing goal of simulating the dynamics of quantum mechanical processes in complex media.

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References

(1) Caldeira, A. O.; Leggett, A. J., Path integral approach to quantum Brownian motion. *Physica A: Statistical Mechanics and its Applications* **1983,** *121*, 587-616.

(2) Caldeira, A. O.; Leggett, A. J., Quantum tunnelling in a dissipative system. *Annals of Physics* **1983,** *149* (2), 374-456.

(3) Weiss, U., *Quantum Dissipative Systems*. World Scientific: Singapore, 1993.

(4) Ruf, B. A.; Miller, W. H., A new (Cartesian) reaction path model for dynamics in polyatomic systems, with application to H atom transfer in malonaldehyde. *J. Chem. Soc., Faraday Trans. 2* **1988,** *84*, 1523-1534.

(5) Miller, W. H.; Handy, N. C.; Adams, J. E., Reaction path Hamiltonian for polyatomic molecules. *J. Chem. Phys.* **1980,** *72*, 99-112.

(6) Leggett, A. J.; Chakravarty, S.; Dorsey, A. T.; Fisher, M. P. A.; Garg, A.; Zwerger, W., Dynamics of the dissipative two-state system. *Rev. Mod. Phys.* **1987,** *59*, 1-85.

(7) Mukamel, S., *Principles of nonlinear optical spectroscopy*. Oxford University Press: New York, 1995.

(8) Cina, J. A., *Getting Started on Time-Resolved Molecular Spectroscopy*. Oxford University Press: Oxford, 2022.

(9) May, V.; Kühn, O., *Charge and energy transfer dynamics in molecular systems*. 3rd ed.; Wiley: 2011.

(10) Makri, N., Numerical path integral techniques for long-time quantum dynamics of dissipative systems. *J. Math. Phys.* **1995,** *36*, 2430-2456.

(11) Makri, N., Quantum dissipative systems: a numerically exact methodology. *J. Phys. Chem.* **1998,** *102*, 4414-4427.

(12) Chandler, D., *Introduction to Modern Statistical Mechanics*. Oxford University Press: New York, 1987.

(13) Makri, N., The linear response approximation and its lowest order corrections: an influence functional approach. *J. Phys. Chem. B* **1999,** *103*, 2823-2829.

(14) Walters, P. L.; Allen, T. C.; Makri, N., Direct determination of harmonic bath parameters from molecular dynamics simulations. *J. Comput. Chem.* **2017,** *38*, 110-115.

(15) Makri, N., Iterative evaluation of the path integral for a system coupled to an anharmonic bath. *J. Chem. Phys.* **1999,** *111*, 6164-6167.

(16) Makri, N.; Makarov, D. E., Tensor propagator for iterative quantum time evolution of reduced density matrices. I. Theory. *J. Chem. Phys.* **1995,** *102*, 4600-4610.

(17) Makri, N.; Makarov, D. E., Tensor propagator for iterative quantum time evolution of reduced density matrices. II. Numerical methodology. *J. Chem. Phys.* **1995,** *102*, 4611-4618.

(18) Ilk, G.; Makri, N., Real time path integral methods for a system coupled to an anharmonic bath. *J. Chem. Phys.* **1994,** *101*, 6708.

(19) Makri, N.; Thompson, K., Semiclassical influence functionals for quantum systems in anharmonic environments. *Chem. Phys. Lett.* **1998,** *291*, 101-109.

(20) Makri, N., Small matrix modular path integral: Iterative dynamics in space and time. *Phys. Chem. Chem. Phys.* **2021,** *23*, 12537-12540.

(21) Makri, N., Small matrix disentanglement of the path integral: overcoming the exponential tensor scaling with memory length. *J. Chem. Phys.* **2020,** *152*, 041104.

(22) Makri, N., Small matrix path integral for system-bath dynamics. *J. Chem. Theory and Comput.* **2020,** *16*, 4038–4049.

(23) Makri, N., Modular path integral: Quantum dynamics via sequential necklace linking. *J. Chem. Phys.* **2018,** *148*, 101101.

(24) Makri, N., Modular path integral methodology for real-time quantum dynamics. *J. Chem. Phys.* **2018,** *149*, 214108.

(25) Makri, N., Small Matrix Decomposition of Feynman Path Amplitudes. *Journal of Chemical Theory and Computation* **2021,** *17*, 3825-3829.

(26) Nakajima, S., On quantum theory of transport phenomena. *Prog. Theor. Phys* **1958,** *20*, 948.

(27) Zwanzig, R., Ensemble method in the theory of irreversibility. *J. Chem. Phys.* **1960,** *33*, 1338-1341.

(28) Caldeira, A. O.; Castro Neto, A. H.; Oliveira de Carvalho, T., DIssipative quantum systems modeled by a two-level-reservoir coupling. *Phys. Rev. B* **1993,** *48*, 13974-13976.

(29) Forsythe, K.; Makri, N., Dissipative tunneling in a bath of two-level systems. *Phys. Rev. B* **1999,** *60*, 972-978.

(30) Kundu, S.; Makri, N., PathSum: A C++ and Fortran suite of fully quantum mechanical real-time path integral methods for (multi-)system + bath dynamics. *The Journal of Chemical Physics* **2023,** *158* (22).