Stochastic unraveling of time-local quantum master equations beyond the Lindblad class

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A method for stochastic unraveling of general time-local quantum master equations (QME) which involve the reduced density operator at time t only is proposed. The present kind of jump algorithm enables a numerically efficient treatment of QMEs that are not of Lindblad form. So it opens large fields of application for stochastic methods. The unraveling can be achieved by allowing for trajectories with negative weight. We present results for the quantum Brownian motion and the Redfield QMEs as test examples. The algorithm can also unravel non-Markovian QMEs when they are in a time-local form like in the time-convolutionless formalism.

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Quantum master equations (QMEs) are frequently used to describe time-independent as well as time-dependent phenomena in chemical physics, quantum optics, solid state physics, biological physics, etc. (see Ref. [1] for a number of typical examples). These QMEs describe the time evolution of density matrices, which are used in order to represent the mixed nature of the states. Stochastic unraveling is an efficient numerical tool for solving such equations. This method allows one to simulate much larger and more complex systems with many degrees of freedom. It can, for example, be used to accurately describe femtochemical experiments in the liquid phase whose description has been limited until now, to models with one or two effective interaction coordinates. In the unraveling scheme one considers an ensemble of stochastic Schrödinger equations (SSEs) which in the limit of a large ensemble resembles the respective QME. The numerical effort scales much more favorably with the size of the basis since one is now dealing with wave functions and not with density matrices anymore (for a comparison of direct integrators, see Ref. [2]). Another aspect of the stochastic methods is the possible physical interpretation of experiments detecting macroscopic fluctuations (e.g., photon counting) in various quantum systems [3]. Most of the unraveling schemes [3–8] have been restricted to QMEs of Lindblad form [9] that ensures that the reduced density matrix (RDM) stays positive semidefinite for all times and all parameters. Nevertheless there are many physical meaningful QMEs that result in positive-definite or almost positive-definite RDMs although they are not of Lindblad form. The increasing interest in descriptions beyond the Lindblad class such as the quantum Brownian motion [10,11], the Redfield formalism [12], non-Markovian schemes [13–15], etc., resulted in various efforts to develop stochastic wave-function algorithms.

Strunz *et al.* [10,11] developed the non-Markovian quantum diffusion model. In general, this method can also be applied to QMEs in Markov approximation even though they might not preserve positivity (see also Ref. [16]). A similar approach was also proposed by Gaspard and Nagaoka [17]. Very recently Stockburger and Grabert [18] developed a method on how to exactly represent the RDM of a system coupled to a linear heat bath in terms of SSEs. The numerical properties of this approach need to be explored. Breuer *et al.* [15] extended a scheme that they had used to calculate the multitime correlation functions [19] to the unraveling of QMEs. Their technique is based on doubling the Hilbert space. Instead of a single stochastic wave function one has a pair of them [15]. This scheme conserves Hermiticity of the RDM only on an average and not for every single realization. Thus, the deviation from Hermiticity is a quantity with statistical error and one has to perform a huge number of realizations in order to achieve a good convergence. Since stability and efficiency are crucial issues for unraveling algorithms we propose in this paper an alternative approach that fulfills these criteria.

The aim is to represent, in terms of quantum trajectories, the solution $\rho(t)$ of a generalized time-local Hermiticity-conserving QME

$$\frac{d\rho(t)}{dt}=A(t)\rho(t)+\rho(t)A^{\dagger}(t)+\sum_{k=1}^{M}\{C_k(t)\rho(t)E_k^{\dagger}(t)+E_k(t)\rho(t)C_k^{\dagger}(t)\} \tag{1}$$

with the total number M of dissipative channels and arbitrary operators $A(t)$, $C_k(t)$, and $E_k(t)$. Examples for these operatores are given below. Here we restrict the operators in such a way that the norm of the solution stays conserved. For readability we shall omit the time arguments in the following.

In order to approach the problem let us define a state vector $(|\psi\rangle,|\phi\rangle)^T$ spanning a doubled Hilbert space as proposed in Ref. [15]. Unlike Ref. [15] the RDM shall be reproduced by an ensemble average (denoted by overbars) of outer products of the vectors $|\psi\rangle$ and $|\phi\rangle$

$$\rho=\overline{|\psi\rangle\langle\phi|}+\overline{|\phi\rangle\langle\psi|}. \tag{2}$$

A particular realization of the stochastic process will be denoted by the pair $(|\psi\rangle,|\phi\rangle)$. The averaging is performed over all trajectories possibly including a weighted sum over pure initial states. A vantage of this averaging is the conservation of Hermiticity for every single trajectory in contrast to

Ref. [15]. We note that this small modification improves the numerical efficiency significantly.

For the SSEs let us consider $2M$ independent possibly complex noise variables $\xi_k^i(t)$. The superscripts denote which of the two terms from the Hermitian pair in the sum in Eq. (1) is taken and subscripts denote the various dissipative channels. All stochastic differentials $d\xi_k^i(t)$ are assumed to have zero mean, to be normalized and uncorrelated [20]

$$\overline{d\xi_k^i}=0, \quad \overline{d\xi_k^{i*}d\xi_l^j}=\delta_{ij}\delta_{kl}dt. \tag{3}$$

Next, as an ansatz we construct a SSE that propagates the pair $(|\psi\rangle,|\phi\rangle)$

$$d|\psi\rangle=D_1|\psi\rangle dt+\sum_{k=1}^{M}\sum_{i=1}^{2} S_{1k}^i|\psi\rangle d\xi_k^i, \tag{4a}$$

$$d|\phi\rangle=D_2|\phi\rangle dt+\sum_{k=1}^{M}\sum_{i=1}^{2} S_{2k}^i|\phi\rangle d\xi_k^i. \tag{4b}$$

The operators D_1 and D_2 govern the deterministic and the operators S_{jk}^i govern the stochastic part of the evolution. In general, they may depend on the state vector and explicitly on time. After differentiating Eq. (2), neglecting all terms higher than first order in dt, and assuming that ensemble averages always factorize [21] one obtains

$$d\rho=[D_1\overline{|\psi\rangle\langle\phi|}+D_2\overline{|\phi\rangle\langle\psi|}]dt+\sum_{k=1}^{M}[S_{1k}^1\overline{|\psi\rangle\langle\phi|}S_{2k}^{1\dagger} + S_{2k}^2\overline{|\phi\rangle\langle\psi|}S_{1k}^{2\dagger}]dt+\text{H.c.} \tag{5}$$

Comparing with Eq. (1) one notes that S_{1k}^1 has to equal S_{2k}^2 and S_{2k}^1 has to equal S_{1k}^2. Moreover, one can see that $S_{2k}^1=C_k+\alpha_k^1$ and $S_{2k}^2=E_k+\alpha_k^2$ with α_k^1 and α_k^2 being arbitrary scalar functions of $(|\psi\rangle,|\phi\rangle)^T$ and possibly of time. Making the latter substitutions in Eq. (5) yields the constraint

$$D_1=D_2=A-\sum_{k=1}^{M}(\alpha_k^{2*}C_k+\alpha_k^{1*}E_k+\alpha_k^1\alpha_k^{2*}). \tag{6}$$

Any quantum jump method is specified by jump rates p_k^i which have to be real scalar functions of $(|\psi\rangle,|\phi\rangle)$. If $n_k^i(t)$ is the number of jumps in channel k and due to term i up to time t, the probability for $n_k^i(t)$ to increase by one, i.e., the expectation value of both dn_k^i and $(dn_k^i)^2$, is equal to $p_k^i dt$ during the infinitesimal time interval dt. Thus, the noise variables ξ_k^i obeying Eq. (3) are related to $dn_k^i(t)$ as [21]

$$d\xi_k^i=\frac{dn_k^i-p_k^i dt}{\sqrt{p_k^i}}e^{i\varphi}. \tag{7}$$

The phase factor $e^{i\varphi}$ does not change the RDM expressions within each realization and can be set to one. Substituting Eq. (7) into Eq. (4) one finds that $\alpha_k^i=-\sqrt{p_k^i}$. So the SSEs for our quantum jump method read

$$d|\psi\rangle=\left(A+\sum_{k=1}^{M}\frac{p_k^1+p_k^2}{2}\right)|\psi\rangle dt+\sum_{k=1}^{M}\left[\left(\frac{E_k}{\sqrt{p_k^1}}-1\right)dn_k^1 + \left(\frac{C_k}{\sqrt{p_k^2}}-1\right)dn_k^2\right]|\psi\rangle, \tag{8a}$$

$$d|\phi\rangle=\left(A+\sum_{k=1}^{M}\frac{p_k^1+p_k^2}{2}\right)|\phi\rangle dt+\sum_{k=1}^{M}\left[\left(\frac{C_k}{\sqrt{p_k^1}}-1\right)dn_k^1 + \left(\frac{E_k}{\sqrt{p_k^2}}-1\right)dn_k^2\right]|\phi\rangle. \tag{8b}$$

The jump rates p_k^1 and p_k^2 still remain as free parameters. In the statistical limit their values have no influence on any averaged physical quantity. Nevertheless, it turns out that they can strongly influence the convergence behavior of the jump algorithm, i.e., they determine the statistical error of the observables calculated. A detailed discussion of this influence and utilization of such free parameters can be found in Ref. [22].

To ensure an efficient scheme with fast convergence one has to require that the norm of every single trajectory is constant in time. Asking for $\langle\phi|\phi\rangle$, $\langle\psi|\psi\rangle$, etc., being constant in time does not create a stable scheme but the condition of norm preservation of $|\psi\rangle\langle\phi|+|\phi\rangle\langle\psi|$

$$\text{Tr}\left\{\frac{d}{dt}[|\psi\rangle\langle\phi|+|\phi\rangle\langle\psi|]\right\}=0 \tag{9}$$

does. Unfortunately, applying this condition does not lead us to positive values of the jump rates p_k^i for all trajectories at all times. However, since the p_k^i are arbitrary real functions, they can be replaced by their absolute values. The price to pay is that we have to introduce an additional weight factor for the trajectories, which jumps between one and minus one. In addition, there is a small deviation of the norm from unity because in the regions where the p_k^i are replaced by their absolute values norm conservation is no longer guaranteed. But in all our tests this deviation was far below 1% and neither affected numerical stability nor efficiency. The negative weights are actually needed to reconstruct RDMs which are, in general, not positive semidefinite. If the RDM stays positive semidefinite during its entire time evolution the negative weights of some trajectories are not needed, i.e., all trajectories can be normalized to unity and represent physically pure states of the open quantum system. In the examples below the RDM can exhibit negative populations. This unphysical situation could probably be cured by applying an initial slippage to the initial state [23,24]. We note that these physically unreasonable RDMs occur because of unphysical initial states or because the QME is not physically correct or is applied in a parameter region where it is not valid. Nevertheless an unraveling scheme has to be able to mimic also this unphysical behavior of the QME because in the ensemble average both should fully coincide.

The condition (9) applied to the QME (1) results in the additional constraint

$$A+A^{\dagger}=-\sum_{k=1}^{M}(E_k^{\dagger}C_k+C_k^{\dagger}E_k) \tag{10}$$

and if applied to the deterministic part of the corresponding SSE (8) it yields the total jump rate

$$p=-\frac{\langle\phi|A+A^{\dagger}|\psi\rangle+\langle\psi|A+A^{\dagger}|\phi\rangle}{\langle\phi|\psi\rangle+\langle\psi|\phi\rangle}. \tag{11}$$

All partial jump rates can be found subsequently making use of Eqs. (10) and (11)

$$p_k^1=\frac{\langle\phi|C_k^{\dagger}E_k|\psi\rangle+\langle\psi|E_k^{\dagger}C_k|\phi\rangle}{\langle\phi|\psi\rangle+\langle\psi|\phi\rangle}, \tag{12a}$$

$$p_k^2=\frac{\langle\phi|E_k^{\dagger}C_k|\psi\rangle+\langle\psi|C_k^{\dagger}E_k|\phi\rangle}{\langle\phi|\psi\rangle+\langle\psi|\phi\rangle}. \tag{12b}$$

In the rest of this paper let us briefly show how the proposed method can be applied to two typical physical problems: the quantum Brownian motion and dissipative electron transfer within Redfield theory. In both cases the systems are described by Markovian QMEs which do not have Lindblad structure. The model of Brownian motion [1] describes a particle with mass m, coordinate q, momentum p, and Hamiltonian H_S interacting with a thermal bath. In the high-temperature limit of a bath of harmonic oscillators the relevant QME has the form

$$\frac{d\rho}{dt}=-\frac{i}{\hbar}[H_S,\rho]-\frac{i\gamma}{2\hbar}[q,\{p,\rho\}]-\frac{m\gamma kT}{\hbar^2}[q,[q,\rho]], \tag{13}$$

where γ is the damping rate. Comparing with Eq. (1) one finds the operators of the jump algorithm ($M=2$)

$$E_1=\sqrt{\frac{\gamma}{2\hbar}}q, \quad C_1=-i\sqrt{\frac{\gamma}{2\hbar}}p, \tag{14a}$$

$$E_2=\sqrt{\frac{m\gamma kT}{\hbar^2}}q, \quad C_2=E_2, \tag{14b}$$

$$A=-\frac{i}{\hbar}H_S+\frac{i\gamma}{2\hbar}qp-\frac{m\gamma kT}{\hbar^2}qq. \tag{14c}$$

Modeling the particle as a harmonic oscillator with eigenfrequency ω one can compute the population dynamics depicted in Fig. 1. The initial state of the oscillator is the pure state $\rho_{33}=1$. As can be seen, the agreement of the results using our stochastic method and a direct integration of the QME is already quite good for one thousand samples.

As a next test for the present quantum jump method we shall demonstrate the stochastic unraveling of the Redfield QME [12,25]

$$\dot{\rho}=-\frac{i}{\hbar}[H_S,\rho]+\frac{1}{\hbar^2}\{[\Lambda\rho,K]+[K,\rho\Lambda^{\dagger}]\} \tag{15}$$

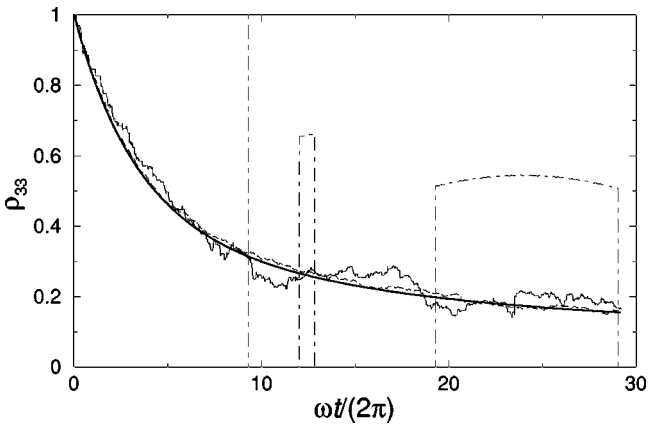

FIG. 1. Time evolution of the third excited state of the harmonic oscillator in the quantum Brownian oscillator model for $\gamma=10^{-3}\omega$, $kT=4.5\omega$. The direct integration of the QME (thick solid line) is compared to the results of the quantum jump method with one trajectory (dot-dashed line), average of 100 (thin solid line), and 1000 (broken line) trajectories.

in which Λ is the relaxation operator and K the system part of the system-bath interaction [12]. Let us consider a model for electron transfer in which the system includes a single reaction coordinate with the Hamiltonian [12,25]

$$H_S=H_1|1\rangle\langle 1|+H_2|2\rangle\langle 2|+v_{12}(|1\rangle\langle 2|+|2\rangle\langle 1|), \tag{16}$$

where H_1 and H_2 are the Hamiltonians of two coupled harmonic oscillators with frequency ω. We choose a potential configuration in the normal region with no barrier between the two harmonic potentials (change of free energy $\Delta E=2\omega$, reorganization energy $\lambda=3\omega$) with intercenter coupling $v_{12}=\omega$. The bath is described by a cutoff frequency $\omega_c=\omega$ and temperature $kT=\omega/4$. The system-bath interaction is characterized by the damping rate $\Gamma=\pi\eta/(\mathcal{M}\exp(1))=\omega/10$ (see Ref. [25] for details). After rearrangement of Eq. (15) one can easily identify the operators involved in Eq. (1) ($M=1$): $C_1=K$, $E_1=\Lambda$, $A=-iH_S-K\Lambda$. A Gaussian wave packet located at the donor state $|1\rangle$ and having energy slightly above the crossing of the harmonic potentials was chosen as initial state. The numerical simulation for about 1000 trajectories provides sufficiently converged and accurate results. Figure 2 shows the relaxation of the ensemble averaged donor population $\overline{P_1}=\overline{\langle\psi|1\rangle\langle 1|\phi\rangle}+\overline{\langle\phi|1\rangle\langle 1|\psi\rangle}$. A widely discussed property of the Redfield equation is that it does not conserve positivity [12]. Although $\overline{P_1}$ is always positive the tiny negative fraction in Fig. 3 is an evidence for the existence of single realizations with negative P_1. The simulation of the same system within the so-called diabatic-damping approximation [25,26] with a Lindblad QME by means of the standard quantum jump method [3–7] keeps all values of P_1 well confined between 0 and 1.

To summarize, a method of stochastic unraveling of QMEs beyond the Lindblad form is proposed and thus large fields of application for stochastic methods are opened. This progress became possible with the use of the wave-function pair in the doubled Hilbert space and the derivation of stable,

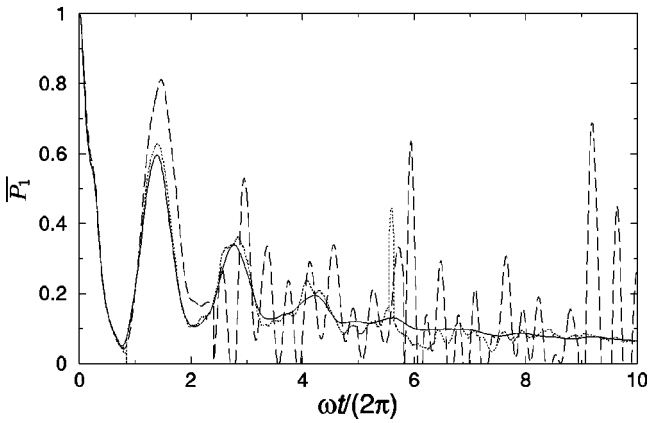

FIG. 2. Relaxation of the donor population for the electron transfer model. The solid line shows the exact solution of the QME, the dashed line one arbitrary trajectory, the dotted line an average over 500 trajectories.

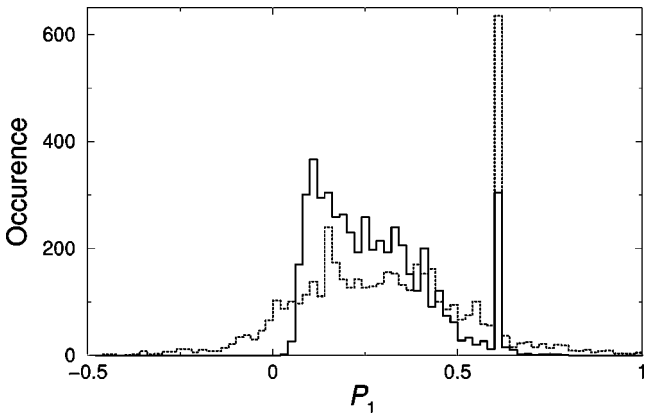

FIG. 3. Occurrence of the expectation values of the population on the donor state produced by the new unraveling scheme for the Redfield QME (dotted line) and the standard normalized jump method for the Lindblad QME (solid line) at time $\omega t/(2\pi)=3$, both with 5000 trajectories.

almost normalized SSEs. The efficiency is determined by the behavior of the norm of every single trajectory. In this sense the jump rates were used as parameters to influence the efficiency. Negative values for the weight of single trajectories allow for the reconstruction of non positive-semidefinite RDMs if required. The method was successfully tested for a simple electron transfer model and for Brownian motion and should allow for better quantum dynamical simulation of large systems. It can also unravel non-Markovian QMEs when they are in a time-local form like in the time-convolutionless formalism [13] or in methods using auxiliary density matrices to include the memory effects [14] as well as post-Markov master equations [23].

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