Small Matrix Quantum-Classical Path Integral

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Abstract

The quantum-classical path integral (QCPI) is a rigorous formulation of nonadiabatic dynamics, where the dynamical interaction between a quantum system and its environment is captured consistently through classical trajectories driven by forces along quantum paths of the system. In this Letter we develop a small matrix decomposition (SMatQCPI) which eliminates the tensor storage requirements of the iterative QCPI algorithm. In the case of a system coupled to a harmonic bath, SMatQCPI provides fully quantum mechanical propagation which also reduces the computational cost to that of a single QCPI step. Further, the SMatQCPI matrices only need to account for quantum contributions to decoherence, allowing high efficiency in challenging regimes of incoherent dynamics. Overall, this new composite algorithm combines the best features of two powerful path integral formulations and offers a versatile tool for simulating condensed phase quantum dynamics.



A number of recent advances in experimental techniques have enabled the characterization of molecular processes at an unprecedented level of spatial, frequency and temporal resolution. These developments have spurred intense theoretical efforts in the direction of developing methods for simulating the dynamics of large molecular systems accurately and reliably. Since many processes of interest are not adequately described by classical mechanics, simulation methods must be able to faithfully account for quantum mechanical effects, such as quantum dispersion, phase interference, tunneling and nonadiabaticity, in the time evolution of the nuclei. The steep increase in the cost of quantum mechanical calculations with the number of degrees of freedom presents a severe challenge. A large body of work has led to the development of many powerful simulation tools, but however, further developments are needed to address the quantum dynamics of complex processes in the condensed phase or biological environments.

Among methods based on the Schrödinger equation, linearized semiclassical approximations,¹⁻⁴ forward-backward semiclassical dynamics⁵⁻⁷ and path integral Liouville dynamics⁸⁻⁹ offer very practical tools for simulating Born-Oppenheimer dynamics in large systems, and may be applied to discrete systems through the mapping Hamiltonian.^{4, 10-11} Methods designed for nonadiabatic dynamics include prescriptions designed to remedy the shortcomings of the Ehrenfest model, such as trajectory surface hopping and spawning,¹²⁻¹⁶ and approaches based on the quantum-classical Liouville equation,^{12,13} Accurate, fully quantum mechanical calculations are possible using the multiconfiguration time-dependent Hartree method,¹⁷⁻¹⁹ as well as approaches based on matrix product states²⁰⁻²¹ and the density matrix renormalization group method.²²⁻²³

Feynman's path integral formulation²⁴⁻²⁵ is appealing because it does not require wavefunction storage. Another distinct advantage of the path integral is the ability to integrate out harmonic degrees of freedom analytically at any temperature.²⁶ The drawbacks are the astronomical number of terms that must be summed to calculate the quantum mechanical amplitude, which in general cannot be sampled by stochastic methods,²⁷ and the nonlocal character of the dynamics that results from eliminating harmonic environments.²⁸ In this Letter we report the integration of two powerful real-time path integral methods, the quantum-classical path integral²⁹⁻³⁰ (QCPI) and the small matrix path integral³¹⁻³² (SMatPI) into an algorithm that offers versatility as well as improved performance, and (perhaps most importantly) which has low storage requirements.

The SMatPI algorithm is based on the quasi-adiabatic propagator path integral (QuAPI) methodology³³ for simulating the dynamics of a small system coupled to a harmonic bath, which has been used to simulate a wide variety of processes. The QuAPI algorithm decomposes the path integral for the system, which is augmented by a time-nonlocal influence functional, into a series of tensor multiplications that lead to iterative evaluation, with cost that scales linearly with propagation time. The main cost of the algorithm is associated with the QuAPI tensors which in principle involve n^{2L} elements and require the evaluation of n^{2L+2} terms in each iteration step,³⁴⁻³⁵ where *n* is the number of system states and *L* is the bath-induced memory length in units of the path integral time step. (We note, however, that powerful filtering techniques can dramatically decrease these numbers in some regimes.) Recent work³¹⁻³² showed that the QuAPI tensors, which capture the correlations among path integral variables within the memory length, can be further decomposed through an analytically derived exact procedure, giving rise to an algorithm that involves a small number of $n^2 \times n^2$ matrices. Elimination of tensor storage makes the SMatPI method applicable to multistate systems and reduces the total cost of the algorithm to that of a single QuAPI propagation step.

For the purpose of simulating processes in complex anharmonic environments, much progress can be made by resorting to classical trajectory treatments. The quantum-classical path integral (QCPI) is a rigorous formulation that emerges when the particles that comprise the environment are treated within the semiclassical stationary phase approximation. As such, QCPI captures the system-solvent interaction correctly, without resorting to Ehrenfest-type averages³⁶ or invoking *ad hoc* assumptions. Further, the coherence-damping effects from the solvent arise entirely from destructive interference of phases obtained from the interaction of the system with the solvent,³⁷ in full atomistic detail.³⁸

Combining the QCPI and SMatPI algorithms can benefit both methods in distinct ways: (i) SMatPI may be used to eliminate tensor storage in the HBR-QCPI algorithm. (ii) In the case of a harmonic bath, the QCPI propagators, which are accurate over larger time steps and allow convergence with shorter memory compared to QuAPI, may be used within the SMatPI algorithm to facilitate convergence.

Consider a small quantum mechanical system, described by the Hamiltonian H_0 , which interacts with a general (anharmonic) environment (e.g. a solvent) described by the phase space variables \mathbf{q}, \mathbf{p} through the potential $V_{\text{sol}}(s, \mathbf{q})$. The isolated system is described in terms of *n* discrete states $|\sigma_i\rangle$, which diagonalize the coordinate operator³⁹⁻⁴⁰ with eigenvalues σ_i . Observables pertaining to the quantum system are conveniently obtained from the reduced density matrix (RDM),

$$\tilde{\rho}_{s_{N}^{\pm}s_{0}^{\pm}}^{(N0)} = \operatorname{Tr}_{\mathrm{sol}}\left\langle s_{N}^{+} \left| e^{-i\hat{H}t_{N}/\hbar} \right| s_{0}^{+} \right\rangle \hat{\rho}_{\mathrm{sol}}(0) \left\langle s_{0}^{-} \left| e^{i\hat{H}t_{N}/\hbar} \right| s_{N}^{-} \right\rangle,$$

$$(0.1)$$

where $\rho_{sol}(0)$ is the initial density operator of the solvent and $t_k = k\Delta t$ is the time in units of the path integral time step Δt . The QCPI expression for the system RDM has the form

$$\tilde{\rho}_{s_{N}^{\pm}s_{0}^{\pm}}^{(N0)} = \int d\mathbf{q}_{0} \int d\mathbf{p}_{0} \ W(\mathbf{q}_{0}, \mathbf{p}_{0}) Q_{s_{N}^{\pm}s_{0}^{\pm}}^{(N0)}(\mathbf{q}_{0}, \mathbf{p}_{0})$$
(0.2)

where W is the Wigner transform⁴¹ of $\rho_{sol}(0)$ and $Q_{s_{N}^{k}s_{0}^{\pm}}^{(N0)}$ is the quantum influence function,²⁹⁻³⁰ which involves a sum of phases along all forward-backward system paths $\{s_{k}^{\pm}\}$,

$$Q_{s_{N}^{\pm}s_{0}^{\pm}}^{(N0)}\left(\mathbf{q}_{0},\mathbf{p}_{0}\right) = \sum_{s_{0}^{\pm}} \sum_{s_{1}^{\pm}} \cdots \sum_{s_{N-1}^{\pm}} K_{\mathbf{q}_{0}\mathbf{p}_{0}}^{\text{ref}}\left(s_{0}^{\pm},t_{0}^{\pm};s_{1}^{\pm},t_{1}^{\pm}\right) \cdots K_{\mathbf{q}_{0}\mathbf{p}_{0}}^{\text{ref}}\left(s_{N-1}^{\pm},t_{N-1}^{\pm};s_{N}^{\pm},t_{N}^{\pm}\right) e^{i\Phi_{\mathbf{q}_{0}\mathbf{p}_{0}}\left(s_{0}^{\pm},s_{1}^{\pm},\ldots,s_{N}^{\pm}\right)/\hbar}$$
(0.3)

Here the reference propagators $K_{\mathbf{q}_0\mathbf{p}_0}^{\text{ref}}$ are given by

$$K_{\mathbf{q}_{0}\mathbf{p}_{0}}^{\mathrm{ref}}\left(s_{k}^{\pm},t_{k};s_{k+1}^{\pm},t_{k+1}\right) = \left\langle s_{k+1}^{+} \left| \hat{U}_{\mathbf{q}_{0}\mathbf{p}_{0}}^{\mathrm{ref}}\left(t_{k+1},t_{k}\right) \right| s_{k}^{+} \right\rangle \left\langle s_{k}^{-} \left| \hat{U}_{\mathbf{q}_{0}\mathbf{p}_{0}}^{\mathrm{ref}}\left(t_{k},t_{k+1}\right) \right| s_{k+1}^{-} \right\rangle$$
(0.4)

where $U_{q_0p_0}^{\text{ref}}$ is the time evolution operator for the time-dependent Hamiltonian

$$\hat{H}_{\mathbf{q}_0\mathbf{p}_0}^{\text{ref}}(t) = \hat{H}_0 + V_{\text{sol}}\left(\hat{s}, \mathbf{q}^{\text{ref}}(t)\right) \tag{0.5}$$

along the particular "reference" trajectory, and $\Phi_{q_0p_0}(s_0^{\pm}, s_1^{\pm}, \dots, s_N^{\pm})$ is the QCPI-discretized net forwardbackward action integral that corresponds to $H - H_{q_0p_0}^{\text{ref}}$. The reference Hamiltonian $H_{q_0p_0}^{\text{ref}}$ augments the system by the external time-varying field from the system-solvent interaction along a classical trajectory $(\mathbf{q}^{\text{ref}}, \mathbf{p}^{\text{ref}})$. The remaining action $\Phi_{q_0p_0}$ arises from the "force" exerted on the solvent by the quantum system (the "back-reaction"). This force is imparted on the solvent through frequent changes of potential surface along each system path, which modify the solvent trajectory. The phase space integral in Eq. (0.2) is evaluated by Monte Carlo methods.⁴² Each quantum path in Eq. (0.6) specifies a unique sequence of forces (i.e. system states) and thus gives rise to a different solvent trajectory, generally resulting in a total of n^{2N} trajectories from each $\mathbf{q}_0, \mathbf{p}_0$. The iterative formulation of QCPI³⁰ restricts trajectory branching to the memory interval $L\Delta t$ and propagates Eq. (0.3) using tensors with n^{2L} elements.

While many choices are possible for the reference Hamiltonian, and the iterative QCPI algorithm can significantly benefit from physically motivated reference trajectories,⁴³⁻⁴⁴ for simplicity we restrict attention to the simple "classical path" reference,³⁰ where the trajectories are obtained by solving the classical equations of motion for the solvent Hamiltonian on a fixed state of the quantum system. With the classical path reference and within the harmonic back-reaction (HBR) approximation⁴⁵⁻⁴⁶ the phase function is independent of trajectory initial conditions and is given by the expression

$$\Phi\left(s_{0}^{\pm}, s_{1}^{\pm}, \dots, s_{N}^{\pm}\right) = \exp\left(-\frac{i}{\hbar} \sum_{k'=0}^{N} \sum_{k''=0}^{k'} \operatorname{Im} \eta_{k'k''}\left(s_{k'}^{+} - s_{k'}^{-}\right)\left(s_{k''}^{+} + s_{k''}^{-}\right)\right),\tag{0.6}$$

where $\eta_{k'k'}$ are the QuAPI⁴⁷-discretized influence functional coefficients³⁴ derived from the solvent correlation function.⁴⁸ Eq. (0.6) captures the back-reaction phase implicitly, without the need to account for trajectory branching.⁴⁵ Thus, the HBR-QCPI algorithm requires only a single classical trajectory per initial condition $\mathbf{q}_0, \mathbf{p}_0$, and iteration may be performed by the QuAPI algorithm³⁵ for the time-dependent system Hamiltonian⁴⁹ $H_{q_0p_0}^{ref}$ (where only the imaginary parts of the $\eta_{k'k'}$ coefficients are utilized). Thus, the iterative HBR-QCPI algorithm formally requires storage of tensors comprising n^{2L} elements and involves $(n^2)^{L+1}$ operations at each iteration step for each trajectory initial condition. Path filtering criteria⁵⁰⁻⁵² and matrix product based singular value decompositions⁵³ may be used to drastically trim the size of the QuAPI tensors. Significant savings are derived by rewriting the HBR-QCPI expression in blip/sojourn variables, $\Delta s_k = s_k^+ - s_k^-$, $\bar{s}_k = \frac{1}{2}(s_k^+ + s_k^-)$, taking advantage of the form of Eq. (0.6). Even without excluding any paths, the blip representation⁵⁴⁻⁵⁵ reduces the cost of the full algorithm to $(n^2 - n + 1)^{L+1}$. Furthermore, contributions from forward-backward paths with multiple blips are exponentially damped and often negligible, allowing additional speedup by large factors.

For each \mathbf{q}_0 , \mathbf{p}_0 , the HBR-QCPI expression is isomorphic to that of the QuAPI-discretized path integral for a system-bath Hamiltonian with a time-dependent system. As such, the HBR-QCPI expression lends itself to the SMatPI decomposition.⁵⁶ In this case the memory length is determined by the imaginary part of the influence functional alone, which corresponds to the strictly quantum mechanical component of decoherence⁵⁷ and in many situations is shorter than the full memory. Further, integration with respect to trajectory initial conditions leads to additional memory damping through classical decoherence,⁵⁷ which is treated exactly and thus does not require a fine time discretization. With these ideas we formulate the SMatQCPI algorithm described below.

Consider the $n^2 \times n^2$ matrix $\mathbf{Q}^{(N0)}(\mathbf{q}_0, \mathbf{p}_0)$ for all possible final and initial states, where the superscript labels the corresponding times t_N and t_0 . The SMatPI decomposition leads to the following expression for propagation beyond the memory length:⁵⁶

$$\mathbf{Q}^{(N0)}(\mathbf{q}_0\mathbf{p}_0) = \sum_{r=1}^{L} \mathbf{M}^{(N,N-r)}(\mathbf{q}_0\mathbf{p}_0) \cdot \mathbf{Q}^{(N-r,0)}(\mathbf{q}_0\mathbf{p}_0), \quad N = L+1,\dots$$
(0.7)

where $\mathbf{M}^{(Nm)}$ are $n^2 \times n^2$ matrices that are constructed from the full path integral expression with the discretized influence functional. The entanglement of the path integral variables is encoded in the SMatPI matrices, which tend to decrease in magnitude with the separation between time points and eventually become negligible. The procedure for evaluating the SMatPI matrices in the presence of time-dependent fields⁵⁸ scales as $(n^2)^{L+1}$, and in the blip representation the scaling reduces to $(n^2 - n + 1)^{L+1}$. While the

number of operations is similar to that in the original HBR-QCPI, no tensors need to be stored in the SMatQCPI algorithm, extending the feasibility of the method to longer memory and multistate systems.

Next we focus on the special case of a harmonic bath,

$$\hat{H}_{\rm sol} = \sum_{j} \frac{\hat{p}_{j}^{2}}{2m_{j}} + \frac{1}{2} m_{j} \omega_{j}^{2} \left(\hat{q}_{j} - \frac{c_{j} \hat{s}}{m_{j} \omega_{j}^{2}} \right)^{2}$$
(0.8)

where the mode frequencies and coupling parameters are collectively specified by the spectral density function $\mathscr{I}(\omega)$.⁵⁹ Consider the amplitude that corresponds to the product of reference propagators and the Wigner phase space function. With the small path integral time step required in discretized path integral methods, the reference propagators contain phases which, upon integration with respect to the phase space variables, produce the classical decoherence component of the influence functional.²⁹ This structure implies that the SMatPI decomposition applies not only to the quantum influence function, but also to its integrated form, i.e. the entire RDM, whose SMatQCPI decomposition becomes

$$\tilde{\boldsymbol{\rho}}^{(N0)} = \sum_{r=1}^{L} \mathbf{M}^{(N,N-r)} \cdot \tilde{\boldsymbol{\rho}}^{(N-r,0)}, \quad N = L+1,\dots$$
(0.9)

The SMatPI matrices in this expression do not depend on trajectory initial conditions and thus are evaluated only once. We also note that it is possible to include residual memory using the extended algorithm.⁵⁶ At each propagation step beyond memory (i.e. for $N = L + 1, ..., L_{ext}$) the RDM is first obtained using Eq. (0.9), then readjusted with the inclusion of influence functional coefficients η_{N0} . The inclusion of memory beyond *L* does not incur additional costs, thus the value of L_{ext} may be as large as desired.

Eq. (0.9) is very similar to the original SMatPI expression, but the SMatQCPI matrices include only the imaginary part of the influence functional, which corresponds to memory of a strictly quantum mechanical origin and tends to be less prominent than its classical counterpart, allowing a larger path integral time step and reaching convergence with smaller values of *L*. Thus, the SMatQCPI expression for a harmonic bath combines the advantages of the QCPI and SMatPI formulations into a powerful algorithm, which is applicable to long-memory processes and multistate systems.

While these potential benefits seem appealing, an obvious concern is that the SMatPI algorithm, which is based on matrices obtained through precisely defined and highly accurate procedures, may not tolerate the statistical error associated with QCPI components. We answer this question by applying the algorithm to four models with diverse dynamical characteristics. Our results indicate that the SMatQCPI algorithm is robust and leads to stable results, which can even be smoother than those obtained from QCPI calculations. Interestingly, in all illustrations (which correspond to diverse phenomena in the physical chemistry literature, involving multiple quantum states of the system and spanning various regimes of the condensed phase environment) the composite SMatQCPI algorithm emerges as a considerably superior method both in terms of computational cost and storage compared to at least one and in some cases both of its constituent formulations.

Each model that follows is based on the Hamiltonian given by Eq. (0.8). All SMatQCPI calculations are performed with a total of 15,000 trajectory initial conditions sampled by Monte Carlo, and the population results have a statistical uncertainty of about 0.01. In three of the models we choose a spectral density of the Ohmic form,⁶⁰

$$\mathscr{I}(\omega) = \frac{2\pi\hbar\xi}{\left(\sigma_n - \sigma_1\right)^2} \omega \, e^{-\omega/\omega_c} \tag{0.10}$$

which peaks at a frequency ω_c , and where the parameter ξ quantifies the system-bath coupling strength.

The first two models comprise symmetric two-level systems (TLS) with

$$\hat{H}_{0} = -\hbar\Omega(|1\rangle\langle 2|+|2\rangle\langle 1|) \tag{0.11}$$

and $\sigma_2 - \sigma_1 = 2$. In Figure 1 we show the time evolution of the initially populated state in a symmetric TLS strongly coupled to a slow bath with $\omega_c = \Omega$, $\xi = 2$ at an intermediate temperature, $\hbar\Omega\beta = 1$. The bath is initially equilibrated with respect to the populated TLS state. These parameters give rise to long-lived memory, presenting a challenge to path integral methods. Recent SMatPI calculations⁵⁶ obtained converged results using L = 18 and $L_{ext} = 100$ with $\Omega\Delta t = 0.25$. The SMatQCPI calculation converged much faster, using L = 7, $L_{ext} = 80$, and required about 10 times less effort.



Fig. 1. Time evolution of initially populated states for a TLS coupled to a slow harmonic bath with $\omega_c = \Omega$, $\xi = 2$ and $\hbar\Omega\beta = 1$. The bath is initially equilibrated with respect to the initially populated state. Black line: converged SMatPI results with L = 18 and $L_{ext} = 100$. SMatQCPI results with L = 7 are shown with dashed lines and circles. Dashed green line: no extended memory. Dashed blue line: $L_{ext} = 20$. Red circles: $L_{ext} = 80$.

In the second TLS example we use parameters pertaining to the ferrocene-ferrocenium (see Figure 2) charge transfer in liquid hexane, which is accompanied by a significant solvent rearrangement. Earlier work³⁸ reported full QCPI simulations in a solvent containing 66 hexane molecules (1320 atoms) interacting through the CHARMM force field,⁶¹ and concluded that the process is strongly nonexponential. Further, QCPI calculations performed on a system-bath model that used the energy gap correlation function obtained from molecular dynamics simulations to map the anharmonic solvent on a harmonic bath produced indistinguishable results, confirming the quantitative validity of Gaussian response for this system.

The coupling between the two charge states is 32 cm⁻¹. The bath was initially equilibrated with respect to the donor state. The spectral density of the harmonic bath that describes the effects of the hexane

solvent on the charge transfer system is shown in the inset of Fig. 2. The large solvent reorganization energy of this system (which exceeds the donor-acceptor coupling by about an order of magnitude), along with the strong coupling of solvent modes in the very low frequency region and several prominent peaks in the spectral density, necessitate a small path integral time step and lead to a very long memory, presenting a challenge to most available methods. Convergence of the QCPI calculations was possible only with the use of the dynamically consistent state hopping (DCSH) trajectory branching scheme.⁴⁴



Fig. 2. Donor state population for the two-state system-bath model that describes the ferrocene-ferrocenium charge transfer complex in liquid hexane at 300 K. The inset shows the spectral density of the effective harmonic bath. The bath is initially equilibrated with respect to the populated system state. The black line shows the DCSH-QCPI results from Ref. ³⁸ Red markers show the SMatQCPI results with L = 30, $L_{ext} = 100$, $\Delta t = 24.2$ fs . The estimated Monte Carlo error is about 0.01.

Fig. 2 shows the SMatQCPI results for the donor population at 300 K and compares to those obtained using the DCSH-QCPI algorithm. The SMatQCPI calculation used a path integral time step of $\Delta t = 24.2$ fs . This large time step was enabled by the use of trajectory-based reference propagators in QCPI. However, the SMatQCPI results were obtained with simple bath reference trajectories on the donor state. Since the present calculation does not take advantage of the DCSH reference, it requires the inclusion of much longer memory. The converged results attained with L = 30, $L_{ext} = 100$ are in excellent agreement with the DCSH-QCPI results. This agreement is remarkable, given the very different nature of reference trajectories and branch selection in the considerably more involved DCSH-QCPI algorithm. In spite of the much longer memory included, the converged SMatQCPI results were obtained with much less effort in comparison to the DCSH-QCPI calculation. Specifically, the acceleration achieved by the SMatQCPI method was over a factor of 50. Further, the SMatQCPI results in Fig. 2 are smoother than those obtained with the DCSH-QCPI algorithm, and required no storage of system paths.

Next, we investigate the performance of the SMatQCPI method in the underdamped regime. The SMatPI algorithm is extremely efficient in this regime, and the use of QCPI is not expected to offer a significant advantage. However, it is important to test the robustness of the SMatQCPI algorithm in this regime as well, as the presence of Monte Carlo error in the SMatPI matrices could affect the stability of the propagation algorithm in situations of long-lived oscillatory evolution beyond the memory interval.

In Figure 3 we present results on symmetric and asymmetric three-state models described by the Hamiltonian

$$\hat{H}_{0} = -\hbar\Omega(|1\rangle\langle 2|+|2\rangle\langle 1|+|2\rangle\langle 3|+|3\rangle\langle 2|) + \varepsilon_{1}|1\rangle\langle 1|+\varepsilon_{2}|2\rangle\langle 2|+\varepsilon_{3}|3\rangle\langle 3|$$
(0.12)

with parameters that exhibit underdamped dynamics. Initially the population of the system is in state 1 and the bath is equilibrated with respect to this state. The system-bath interaction parameters are specified by $\sigma_1 = 0$, $\sigma_2 = 1$, $\sigma_2 = 2$, $\omega_c = 7.5\Omega$, $\xi = 0.1$, and the temperature $\hbar\Omega\beta = 1$. This model is characteristic of coherent energy transfer in a molecular trimer.



Fig. 3. Dynamics of a three-level system coupled to a bath in the coherent regime with ω_c = 7.5Ω, ξ = 0.1 and ħΩβ = 1. The populations of states 1,2 and 3 are shown in blue, green and orange/red, respectively. SMatPI results are plotted as lines, while markers show the analogous SMatQCPI results. All results use L = 4, ΩΔt = 0.25.
(a) Symmetric three level system (ε₁ = ε₂ = ε₃ = 0). (b) Asymmetric three-level system (ε₁ = 0.8ħΩ, ε₂ = ħΩ, ε₃ = 0).

Fig. 3a shows the populations for a symmetric three-state system ($\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = 0$). This weaklycoupled, high-frequency bath is effectively at a low temperature ($\hbar \omega_c \beta = 7.5$), thus this parameter set is in the coherent regime. The dynamics of this system is largely underdamped, and the ensuing population is oscillatory up to long evolution times. The equilibrium values of the two edge state populations are lower than the population of state 2, reflecting the composition of the ground eigenstate. The SMatQCPI results converged with L = 4, $\Omega \Delta t = 0.25$ and are in excellent agreement with fully converged SMatPI results. Not surprisingly, the effects of quantum memory are just as important as their classical counterparts in this parameter regime,⁵⁷ thus the QCPI reference does not shorten the required memory. Fig. 3b shows results for an asymmetric arrangement of the site energies, $\varepsilon_1 = 0.8\hbar\Omega$, $\varepsilon_2 = \hbar\Omega$, $\varepsilon_3 = 0$, state 2 represents a lowlying bridge. Again, large amplitude oscillatory features are observed initially, but they are much shorter lived in this case due to the energetic separation of the states. The agreement between SMatPI and SMatQCPI results is excellent here as well.

Last, we illustrate the algorithm on a six-state vibronic model. Such models are often constructed for exciton dimers. The Hamiltonian has two electronic states, labeled 1 and 2, which interact according to Eq. (0.11) and which are coupled to the usual dissipative bath and also to a special vibrational mode of coordinate Q and frequency $\omega_Q = 3\Omega$ according to the Hamiltonian

$$\hat{H} = \hat{H}_0 + \frac{\hat{P}_j^2}{2m} + \frac{1}{2}m\omega_Q^2 \left(\hat{Q} - \frac{C\hat{s}}{m\omega_Q^2}\right)^2 + \sum_j \frac{\hat{P}_j^2}{2m_j} + \frac{1}{2}m_j\omega_j^2 \left(\hat{q}_j - \frac{c_j\hat{s}}{m_j\omega_j^2}\right)^2$$
(0.13)

where the coupling parameter *C* is such that the Huang-Rhys factor of the mode is S = 0.05. These parameters are representative of intramolecular vibrations relevant to the exciton dynamics of chromophore dimers. We treat this mode as a part of the system Hamiltonian using three harmonic oscillator basis states, such that the composite vibronic system Hamiltonian comprises a total of six states. We use a moderate peak frequency of the bath, $\omega_c = 3\Omega$, a moderately large system-bath coupling parameter $\xi = 0.8$, and monitor the dynamics at a temperature that corresponds to $\hbar\Omega\beta = 0.5$.



Fig. 4. Electronic state population for a vibronic six-state system. Black line: SMatPI results with $\Omega\Delta t = 0.3$, L = 6. Red markers: SMatQCPI results with $\Omega\Delta t = 0.4$, L = 3. The inset shows the population over a longer period (red), along with the expectation value of the coordinate of the vibronic mode (blue). SMatPI and SMatPI results are indistinguishable.

Figure 4 shows the population of the electronic state 1 after summing over the basis states of the vibronic mode. Persistent small-amplitude oscillations owing to the vibronic mode are observed following the initial rapid decay of the population, which gradually phase out on a much longer time scale shown in the inset. We also show the average coordinate of the vibronic mode, which is seen to oscillate for very long times, while slowly losing amplitude to the continuous bath. We note that the energy exchange process is very slow because the vibronic mode is coupled to the bath only indirectly through the electronic system. The SMatPI results converged with a time step $\Omega\Delta t = 0.3$ and a memory parameter L = 6. Because of the exact treatment of classical memory in the QCPI reference propagators, the SMatQCPI results converged with $\Omega\Delta t = 0.4$ and L = 3. In this case the SMatQCPI calculation was considerably faster than SMatPI.

In conclusion, SMatQCPI combines the best features of the QCPI and SMatPI algorithms into a simple, yet powerful method which eliminates the storage demands of iterative HBR-QCPI calculations. The model calculations presented above show that the algorithm is stable and highly accurate in all parameter regimes. When used on system-bath Hamiltonians the SMatQCPI algorithm yields exact, fully quantum mechanical results. By avoiding the full path evaluation at each iteration step, SMatQCPI reduces the computational effort of iterative HBR-QCPI by a factor equal to the number of propagation time steps.

Further, the SMatQCPI matrices only need to account for quantum decoherence, leading to shorter effective memory and faster convergence compared to SMatPI in the incoherent regime. The elimination of tensor storage, along with the very significant increase of efficiency in comparison to the HBR-QCPI and SMatPI algorithms, suggest that the SMatQCPI will be the method of choice for simulating the dynamics of multistate systems in challenging regimes, where earlier methods may be prohibitively expensive.

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