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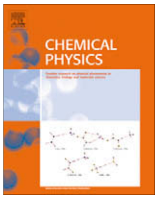

Linearized approximations for condensed phase non-adiabatic dynamics: Multi-layered baths and Brownian dynamics implementation

P. Huo [a], S. Bonella [c], L. Chen [d], D.F. Coker [a,b,*]

[a] Department of Chemistry, Boston University, 590 Commonwealth Avenue, Boston, MA 02215, United States
[b] Department of Physics, University College Dublin, Belfield, Dublin 4, Ireland
[c] Dipartimento di Fisica, Università "La Sapienza", Piazzale Aldo Moro, 2, 00185 Roma, Italy
[d] Department of Chemistry, University of Illinois, Urbana-Champagne, 505 South Mathews Avenue, Urbana, IL 61801, United States

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ABSTRACT

Several approximate methods for propagating the density matrix of systems coupled to baths based on linearized approximations have been presented. Using influence functional formalism this approximation is explored in various limits for a condensed phase model. A new iterative stochastic propagation scheme is introduced that integrates out some of the bath degrees of freedom giving an effective evolution resembling Brownian dynamics. We show that this approach satisfies the fluctuation–dissipation theorem in various limits. The method is compared with alternative approximate full dimensional propagation schemes for the spin-boson model. The accuracy of the results is surprising since the scheme makes approximations about initialization at each iteration. This accuracy is encouraging since these kind of approaches hold significant potential computational saving for condensed phase quantum dynamics simulations as they give a systematic way of eliminating the explicit integration of a large number of environmental degrees of freedom.

1. Introduction

Recent work in the field of mixed quantum-classical dynamics [1–8] has employed linearized approximations to the evolution of the full system. The linearized approximation is applied in particular when calculating the time dependent density matrix of a non-equilibrium system or equilibrium time correlation functions. The general idea is to first separate the interacting degrees of freedom of the condensed phase system of interest into a quantum subset and a classical bath based on relative thermal wavelength or energy considerations. The forward and backward time propagators in the evolution of the density matrix, or of the correlation function, are represented as path integrals. The phase in the integrands of these expressions is then expanded to linear order in the difference between the forward and backward paths of the bath. The resulting approximate form still contains the full evolution of the quantum subsystem. If an appropriate representation for this dynamics is available (e.g. the mapping Hamiltonian or some semiclassical formulation) the linearized approximation can be computed using classical trajectories. While the benefits of the truncation to linear order in the difference paths for the bath variables are well known and have been exploited in a number of applications [9–13], work is still in progress to obtain a general understanding of the conditions under which the approximation is reliable [14].

Depending on the interplay between the parameters in the Hamiltonian, the linearized expression can provide a good approximation for evolving the density matrix over different periods of time. When the linearized approximation is reliable only for short times, correction schemes can be applied. Recently, an iterative scheme employing the linearized approximation for the mixed quantum-classical propagator in the mapping Hamiltonian formulation as a short time approximation in a path integral expression for long time propagation has been suggested [15]. The approach provides a systematic way to extend the linearized approximation to longer times but this comes at a numerical cost that can be substantially reduced in conditions where linearization is reliable for longer times. Similar computational problems affect the work of other groups that have proposed employing approximate short time propagators to iteratively evolve the density matrix. For example, Kapral, Ciccotti, and co-workers have developed an iterative solution for the mixed quantum-classical Wigner-Liouville equation [16–18] based on the Dyson series. The term that is lowest order in the interaction between the quantum and classical subsystems in the propagator gives the classical Liouvillian. Higher

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[*] Corresponding author. Address: Department of Chemistry, Boston University, 590 Commonwealth Avenue, Boston, MA 02215, United States. Tel.: +1 617 353 2490; fax: +1 617 353 6466.
E-mail address: coker@bu.edu (D.F. Coker).

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order terms are represented as combinations of classical dynamics and transitions among states.

Given the computational advantages of the fully linearized scheme, an appreciation of how it becomes accurate for model systems important in condensed phase chemical physics is crucial. In this work we consider and explore one such model: a quantum system is coupled to a local bath, which in turn interacts with an environment represented as a set of harmonic oscillators with bilinear coupling. Such multi-level baths have been studied in various contexts from the early work of Garg et al. [19], who used a very similar path integral influence functional approach to the one we employ here, to explore the qualitative effects of environmental friction and solvent modes (the global bath) on the nuclear reaction coordinates (the local bath) in determining, for example, electron transfer rates (the quantum subsystem). The various approaches we develop here, however, offer a general methodology for developing mixed quantum-classical trajectory based methods, built on these ideas, to propagate an approximation to the density operator for such systems. The same basic ideas underlie the Brownian oscillator models [20,21] that have been so pivotal in the development of the theory of nonlinear spectroscopy of complex systems. More recently [22,23], the spin-boson model with a hierarchical, Brownian oscillator-like bath was employed to develop an approach that combines accurate quantum dynamics for the local bath together with a master equation for the global bath. This marriage of different quantum dynamics methodologies to treat different parts of a system is the powerful idea that forms the basis of the methods we develop in this paper.

A similar model, employing only one harmonic local bath mode, has been used by Shiokawa and Kapral [24] to study the emergence of quantum-classical dynamics in an open quantum environment. These authors showed how the relative time-scales of the quantum subsystem and local bath coherent dynamics change depending on the couplings and on the choice of the model for the spectral density (Ohmic and super-Ohmic) for the baths. In particular, they found that, at high temperatures and for weak couplings, the onset of decoherence can be much faster for the local bath than for the quantum subsystem thus enabling a mixed quantum-classical description of the combined system. This analysis was based on the influence functional formalism [25], which has a long history of development and application, starting in the context of open system dynamics with the early work of Caldeira and Leggett and others [26,27] who investigated the dissipative dynamics of a quantum system coupled to a harmonic bath. In simulations, the influence functional approach has also been used by Makri and co-workers to study the reduced (quantum or semiclassical) dynamics of such systems [28]. As an alternative Pollak and co-workers have extended semiclassical initial value ideas and developed continuum limit methods for treating the quantum dynamics of open dissipative systems [29–31]. Shi and Geva [32], on the other hand, employed a path integral formalism to show how the mixed quantum-classical Liouville equation can be obtained, for given choices of the quantum subsystem basis (diabatic and adiabatic), from linearization of an influence functional. In all these numerical applications, the quantum subsystem was directly coupled to the harmonic bath. In this work we rely on the influence functional formalism to identify conditions in which our linearized dynamics is accurate for the hierarchical bath model outlined above. In the theory section we summarize the most relevant aspects-some known from the literature [27], some based on our developments of the influence functional approach and explore the characteristics of the dynamics of the system when an Ohmic spectral density is used for the local and global baths. As expected from the previous work [24], we find that the critical parameters that control the accuracy of the linearized dynamics for this system are the temperature, the cutoff frequencies of the bath's spectra, and the relative strength of the coupling among the various subsystems.

In addition to this analysis we present a new algorithm to efficiently simulate the evolution of this type of hierarchical bath model. The scheme takes advantage of the influence functional to integrate out the degrees of freedom of the global, harmonic, environment. The evolution of the quantum subsystem and of the local bath is thus reduced to a scheme that has similarities to Brownian dynamics. We show that this new approach satisfies the fluctuation–dissipation theorem in appropriate limits. The new algorithm is potentially very useful for reducing the numerical effort needed to compute the properties of condensed phase systems for which the hierarchical bath model is reasonable. The accuracy of the new algorithm will be tested in benchmark calculations exploring the relevant range of parameters in the special case of a spin coupled to a local harmonic bath (spin-boson), that is bilinearly coupled to a global harmonic environment.

2. Theory

2.1. Hierarchical system-bath model: an influence functional analysis

2.1.1. The model

Condensed phase chemical systems can often be represented in terms of a quantum system (e.g. electrons, protons, or high frequency vibrations, etc.) that may be influenced by its local environment, the "local bath". This local bath essentially screens the quantum subsystem from the rest of the environment or "global bath". For simplicity we will thus assume that there is no direct interaction between the quantum subsystem and the global bath, but the local environment and the quantum subsystem are coupled. The local and global baths also of course can interact in our model.

For convenience we will define the system-local bath interaction Hamiltonian

$$\hat{h}(\hat{s},\hat{r}) = \widehat{H}_s + V_b(\hat{r}) + \Phi_{s-b}(\hat{s},\hat{r}) \tag{1}$$

where $\widehat{H}_s$ is the quantum subsystem Hamiltonian, including the kinetic energy operator, $\hat{s}$ and $\hat{r}$ are the system and local bath coordinate operators respectively, and the full Hamiltonian for the condensed phase models we will consider is thus

$$\widehat{H} = \frac{\hat{p}^2}{2M_b} + \hat{h}(\hat{s},\hat{r}) + \sum_J \left[\frac{\widehat{P}_J^2}{2M_B} + \frac{1}{2} M_B \Omega_J^2 \widehat{R}_J^2 + C_J \widehat{R}_J \hat{r} \right] \tag{2}$$

Here the last square bracketed term on the right hand side represents the global bath with phase space operators $\{P_J, R_J\}$ as a set of harmonic oscillators that are bilinearly coupled to the local bath coordinate operators $\hat{r}$, which, in principle, could be highly dimensional. While the Hamiltonian above is a well defined model when the values of the parameters C_J are small, it is known [27,24] that it can exhibit pathological behavior in the limit of strong coupling between the local and global bath. This behavior is usually corrected by modifying the Hamiltonian via the introduction of the so-called "counter-term", thus

$$\begin{aligned}\widehat{H}_{ct} &= \frac{\hat{p}^2}{2M_b} + \hat{h}(\hat{s},\hat{r}) + \sum_J \left[\frac{1}{2}\left(\frac{\widehat{P}_J^2}{M_B} + M_B \Omega_J^2 \widehat{R}_J^2 \right) + C_J \widehat{R}_J \hat{r} + \frac{C_J^2}{2M_B\Omega_J^2}\hat{r}^2 \right] \\ &= \frac{\hat{p}^2}{2M_b} + \hat{h}(\hat{s},\hat{r}) + \sum_J \left[\frac{\widehat{P}_J^2}{2M_B} + \frac{1}{2} M_B \Omega_J^2 \left(\widehat{R}_J + \frac{C_J}{M_B\Omega_J^2}\hat{r} \right)^2 \right]\end{aligned} \tag{3}$$

The counter-term completes the square in the bilinear coupling between the baths and makes the hessian in the bath degrees of freedom positive definite for this model. The motion of all degrees of freedom is thus bound and this ensures that the coupling be-