Finite temperature application of the corrected propagator method to reactive dynamics in a condensed-phase environment

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(Received 26 October 2010; accepted 4 January 2011; published online 20 January 2011)

The recently proposed mixed quantum-classical method is extended to applications at finite temperatures. The method is designed to treat complex systems consisting of a low-dimensional quantum part (the primary system) coupled to a dissipative bath described classically. The method is based on a formalism showing how to systematically correct the approximate zeroth-order evolution rule. The corrections are defined in terms of the total quantum Hamiltonian and are taken to the classical limit by introducing the frozen Gaussian approximation for the bath degrees of freedom. The evolution of the primary system is governed by the corrected propagator yielding the exact quantum dynamics. The method has been tested on a standard model system describing proton transfer in a condensed-phase environment: a symmetric double-well potential bilinearly coupled to a bath of harmonic oscillators. Flux correlation functions and thermal rate constants have been calculated at two different temperatures for a range of coupling strengths. The results have been compared to the fully quantum simulations of Topaler and Makri [*J. Chem. Phys.* **101**, 7500 (1994)] with the real path integral method. © 2011 American Institute of Physics. [doi:10.1063/1.3545978]

I. INTRODUCTION

Quantum-mechanical treatment of complex systems consisting of many degrees of freedom (DoF) remains a challenging task. The exact solution of the time-dependent Schrödinger equation for such systems is not feasible yet, since the numerical effort scales exponentially with the number of DoF. A common approach to minimizing the numerical effort involves separating the total system into a small subsystem, consisting of a few physically relevant DoF, and a large bath, consisting of the remaining DoF.^{1,2} The former, which can be called the primary system, is treated explicitly, while the latter is described implicitly. The ultimate goal of the system–bath separation is to derive equations of motion for the primary system alone, by tracing out the bath DoF.

An alternative way to reduce the exponential scaling of the fully quantum dynamics is employed by mixed quantum-classical methods.³ These methods approximate the dynamics of the bath by classical equations of motion, while the primary system is treated quantum mechanically. The strategy is particularly well suited to reactions in large biological systems (e.g., enzymes), where strong quantum effects may be limited to a small number of DoF (e.g., those describing proton transfer). At the same time, a very large system combined of heavy atoms (the rest of the enzyme) can be described by classical dynamics. The approach enables the study of a large number of DoF in a detailed level while reducing the computational effort dramatically.

The main challenge of the mixed quantum-classical methods remains the definition of the interaction term between the quantum and classical parts. There are two main groups of methods that differ in the way they combine quantum and classical dynamics. One group is based on a mean-field approximation and includes the classical path method known as Ehrenfest dynamics,⁴ and the time-dependent self-consistent field approximation (TDSCF).^{5,6} In these methods, the dynamics of the quantum part is governed by the time-dependent Hamiltonian, consisting of the potential, averaged with respect to the classical subsystem. The classical part evolves according to Newton's equations of motion on the potential given by the expectation value of the quantum coordinate. The mean-field methods work reasonably well in the case of weak coupling between quantum and classical subsystems. However, they fail to describe nonadiabatic transitions or treat correctly dynamics of a system that involves tunneling.⁷ The drawbacks of the mean-field approximation can be partially improved by multiconfigurational extensions of the TDSCF,^{7–10} which include important correlations between the subsystems, neglected in the single configuration scheme.

The second branch of the mixed quantum-classical methods includes the surface-hopping approach¹¹ and its numerous variations.^{12–18} In these methods, the classical trajectories evolve on adiabatic potential energy surfaces with transitions governed by a stochastic algorithm, which varies in different schemes. While quantum decoherence is neglected in the original surface-hopping method, it has been introduced in later extensions.^{19,20} The surface-hopping

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methods have been shown to work in many cases where the mean-field approximation fails.

The recently developed corrected propagator method²¹ follows the general framework of mixed quantum-classical methods: the low-dimensional primary part is described quantum mechanically, whereas the bath is treated classically. The basic idea of the method is to correct *any* approximate rule for the evolution of the total system. We assume that the exact evolution operator can be written as (hereafter, $\hbar = 1$)

$$\hat{U} = \hat{U}_0 \hat{U}' = \hat{U}_0 \hat{T} e^{-i \int_0^t \hat{H}' dt'} , \quad (1)$$

where $\hat{U}_0$ is the zeroth-order *approximate* propagator, $\hat{U}'$ is the correction that yields exact quantum dynamics, and $\hat{T}$ is the time-ordering operator. The corrected propagator method derives corrections to an approximate evolution operator, rather than to an approximate Hamiltonian. After taking the time derivative of both sides of Eq. (1) and some rearrangement, one can define the time-dependent correction Hamiltonian in terms of the full Hamiltonian and the zeroth-order propagator:

$$\hat{H}'(t) = \hat{U}_0^\dagger \hat{H} \hat{U}_0 - i \hat{U}_0^\dagger \frac{\partial}{\partial t} \hat{U}_0 . \quad (2)$$

The above expression is formally exact, but in order to obtain a computationally feasible scheme it requires additional approximations. In recent publications^{21,22} we have derived the correction to the specific choice of the zeroth-order propagator, namely the adiabatic product $\hat{U}_s \hat{U}_b$, where $\hat{U}_s$ is the quantum propagator for the primary system in the adiabatic environment. Furthermore, we assumed that the bath is fairly classical in nature and can be described by as a set of coherent states. Thus, the dynamics of the bath is given by classical equations of motion for the average positions and momenta of the coherent states, while the primary system evolves according to the corrected quantum propagator. Previously, the method has been applied to describe the dissipative dynamics in one-dimensional systems coupled to a harmonic bath at zero temperature.²³ The results have been compared to the exact quantum-mechanical simulations with the surrogate Hamiltonian method.²⁴ Overall, a good agreement between the two methods has been demonstrated, and the corrected propagator was able to capture the correct dynamics (including the tunneling effect), while the adiabatic and the mean-field approximations failed.

The usefulness of the method depends, however, on its ability to treat multidimensional systems at finite temperatures, which present an additional challenge. Since in this case the system cannot be described by a pure state, calculating thermal observables involves averaging over a large number of eigenstates. The direct averaging makes the fully quantum treatment not feasible, leading to the development of methods incorporating some sort of stochastic averaging.^{25–27}

In this paper, we have extended the corrected propagator method to finite-temperature simulations and calculated a quantum reaction rate in a condensed-phase environment. Quantum rate processes in a condensed phase has been studied extensively by a variety of methods.^{28–38} We apply

the corrected propagator to the study of a model system, consisting of a symmetric double-well potential, bilinearly coupled to a bath of harmonic oscillators. The thermal rate constant for this model system has been calculated using a number of approximate methods. Numerically exact quantum-mechanical calculations, including the path integral technique³⁹ and the multilayer multiconfigurational time-dependent Hartree approach,²⁵ have been used as benchmark results to evaluate the accuracy of different methods.

The structure of the paper is as follows. Section II A summarizes the proposed approach to calculate the thermal rate from the reactive flux formalism with the corrected propagator method. The derivation of the method is given in Sec. II B. In Sec. III, the method is applied to a model system of a symmetric double-well bilinearly coupled to the bath of harmonic oscillators. The conclusions are given in Sec. IV.

II. THEORY

A. Thermal rate constant via flux-side correlation function

To study the reactive dynamics of a quantum system in the condensed-phase environment, we separate the total system into a primary part, consisting of a few DoF that are the most important in the reaction, and their environment. The general Hamiltonian of the combined system is given by

$$\hat{H} = H_s(\hat{\mathbf{p}}, \hat{\mathbf{s}}) + H_b(\hat{\mathbf{P}}, \hat{\mathbf{Q}}) + H_{sb}(\hat{\mathbf{s}}, \hat{\mathbf{Q}}). \quad (3)$$

Here $H_s(\hat{\mathbf{p}}, \hat{\mathbf{s}})$ is the Hamiltonian of the primary system, describing the dynamics along a reaction path, $H_b(\hat{\mathbf{P}}, \hat{\mathbf{Q}})$ is the bath Hamiltonian, and $H_{sb}(\hat{\mathbf{s}}, \hat{\mathbf{Q}})$ describes the interaction between the primary system and the bath. The evolution of the total system is governed by the exact quantum propagator $\hat{U} = e^{-i\hat{H}t}$, which is assumed to be in the form of Eq. (1): a product of the zeroth-order approximate propagator and the correction that yields the exact quantum dynamics.

The quantum reaction rate can be formulated exactly in terms of flux correlation functions.^{40,41} Depending on the ordering of the operators, there are several formally exact expressions. We calculate the thermal rate constant $k(T)$ using the cross correlation function between the position and the flux (the flux-side function):

$$C_{fs}(t) = \text{tr}\{e^{-\beta\hat{H}/2} \hat{F} e^{-\beta\hat{H}/2} e^{i\hat{H}t} \hat{h} e^{-i\hat{H}t}\} . \quad (4)$$

Here $\beta = (k_B T)^{-1}$ and $\hat{F}$ is the reactive flux operator defined as

$$\hat{F} = i[\hat{H}, \hat{h}] . \quad (5)$$

The Heaviside function $\hat{h} = h(\hat{\mathbf{s}})$ is a system operator that projects the wave function onto the product side (in the following numerical example we consider a one-dimensional reaction barrier centered at $s = 0$).

The thermal rate constant is defined as the long time limit of the flux-side correlation function:

$$k(T)Q_r(T) = \lim_{t \rightarrow \infty} C_{fs}(t) , \quad (6)$$

where $Q_r(T)$ is the partition function of the reactants:

$$Q_r(T) = \text{tr}\{e^{-\beta\hat{H}}(1 - \hat{h})\}. \quad (7)$$

The early numerical schemes used to calculate the flux correlation functions included propagation of the thermal wave function⁴² or used Lanczos iterative procedure for diagonalization of the flux operator.⁴³ Later, a more efficient procedure for calculating the flux correlation functions has been developed. It based on the dynamics of the eigenstates of the Boltzmannized flux operator⁴³ (which is not singular as $\hat{F}$) defined as

$$\hat{F}_\beta = e^{-\beta\hat{H}/2} \hat{F} e^{-\beta\hat{H}/2}. \quad (8)$$

For systems with a few DoF the number of the eigenstates of $\hat{F}_\beta$, which are significantly different from zero, is relatively small.⁴³⁻⁴⁶ Thus, the trace in Eq. (4) can be efficiently calculated in the small basis of the eigenstates of $\hat{F}_\beta$. Finally, the calculation of the flux correlation function involves only a small number of wave packet propagations:

$$C_{fs}(t) = \sum_{k=1}^{N_f} f_k \langle u_k(t) | \hat{h} | u_k(t) \rangle. \quad (9)$$

Here $\{f_k\}$ and $\{|u_k\rangle\}$, $k = 1, N_f$ are the eigenvalues and the eigenvectors of $\hat{F}_\beta$, respectively.

However, for a system in the condensed-phase environment the Boltzmannized flux operator is no longer a low rank operator. Therefore, the calculation of thermal observables will require finding a large number of eigenstates followed by their real-time propagation. To overcome the first obstacle, we employ a Monte Carlo importance sampling to the bath states while performing a direct summation of the eigenstates of the system Boltzmannized flux operator. This technique has been successfully applied for condensed-phase reactive systems by Wang et al.^{36,47} using a multilayer multiconfigurational time-dependent Hartree method.⁴⁸ In our application, the dynamics of the bath and the primary system is governed by the corrected propagator.

Since within the corrected propagator the bath dynamics is described by the classical equations of motion, the operators ($\hat{\mathbf{P}}, \hat{\mathbf{Q}}$) are replaced by their corresponding classical phase space variables ($\mathbf{P}_t, \mathbf{Q}_t$). If we neglect the interaction term $\hat{H}_{sb}$ in the Boltzmann operator and assume that the flux operator $\hat{F}$ depends on DoF of the primary system only, the flux-side correlation function can be written as

$$C_{fs}(t) = \frac{1}{Q_b} \int d\mathbf{P}_0 \int d\mathbf{Q}_0 \rho_b(\mathbf{P}_0, \mathbf{Q}_0) \text{tr}_s\{\hat{F}_\beta(\hat{\mathbf{s}}) \hat{U}^\dagger \hat{h} \hat{U}\}, \quad (10)$$

where the trace is over the primary system DoF. Here the Boltzmannized flux operator is defined as

$$\hat{F}_\beta(\hat{\mathbf{s}}) = e^{-\beta\hat{H}_s/2} \hat{F}_s e^{-\beta\hat{H}_s/2}, \quad (11)$$

where $\hat{F}_s = i[\hat{H}_s, \hat{h}]$. The initial phase space distribution of the bath $\rho_b(\mathbf{P}_0, \mathbf{Q}_0)$ is given by the Wigner distribution function:⁴⁹

$$\rho_b(\mathbf{P}, \mathbf{Q}) = \frac{1}{(2\pi)^N} \int d\Delta \mathbf{Q} e^{-i\mathbf{P}\Delta\mathbf{Q}} \times \langle \mathbf{Q} + \Delta\mathbf{Q}/2 | e^{-\beta\hat{H}_b} | \mathbf{Q} - \Delta\mathbf{Q}/2 \rangle, \quad (12)$$

where N is the number of bath DoF. The integral over the phase space gives the partition function of the bath:

$$Q_b(T) = \int d\mathbf{P}_0 \int d\mathbf{Q}_0 \rho_b(\mathbf{P}_0, \mathbf{Q}_0) = \text{tr}_b\{e^{-\beta\hat{H}_b}\}. \quad (13)$$

The transformation between the quantum density operator $\hat{\rho} = e^{-\beta\hat{H}_b}/Q_b$ and the corresponding classical phase space distribution is not unique, and other distribution functions⁵⁰ (such as Husimi) can be employed. This form of the sampling is restricted to harmonic baths, and for anharmonic systems (where the Wigner distribution can be negative) approximations are required.

The Lanczos iteration scheme⁵¹ can be efficiently employed for the diagonalization of the Boltzmannized flux operator since it includes only the system DoF. Using a grid representation for the system wave function, we apply the Chebychev propagator^{52,53} to perform the imaginary time propagation.

In the basis of eigenstates $\{|u_k\rangle\}$ of the Boltzmannized flux operator, the flux-side correlation function reads

$$C_{fs}(t) = \int d\mathbf{P}_0 \int d\mathbf{Q}_0 \rho_b(\mathbf{P}_0, \mathbf{Q}_0) \sum_k f_k \langle u_k(t) | \hat{h} | u_k(t) \rangle, \quad (14)$$

where the real-time propagation is governed by the corrected propagator $\hat{U}_0 \hat{U}'$. Below, we summarize the derivation of the corrected propagator method.

B. The corrected propagator method

We derive the correction to a specific choice of the zeroth-order propagator $\hat{U}_0$, namely an adiabatic product. This approximation is employed by the TDSCF methods,^{5,7} with the evolution operator factorized according to

$$\hat{U}_0 = \hat{U}_s \hat{U}_b. \quad (15)$$

Each of the operators in Eq. (15) acts in a separate subspace: that of the primary system and that of the bath. The interaction term $H_{sb}(\hat{\mathbf{s}}, \hat{\mathbf{Q}})$ enters as an expectation value, resulting in a mean-field approximation. In the mixed quantum-classical TDSCF methods, the dynamics of the bath is described by classical trajectories. The time evolution of the primary system is governed by the quantum propagator $\hat{U}_s$ consisting of the time-dependent coupling term $H_{sb}(\hat{\mathbf{s}}, \mathbf{Q}_t)$, with the operator $\hat{\mathbf{Q}}$ replaced by its expectation value $\langle \hat{\mathbf{Q}} \rangle = \mathbf{Q}_t$.

The corrected propagator method goes beyond the mean-field approximation by introducing a correction to the zeroth-order propagator $\hat{U}_0$. To derive the exact form of the correction we rewrite the total Hamiltonian in Eq. (3) in the following way:

$$\hat{H} = \tilde{H}_s(\hat{\mathbf{p}}, \hat{\mathbf{s}}; \mathbf{Q}_t) + H_b(\mathbf{P}, \mathbf{Q}) + \Delta V. \quad (16)$$

Here $H_b(\mathbf{P}, \mathbf{Q})$ is the classical bath Hamiltonian and $\tilde{H}_s(\hat{\mathbf{p}}, \hat{\mathbf{s}}; \mathbf{Q}_t)$ is a quantum Hamiltonian of the primary system:

$$\tilde{H}_s(\hat{\mathbf{p}}, \hat{\mathbf{s}}; \mathbf{Q}_t) = H_s(\hat{\mathbf{p}}, \hat{\mathbf{s}}) + H_{sb}(\hat{\mathbf{s}}, \mathbf{Q}_t), \quad (17)$$

where operator $\hat{\mathbf{Q}}$ is replaced by its expectation value $\langle \hat{\mathbf{Q}} \rangle = \mathbf{Q}_t$. Finally, we define ΔV as the difference between the system-bath interaction term with position operators

in the all DoF and with $\hat{\mathbf{Q}}$ replaced by its expectation value:

$$\Delta V = H_{\text{sb}}(\hat{\mathbf{s}}, \hat{\mathbf{Q}}) - H_{\text{sb}}(\hat{\mathbf{s}}, \mathbf{Q}_t). \quad (18)$$

The zeroth-order propagator is given by the Trotter product:

$$\hat{U}_0 = \hat{U}_s U_b = e^{-i\hat{H}_s t} e^{-iH_b t}, \quad (19)$$

where U_b is the classical propagator associated with the uncoupled Hamiltonian $H_b(\mathbf{P}, \mathbf{Q})$, and $\hat{U}_s$ is the quantum propagator of the $\hat{\mathbf{s}}$ DoF with $\hat{\mathbf{Q}}$ fixed at the classical value $\mathbf{Q}_t$ [the interaction term $H_{\text{sb}}(\hat{\mathbf{s}}, \mathbf{Q}_t)$ is grouped with the primary system Hamiltonian H_s]. Thus, the evolution of the quantum subsystem according to Eq. (19) is essentially the mean-field approximation.

Next, we consider the limit, where the bath is assumed to be fairly classical and its DoF can be well described by a product of N one-dimensional coherent states:⁵⁴

$$|\mathbf{Q}'\mathbf{P}'\rangle = \prod_{j=1}^N \left(\frac{2\alpha_j}{\pi} \right)^{1/4} \exp[-\alpha_j(\mathbf{Q}_j - \mathbf{Q}_j^t)^2 + i\mathbf{P}_j^t(\mathbf{Q}_j - \mathbf{Q}_j^t)], \quad (20)$$

where N is the number of the bath DoF. Thus, the dynamics of the bath is approximated by classical equations of motion for the average positions and momenta $(\mathbf{Q}', \mathbf{P}')$ of the bath DoF. The width parameter, α_j , is assumed to be real and time independent, resulting in the frozen Gaussian approximation.⁵⁵

The correction to the mean-field dynamics is given by $\hat{U}'$ with the time-dependent Hamiltonian defined by Eq. (2). After some algebra (the full derivation is given in Ref. 21) we find the exact expression of the correction Hamiltonian:

$$\hat{H}' = U_b^\dagger H_b U_b - i U_b^\dagger \frac{dU_b}{dt} + U_b^\dagger \hat{U}_s^\dagger \Delta V \hat{U}_s U_b. \quad (21)$$

Assuming that the initial state is given by an uncorrelated product $|\psi(\mathbf{s})\rangle|\mathbf{Q}_0\mathbf{P}_0\rangle$, we insert a complete set of coherent states to derive the actual propagation scheme:

$$\hat{U}_s U_b \int \int d\mathbf{P} d\mathbf{Q} |\mathbf{Q}\mathbf{P}\rangle \langle \mathbf{Q}\mathbf{P} | \hat{U}' | \mathbf{Q}_0\mathbf{P}_0 \rangle |\psi(\mathbf{s})\rangle. \quad (22)$$

Here, $|\mathbf{Q}_0\mathbf{P}_0\rangle$ is a product of coherent states describing the initial state of the bath, and $|\psi(\mathbf{s})\rangle$ is a wave function describing the initial state of the primary quantum system. In order to propagate the initial wave function, we interpret Eq. (22) as a sequential propagation of the classical trajectories, followed by the quantum propagation with its associated correction in $\hat{U}'$. The evolution of the quantum subsystem is governed by the corrected propagator $\hat{U}_s \hat{U}'$, which is evaluated in the basis of the coherent states.

The correction $\hat{U}'$ involves a time ordered exponential of the time-dependent Hamiltonian and requires an additional approximation. Keeping the time step small, we approximate the correction term using the first order cumulant expansion:

$$\langle \mathbf{Q}\mathbf{P} | e^{-iH'\Delta t} | \mathbf{Q}_0\mathbf{P}_0 \rangle \approx \langle \mathbf{Q}\mathbf{P} | \mathbf{Q}_0\mathbf{P}_0 \rangle e^{-i\bar{H}'\Delta t} \quad (23)$$

with

$$\bar{H}' = \frac{\langle \mathbf{Q}\mathbf{P} | H' | \mathbf{Q}_0\mathbf{P}_0 \rangle}{\langle \mathbf{Q}\mathbf{P} | \mathbf{Q}_0\mathbf{P}_0 \rangle}. \quad (24)$$

The matrix elements of the correction Hamiltonian defined in Eq. (21) are given by

$$\begin{aligned} \langle \mathbf{Q}\mathbf{P} | H' | \mathbf{Q}_0\mathbf{P}_0 \rangle &= \langle \mathbf{Q}^{\Delta t} \mathbf{P}^{\Delta t} | H_b | \mathbf{Q}_0^{\Delta t} \mathbf{P}_0^{\Delta t} \rangle \\ &\quad - i \frac{\partial}{\partial t} \langle \mathbf{Q}^{\Delta t} \mathbf{P}^{\Delta t} | \mathbf{Q}_0^{\Delta t} \mathbf{P}_0^{\Delta t} \rangle \\ &\quad + \langle \mathbf{Q}^{\Delta t} \mathbf{P}^{\Delta t} | U_s^\dagger \Delta V U_s | \mathbf{Q}_0^{\Delta t} \mathbf{P}_0^{\Delta t} \rangle, \end{aligned} \quad (25)$$

where coherent states $|\mathbf{Q}\mathbf{P}\rangle$ evolve according to the bath *uncoupled* propagator U_b . Using the coherent state representation allows us to evaluate the multidimensional integrals in Eq. (25) analytically.⁵⁶ This stage of the derivation bears a problem common to other methods employing the multigaussian expansion. Since Eq. (25) involves the matrix elements of the potential $\langle \mathbf{Q}'\mathbf{P}' | V(\mathbf{Q}) | \mathbf{Q}_0'\mathbf{P}_0' \rangle$ and the interaction term, the analytical evaluation is possible only for systems in which the potential and the interaction can be approximated by a polynomial in Q and d/dQ . In other cases, numerical integration or additional approximations have to be carried out.

The propagation procedure involves the following steps:

1. The evolution of the coherent states is reduced to propagating the centers of the Gaussians in the phase space $(\mathbf{Q}_i, \mathbf{P}_i)$ according to the classical Hamilton's equations of motion:

$$\dot{\mathbf{Q}}_i(t) = \frac{\partial H_b}{\partial \mathbf{P}_i}, \quad (26)$$

$$\dot{\mathbf{P}}_i(t) = -\frac{\partial H_b}{\partial \mathbf{Q}_i}.$$

The classical equations of motion have been solved by using the Adams–Moulton predictor–corrector method. The complete set of Gaussian states $\{|\mathbf{Q}_i\mathbf{P}_i\rangle\}$ of the identity resolution in Eq. (22) is replaced by a finite number with $i = 1, N_g$. The states are sampled randomly from a Gaussian distribution centered around the initial bath state $(\mathbf{Q}_0, \mathbf{P}_0)$ with a “compression” parameter.⁵⁷ The widths α_i of all coherent states are assumed to be real and time independent, resulting in the frozen Gaussian approximation. We chose a width of the Gaussian wave packets equal to that of the coherent state of a harmonic oscillator. The coherent states are propagated according to the bath Hamiltonian H_b .

2. The initial state of the bath is described by a product of coherent states centered at $(\mathbf{Q}_0, \mathbf{P}_0)$. The phase space averaging is performed by using the Monte Carlo procedure with the initial coordinates and momenta $(\mathbf{Q}_i, \mathbf{P}_i)_{i=1}^K$ randomly chosen from the Wigner distribution. Here, K is the number of trajectories required for the convergence. For the bath of harmonic oscillators, the normalized Wigner distribution is given by

$$\begin{aligned} \rho_b(\mathbf{P}_0, \mathbf{Q}_0) &= \prod_i \frac{\tanh(\beta\omega_i/2)}{\pi} \\ &\quad \times \exp \left[-\frac{2 \tanh(\beta\omega_i/2)}{\omega_i} \left(\frac{P_i^2}{2} + \frac{\omega_i^2}{2} Q_i^2 \right) \right]. \end{aligned} \quad (27)$$

The bath initial state $|\mathbf{Q}_0\mathbf{P}_0\rangle$ evolves according to the corrected propagator, with the correction imposing a momentum shift δP .²¹ The momentum shift is completely equivalent to the Hellman–Feynman force applied in the TDSCF schemes:

$$F_Q(t) = -\left\langle \psi(\hat{s}, t) \left| \frac{\partial}{\partial Q} \Delta V(\hat{s}, Q) \right| \psi(\hat{s}, t) \right\rangle. \quad (28)$$

- Since we employed the first order cumulant approximation for the correction propagator, we need to calculate the matrix elements of the correction Hamiltonian according to Eq. (25). This approximation requires small time steps and is not valid for strong system–bath couplings. Finally, the real-time evolution by the zeroth-order propagator is carried out using the split-operator algorithm.⁵⁸

III. RESULTS

A. Model

In order to test the corrected propagator method, we consider a system of the one-dimensional reaction coordinate bilinearly coupled to the bath of harmonic oscillators. In mass-weighted coordinates, the Hamiltonian of the combined system is given by⁵⁹

$$\hat{H} = \frac{\hat{p}_s^2}{2} + V(\hat{s}) + \frac{1}{2} \sum_k \left[\hat{p}_k^2 + \omega_k^2 \left(\hat{Q}_k - \frac{c_k \hat{s}}{\omega_k^2} \right)^2 \right], \quad (29)$$

The reaction barrier is defined as a symmetric double well:

$$V(\hat{s}) = -\frac{1}{2} \omega_b^2 \hat{s}^2 + \frac{\omega_b^4}{16 V_b^\ddagger} \hat{s}^4, \quad (30)$$

where ω_b is the imaginary frequency at the top of the barrier and $V_b^\ddagger$ is the barrier height. The product projection operator for the system is given by the Heaviside function, $h(s) = 1$ for $s > 0$, and zero otherwise.

The influence of the bath is fully characterized by the spectral density function:

$$J(\omega) = \frac{\pi}{2} \sum_k \frac{c_k^2}{\omega_k} \delta(\omega - \omega_k). \quad (31)$$

We have chosen the harmonic bath with an Ohmic spectral density with an exponential cutoff,⁵⁹

$$J(\omega) = \eta \omega e^{-\omega/\omega_c}, \quad (32)$$

which has a frequency-independent damping rate in the continuum limit. Here, ω_c is the cutoff frequency and η is the system–bath coupling strength. We have constructed a discrete bath with an equally spaced sampling of the energy range:

$$\omega_k = k \Delta\omega = k \frac{\omega_c}{N}, \quad (33)$$

where N is the number of bath modes and $k = 1, \dots, N$. The couplings are given by

$$c_k = \omega_k \left(\frac{2}{\pi} \frac{\eta \omega_c}{N} \right)^{1/2}. \quad (34)$$

FIG. 1. Flux-side correlation function of a double-well potential bilinearly coupled to the harmonic bath at $T = 300$ K for two different system–bath coupling strengths: (a) $\eta/\omega_b = 0.95$ and (b) $\eta/\omega_b = 0.1$.

The specific parameters employed in our calculations correspond to the DW1 model studied by Topaler and Makri,³⁹ i.e., $\omega_b = 500$ cm^{-1} , $V_b^\ddagger = 2085$ cm^{-1} , and $\omega_c = 500$ cm^{-1} . The quantum-mechanical thermal rate constants, obtained by Topaler and Makri with the real path integral method, have been used as a benchmark to check the accuracy of our method.

In order to compare our calculations with the benchmark results, we have calculated the transmission coefficient defined as

$$\kappa = \frac{k(T)}{k_{\text{TST}}^{\text{cl}}(T)}, \quad (35)$$

where $k(T)$ is the thermal rate constant defined in Eq. (6) as a long time limit of the flux-side correlation function, and $k_{\text{cl}}^{\text{TST}}$ is the classical transition state theory rate constant for the one-dimensional double-well potential. Within the harmonic approximation of the reactants partition function the classical rate constant is given by

$$k_{\text{TST}}^{\text{cl}}(T) = \frac{1}{2\pi\beta} \frac{e^{-\beta V_b^\ddagger}}{Q_r^{\text{cl}}(T)} \simeq \frac{\omega_b}{\sqrt{2\pi}} e^{-\beta V_b^\ddagger}. \quad (36)$$

The numerical calculations were performed at two different temperatures $T = 300$ K and $T = 200$ K for

FIG. 2. Transmission coefficient $\kappa = k/k_{\text{TST,CL}}$ as a function of the reduced coupling strength η/ω_b at $T = 300$ K. The open squares refer to the results obtained by the corrected propagator method. The solid circles are the quantum path integral calculations of Topaler and Makri, Ref. 39 (the actual data is from Ref. 34).

different values of the coupling strengths. A bath consisting of $N = 100$ harmonic oscillators have been used in all calculations. The number of classical trajectories K in Monte Carlo sampling was 2500 and between 10 to 40 basis coherent states (N_g) per bath mode were sufficient to obtain converged results.

The time evolution of the flux-side correlation function is shown in Fig. 1. The calculations are performed at $T = 300$ K for two different system–bath couplings, one above and one below the turnover point. The results are shown in terms of the time-dependent transmission coefficient $\kappa(t)$. In the case of strong coupling (the spatial diffusion regime), the transmission coefficient reaches a well-defined “plateau” on a time scale of $\beta\hbar = 27$ fs. The weak-coupling case (the energy-diffusion regime) shows that a number of recrossings occur after the transition state theory plateau reached. The dynamical behavior of the system captured by the corrected propagator method is in a good agreement with the results obtained by other methods.^{25,28,33,37,39}

Figure 2 shows the transmission coefficient as a function of the reduced system–bath coupling strength η/ω_b at $T = 300$ K. The solid circles refer to the exact path-integral results of Topaler and Makri.³⁹ The turnover effect predicted by Kramers⁶⁰ is reproduced, and the overall agreement with the exact quantum results is good.

Finally, the transmission coefficient at $T = 200$ K is shown in Fig. 3. Although the method is able to capture the turnover effect, the accuracy clearly deteriorates, especially for stronger system–bath couplings. This can be attributed to the use of the first order cumulant expansion of the correction term. This approximation is expected to fail as the coupling between the quantum subsystem and the classical bath increases. Furthermore, since at lower temperatures quantum effects in the bath can be significant, the bath dynamics cannot be described anymore by evolution of the fixed-width coherent states. However, the last limitation is not expected to be critical for biological processes, since most of them occur near room temperature.

FIG. 3. Transmission coefficient $\kappa = k/k_{\text{TST,CL}}$ as a function of the reduced coupling strength at $T = 200$ K. The open squares refer to the results obtained by the corrected propagator method. The solid circles are the quantum path integral calculations of Topaler and Makri, Ref. 39.

IV. CONCLUSIONS

In this work, we extended the applicability of the corrected propagator method to systems at a finite temperature. The method has been tested on a model system consisting of a one-dimensional reactive coordinate coupled bilinearly to the bath of harmonic oscillators. The thermal reaction rate has been calculated for two temperatures and for a range of system-bath couplings. The fully quantum calculations employing the quasiadiabatic propagator path integral method were used as a benchmark to test the accuracy of our method.

Overall, encouraging results have been obtained and the method was able to capture the turnover effect as well as the quantum enhancement to the reaction rate. The correct dynamics of the system for both weak and intermediate couplings has been reproduced. The results at $T = 300$ K are in a good agreement with the exact quantum calculations with an error of less than 5%. At the lower temperature, $T = 200$ K, the accuracy of the corrected propagator deteriorated, especially for strong couplings. For comparison, the quantum-classical TDSCF method, which serves as the zeroth-order approximate propagator, fails to produce a good accuracy even at $T = 300$ K (showing rate constants at least twice as large as the exact quantum results).²⁸

Previous applications^{22,23} of the corrected propagator method have shown its ability to capture important quantum effects (such as tunneling) in systems where single configurational TDSCF failed.⁷ Since the mean-field adiabatic approximation serves as a zeroth-order propagator in our method, we can conclude that the correction term essentially leads to the correct quantum dynamics of the primary system. Using coherent states (or frozen Gaussians) to describe the bath DoF enable an efficient treatment of truly multidimensional systems, as well as an analytical evaluation of most of the correction propagator.

The applications to more realistic systems present a few challenges that have to be addressed. Since the first order cumulant expansion of the correction term limits the applicability of the method to a relatively short-time dynamics,

including higher order cumulants might be required. The choice of the primary system and the bath is expected to be a critical issue for truly complex biological systems. In real system with complex potentials that are not separable into a simple form such as we have assumed, an alternative definition of the system propagator and the correction is needed. This work is under way for a reaction in an enzymatic system.

ACKNOWLEDGMENTS

This research was supported by the NSF through Grant No. CHE-0714118. D. G. is grateful to Dr. Dimitri Antoniou for numerous helpful discussions.

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