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Letter

Incorporation of Empirical Gain and Loss Mechanisms in Open Quantum Systems through Path Integral Lindblad Dynamics

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ABSTRACT: Path integrals offer a robust approach for simulating open quantum dynamics with advancements transcending initial system size limitations. However, accurately modeling systems governed by mechanisms that do not conserve the number of quantum particles, such as lossy cavity modes, remains a challenge. We present a method to incorporate such empirical source and drain mechanisms within a path integral framework using quantum master equations. This technique facilitates rigorous inclusion of bath degrees of freedom while accommodating empirical time scales via Lindbladian dynamics. Computational costs are primarily driven by the path integral method with minimal overhead from Lindbladian terms. We use it to study exciton transport in a four-site Fenna–Matthews–Olson model, examining the potential loss of the exciton to the reaction center. This path integral Lindblad method promises an enhanced ability to simulate dynamics and will be fundamental to simulation of spectra in diverse quantum processes in open systems.



S imulation of the dynamics of open quantum systems is the holy grail of chemistry. The exponential scaling of quantum mechanics with the number of degrees of freedom combined with the difficulty of describing thermal dynamics contributes to the unparalleled challenges in simulating the dynamics of bulk systems. Methods based on propagating wave functions, such as the density matrix renormalization group (DMRG),¹⁻³ the family of multi-configuration time-dependent Hartree (MCTDH) method,^{4,5} and Gaussian wavepacket dynamics,⁶⁻⁸ cannot handle a continuum of vibrational modes or solvent degrees of freedom held at a constant temperature.

Methods based on reduced density matrices (RDMs) can overcome many of these difficulties. After judiciously separating the problem into a "system" of interest and the "environment", these methods aim to solve the dynamics corresponding to the system while incorporating the effects of the environment. While this system-solvent separation is critical in decreasing the dimensionality of the system space, it makes the dynamics non-Markovian. Approximate simulations of RDMs can be done quite simply using the perturbative Bloch–Redfield master equation^{9,10} or through the empirical Lindblad master equations.^{11,12} However, the results obtained from such simulations are not systematically improvable. Most crucially, simulations involving these two methods usually assume that the dynamics can be approximated in a Markovian fashion. These shortcomings are alleviated for a certain class of problems using numerically exact methods for simulating the dynamics. The hierarchical equations of motion $(\text{HEOM})^{13-15}$ and the quasiadiabatic propagator path integral (QuAPI) method^{16,17} based on the Feynman–Vernon influence functional¹⁸ are the most common mathematically rigorous frameworks available.

Over the years, much work has gone into improving the performance of these methods. The original HEOM was primarily limited to handling Drude–Lorentz spectral densities. Various approaches are now being developed to handle other spectral densities, including approaches involving Chebyshev polynomials^{19,20} and improvements using tensor networks.¹⁵ Similarly, QuAPI has been developed in a variety of manners to improve the performance. Notable among these are the small matrix decomposition of path integral (SMatPI),²¹ which is conceptually similar to the transfer tensor method (TTM) based on dynamical maps for non-Markovian processes,^{22–24} and methods based on tensor networks.^{25–28} Tensor network algorithms have also been extended to handle extended open quantum systems²⁹ and simulation of thermal correlation functions.³⁰ All of these developments have enabled simulations of larger systems up to longer times.^{31–33}

Although lucrative and now significantly more affordable, application of these rigorous methods requires detailed analysis of the system—environment interactions resulting in calculation of spectral densities. This may not always be possible. For instance, spontaneous emission of excited states of molecules in systems with Frenkel exciton transport or polaritonic dynamics in the presence of leaky cavities is not easily characterized by a spectral density. Similarly, it becomes difficult to describe the

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presence of source terms for quantum particles in an open quantum system. These phenomena can be modeled using the empirical Lindblad master equation^{11,12} or using non-Hermitian descriptions of the system. While the empirical Lindblad approach is incompatible with rigorous path integral simulations, path integral calculations have recently been done with non-Hermitian systems.³⁴ However, the non-Hermitian dynamics, while simple to implement, is non-unitary. Consequently, the trace of the density matrix is not conserved, leading to spurious artifacts in the most general case. Consider, for example, the particular case of spontaneous emission from the singly excited state. If a simulation is done in the space of the excited and ground states, the population of the ground state is supposed to increase as the excited state population decreases, keeping the trace conserved. When this process is simulated using non-Hermitian systems, the decay of the excited state is not accompanied by a corresponding increase of the ground state population (this is demonstrated in the Supporting Information). Quantities like absorption spectra, which are obtained as a Fourier transform of the dipole moment autocorrelation function and connect the ground state with the singly excited manifold, would consequently suffer from spurious effects of the population of the ground state not growing commensurate to the leakage of the excited state.

The Lindblad evolution is unitary and does not suffer from this problem. The resultant dynamic maps are known to be completely positive and trace-preserving. However, it does not lend itself to a simple incorporation in the path integral framework. One approach to incorporating everything might be to map the well-characterized environment onto other Lindblad operators and then solve the Lindblad master equation for everything. While this treats everything on the same footing, this approach has the disadvantage of making the dynamics approximate. We no longer even account for the thermal environment in a numerically exact manner. Implicit in the Lindblad treatment is the Markovian approximations to the dynamics and the assumption of a weak system-environment coupling. The other complementary approach would be to try to postulate a bath and a spectral density for the processes for which we do not have the details. If one does that, then there is a lot of guesswork associated with the forms of the spectral density and the nature of the bath. These questions are not typically well-settled. Therefore, we effectively not only increase the complexity of the simulation by adding completely fictitious baths to describe the processes that are not simple to parametrize but also add extra artifacts brought in by our choices of these baths.

The ideal approach, therefore, is neither of the two discussed above but to resort to a combination of both. We want to describe the open quantum system in a fully non-Markovian and non-perturbative manner while incorporating the Lindblad master equation into it without any additional cost. This work aims at this fundamental goal. This hybrid approach has the advantage of being (1) ideal in terms of computational costs, because solving the Lindblad master equation is minimal compared to the full path integral simulation, and (2) giving the optimally accurate dynamics according to our ability to characterize the processes. A similar motivation has led to the development of a recent classical trajectory-based method by Mondal et al.35 that incorporates the Lindblad loss into the partial linearized density matrix dynamics.^{36,37} The path integral Lindblad dynamics developed here is independent of the method of simulation of the open quantum dynamics and allows

for a decoupling of the path integral simulations for incoporation of the environment degrees of freedom from the solution to the Lindblad operators. We develop this path integral Lindblad master equation approach by going through the Nakajima– Zwanzig master equation,^{38,39} via the transfer tensor method.²² This decoupling has the added advantage of making the cost of adding different Lindblad jump operators to a system merely involve solving the master equation. The path integral simulation does not need to be redone.

Consider an open quantum system described by the Hamiltonian

$$H = H_0 + H_{\rm env} \tag{1}$$

where H_0 is the system Hamiltonian and H_{env} is the system– environment Hamiltonian. Also, suppose that, while most of the environment has been properly described in H_{env} , there are features like spontaneous decay, leakage of quantum particles, etc. that cannot be characterized accurately using thermal baths. For these processes, additionally, the system is also subject to interactions parametrized by a set of Lindblad jump operators L_i . We want to understand the dynamics of the system under the open quantum Hamiltonian, eq 1, and under the action of the Lindblad jump operators.

If the initial state can be written in a separable form $\rho_{\text{total}}(0) = \rho(0) \otimes \frac{e^{-\beta H_{\text{env}}}}{Z}$, the time evolution of the reduced density matrix corresponding to the system in the absence of the Lindblad jump operators can be simulated using path integrals as^{16,17}

$$\langle s_{N}^{+} | \rho(N\Delta t) | s_{N}^{-} \rangle = \sum_{s_{0}^{\pm}} \sum_{s_{1}^{\pm}} \dots \sum_{s_{N-1}^{\pm}} \langle s_{N}^{\pm} | \mathcal{E}_{0}(\Delta t) | s_{N-1}^{\pm} \rangle$$

$$\langle s_{N-1}^{\pm} | \mathcal{E}_{0}(\Delta t) | s_{N-2}^{\pm} \rangle \dots \langle s_{1}^{\pm} | \mathcal{E}_{0}(\Delta t) | s_{0}^{\pm} \rangle$$

$$\times \langle s_{0}^{+} | \rho(0) | s_{0}^{-} \rangle F[\{s_{j}^{\pm}\}]$$

$$(2)$$

where

$$F[\{s_j^{\pm}\}] = \exp\left(-\frac{1}{\hbar}\sum_{k=0}^{N} (s_k^{+} - s_k^{-})\sum_{k'=0}^{k} (\eta_{kk'}s_{k'}^{+} - \eta_{kk'}^{*}s_{k'}^{-})\right)$$
(3)

The bare forward-backward propagator, $\mathcal{E}_0(t) = \exp(-iH_0t/\hbar) \otimes \exp(iH_0t/\hbar)$, is the dynamical map corresponding to the bare system; s_i^{\pm} is the state of the system at the *j*th time point; and $F[\{s_j^{\pm}\}]$ is the State of the system at the *j*th time point; and $F[\{s_j^{\pm}\}]$ is the Feynman–Vernon influence functional¹⁸ along the path s_j^{\pm} . The influence is calculated in terms of the η coefficients,^{16,17} which are discretizations of the bath response function.⁴⁰ The influence functional makes the dynamics non-Markovian by depending upon the entire history of the path. In condensed phases, this dependence upon the history dies away and can be truncated at some finite memory length. The cost of these calculations, when done in a naive manner, grow exponentially with the number of time steps within memory, $O(d^{2K})$, where d is the system dimensionality and K is the memory length. To obtain the reduced density matrix beyond the memory length, $\tau_{mem} = K\Delta t$, various iteration techniques can be used, which reduce the computational complexity from exponential to linear with time. Recent developments have focused on improving the performance of these path integral calculations.^{25,27,29,4}

These path integral simulations do not allow for the simple incorporation of the Lindblad jump operators. To incorporate them, we start with the Nakajima–Zwanzig master equation.^{38,39} The reduced density matrix of the system, $\rho(t)$, simulated using eq 2, also satisfies the Nakajima–Zwanzig master equation

$$\dot{\rho}(t) = -\frac{i}{\hbar} \mathcal{L}_0 \rho(t) + \int_0^{\tau_{\text{mem}}} \mathcal{K}(\tau) \rho(t-\tau) \mathrm{d}\tau$$
(4)

where $\tau_{\rm mem}$ is the length of the non-Markovian memory and $\mathcal{L}_0 \cdot = [H_0, \cdot]$ is the system Liouvillian. Generally, obtaining the memory kernel is a tricky affair. Much work has gone into trying to obtain these memory kernel elements accurately from either approximate^{42,43} or numerically exact⁴⁴ quantum dynamical simulations of the evolution of the reduced density matrix.

A simpler and more aesthetically pleasing route was proposed by Cerrillo and Cao.²² They showed that, from the dynamical maps that relate the time-evolved density matrix $\rho(t)$ to the initial density matrix $\rho(0)$ under the influence of the environment, $\rho(t) = \mathcal{E}(t)\rho(0)$, one can derive the transfer tensors, T_{k} , that satisfy

$$\rho(t_n) = \sum_{k=1}^{n} T_k \rho(t_{n-k})$$
(5)

The dynamical maps, including the environment effects, can be simulated using eq 2 by not contracting the initial reduced density matrix. The transfer tensor method (TTM) has already been used with path-integral-based simulations.^{33,45} It has also been shown that, for short time steps, the transfer tensors can be related to the memory kernel by²²

$$T_k = (1 - i\mathcal{L}_0\Delta t)\delta_{k,1} + \mathcal{K}_k\Delta t^2$$
⁽⁶⁾

For longer time steps, this would break down because it is based on a discretization of the time derivative of $\rho(t)$ correct to $O(\Delta t)$. A better mapping can be obtained by converting to the reduced density matrix to the interaction picture with respect to the bare system Hamiltonian, H_{0} , in terms of the bare dynamical map, $\mathcal{E}_0(t)$,

$$\tilde{\rho}(t) = \mathcal{E}_0^{-1}(t)\rho(t) \tag{7}$$

where

$$\mathcal{E}_{0}(t)\rho(t) = \exp\left(\frac{-iH_{0}t}{\hbar}\right)\rho(t)\exp\left(\frac{iH_{0}t}{\hbar}\right)$$
(8)

The equation of motion for the reduced density matrix in this interaction picture becomes

$$\dot{\rho}(t) = \mathcal{E}_0^{-1}(t) \int_0^{\tau_{\text{mem}}} \mathcal{K}(\tau) \mathcal{E}_0(t-\tau) \tilde{\rho}(t-\tau) \mathrm{d}\tau$$
(9)

which upon time-discretization leads to

$$\tilde{\rho}(t_n) = \tilde{\rho}(t_{n-1}) + (\Delta t)^2 \mathcal{E}_0^{-1}(t_n) \sum_{k=1}^L \mathcal{K}_k \mathcal{E}_0(t_{n-k}) \tilde{\rho}(t_{n-k})$$
(10)

With the conversion of eq 5 to the interaction picture, the corresponding equation in terms of the transfer tensors becomes

$$\tilde{\rho}(t_n) = \mathcal{E}_0^{-1}(t_n) \sum_{k=1}^{L} T_k \mathcal{E}_0(t_{n-k}) \tilde{\rho}(t_{n-k})$$
(11)

Comparing eqs 10 and 11, we obtain

$$T_k = \mathcal{E}_0(\Delta t)\delta_{k,1} + \mathcal{K}_k \Delta t^2$$
(12)

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as an analogue of eq 6.²² The main benefit is that this allows us to take advantage of the larger time steps enabled by ideas like the quasi-adiabatic propagator.⁴⁶ Earlier work involving evaluating the memory kernel from numerically exact quantum dynamical simulations⁴⁴ required interpolation of the path integral results, which can bring in errors if not done carefully.

To incorporate the Lindbladian jump operators, we modify the Nakajima–Zwanzig master equation for the reduced density matrix, eq 4, as

$$\dot{\rho}^{(L)}(t) = -\frac{i}{\hbar} \mathcal{L}_0 \rho^{(L)}(t) + \int_0^{\tau_{\text{mem}}} \mathcal{K}(\tau) \rho^{(L)}(t-\tau) d\tau + \sum_j \left(L_j \rho^{(L)}(t) L_j^{\dagger} - \frac{1}{2} \{ L_j^{\dagger} L_j, \rho^{(L)}(t) \} \right)$$
(13)

where the superscript (L) denotes that this equation involves the empirical terms from the Lindbladian master equation.

Let us, once again, cast the density matrix in an interaction picture vis-à-vis the bare system evolution, eq 7, which in the presence of the jump operators satisfies

$$\dot{\rho}^{(L)}(t) = \mathcal{E}_{0}^{-1}(t) \Biggl(\int_{0}^{\tau_{\text{mem}}} \mathcal{K}(\tau) \rho^{(L)}(t-\tau) d\tau + \sum_{j} \Biggl(L_{j} \rho^{(L)}(t) L_{j}^{\dagger} - \frac{1}{2} \{ L_{j}^{\dagger} L_{j}, \rho^{(L)}(t) \} \Biggr) \Biggr)$$
(14)

Consequently, we have the following expression for the time evolution of the reduced density matrix:

$$\rho_n^{(L)} = \mathcal{E}_0(\Delta t)\rho_{n-1}^{(L)} + \sum_{j=1}^L \mathcal{K}_j \rho_{n-j}^{(L)} \Delta t^2 + \sum_j \left(L_j \rho_{n-1}^{(L)} L_j^{\dagger} - \frac{1}{2} \{ L_j^{\dagger} L_j, \rho_{n-1}^{(L)} \} \right) \Delta t$$
(15)

which along with eq 12 forms the final results of this letter. The transfer tensors may be obtained directly from the augmented propagators or dynamical maps produced by any path integral technique.^{16,21,25,27} The main complexity of the simulation is primarily limited to this path integral simulation. The solution of eq 15, once the memory kernel was evaluated, is extremely cheap. The path integral simulation does not need to be rerun even if the Lindbladian jump operators are changed.

As an example of this methodology, consider the four-site model of the Fenna–Matthews–Olson complex, Figure 1, studied in ref 48. This model is described by the vibronic Hamiltonian

$$H = H_0 + H_{\rm env} \tag{16}$$

$$H_{0} = \sum_{j=1}^{4} \varepsilon_{j} |j\rangle \langle j| + \sum_{j < k} h_{jk} (|j\rangle \langle k| + |k\rangle \langle j|)$$
(17)

$$H_{\rm env} = \sum_{k=1}^{4} \sum_{j=1}^{N_{\rm osc}} \frac{p_{jk}^2}{2m_{jk}} + \frac{1}{2} m_{jk} \omega_{jk}^2 \left(x_{jk} - \frac{c_{jk} |k\rangle \langle k|}{m_{jk} \omega j k^2} \right)^2$$
(18)

where H_0 is the electronic "system" Hamiltonian and H_{env} describes the environment and its interaction with the system. This environment consisting of molecular nuclear motion and motion of the protein scaffolding is mapped to site-specific baths of harmonic oscillators. The frequency and coupling of the *j*th



Figure 1. Fenna–Matthews–Olson complex, with four-site coarse graining as indicated by the colors.

bath mode corresponding to the kth chromophoric site are characterized by a spectral density

$$J_k(\omega) = \frac{\pi}{2} \sum_{j=1}^{N_{\text{osc}}} \frac{c_{jk}^2}{m_{jk}\omega_{jk}} \delta(\omega - \omega_{jk})$$
(19)

which can be obtained from classical trajectory-based simulations of bath correlation functions. The spectral density corresponding to the molecular vibrations and protein scaffolding was characterized by Maity et al.⁴⁷ using quantum mechanics (QM)/molecular mechanics (MM). The spectral densities corresponding to the first four sites are shown in Figure 2. Also note that $|j\rangle$ corresponds to the singly excited state, where the *j*th molecule is excited and all of the others are in the ground state.



Figure 2. Site-specific and average spectral densities (black solid line), obtained by Maity et al.,⁴⁷ characterizing the chemical environment of the chromophores.

Now, this Hamiltonian describes a Frenkel–Holstein model and, therefore, does not account for the extraction of the exciton at chlorophyll site number 3. We use the path integral Lindblad dynamics approach developed here to incorporate this feature. First, we need to expand our Hilbert space by also considering I $g\rangle$ corresponding to the state in which all of the chlorophyll molecules are in the ground state. In this case, there is only one jump operator, $L = \gamma |g\rangle \langle 3|$, which is a non-Hermitian lowering operator that de-excites the third molecule. The time scale in which this effect happens is given by $\frac{1}{\gamma^2}$ (the effect of this jump operator and the identification of the time scale with $\frac{1}{\gamma^2}$ is demonstrated for a single molecule in the Supporting Information).

The base dynamics without the Lindblad jump operators was first calculated with a time step of $\Delta t = 3$ fs. The dynamical maps, $\mathcal{E}(t)$, were generated using the time-evolving matrix product state (TEMPO) algorithm^{25,28} as implemented in the QuantumDynamics, jl package⁴⁵ up to a maximum time of 300 fs. For these calculations, the full path simulation was done up to a memory length of $\tau_{mem} = K\Delta t = 150$ fs, beyond which an iterative algorithm was used to generate $\mathcal{E}(t)$ (a naïve calculation of this problem would need to sum over $25^{50} \approx 7.9 \times 10^{69}$, and the tensor network approach manages to make this computation totally feasible). The transfer tensors were derived from these data and used to propagate the dynamics up to a time of 5 ps via eq 5. The dynamics corresponding to $\rho(0) = |1\rangle\langle 1|$ is shown in Figure 3. The Frenkel model of exciton transport conserves the



Figure 3. Dynamics of the excitonic population without the Lindbladian jump operators.

number of excitons. Consequently, when we start with an initial excitation on $\rho(0) = |1\rangle\langle 1|$, the dynamics remain in the manifold of singly excited states. The population of the ground state remains identically zero throughout the dynamics.

Now, we add the Lindbladian jump operator with a range of different time scales, $\frac{1}{x^2}$ = 2.5, 5, 10, and 200 ps. We solve eq 15 using the memory kernel obtained from the transfer tensors in the previous step. The results are listed in Figure 4. Once the memory kernel has been generated from the path integral dynamical maps, the incorporation of the Lindbladian jump operators is as costly as the solution of eq 15. As expected, the rate of the growth of the population of the ground state, $|g\rangle$, is directly related to the time scale of the decay. However, this decay of the third site leads to subtle changes in the population dynamics of the other sites as well. These are quantitatively taken into account. The dynamics under a very long decay time of $\frac{1}{x^2}$ = 200 ps, Figure 4d, is shown to demonstrate the asymptotic convergence of the path integral Lindblad dynamics to the path integral dynamics in the absence of any Lindblad jump operators (Figure 3). Finally, probably the change as a result of the decay from the third site is the greatest if we take an initial condition localized on the fourth site $(\rho(0) = |4\rangle\langle 4|)$. As



Figure 4. Dynamics of the excitonic population with different decays on the third chromophore. The colors used are the same as Figure 3.

shown in Figure 5, the rise in the other sites is all but quenched when the decay is incorporated.





In this case, once the memory kernels were obtained from the initial path integral simulations via the transfer tensors, adding any jump operator or changing the strength of the jump operator amounts to resolving eq 15 with the corresponding changes. Because this is just a solution of a difference equation, it is effectively free and can be done with great efficiency.

In this paper, we have developed a method for doing path integral Lindblad dynamics. The goal is to unify the rigorous path integral methods for the environment degrees of freedom that can be properly characterized in terms of spectral densities with the Lindblad master equation approach of dealing with phenomena that are described only by some empirical time scales. This approach brings together the best of both worlds, maximizing the numerical accuracy of the simulations while not incurring any additional costs. This path integral Lindblad dynamics method can be used to incorporate a variety of empirically specified phenomena like spontaneous emission lifetime of states, leakage from particular states, and others, with rigorous path integral descriptions of dynamics under the influence of thermal environments specified by spectral densities. While the example considered here uses only a drain or loss term, it is trivial to study systems with a source term by suitably choosing the jump operators. This combination of Lindblad terms with path integrals can be done at no extra cost, because the solution to the master equation is negligible in comparison to the path integral simulation. Even changing the Lindbladian jump operators to model different processes can be done extremely efficiently once the memory kernels have been initially obtained.

While this method is already very useful in studying realistic problems, future developments are able to leverage its power even more significantly. We will extend the path integral Lindblad equations to study the changes brought about by the presence of thermal environments by phenomena represented by Lindblad jump operators. For example, it would be interesting to understand how the presence of a leaky cavity changes the absorption spectrum and transfer pathways of an exciton-polaritonic system. The effects of a combination of source and loss terms on the dynamics of an open quantum system are also be studied. The path integral Lindblad dynamics method has been implemented in the QuantumDynamics.jl package⁴⁵ for simulating the dynamics of open quantum systems. Finally, this idea transcends the use of path integral methods. While in this work, the path integral has been used to generate the dynamical maps that were used to obtain the memory kernel, in principle, any other method can also be used just as easily.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.4c00489.

Demonstration of the non-conservation of the trace with non-Hermitian descriptions of the loss of the exciton and description of the Lindbladian approach for loss mechanisms like spontaneous emission (PDF)

Transparent Peer Review report available (PDF)

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Notes

The author declares no competing financial interest.

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