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Small Matrix Modular Path Integral: Iterative Quantum Dynamics in Space and Time

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The modular path integral (MPI) formulation for one-dimensional extended systems, such as spin arrays or molecular aggregates, allows evaluation of spin- or exciton-vibration dynamics with effort that scales linearly with the number of units. This work presents a small matrix decomposition of MPI, which eliminates tensor storage and enables iterative long-time propagation.

Systems composed of segments with a basic one-dimensional topology are common in chemistry. Molecular aggregates, such as those found in photosynthetic light harvesting complexes and structures of stacked chromophores, are of interest from the perspective of understanding and optimizing excitation energy transfer. Spin arrays are encountered in magnetic materials and are also important for understanding quantum phase transitions as well as qubit coherence and entanglement. Each unit in such systems is often characterized by two or more discrete (electronic or spin) states, which are coupled to a large number of intramolecular vibrations. The ensuing dynamics can be quite complex, and behaviours observed in experiments may be hard to decipher.

Theoretical analysis combined with simulation can offer invaluable information for understanding the complex interplay of electron- and spin-vibration dynamics. Further, the insights gained from studying Hamiltonian-to-dynamics relations can aid in the design of molecular units with optimal parameters. However, the full quantum mechanics of such large systems is inaccessible to conventional methods. Even if only the electronic (or spin) states are included, the resulting Hilbert space can be very large. For example, a chain or 10 two-level systems (TLS) gives rise to 2^{10} states. When each of these states is coupled to ~10^2 intramolecular vibrational degrees of freedom, each of which may have several thermally populated states, obtaining the dynamics through wavefunction-based methods becomes impractical.

A significant advantage in this regard is offered by the path integral formulation of quantum mechanics,[1, 2] which replaces wavefunction computation and storage by a sum of amplitudes along all paths. The main difficulty in the path integral is the exponential scaling of the number of paths with propagation time, which leads to astronomical numbers of terms. Early work developed optimal discretized path integral representations that minimize the number of path integral variables and formulated a time-iterative decomposition of the path sum for a small system coupled to a dissipative harmonic bath.[3, 4] The underlying principle that enables this decomposition is the finite length of correlations (the "memory") between path integral variables. The resulting quasi-adiabatic propagator path integral (QuAPI) algorithm accounts for such correlations within the memory length, which serves as a convergence parameter, achieving linear scaling with propagation length.[5] Recent work showed that the path integral variables can be disentangled even within the memory length, replacing the QuAPI tensors by matrices of size equal to that of the system's reduced density matrix (RDM). The fully quantum mechanical small matrix decomposition of the path integral[6, 7] (SMatPI) allows the treatment of multistate quantum systems coupled to diverse harmonic environments whose parameters may be obtained from phonon spectra or from molecular dynamics simulations.

The modular decomposition of the path integral[8, 9] (MPI) is a spatial tensor decomposition, which is designed for extended one-dimensional systems characterized by short-range interactions. In the case of nearest-neighbour interactions between units that are local in the single-unit basis states, the path integral variables form a rectangular lattice[8, 9] where connections between adjacent vertices along the time direction correspond to short time propagators within each unit, while the lines connecting different units represent coupling terms. (In the more general case where the coupling terms are not diagonal, the MPI lattice becomes slightly more complex.[10]) In general, the algorithm proceeds by linking the path variables between units sequentially, achieving linear scaling with

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aggregate length. The dynamical effects from any number of intramolecular vibrations, at zero or finite temperature, can also be included through an influence functional, which is available analytically and does not increase the computational cost.[11] The MPI path linking process can be further factorized, such that the cost of treating each unit scales almost linearly with the number of paths.[12] Filtering criteria[13-15] may be employed to reduce the number of contributing paths in each unit. The MPI methodology has been used to obtain fully quantum mechanical results for the dynamics of excitation energy transfer in bacteriochlorophyll aggregates and the 18-unit LH2 ring, where 50 normal modes on each molecule were included with parameters from experimental Huang-Rhys factors,[16] and also in 25-unit J-aggregates of perylene bisimide (PBI).[17]

The main limitation of the MPI algorithm is the path storage requirement, which effectively restricts the accessible time length. For example, unless filtering procedures can eliminate the majority of paths, MPI calculations of spin arrays are practical only up to N ; 10 path integral time steps. While the resulting time length is often sufficient for extracting the dynamical properties of interest, there are many situations where accessing longer simulation times is highly desirable.

The present paper removes this limitation by devising a small matrix formulation of the modular path integral (SMatMPI). Such a formulation does not appear feasible at first glance, as the influence functional arising from coupled spin units is not expected to have the simple Gaussian form that led to the SMatPI decomposition[6, 7] in the harmonic bath case, and is not even available in analytical form. However, the small matrix decomposition may also be applied to the path amplitudes, where the relevant matrices are obtained through a generalization of the SMatPI procedure. Once the path amplitudes are available, the MPI linking algorithm is easily performed, sequentially summing the path amplitudes of successive units until the tagged unit (the "system") is reached. The obtained SMatMPI matrices for the system contain all the effects from the rest of the spin chain. In most situations, e.g. in quantum Ising Hamiltonians, the large Hilbert space of a multi-unit chain produces effects to the system that mimic those from a dissipative environment, regardless of whether the individual units are coupled to harmonic baths. As a result, the SMatMPI matrices may be used to obtain long-time dynamics through repeated small matrix operations.

Consider a single-file arrangement of l units, labelled α, which are coupled through nearest-neighbour interactions, and suppose that the tagged system of interest is the last unit. (This assumption is only used for convenience and is not a limitation of the algorithm.) Each unit consists of n discrete (electronic or spin) states $\left|\sigma_i^\alpha\right\rangle$ which are coupled to a harmonic bath. The total Hamiltonian can be written as

$$\hat{H} = \sum_{\alpha=1}^{\mathrm{l}} \hat{H}_0^\alpha + \sum_{\alpha=1}^{\mathrm{l}-1} J^{\alpha,\alpha+1} \hat{V}^\alpha \hat{V}^{\alpha+1} \tag{2}$$

where

$$\hat{H}_0^\alpha = \sum_{i=1}^{n}\sum_{j=1}^{n} \hat{h}_{ij}^\alpha \left|\phi_i^\alpha\right\rangle\left\langle\phi_j^\alpha\right| + \sum_{i=1}^{n}\sum_{k} \frac{\hat{p}_k^{\alpha\,2}}{2m} + \frac{1}{2} m\omega_k^{\alpha\,2} \hat{q}_k^{\alpha\,2} - c_{ik}^\alpha \left|\phi_i^\alpha\right\rangle\left\langle\phi_i^\alpha\right|, \tag{3}$$

$$\hat{V}^\alpha = \sum_{i=1}^{n} s^\alpha \left|\phi_i^\alpha\right\rangle\left\langle\phi_i^\alpha\right| . \tag{4}$$

The unit operators $\hat{H}_0^\alpha$ include harmonic bath degrees of freedom arising from molecular vibrations, which are assumed diagonal in the unit basis.

The first step in the MPI algorithm involves constructing the arrays $\mathbf{R}_1$ and $\mathbf{R}_2$ of paths for the first two units, linking these paths by multiplying their amplitudes by phase factors that arise from the potential interactions between the two units[18] in the discretized path integral expression[19] and summing the amplitudes of unit 1. Earlier implementations of MPI required storing the array of paths for one unit at a time, updating this array after it is linked to the adjacent unit.[8, 9] In the absence of filtering procedures, the original MPI algorithm requires the storage of $n^{2(N+1)}$ amplitudes for propagation to $N\Delta t$ (where Δt is the path integral time step). Factorization of the linking process[12] leads to almost linear scaling with the number of paths. Thus, the storage requirement is the main obstacle that prevents application to very long propagation times.

The starting point of the new formulation is the general small matrix (SMat) decomposition of path integral amplitudes, whose sum produces the RDM of a single unit. For a system interacting with a general environment, the amplitude of a path of length *N* time steps can be written in the SMatPI form,

$$R_{s_0^\pm, s_1^\pm, \mathrm{L}, s_N^\pm} = c_N^{(N)} S^{(N,N-1)}_{s_N^\pm, s_{N-1}^\pm} \mathrm{L}\; S^{(10)}_{s_1^\pm, s_2^\pm} + \mathrm{L} + c_2^{(N)} \prod_{k=1}^{N-1} S^{(Nk)}_{s_N^\pm, s_{N-k}^\pm} S^{(k0)}_{s_k^\pm, s_0^\pm} + c_1^{(N)} S^{(N0)}_{s_N^\pm, s_0^\pm} \tag{5}$$

Here $s_k^\pm$ denotes the states of this unit at the time $t_k = k\Delta t$ along a particular forward-backward path, and $\mathbf{S}^{(kk')}$ are $n^2 \times n^2$ matrices. In the special case of a harmonic bath, these are the SMatPI matrices $\mathbf{M}^{(kk')}$, which encode (through a decomposition of the analytical influence functional[20]) the effects of the harmonic modes of this unit on the discrete system along the particular path and are obtained by evaluating the path integral for the RDM at all time points $t_k = 1, \mathrm{K}\ , N$.

The SMat representation of path amplitudes invites a formulation of MPI that eliminates array storage. To begin, the array of amplitudes for units 1 and 2 (which are initially isolated) are expressed in terms of the SMatPI matrices $\mathbf{M}^{(kk')}$ according to Eq. (5). The units are then linked through the appropriate potential factors at each time point and the amplitudes are summed with respect to the variables of unit 1, excluding the path endpoints $s_N^\pm, s_0^\pm$, without storing these arrays, to obtain the RDMs for unit 2 at the times $t_k = 1, \mathrm{K}\ , N$. These RDMs are then used to decompose the path amplitudes for unit 2 in terms of new matrices $\mathbf{S}_2^{(kk')}$, which provide the SMat representation of this unit. Note that the effective influence functional for unit 2 is no longer that of a harmonic bath alone, thus the $\mathbf{S}_2^{(kk')}$ matrices are not equal to the SMatPI matrices $\mathbf{M}^{(kk')}$.

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Once the SMatMPI matrices $\mathbf{S}_2^{(kk')}$ are available, the amplitudes are linked to those of the next unit, which initially is uncoupled and thus is described by the $\mathbf{M}^{(kk')}$ matrices. Applying the linking procedure with the potential interaction factors to obtain the RDMs for unit 3 and repeating the SMatMPI decomposition, one obtains the matrices $\mathbf{S}_3^{(kk')}$. This process is performed until the last unit is reached. Note that a simple modification of the MPI algorithm yields the RDM of non-terminal units, and can also lead to results for branched chains or ring structures.[9]

In the system-bath case, the expansion of path amplitudes is performed up to a length $N = r_{\max}$, where $r_{\max}$ is the influence functional entanglement length,[6] which in practice is equal to the length of memory induced by the system's enrivonment. Unlike the harmonic influence functional, in the more general case memory arises through the trace with respect to the other units of the aggregate, which may or may not be coupled to dissipative baths. Once converged with respect to this parameter, the SMatMPI procedure yields the RDM of the unit of interest over the time points $t_k = 1,\mathsf{K}\ ,r_{\max}$.

Provided that the remaining units of the chain introduce adequate dissipative effects, the projected dynamics is a finite-memory process. Under these conditions, all matrices $\mathbf{S}_{\mathsf{l}}^{(N0)}$ for $N > r_{\max}$ are smaller than the acceptable error and may be dropped. SMatMPI matrices may be used to iteratively propagate the tagged unit to longer times. If the observables of interest pertain to the last unit, the RDM at future times is given by[6, 7]

$$\mathbf{U}^{(N0)} = \sum_{r=1}^{r_{\max}} \mathbf{S}_{\mathsf{l}}^{(N,N-r)} \cdot \mathbf{U}^{(N-r,0)}, \quad N = r_{\max}+1,\mathsf{K} \tag{6}$$

To illustrate the SMatMPI approach, consider a quantum Ising chain[21] of $\mathsf{l} = 10$ units, described by the Hamiltonian of Eq. (4), which is rewritten in the form

$$\begin{aligned} \hat{H} = &-\hbar\Omega\sum_{\alpha=1}^{\mathsf{l}} \hat{\sigma}_x^{\alpha} - J\sum_{\alpha=1}^{\mathsf{l}} \hat{\sigma}_z^{\alpha}\hat{\sigma}_z^{\alpha+1} \\ &+\sum_{\alpha=1}^{\mathsf{l}} \sum_k \frac{\hat{p}_k^{\alpha\,2}}{2m} + \frac{1}{2}m\omega_k^{\alpha\,2}\hat{q}_k^{\alpha\,2} - c_k^{\alpha}\hat{\sigma}_z^{\alpha}\hat{q}_k^{\alpha} \end{aligned} \tag{7}$$

The quantum Ising chain has attracted much interest as a simple paradigm of a quantum phase transition.[21, 22] Further, the coherence and entanglement dynamics of coupled qubits is of interest in quantum computing. Each unit in Eq. (7) is a two-level system (TLS), $-\hbar\Omega$ is the tunnelling matrix element, and $\hat{\sigma}_x^{\alpha}$ and $\hat{\sigma}_z^{\alpha}$ are Pauli spin matrices for each unit. The strength of coupling between adjacent units is J. The frequencies and coupling coefficients to harmonic bath modes are collectively specified through the bath spectral density,[23] which is assumed to have the common Ohmic form, $J(\omega) = \frac{1}{2}\pi\hbar\omega\xi\, e^{-\omega/\omega_{\mathrm{c}}}$ where the Kondo parameter ξ quantifies the strength of dissipative effects and ω_{c} is the bath cutoff frequency. Note that the MPI methodology is not restricted to this form of system-bath coupling, and that each TLS may have its own parameters.

Figure 1 shows the survival probability of the edge spin for Ising chains with weakly coupled spins, $J = 0.2\hbar\Omega$, which are not attached to dissipative baths, for lengths $\mathsf{l} = 2$ and $\mathsf{l} = 10$. All spins are initially placed in the "up" state (i.e. the same eigenstate of σ_z). The spin population dynamics is the result of phase interference among 2^{l} eigenvalues, which leads to a very complex composite density matrix, and the apparent damping is a consequence of averaging the populations with respect to the $\mathsf{l}-1$ unobserved spins. It is seen that the peaks are initially synchronized with those of an isolated TLS, but a jitter is observed around $\Omega t\ ;\ 8$, after which the population oscillates out of phase. This is a consequence of the non-uniform level distribution of the Ising chain. From the perspective of convergence, this regime is challenging, as the memory induced by the Ising chain in the absence of harmonic bath effects is very long. The lack of adequate damping in this regime is evidenced by the persisting oscillatory dynamics of the edge spin population. With only two coupled spins a full revival is observed early on. In the chain of $\mathsf{l} = 10$ recurrences are expected much later. The population dynamics of an isolated TLS, obtained using the quasi-adiabatic propagator path integral (QuAPI) algorithm,[5] is also shown for reference.

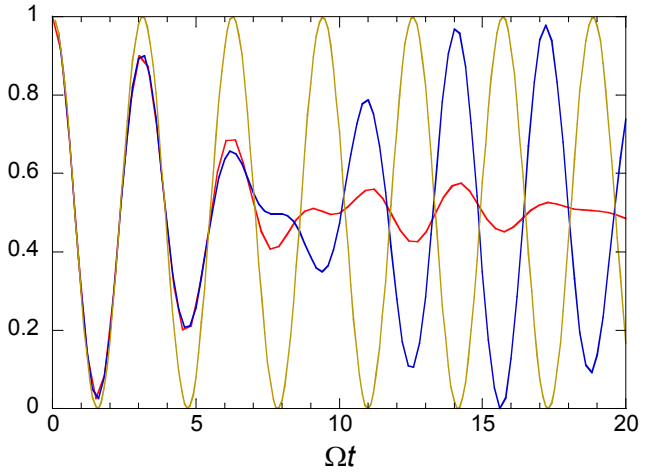

Fig. 1. Survival probability for the edge TLS in two quantum Ising chains with $J = 0.2\hbar\Omega$, which are not coupled to dissipative baths. All spins are initially placed in the same eigenstate of σ_z. Blue: $\mathsf{l} = 2$. Red: $\mathsf{l} = 10$. For reference, results for a single TLS are also shown in gold.

The edge spin population dynamics with $J = 0.2\hbar\Omega$ are compared to those obtained in the presence of harmonic dissipative environments of different parameters in Figure 2. In the first case the bath is characterized by $\xi = 0.05$, $\hbar\Omega\beta = 5$ and $\omega_{\mathrm{c}} = 5\Omega$. The weak dissipation and low temperature leads to underdamped dynamics. The jitter effect is still noticeable on the edge spin of the Ising chain, although the feature is strongly diminished in the presence of a bath. Comparison against Fig. 1 indicates that the damping effect of a long Ising chain whose spins are not coupled to bath modes is somewhat stronger than that of a harmonic bath with the present parameters. A seen in Fig. 2, interaction of the probed TLS with this bath and the Ising chain leads to faster damping, suggesting that the effects from these two environments are cumulative. However, the specifics of the spin dynamics differ in important ways.

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In the second case the TLS-bath coupling is stronger, given by $\xi = 0.25$, and the bath is at an intermediate temperature with $\hbar\Omega\beta = 1$ and $\omega_c = 5\Omega$. These conditions lead to faster damping, causing the population to fall below the equilibrium value of 0.5 only once. In this case the harmonic bath is primarily responsible for the quenching of the TLS coherent oscillation, and the additional damping effects from the weakly coupled TLS chain are relatively minor. Since the chain effects are not felt during the first half of the oscillation cycle with this weak spin-spin coupling and the TLS populations equilibrate rapidly with these parameters, the dynamics of the quantum Ising and single spin dynamics are nearly indistinguishable in this case.

The dynamics of system-bath Hamiltonians can be followed accurately in many regimes of interest using several approaches. The MPI methodology has extended treatment to arrays of multiple units, each interacting with harmonic baths representing intramolecular vibrations, but the time length reachable this way was previously limited by the need for storing the array of path amplitudes for each unit.

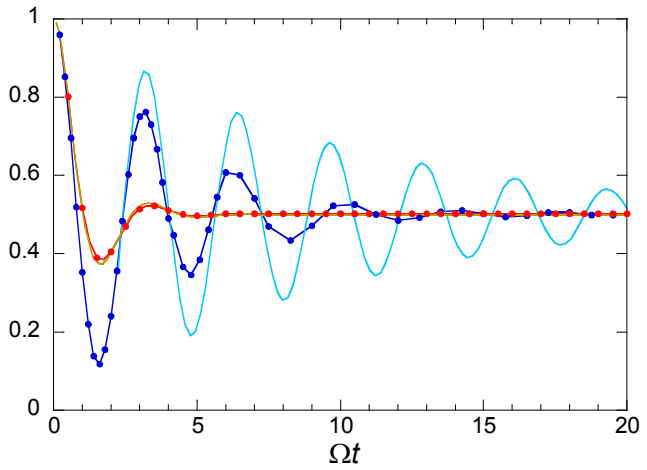

Fig. 2. Survival probability for the edge TLS in two quantum Ising chains with $J = 0.2\hbar\Omega$, which are coupled to dissipative baths. All spins are initially placed in the same eigenstate of σ_z. Blue markers and line: Ising chain with $\mathrm{I} = 10$, $\xi = 0.05$, $\hbar\Omega\beta = 5$. Cyan line: same bath parameters for a single TLS. Red markers and line: $\mathrm{I} = 10$, $\xi = 0.25$, $\hbar\Omega\beta = 1$. Gold line: same parameters for a single TLS.

The SMatMPI decomposition described in this Communication circumvents the need for array storage by representing the unit path amplitudes in terms of small matrices, whose dimension is the same as the unit's RDM. This way the MPI linking can be performed over longer segments and potentially for multistate units. Once the linking process is complete over the memory length, the constructed SMatMPI matrices are used in an iterative fashion to generate long-time RDM dynamics for the tagged unit. Thus the SMatMPI algorithm combines the ability of the MPI algorithm to treat multi-unit arrays with the long-time capabilities of time-iterative methods. The absence of tensor storage requirements opens up the road to the treatment of aggregates where each unit is composed of multiple states that may also be coupled to long-memory environments.

The interplay of spin-spin coupling in TLS arrays and the dissipative effects from intramolecular vibrations leads to rich dynamical behaviours, which will be reported in other publications.

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Conflicts of interest

There are no conflicts to declare.

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