Positivity preserving non-Markovian master equations

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A general class of integrodifferential non-Markovian master equations is developed which is representative of the dynamics of small subsystems interacting with open reservoirs with memory. Conditions which guarantee positivity of the subsystem reduced density are established.

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Master equation approaches remain an important tool for predicting the quantum mechanical dynamics of small subsystems interacting with open reservoirs. More rigorous approaches, such as the Feynman-Vernon influence functional method [1–3], while preferable in principle, suffer the disadvantage that they can at present only be applied to simple model systems such as the spin-boson model [2,4]. Numerical methods for calculating the influence functionals of more general reservoirs are still in the early stages of development [5]. Applications of the exact Nakajima-Zwanzig master equation [6] are also hampered by high computational costs. Approximate master equation approaches are often the only method available for application to systems of current experimental interest, and efforts to improve the accuracy of these equations are therefore ongoing.

The issue of positivity has drawn the most attention. Matrix elements $\langle\phi|\rho(t)|\phi\rangle$ of the subsystem density $\rho(t)$ are occupation probabilities, and they should be positive for any state ϕ. For some initial densities $\rho(0)$ the popular Redfield master equation [7] is known to produce time evolving densities $\rho(t)$ which violate positivity. Slipped initial conditions [i.e., special $\rho(0)$] correct this problem for the spin-boson system [8,9], but have not been shown to work in general. The only master equations which are known to produce positive $\rho(t)$ for all $\rho(0)$ are of the completely positive dynamical semigroup (CPDS) form [10,11]. This class of equations is very general and includes master equations derived in many different ways [12]. All CPDS equations have the form [10,11]

$$d\rho(t)/dt=-iL\rho(t)-\tau L_D\rho(t), \tag{1}$$

where L is a nondissipative Liouville operator,

$$L\rho=\frac{1}{\hbar}[H,\rho], \tag{2}$$

and L_D is a positive semidefinite Lindblad operator [11]:

$$L_D\rho=\frac{1}{\hbar^2}\sum_{\mu,\nu}C_{\mu,\nu}\{[\rho S_\nu,S_\mu]+[S_\nu,S_\mu\rho]\}. \tag{3}$$

Here H is an effective subsystem Hamiltonian, τ is the relaxation time of the reservoir, the Hermitian operators S_μ mediate interactions of the subsystem with the reservoir, and $C_{\mu,\nu}$ is a positive definite Hermitian matrix.

The Redfield and CPDS master equations share a common limitation: they can only be applied when the reservoir relaxes to equilibrium much more quickly than the subsystem. Situations where this separation of time scales may not exist include relatively slow processes such as electron transfer in biological molecules [13], destruction of local orientational order in supercooled water [14], and vibrational relaxation of ions in solution [15]. Breakdown of this separation of time scales is also characteristic of faster processes such as chemical reactions in solution. Approximate master equations therefore need to be, and are being [2,4,16–19], developed for this non-Markovian regime.

Here we construct a general class of non-Markovian master equations, analogous to the Markovian CPDS equation (1), and establish conditions which guarantee positivity of the subsystem density $\rho(t)$. When the reservoir relaxation time is comparable to the time scale of the subsystem dynamics, information about the history of the subsystem is stored in the phases of subsystem-reservoir interaction modes. Because the interaction modes influence the subsystem, the history of the subsystem plays a role in determining its future. Thus, from a mathematical perspective, master equations in the non-Markovian regime must take the form of integrodifferential equations. A promising class of suitable integrodifferential equations can be obtained by a straightforward generalization of CPDS theory,

$$d\rho(t)/dt=f(t)-iL\rho(t)-\int_0^t dt'\,W(t-t')L_D\rho(t'), \tag{4}$$

where L is the nondissipative Liouville operator, [Eq. (2)], and L_D is the dissipation operator [Eq. (3)]. Equations like Eq. (4) can be viewed as approximations to the exact Nakajima-Zwanzig equation [6]. $W(t)$ is a memory function which weights the integral over the history of the subsystem, while the Hermitian operator $f(t)$ is an inhomogeneous term introduced to include the effects of initial subsystem-reservoir correlation [19]. If $\int_0^\infty dt\,W(t)=\tau<\infty$ and if $f(t)$ is zero outside the initial non-Markovian regime, then Eq. (4) reduces to CPDS form [Eq. (1)] at long times. Performing a trace over both sides of Eq. (4) yields $d\,\mathrm{Tr}\,\rho(t)/dt=\mathrm{Tr}\,f(t)$, and so if $\mathrm{Tr}\,f(t)=0$ then probability is conserved. It is also straightforward to show that $\rho(t)$ and $\rho^\dagger(t)$ satisfy the same equation with the same initial condition, and therefore the solutions of Eq. (4) are Hermitian operators. Thus Eq. (4) has a number of important physical properties.

The fact that Eq. (4) reduces to CPDS form at long time proves useful for establishing positivity criteria. Defining $M(t)=\tau\delta(t)-W(t)$, Eq. (4) can be rewritten in the form

$$d\rho(t)/dt=f(t)-(iL+\tau L_D)\rho(t)+\int_0^t dt' M(t-t')L_D\rho(t'), \tag{5}$$

where we have separated out the generator $-(iL+\tau L_D)$ of the long time Markovian dynamics. Since L and L_D do not in general commute, it would be easier to analyze Eq. (5) if we could treat the second and third terms on the right-hand side independently. This can be done by converting the integro-differential equation (5) to a larger set of differential equations. Defining a new operator $\chi(t,u)$ which depends on time t, and a new timelike variable u,

$$\frac{d}{dt}\begin{pmatrix}\rho(t)\\ \chi(t,u)\end{pmatrix}=\begin{pmatrix}-(iL+\tau L_D) & \delta_0\\ M(u)L_D & \frac{\partial}{\partial u}\end{pmatrix}\begin{pmatrix}\rho(t)\\ \chi(t,u)\end{pmatrix},$$

where the usual initial conditions apply for $\rho(t)$ and $\chi(0,u)=f(u)$. The linear functional δ_0 is defined via $\delta_0 g(u)=g(0)$. The equivalence of

$$\frac{d\rho(t)}{dt}=-(iL+\tau L_D)\rho(t)+\delta_0\chi(t,u), \tag{6}$$

$$\frac{d\chi(t,u)}{dt}=M(u)L_D\rho(t)+\frac{\partial\chi(t,u)}{\partial u} \tag{7}$$

to Eq. (5) can be easily established. Solving Eq. (7) for $\chi(t,u)$ in terms of $\rho(t)$ gives

$$\chi(t,u)=e^{t\partial/\partial u}\chi(0,u)+\int_0^t dt' e^{(t-t')\partial/\partial u}M(u)L_D\rho(t') \tag{8}$$

$$=f(t+u)+\int_0^t dt' M(t-t'+u)L_D\rho(t'), \tag{9}$$

from which it then follows that

$$\delta_0\chi(t,u)=f(t)+\int_0^t dt' M(t-t')L_D\rho(t'). \tag{10}$$

Substituting this result into Eq. (6) then gives Eq. (5). Thus Eqs. (8) and (9) are equivalent to Eq. (5), but have a more convenient form. This method of converting integrodifferential equations to differential equations, first introduced by Chen and Grimmer [20], is closely related to the t, t' method, which is used to solve the Schrödinger equation for time-dependent Hamiltonians [21].

The solutions of Eqs. (6) and (7) can be expressed as a propagator of exponential form acting on the initial conditions,

$$\begin{pmatrix}\rho(t)\\ \chi(t,u)\end{pmatrix}=\exp\left[\begin{pmatrix}-(iL+\tau L_D) & \delta_0\\ M(u)L_D & \frac{\partial}{\partial u}\end{pmatrix}t\right]\begin{pmatrix}\rho(0)\\ f(u)\end{pmatrix},$$

which allows us to use methods developed for the propagator of the Schrödinger equation. Applying the Trotter product formula [22],

$$\begin{pmatrix}\rho(t)\\ \chi(t,u)\end{pmatrix}=\lim_{N\to\infty}\left\{\exp\left[\begin{pmatrix}-(iL+\tau L_D) & 0\\ 0 & 0\end{pmatrix}\frac{t}{N}\right]\times\exp\left[\begin{pmatrix}0 & \delta_0\\ M(u)L_D & \frac{\partial}{\partial u}\end{pmatrix}\frac{t}{N}\right]\right\}^N\begin{pmatrix}\rho(0)\\ f(u)\end{pmatrix},$$

and the desired separation of Markovian and non-Markovian evolutions is achieved.

Since the CPDS propagator $e^{-(iL+\tau L_D)t}$ preserves positivity, we also know that

$$\exp\left[\begin{pmatrix}-(iL+\tau L_D) & 0\\ 0 & 0\end{pmatrix}t\right]=\begin{pmatrix}e^{-(iL+\tau L_D)t} & 0\\ 0 & 1\end{pmatrix}$$

preserves positivity. Thus, Eq. (5) will preserve positivity if the operator

$$\exp\left[\begin{pmatrix}0 & \delta_0\\ M(u)L_D & \frac{\partial}{\partial u}\end{pmatrix}t\right]$$

preserves positivity, and we may thus confine our attention to the simpler integrodifferential equation

$$d\rho(t)/dt=f(t)+\int_0^t dt' M(t-t')L_D\rho(t') \tag{11}$$

generated by this operator.

Equations like Eq. (11) were studied by Prüss [23], who showed that solutions of Eq. (11) will be positive if the function

$$a(t)=\int_0^t dt' M(t')=\tau-\int_0^t dt' W(t') \tag{12}$$

is (i) positive or (ii) nonincreasing, (iii) if $\log a(t)$ is convex (i.e., $a(t)[d^2a(t)/dt^2]-[da(t)/dt]^2\geqslant 0$), and (iv) if $f(t)$ is positive. Clearly $a(t)$ will be positive and nonincreasing if $W(t)$ is positive and nonincreasing, conditions consistent with the role of $W(t)$ as a memory function.

We now explain how these conditions arise. Laplace transforming both sides of Eq. (11)—and denoting the Laplace transforms of $M(t)$, $a(t)$, $f(t)$, and $\rho(t)$ by $\tilde{M}(z)$, $\tilde{a}(z)$, $\tilde{f}(z)$, and $\tilde{\rho}(z)$—one can show that

$$\tilde{\rho}(z)=[z-\tilde{M}(z)L_D]^{-1}[\rho(0)+\tilde{f}(z)]. \tag{13}$$

The trick now is to rewrite

$$[\text{-}z-\tilde{M}(z)L_D]^{-1}=\int_0^\infty d\tau' e^{-[z-\tilde{M}(z)L_D]\tau'} \tag{14}$$

$$=\int_0^\infty d\tau\, e^{L_D\tau}\tilde{h}(z,\tau), \tag{15}$$

where $\tau = \tau'/\tilde{M}(z)$ and $\tilde{h}(z,\tau) = e^{-z\tau/\tilde{M}(z)}/\tilde{M}(z) = e^{-\tau/\tilde{a}(z)}/z\tilde{a}(z)$. Combining Eqs. (13) and (15), one can show that

$$\rho(t) = S(t)\rho(0) + \int_0^t dt' S(t-t') f(t'), \tag{16}$$

where

$$S(t) = \int_0^\infty d\tau e^{L_D \tau} h(t,\tau) \tag{17}$$

is the inverse Laplace transform of Eq. (15), and $h(t,\tau)$ is the inverse Laplace transform of $\tilde{h}(z,\tau)$. Now, clearly, $e^{L_D \tau}$ preserves positivity, since L_D is of Lindblad type [11], and so if $h(t,\tau)$ is positive for all t, and τ then $S(t)$ will be positive. A necessary and sufficient condition for $h(t,\tau)$ to be positive (Bernstein's theorem [24]) is that $\tilde{h}(z,\tau)$ be completely monotonic, [i.e., $(-1)^n (d^n/dz^n)\tilde{h}(z,\tau) \geqslant 0$, for $z \in (0,\infty)$. Prüss [23] showed that (i)–(iii) are sufficient to guarantee that $\tilde{h}(z,\tau)$ is completely monotonic with respect to z. Finally, if $S(t)$ preserves positivity, then solutions of Eq. (16) will be positive if $f(t)$ is positive.

In summary, if requirements (i)–(iv) are satisfied, then the operator

$$\exp\left[\begin{pmatrix} 0 & \delta_0 \\ M(u)L_D & \dfrac{\partial}{\partial u} \end{pmatrix} t\right]$$

preserves positivity. Both the Markovian and non-Markovian evolutions then preserve positivity, and hence their product

$$\exp\left[\begin{pmatrix} -(iL+\tau L_D) & 0 \\ 0 & 0 \end{pmatrix} t\right] \exp\left[\begin{pmatrix} 0 & \delta_0 \\ M(u)L_D & \dfrac{\partial}{\partial u} \end{pmatrix} t\right]$$

preserves positivity. Finally, it follows that the limit

$$\lim_{N\to\infty}\left\{\exp\left[\begin{pmatrix} -(iL+\tau L_D) & 0 \\ 0 & 0 \end{pmatrix} \frac{t}{N}\right] \times \exp\left[\begin{pmatrix} 0 & \delta_0 \\ M(u)L_D & \dfrac{\partial}{\partial u} \end{pmatrix} \frac{t}{N}\right]\right\}^N$$

must also preserve positivity.

Thus, the results of Prüss [23] for Eq. (11) can be readily extended to Eq. (5), and therefore equations like Eq. (4) have positive solutions if $f(t)$ is positive and if $W(t)$ satisfies conditions (i)–(iii). In addition, the condition that $\mathrm{Tr}\, f(t) = 0$ must be satisfied, so that probability is conserved. Thus we have shown that a large class of non-Markovian positivity preserving master equations can be constructed. Since several recently derived master equations [19,25] are of the form of Eq. (4), this class of equations is worthy of further study.

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