Modeling vibrational resonance in linear hydrocarbon chain with a mixed quantum-classical method

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The quantum dynamics of a vibrational excitation in a linear hydrocarbon model system is studied with a new mixed quantum-classical method. The method is suited to treat many-body systems consisting of a low dimensional quantum primary part coupled to a classical bath. The dynamics of the primary part is governed by the quantum corrected propagator, with the corrections defined in terms of matrix elements of zeroth order propagators. The corrections are taken to the classical limit by introducing the frozen Gaussian approximation for the bath degrees of freedom. The ability of the method to describe dynamics of multidimensional systems has been tested. The results obtained by the method have been compared to previous quantum simulations performed with the quasiadiabatic path integral method. © 2009 American Institute of Physics.

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I. INTRODUCTION

An exact quantum dynamical description of many-body systems remains out of reach for current methodologies. The computational effort required to solve the time-dependent Schrödinger equation grows exponentially with the number of degrees of freedom. As a result, a direct solution of the quantum dynamics has been obtained only for systems of relatively moderate size. There is then an ongoing effort to develop approximate schemes to treat multidimensional systems.

One of the ways to reduce complexity is by introducing a “system plus bath” partition. The main idea is to treat only a small part of the system explicitly, assuming that this part can be probed experimentally. While the rest of the degrees of freedom form the bath, which is treated implicitly. A number of fully quantum methods have been developed based on the “system and bath” methodology. The methods based on the path integral formulation of quantum mechanics\textsuperscript{1} and the multiconfigurational time-dependent Hartree\textsuperscript{2,3} (MCTDH) employ the harmonic description of the bath. In the case of the harmonic bath and linear coupling an exact derivation is possible. The surrogate Hamiltonian method\textsuperscript{4,5} treats the environment degrees of freedom as a spin bath. Since both the MCTDH and the surrogate Hamiltonian methods solve the dynamics of the total system plus bath entity, the drawback of the exponential scaling have not been solved completely. However, a considerable progress in reducing a computational effort has been achieved,\textsuperscript{6–8} enabling to treat truly multidimensional systems.

There are systems, however, that can be described to a certain level in an approximate “mixed quantum-classical” way.\textsuperscript{9} The central idea of the mixed methods is to describe a few (physically relevant) degrees of freedom quantum mechanically, while the rest of the system, to a good approximation, is treated classically. This framework enables the study of a large number of the bath degrees of freedom in a detailed level, and yet reduces the computational effort dramatically.

The separation of the quantum and the classical subsystems is generally based on the mass (or energy) ratio between different degrees of freedom. While the separation criterion is relatively simple, inventing an ansatz for the coupling between the quantum and the classical parts remains a challenge. The methods differ by the way in which the coupling term is defined.

One group of methods is based on a mean-field approximation, and includes the classical path method known as Ehrenfest dynamics,\textsuperscript{10} and the time-dependent self-consistent field approximation.\textsuperscript{11,12} The second branch of the mixed quantum-classical methods include the surface-hopping approach\textsuperscript{13,14} and its numerous variations.\textsuperscript{15–20} Another approach we should mention is based on the quantum-classical Liouville description.\textsuperscript{18,21–24}

The method introduced in our previous work\textsuperscript{25,26} follows the general framework of the quantum-classical approaches: we use a quantum mechanical description for the low dimensional primary system, while the bath degrees of freedom are described by classical trajectories. The novelty of the method is in the definition of the evolution rule for the quantum subsystem. The primary system evolves according to the quantum corrected propagator. The core idea is to find a correction to the zeroth order evolution operator. The latter is a guess for the propagator for the full Hamiltonian instead of an exact propagator for an approximate Hamiltonian.

The dynamics of the bath degrees of freedom is described by a propagation of the frozen Gaussians.\textsuperscript{27} Thus the matrix elements of the correction propagator are evaluated in
the basis of Gaussian wave packets propagated according to the classical equations of motion. The similar concept of correcting an approximation to the exact propagator has been implemented differently to a semiclassical initial value representation (IVR) propagator by Pollak and co-workers.28–30

Following the original work of Heller,31 a large family of mixed quantum-classical and semiclassical methods based on the coherent state representation has been developed.19,20,30,32–48 Among these methods we should particularly mention the Gaussian-MCTDH (Refs. 49 and 50) and the local coherent state approximation,47 which employ the exact description of the primary subsystem coupled to the bath (or “secondary” degrees of freedom), while the latter is described by the coherent states. What makes our approach novel is the following: instead of calculating the coupling using classical variables for the bath part, we start from exact quantum mechanics and calculate the coupling between the quantum and classical subsystems in the quantum limit (in terms of the quantum correction propagator). Then these corrections are taken to a classical limit, by assuming the frozen Gaussian approximation for the bath degrees of freedom.

In the previous work25,26 the method has been applied to model low dimensional systems consisting of a double-well potential coupled to a harmonic oscillator. While the chosen system was relatively simple, the case of the linear coupling between the primary system and the bath represented a challenging case. It is well known that the single configuration mean-field methods fail to describe wave packet splitting, and in the case of bilinear coupling the tunneling is simply blocked.51 Our method was able to produce accurate results for simulating tunneling in an asymmetric double-well potential with a single configuration description employed for the quantum subsystem.

In this article we apply our method to studying the dynamics of the overtone relaxation in a linear hydrocarbon chain. The intramolecular vibrational relaxation in model hydrocarbon systems has been studied extensively by quantum,52,53 semiclassical,54 and classical55–57 methods. The linear hydrocarbon chains53,58,59 represent a simplified system, which is a good candidate for a mixed quantum-classical approach. This system consists of a high frequency CH overtone coupled to a slow bath of the carbon chain atoms. The former has a high zero-point energy, which requires a quantum mechanical treatment. The chain of heavier carbon atoms, weakly coupled to the CH stretch, can be approximately described by classical trajectories. Although the combined system is often considered classical-like, the importance of inclusion of the zero-point energy for the CH mode has been discussed in the number of works.56–58 The benchmark results for this system have been provided by the only quantum simulations, performed by Topaler and Makri with the quasidiabatic path integral method.53 The conclusions are discussed in Sec. IV. It should be noted that atomic units are used throughout the paper (\(\hbar = 1\)).

II. THEORY

The goal of the method introduced in our previous work25,26 was to treat a general mixed quantum-classical system. This kind of a system includes a primary part treated quantum mechanically, while the rest of the degrees of freedom are described classically. We start with the assumption that the Hamiltonian of our system can be separated and written in the general system plus bath form:

\[ H = H_s(\hat{s}) + H_b(\hat{Q}) + V(\hat{s}, \hat{Q}). \]

(1)

Here \(H_s(\hat{s})\) is the Hamiltonian of the primary system, which has to be treated explicitly, \(H_b(\hat{Q})\) refers to the bath Hamiltonian and \(V(\hat{s}, \hat{Q})\) describes the interaction between the system and the bath.

The evolution of the combined system is governed by the total propagator \(U\), which can be written as

\[ U = U_0U' = U_0Te^{-i\int_0^t H' dt'}, \]

(2)

where \(U_0\) is the zeroth order evolution operator, \(U'\) is the correction propagator and \(T\) is the time-ordering operator.

The basic idea of the proposed method is to calculate corrections to the zeroth order propagator \(U_0\), yielding an exact quantum propagation of the primary subsystem. After taking the time derivative of both sides of Eq. (2), the time-dependent correction Hamiltonian is obtained in terms of the full Hamiltonian and the zeroth order propagator:

\[ H' = U_0^{-1}HU_0 - iU_0^{-1}\frac{dU_0}{dt}. \]

(3)

In order to develop a computationally feasible propagation scheme we introduce the following approximations. We consider the limit where the bath degrees of freedom \(\hat{Q}\) are described satisfactorily by the frozen Gaussian wave packets.27 Thus the dynamics of the bath is described by the classical equations of motion, while the dynamics of the primary system is governed by the corrected quantum propagator.

We rewrite the total Hamiltonian in Eq. (1) in the following way:

\[ H = \tilde{H}_s(\hat{s}, \hat{Q}) + H_b(\hat{Q}) + \Delta V. \]

(4)

Here \(H_b(\hat{Q})\) describes the classical bath and \(\tilde{H}_s(\hat{s}, \hat{Q})\) is a quantum Hamiltonian with operator \(\hat{Q}\) replaced by its expectation value \(\langle \hat{Q} \rangle = Q\):

\[ \tilde{H}_s(\hat{s}, Q) = H_s(\hat{s}) + V(\hat{s}, Q). \]

(5)

Finally we define \(\Delta V\) as the difference between a coupling term with operators in all degrees of freedom and one with \(\hat{Q}\) replaced by its classical value:

\[ \Delta V = V(\hat{s}, \hat{Q}) - V(\hat{s}, Q). \]

(6)
Next we define the zeroth order propagator as an adiabatic approximation (the Trotter propagator):

\[ U_0 = U_s^o U_b^o = e^{-iH_0 t} e^{-iH_b t}, \]

(7)

where the coupling part \( V(\hat{s}, \hat{Q}) \) is grouped with the primary system Hamiltonian \( H_s \). The zeroth order propagator defined by Eq. (7) consists of the frozen Gaussian propagator \( U^o_s \) associated with the uncoupled Hamiltonian \( H_s(Q) \), and the quantum propagator \( U^o_b \) of the \( \hat{s} \) degree of freedom with \( \hat{Q} \) fixed at the classical value \( Q_c \). Thus the evolution of the quantum subsystem according to Eq. (7) is essentially a mean-field approximation.

After some algebra one can derive the expression for the correction Hamiltonian:

\[ H' = U_b^{-1} H_b U_b^o - i U_b^{-1} \frac{dU_b^o}{dt} + U_b^{-1} U_s^{-1} \Delta V U_s^o U_b^o \]

(8)

where \( \Delta V = V(\hat{s}, \hat{Q}) - V(\hat{s}, \hat{Q}_c) \). Note that in Eq. (8) all corrections are defined in terms of zero order propagators.

We assume that the initial wave function of the combined system is approximated by an uncorrelated product state and evolves according to

\[ \Psi(\hat{s}, \hat{Q}; t) = U^o_s U^o_b e^{-iH't} |\psi_o\rangle |\Phi(\hat{Q})\rangle, \]

(9)

with the bath degrees of freedom described by multidimensional Gaussian wave packets:

\[ \Phi(\hat{Q}) = \left( \frac{2\alpha_0}{\pi} \right)^{3N/4} \exp[-\alpha_0 (Q - Q_0)^2 + iP_0 (Q - Q_0)]. \]

(10)

The coordinates and momenta of the bath degrees of freedom are given by the vectors \( \hat{Q} = \{Q_k\} \) and \( \hat{P} = \{P_k\} \) with \( k = 1, \ldots, N \) respectively. For the system considered in this article, the multidimensional Gaussian functions are constructed as a product of one-dimensional Gaussians describing each of the \( N \) bath degrees of freedom. The evolution of the bath is governed by the frozen Gaussian propagator \( U^o_b \). Thus the widths of the wave packets \( \alpha_0 \) are assumed to be real and time independent.

In order to derive the actual propagation scheme we insert into Eq. (9) a complete set of Gaussian states:

\[ U^o_s U^o_b \int d\hat{P} d\hat{Q} |\Phi(\hat{Q})\rangle \langle \Phi(\hat{Q})| e^{-iH't} |\Phi(\hat{Q})\rangle |\psi_o\rangle. \]

(11)

Here, \( \Phi(\hat{Q}) \) is the initial state of the bath. In order to propagate the initial wave function, we interpret Eq. (11) as a sequential propagation of the classical trajectories \( \{Q_k\} \), followed by the quantum part with its associate correction in \( U' \). The evolution of the quantum subsystem is governed by the corrected propagator \( U' s U' b \), which is evaluated in the basis of Gaussian wave functions.

The first application of the method\(^{25}\) has assumed infinitely narrow Gaussian wave packets to describe the bath degrees of freedom. As a result, only a single matrix element of the correction propagator survives in Eq. (11), namely the overlap with the initial state of the bath. Since the single Gaussian scheme has shown to work only in limited number of cases, the assumption of sharp Gaussians was abandoned.\(^{26}\) Thus the propagation algorithm includes an evaluation of a high dimensional phase space average, using Monte Carlo or other methods.

The autocorrelation function of the system is given by

\[ C(t) = \int_{-\infty}^{\infty} d\hat{P} \int_{-\infty}^{\infty} d\hat{Q} \langle \Phi(\hat{Q})| \Phi(\hat{Q}; t) \rangle \times \langle \Phi(\hat{Q}; t)| U^o_s |\Phi(\hat{Q})\rangle |\psi_o\rangle. \]

(12)

Thus the overlap between the initial bath state and the other Gaussians \( |\langle \Phi(\hat{Q})| \Phi(\hat{Q}; 0) \rangle\rangle \) represents a sampling function for the Monte Carlo integration. The Gaussian wave packets \( |\Phi(\hat{Q}; t)\rangle \) in Eq. (12) evolve according to the propagator \( U^o_b \) associated with the uncoupled Hamiltonian \( H_b(Q) \). Thus the influence of the quantum subsystem on the bath is omitted. In order to include the effect of the primary system on the bath, the correction propagator has to be applied on the bath wave function as well.

The propagation procedure involves the following steps:

1. The evolution of the Gaussian wave functions is reduced to propagating the centers of the Gaussians in the phase space \( (\hat{Q}, \hat{P}) \) according to the classical Hamilton’s equations of motion:

\[ \dot{Q}_i(t) = \frac{\partial H_b}{\partial P_i} = P_i(t)/M, \]

\[ \dot{P}_i(t) = -\frac{\partial H_b}{\partial Q_i} = -V_b(Q_i). \]

(13)

2. The initial state of the bath is given by \( |\Phi(\hat{Q}_0, P_0)\rangle \). The complete set of Gaussian states \( \{\Phi(\hat{Q})\} \) of the identity resolution in Eq. (11) is replaced by a finite number with \( i = 1, K \). The initial coordinates and momenta \( \{Q_i, P_i\}\) are randomly chosen from the Wigner distribution.\(^{60}\)

3. We propagate the quantum wave function, introducing an additional approximation: keeping the time step small, the matrix elements of the time-dependent correction propagator are calculated using a first order cumulant expansion. The total evolution operator is then expanded in the adiabatic basis of the Hamiltonian \( H_s(\hat{s}, \hat{Q}) \). The set of eigenfunctions \( \{|n\rangle\} \) and the associated eigenvalues \( E_{nQ}^D \) which depend parametrically on the position of the classical particles, are defined for each configuration of \( \hat{Q} \). Then the total propagator is expanded in the adiabatic basis of the quantum subsystem states. The detailed derivation is given in Ref. 25.

4. The matrix elements of the correction Hamiltonian, given in Eq. (8), are given by

\[ \langle \Phi(\hat{Q}; t)| H_s(\hat{s}, \hat{Q}) |\Phi(\hat{Q})\rangle = \langle \Phi(\hat{Q}; t)| H_s(\hat{s}) |\Phi(\hat{Q}; t)\rangle - i \langle \Phi(\hat{Q}; t)| H_s(\hat{s}) |\Phi(\hat{Q}; t)\rangle \]

\[ + \langle \Phi(\hat{Q}; t)| U^o_s \Delta V(\hat{s}, \hat{Q}) U^o_s |\Phi(\hat{Q}; t)\rangle \]


\[ -\mathbf{Q}_0(t) \cdot \langle \Phi_i(\mathbf{Q}; t) | U_{\text{c}}^{-1} V(\mathbf{s}) U_{\text{c}} \rvert \Phi_0(\mathbf{Q}; t) \rangle. \]  

In general, these multidimensional integrals can be calculated analytically.\textsuperscript{61} They are all proportional to the time-dependent overlap between the initial bath state and the Gaussians of the expansion in Eq. (11):

\[ \exp \left[ -\frac{\Delta \mathbf{Q}^2}{2} \right] \exp \left[ -\frac{\Delta \mathbf{P}^2}{8\alpha_0} \right] \exp \left[ i\Delta \mathbf{Q} \cdot \mathbf{P} \right], \]

where \( \Delta \mathbf{Q} = \mathbf{Q}_0(t) - \mathbf{Q}_i(t) \), \( \Delta \mathbf{P} = \mathbf{P}_0(t) - \mathbf{P}_i(t) \), and \( \mathbf{P}_i = \frac{1}{2} (\mathbf{P}_i(t) + \mathbf{P}_0(t)) \). We chose a width of the Gaussian wave packets equal to that of the coherent state of a harmonic oscillator \( \alpha_0 = M \omega / 2 \). This stage of the derivation bears a problem common to other methods employing the multi-Gaussian expansion.\textsuperscript{32,40,62} The analytical evaluation of the matrix elements of the correction propagator is possible for systems in which the potential and the coupling terms can be approximated by a polynomial in \( \mathbf{Q} \) and \( d/d\mathbf{Q} \). Numerical integration or an approximation has to be carried out in other cases.

III. RESULTS

A. Model

In this section we use the corrected propagator method to study a vibrational relaxation in the linear hydrocarbon chains \( \text{HC}_n \). The simplified model, consisting of an anharmonic CH bond coupled to a chain of harmonic CC bonds, has been previously employed in a number of theoretical works.\textsuperscript{53,57-59} The path integral calculations by Topaler and Makri\textsuperscript{53} have provided the benchmark results of the dynamics of CH overtone relaxation in the \( \text{HC}_6 \) linear chain. To test the ability of our method to treat dynamics of multidimensional systems we apply it to the model system used in Ref. 53.

The model Hamiltonian, in a form where the particles’ coordinates and momenta have been canonically transformed to the bond coordinate and momenta, is given by

\[ H = \frac{1}{2} \mu_{\text{CH}} \mathbf{P}_i^2 + V_{\text{CH}}(r_i) + \sum_{i=1}^{n-1} \left[ \frac{1}{2} \mu_{\text{CC}} \mathbf{P}_i^2 + V_{\text{CC}}(r_i) - \frac{p_mp_{i+1}}{m_{\text{C}}^2} \right], \]

where \( r_i \), \( p_i \), and \( p_{i+1} \) are the coordinates and the conjugated momenta of the CH and CC bonds, respectively, and \( \mu_{\text{CH}} \) and \( \mu_{\text{CC}} \) are the reduced masses, while \( m_{\text{C}} \) is the mass of the carbon atom.

The carbon chain consists of \( n-1 \) identical harmonic potentials:

\[ V_{\text{CC}}(r_i) = \frac{1}{2} \mu_{\text{CC}} \omega_{\text{CC}}^2 r_i^2; \quad i = 1, \ldots, n-1, \]

with the harmonic frequency \( \omega_{\text{CC}} = 1850 \text{ cm}^{-1} \). The hydrogen-carbon bond is described by a Morse oscillator:

\[ V_{\text{CH}}(r_i) = D_{\text{CH}} (1 - \exp(-\beta_{\text{CH}} r_i))^2, \]

with the dissociation energy of 3.647 eV and \( \beta_{\text{CH}} = 1.03 a_0^{-1} \). The Hamiltonian in Eq. (16) contains coupling terms that depend on the bond momenta.

Following the derivation given in the Ref. 53, the Hamiltonian of Eq. (16) is transformed to a Hamiltonian with diagonal kinetic energy and potential coupling. After performing a canonical transformation to the normal mode coordinates of the whole molecule \( (s, p_s, Q_i, p_i) \) one can eliminate the kinetic energy coupling. The coupling term then appears as the off-diagonal elements in the potential energy. The new Hamiltonian takes the following form:

\[ H = H_s + \sum_{k=1}^{n-1} h_k \sum_{i=1}^{n-1} f_k(s) Q_i, \]

where

\[ U(s, Q_i, Q_{i+1}) = V_{\text{CH}}(s) - \frac{1}{2} \mu_{\text{CH}} \omega_{\text{CH}}^2 r_i^2. \]

The bath Hamiltonian is given by

\[ h_k = \frac{1}{2} P_k^2 + \frac{1}{2} \omega_k^2 Q_k^2. \]

After expanding the total potential \( U(s, Q_1, \ldots, Q_{n-1}) \) up to the first order in \( Q_k \), the coupling terms take a form of

\[ f_k(s) = -\frac{\partial U(s, Q_1, \ldots, Q_{n-1})}{\partial Q_k} \bigg|_{Q_1=\ldots=Q_{n-1}=0}. \]

We assume in accordance with the previous work\textsuperscript{53,58} that only terms linear in the bath coordinates contribute to the dynamics.

The local mode initial state \( \psi_0 = \psi(r_i) \Pi_{i=1}^{n-1} \phi_i(Q_i) \) of the full Hamiltonian (16) is replaced by the approximate shifted product\textsuperscript{53}

\[ \Psi_{\text{a}}(s, Q) = \psi(a) \prod_{i=1}^{n-1} \phi_{0,i}(Q_i - b_i s), \]

where \( \psi_a \) is an eigenfunction of the Morse oscillator and \( \phi_{0,i} \) are the ground state harmonic oscillator eigenfunctions. The constants \( b_i \) and \( a \) are chosen so that \( \Psi_{\text{a}}(s, Q) \) is equal to the local mode initial state \( \psi_0 \). The choice of the linearized system-bath coupling as well as the shifted form of the initial state are defined solely for the purpose of comparison to the available benchmark results.\textsuperscript{53}

B. Comparison with exact quantum mechanical calculations

First we consider a two-dimensional system of \( \text{HC}_2 \) chain, for which the exact quantum treatment is feasible. We
calculate the survival probability defined as the square of the autocorrelation function:

\[ P(t) = |\langle \Psi(s, Q; 0) | \Psi(s, Q; t) \rangle|^2. \]  

Figures 1 and 2 present results obtained by three different methods: a fully quantum mechanical simulation we carried out, the path integral method and the corrected propagator calculations. The exact quantum calculations have been performed using the Hamiltonian with linearized coupling (19) and the same initial conditions as in Ref. 53.

The initial state is given by the product where the CH bond was set as either the \( v = 5 \) or the \( v = 8 \) eigenstate of the Morse potential, while the CC bond is described by a shifted ground state of the harmonic oscillator. The fully quantum calculations employ the Chebychev polynomial expansion for the representation of the evolution operator, while the kinetic energy operator is applied in a Fourier space using the fast Fourier transform.

For the corrected propagator calculations the initial state of the quantum subsystem \( \psi_0(s) \) is chosen the same as \( \psi_h \) in the fully quantum simulations. The classical subsystem is defined by the Gaussian centered at \( Q_0 = 0 \) and \( P_0 = 0 \). The initial coordinate and momenta of the Gaussian wave packets \( (Q_i, P_i^{(K)}) \) are selected randomly from the appropriate Wigner distribution:

\[ f_W(Q, P) = \frac{1}{\pi} \exp[-\alpha(Q - b(s))_0^2] \exp[-P^2/\alpha], \]  

where \( \alpha = \mu_{CC} \omega_{CC} \). The initial distribution has been shifted in the coordinate by \( b(s)_0 \), according to the choice of the initial state in Ref. 53.

The classical equations of motion have been solved by using the Adams–Moulton predictor-corrector method. The converged results for propagation of the quantum subsystem have been obtained with a relatively small number of Gaussians \( (K=20) \), and the 8–12 adiabatic eigenfunctions of the \( \tilde{H}(s, Q) \) were sufficient to expand the corrected propagator. The propagation time step was set to \( \Delta t = 0.15 \) fs.

Figure 1 shows the results for a short time scale. The survival probability has been calculated for two different initial states of the HC\(_2\) molecule (the \( v = 5 \) and \( v = 8 \) overtones of CH). The results obtained with the quasadiabatic propagator path integral method are given as a reference. For the time scale shown in Fig. 1, the overall agreement is good. The decay and the recurrences of the correlation function are reproduced with a good accuracy. The high frequency beats of the survival probability have slightly higher amplitudes, but their period is in a good agreement with the exact results.

In Fig. 2 we compare the results of the simulations performed with a relatively long time scale. While the path integral calculations have provided the converged results for a very short time scale (50–70 fs), the corrected propagator seemed to reproduce well the exact survival probability up to \( t = 0.5 \) ps. The agreement clearly deteriorates with a time,
suggesting that higher order terms in the expansion of the corrected propagator are required. However, the dominant period of the oscillations is reproduced with a remarkably good accuracy even within the first order expansion.

C. Longer chains

Next we consider the dynamics for longer chains including up to eight carbon atoms. These systems are expected to undergo the irreversible behavior due to the increasing size of the bath (the chain of carbon atoms). The classical simulations of the linear hydrocarbon chains [56] have shown that the relaxation time is essentially independent of the chain length and the irreversible energy transfer is possible even in small chains.

In Fig. 3 the survival probability is shown as function of time for the overtone $\nu=8$ of HC$_n$ molecule. The results obtained with the corrected propagator (the solid line) are compared to the benchmark results of Topaler and Makri [53] (shown by the dashed line). In the corrected propagator calculations the initial state of the bath $\Phi_0(s)$ was defined by the product of one-dimensional Gaussians each centered at $Q_0=0$ and $P_0=0$. The initial coordinate and momenta of the Gaussian wave packets $(Q_i, P_i)_{i=1}^K$ were selected randomly from the appropriate Wigner distributions. The normal mode frequencies $\omega_k$ of the bath are given by 2903, 2518, 2245, 1829, 1291, and 668 cm$^{-1}$.

The path integral calculations have provided the converged results for time up to five vibrational periods of the CH bond (about 50 fs). The survival probability calculated with the corrected propagator is shown up to 150 fs. The results are in an excellent agreement. The initial decay of the survival probability within 50 fs is reproduced exactly with the corrected propagator method. There is a recurrence centered around 75 fs. While there are no quantum calculations available up to this time, the recurrences due to the finite size of the CC chain are expected to occur. These recurrences should occur at later times, as the chain of the CC bonds grows.

To verify this assumption we performed dynamical simulations of the HC$_n$ molecule with the chain size varied up to $n=8$. The results for the chains with $n=4,6,8$ are shown in the Fig. 4. The initial decay of the survival probability is roughly independent on the chain length. The first recurrence, however, occurs at the different times (later for the larger bath). The results for the longest chain HC$_8$ show no recurrences up to 150 fs.

Figure 5 displays the survival probability of the overtone $\nu=8$ of HC$_n$ molecule calculated with a different number of Gaussian wave packets per bath degree of freedom. The convergence is achieved with $K=100$. For longer chains, the convergence requires a slightly larger number of Gaussians ($K=150$).

IV. CONCLUSIONS

In this work we have applied the previously developed mixed quantum-classical method to the study of vibrational relaxation in the linear hydrocarbon chains. The model system consisted of a high frequency part (the CH stretch) coupled to a slow classical-like bath of the CC bonds represented by harmonic oscillators. The fully quantum calculations employing the quasidiabatic propagator path integral method [53] have provided the benchmark results to test the validity of different approximate methods. The path integral calculations have produced the exact results within a short time scale and showed that the adiabatic approximation...
alone is not sufficient to describe the dynamics correctly. Since the corrected propagator method goes beyond the adiabatic approximation by introducing corrections to the zeroth order propagator, we expect the method to be well suited for the current system.

The method starts with a formal derivation that shows how to correct the approximate rule for the evolution of the total system. The coupling between the primary system and the bath arises from the quantum correction operator. In the following step these corrections are taken to the classical limit by introducing the frozen Gaussian description of the bath degrees of freedom. Although the bath dynamics is described by the classical trajectories, the evolution of the primary system is governed by the corrected propagator yielding the exact quantum dynamics. The main restriction of the method is due to including only the first order correction in the cumulant expansion of the corrected propagator. This limits the application to a short time scale and a relatively weak coupling. An additional approximation has been made in the calculation of the matrix elements of the correction propagator. As a result, the effect of the correction propagator on the bath degrees of freedom is omitted and the Gaussian wave packets evolve according to the uncoupled propagator.

Nevertheless, for the current system the method was able to describe the dynamics with a high accuracy for a relatively long time. Interestingly, a low dimensional problem of two coupled oscillators has been more challenging for the mixed quantum-classical methods, especially if one of the oscillators is highly anharmonic. Yet, the corrected propagator method produced the results in a good agreement with the exact quantum calculations.

The previous application of the method validated its ability to describe correctly the splitting of the wave packet due to tunneling in the double-well potential bilinearly coupled to a harmonic oscillator. The initial assumption of infinitely narrow Gaussian wave packets has been abandoned and the matrix elements of the corrected propagator were evaluated in the multi-Gaussian basis. Overall encouraging results have been obtained, although the considered systems were oversimplified. For further validation it is important to apply our method to more realistic dissipative systems and especially to verify the importance of including high order correction terms.

The initial motivation was to develop a method able to describe a low dimensional quantum system coupled to a classical bath. This strategy is particularly well suited to reactions in biological environments, such as proton transfer in enzymes. The strong quantum effects (such as proton transfer) are limited to a small number of degrees of freedom, while the bath (the rest of the protein) is assumed to be classical. For this kind of systems the potential of the whole system is not easily expressed in the form of system plus bath and no clear system-bath coupling is identified. A new challenge to be addressed includes a derivation of methodology allowing higher order corrections and applications to a complex potential not separable into a simple form.

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