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Alexey V. Akimov, Run Long, and Oleg V. Prezhdo

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Coherence penalty functional: A simple method for adding decoherence in Ehrenfest dynamics

Alexey V. Akimov,1,2,a) Run Long,3 and Oleg V. Prezhdo1,a)
1Department of Chemistry, University of Rochester, Rochester, New York 14627, USA
2Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, USA
3School of Physics, Complex and Adaptive Systems Laboratory, University College Dublin, Dublin 4, Ireland

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We present a new semiclassical approach for description of decoherence in electronically non-adiabatic molecular dynamics. The method is formulated on the grounds of the Ehrenfest dynamics and the Meyer-Miller-Thoss-Stock mapping of the time-dependent Schrödinger equation onto a fully classical Hamiltonian representation. We introduce a coherence penalty functional (CPF) that accounts for decoherence effects by randomizing the wavefunction phase and penalizing development of coherences in regions of strong non-adiabatic coupling. The performance of the method is demonstrated with several model and realistic systems. Compared to other semiclassical methods tested, the CPF method eliminates artificial interference and improves agreement with the fully quantum calculations on the models. When applied to study electron transfer dynamics in the nanoscale systems, the method shows an improved accuracy of the predicted time scales. The simplicity and high computational efficiency of the CPF approach make it a perfect practical candidate for applications in realistic systems. © 2014 AIP Publishing LLC, [http://dx.doi.org/10.1063/1.4875702]

I. INTRODUCTION

Quantum non-adiabatic processes in molecular systems are widespread in nature and technology.1–6 They include electron and proton migration,7–18 charge and energy transfer,19–24 and similar phenomena, which take place in natural and artificial systems. The interest in these processes stimulates development of new theoretical methodologies and simulation techniques.12–14, 25–46 Quantum dynamics requires solution of the time-dependent Schrödinger equation (TD-SE). Accurate, fully quantum and advanced semiclassical and quantum-classical solutions based on numerically exact integration and wavepacket propagation,18, 35, 47–54 quantum-classical Liouville equation and entangled trajectories,55–59 Bohmian trajectories,60–63 and initial value representation64, 65 have been developed. For a more detailed discussion of these and related methods for quantum non-adiabatic dynamics we refer the reader to the recent review on the subject.4 Despite exceptional accuracy and rigorous mathematical foundation of the above methods, they are often restricted to relatively small systems. Approximate semiclassical treatments are unavoidable for realistic, large-scale systems.

The fewest switches surface hopping (FSSH) algorithm25–26 for molecular dynamics (MD) with electronic transitions is among the most popular semiclassical approaches. In this method, the probability of transition from a current electronic state to all other states is computed along a nuclear evolution trajectory, using solution of the approximate, semiclassicalTD-SE. On the basis of the computed wavefunction amplitudes, {ci(t)}, a stochastic hop from the current quantum state to one of the accessible states is performed. Making FSSH very popular, its main advantages include conceptual and implementation simplicity and, most importantly, ability to correctly describe branching of quantum trajectories. The latter feature ensures that after a scattering event the system’s wavefunction collapses onto one of its pure states (eigenstate). In addition, the method is capable of approximately reproducing the Boltzmann distribution of the excited states,66 which is important for accurate description of relaxation to thermal equilibrium and thermodynamic properties.

Although the FSSH method has been successful in many applications, there are cases in which it may be inadequate or performs less accurately than the mean-field (MF) approaches.27, 67 The FSSH is not straightforward to apply to systems with a continuum of states. A preliminary discretization of the continuum is required.30 On the contrary, the MF calculation can be easily performed.26 In addition, with increasing density of states, characteristic of large-scale systems, the chances to encounter conical intersections, as well as numerically problematic “unavoided” or trivial crossings, increase. They start to dominate the physically interesting avoided crossings, forcing one to keep track of state indexing and to apply corrections to the standard FSSH procedure.68, 69 This problem is naturally overcome by the mean-field Ehrenfest technique.

Neglect of decoherence effects induced in the electronic subsystem by the nuclear bath constitutes a well-known problem of the most commonly used, original version of FSSH.25 The method is often overcoherent, because solution of the semiclassical TD-SE, {ci(t)}, preserves coherences, c†icj, when they should decay to zero and the wavefunction should collapse to an eigenstate according to the fully quantum description of the electron-nuclear system. In his pioneering work Tully did point this out and proposed a simple ad hoc
scheme that achieved decoherence via damping of the off-diagonal elements of density matrix. Many other decoherence correction schemes for FSSH have been proposed later, based on different principles. These schemes either introduce a stochastic element to the wavefunction evolution or deal with the density matrix. Stochastic evolution of the wavefunction creates additional computational challenges, while introduction of the density matrix increases the size of the problem from N to N^2, where N is the basis set size.

The MF or Ehrenfest approach provides an alternative formulation of non-adiabatic MD (NA-MD). Here, the evolution of a mixed quantum-classical system is treated self-consistently on the average potential energy surface. The trajectories generated in the Ehrenfest dynamics are continuous, and there are no stochastic changes of quantum states. Although simple, the approach has a number of serious limitations. One of the commonly discussed examples is its inability to collapse system’s wavefunction on a pure state. For instance, after an interaction event has occurred, the resulting wavefunction remains a mixture of nearby adiabatic states, even in regions with negligible coupling between the states. One can resolve this deficiency by a proper interpretation. Namely, the results given by the Ehrenfest solutions should not be explained from the point of view of instantaneous properties of a system. Rather, it is a solution for the average properties and their distributions. Similarly, quantum mechanics can be formulated in the Heisenberg representation, in which one solves the Heisenberg equation for the expectation values (averages), 〈A〉, of a given operator A. These quantities cannot be interpreted in terms of instantaneous trajectories and wavefunction collapse. They have only a probabilistic and statistical interpretation.

Keeping in mind the above discussion, one finds that the semiclassical Ehrenfest solution of the TD-SE still misses important physical effects. In particular, the dynamics does not account for decoherence. This is because the nuclear component of the wavefunction reduces to a classical delta distribution (phase space point), when the transition from the fully-quantum TD-SE to the semiclassical TD-SE is made. In a 2-level system, the complete loss of coherence between the pair of electronic states is only possible in the Ehrenfest method if and only if the population of one of the states is zero.

Neglect of electronic decoherence in FSSH and related schemes is known to overestimate electronic transition rates. This problem has been mitigated by ad hoc decoherence correction schemes. Application of decoherence corrections to the Ehrenfest dynamics has led to approaches, such as the stochastic MF approximation, that contain a stochastic element and resemble surface hopping rather than the fully deterministic MF evolution. There has been a number of mixed MF/SH schemes targeted at accounting for decoherence effects. For example, in the self-consistent decay of mixing and in the subsequent coherent switching with decay of mixing, the density matrix is propagated deterministically to conserve the angular momentum of the mapped electronic variables – the condition not necessarily satisfied in the standard Ehrenfest formulation. The equations lead to deterministic decay of the off-diagonal elements of the density matrix. Stochastic surface hops are then undertaken, similarly to FSSH. Therefore, they retain the stochastic flavor of SH and require averaging over a large number of stochastic realizations. Similar in spirit to the MF approaches are the methods based on the quantum-classical Liouville equation of motion for density matrix. These techniques are fully deterministic and capable of describing decoherence, but are sophisticated and computationally demanding. The Liouvillian formulation of equations of motion does not necessarily imply existence of a Hamiltonian structure for the considered dynamical system.

In this work, we propose a simple empirical decoherence correction scheme for the Ehrenfest dynamics. In addition, we formulate this method within the fully Hamiltonian framework. The effects of decoherence are introduced in on average sense directly via the wavefunction, to affect the dynamics of the expectation values. Unlike many other approaches correcting for decoherence, we achieve this goal via continuous unitary dynamics of the wavefunction, rather than via stochastic, non-unitary, or density matrix techniques.

II. THEORY

A. Formulation of the coherence penalty functional method

We start by referring to the works of Meyer and Miller, and Stock and Thoss, who established a mapping between the TD-SE and the fully classical Hamiltonian formulation of the equations of motion for quantum variables. The original work of Meyer and Miller used a specific choice of the variables that represent quantum degrees of freedom. The choice is not unique, and the variables may be selected quite arbitrarily. Depending on the representation of potential, it may be more convenient to choose one set over another. In particular, it can be shown that in the variables and = Re (ci) and = Im (ci), the semiclassical TD-SE,

\[ i\hbar \frac{\partial c_i(t)}{\partial t} = \sum_j E_j \delta_{i,j} - \hbar \frac{P}{M} \frac{\partial}{\partial q_j} c_j(t), \]

is equivalent to the Hamiltonian equations of motion:

\[ \dot{q}_i = -\frac{\partial H}{\partial p_i}, \]

\[ \dot{p}_i = \frac{\partial H}{\partial q_i}, \]

with the effective mapped Hamiltonian given by

\[ H = \sum_i \frac{E_i}{2\hbar} (q_i^2 + p_i^2) - \frac{P}{m} \sum_{i,j} c_{ij} p_i q_j. \]

To account for decoherence effects in the dynamics generated by Hamiltonian Eq. (3), we introduce the following augmented Hamiltonian:

\[ \tilde{H} = H + \sum_{i,j} \lambda_{ij} \left( q_i^2 + p_i^2 \right) \left( q_j^2 + p_j^2 \right), \]
The term \((q_i^2 + p_i^2)(q_j^2 + p_j^2) = |c_i^*c_j|^2\) is simply a square of the magnitude of coherence between the pair of states \(i\) and \(j\). This term penalizes coherence development, each pair having a different penalty determined by the constant \(\lambda_{ij}\). Therefore, we call the sum in the right-hand side of Eq. (4), and the overall methodology, the coherence penalty functional (CPF). The role of the functional is easy to understand by considering the effective energy surface in the phase space spanned by the quantum variables \(\{(q_i, p_i)\}\). Each term \((q_i^2 + p_i^2)(q_j^2 + p_j^2)\) creates an additional potential that biases system’s dynamics to choose its evolution pathways such that they minimize the developed coherences (provided \(\lambda_{ij} > 0\)). When the system accumulates coherence between the pair of states \(i\) and \(j\), the point in the phase space of the dynamical system is located uphill the bias potential. The gradient of the effective energy surface acts in the opposite direction and moves the phase space point away from the regions of large coherences. Therefore, the system avoids developing large coherences. In the on average sense, the effective coherences are minimized. Such avoidance of the regions with large coherences can affect the average populations of the electronic states as functions of time, by changing the rates of transitions between them.

**B. Analogy of the CPF method with exchange-correlation functionals in DFT**

The CPF may be interpreted from a different viewpoint. The idea of the CPF for the Ehrenfest dynamics has a lot in common with the density functional theory (DFT). Partially because of this analogy, the name of our current approach contains the word “functional.” As any other MF theory, the Ehrenfest dynamics has a serious problem accounting for correlation/entanglement effects. The dynamics of electronic states is not correlated with nuclear evolutions to yield desired asymptotic properties. Overcoherence can also be considered a consequence of the lack of dynamic correlation. In the conventional electronic structure theory, the lack of correlation in the MF Hartree-Fock method is well recognized, and multiple approaches for incorporating correlation have been developed. Dynamic correlation arises in the electronic structure theory due to interactions of electrons, leading them to undergo correlated motions. (No analogies are drawn here with respect to the non-dynamic correlation of the electronic structure theory.)

Having discussed the relationship between the Ehrenfest dynamics of electronic states in the mixed quantum-classical evolution and the mean-field dynamics of electrons in the electronic structure theory, and having identified the missing correlation, we can consider how theories in one field can help develop theories in the other field. Namely, introduction of universal exchange-correlation functional constitutes the central idea of the DFT approach to the electronic structure theory. It is true that the exact form of such functional is not known, in general, and its approximations are difficult to construct. At the same time, a wide variety of density functionals has been developed over the last few decades, ranging in accuracy, efficiency, and applicability. One can regard CPF as a counterpart of density functionals, which is aimed at correcting one of the correlation-related issues (decoherence) with the Ehrenfest dynamics. The CPF plays the same role in the Ehrenfest dynamics as the correlation functionals in DFT. Similar to the electronic structure density functionals, the CPF depends on the density (matrix), is hard to derive, in general, and provides a correction to correlation-related problems. The functional form of the CPF given by Eq. (4) is one of the possible approximations. It may be much more complex.

**C. Choice of parameters and functional form**

The parameters \(\lambda_{ij}\) determine the strength with which coherences of each pair of states \(i\) and \(j\) are suppressed. From the dimensional analysis, the variable \(\lambda_{ij}\) has units of inverse time, and therefore, it has the meaning of rate. Because \(\lambda_{ij}\) controls coherences, it is natural to assume that the rate we refer to is proportional to the decoherence rate. Determination of decoherence rates is not a simple task. An attempt to describe decoherence effects by a single parameter constitutes a strong approximation, which becomes accurate in large systems with fast decoherence.

There exists a variety of ways to define the decoherence rate, and there are certain conditions under which those definitions work. Expressions for decoherence times are based on consideration of wavepacket dynamics, often in the frozen Gaussian short-time limit. The common result is that the decoherence time can be estimated as the timescale of the decay of overlap of frozen Gaussians representing nuclear degrees of freedom correlated with different electronic states. An example of a frozen Gaussian expression is given by Schwartz,81, 92

\[
\frac{1}{\tau_{ij}} = \sum_n \frac{|F^0_n(t) - F^0_n(t)|}{2\hbar\sqrt{a_n}}, \tag{5}
\]

where \(F_i\) is the force in the adiabatic level \(i\) and \(a_n\) is the effective width of the nuclear wavepacket. According to Schwartz and co-workers, the width of the nuclear wavepacket can be approximated by

\[
a_n = \left[\frac{(w/a_0)^2}{2\lambda_D(t)}\right]^2 = \frac{m (w/a_0)^4 m v^2}{2\hbar} = \frac{(w/a_0)^4}{2\hbar} E_{\text{kin}}, \tag{6}
\]

where \(m\) is the effective mass of the particle, \(w\) is the spatial extent of non-adiabatic coupling, \(a_0\) is the Bohr radius, \(\hbar\) is the Planck constant, \(v_0\) is the velocity of the particle, and \(\lambda_D(t) = \frac{\hbar}{m v_0(t)}\) is the instantaneous de Broglie wavelength. Note that the quantities \(m\) and \(w\) are defined semiquantitatively; therefore, the entire prefactor \(\frac{(w/a_0)^4}{2\hbar}\) can be considered an empirical parameter.

A more general approach to the derivation of the decoherence times has been developed by Subotnik and co-workers on the basis of the Wigner transform of the electron-nuclear wavefunction and the quantum-classical Liouville equation.55, 59 The general result for a 2-level system suggests
the state-dependent decoherence rates:

\[
\frac{1}{\tau_{i12}} \approx \frac{1}{2} \sum_{n} \left( F_{i1}^{n} - F_{22}^{n} \right) \frac{1}{A_{12}^{(1)}} \frac{\partial A_{12}^{(1)}}{\partial P_{n}},
\]

(7a)

\[
\frac{1}{\tau_{125}} \approx -\frac{1}{2} \sum_{n} \left( F_{i1}^{n} - F_{22}^{n} \right) \frac{1}{A_{12}^{(2)}} \frac{\partial A_{12}^{(2)}}{\partial P_{n}}.
\]

(7b)

Here, \( F_{ij}^{n} = -\langle \Phi_{j} | \frac{\partial V}{\partial R_{n}} | \Phi_{i} \rangle \) are the generalized forces: the diagonal elements are the standard forces, while the off-diagonal elements are proportional to the nonadiabatic coupling. \( A_{12}^{(i)} \) is the element of the Wigner transform of the joint electron-nuclear wavefunction for \( \lambda \)th active electronic state. \( P_{n} \) is the momentum of the \( n \)th nuclear mode. The results for the Gaussian wavepacket propagation, similar to Eq. (5), can be obtained as a specific case of Eq. (7), by proper ansatz of the nuclear wavefunction.

In the decay of mixing scheme, Truhlar and co-workers utilized the phenomenological expression for the decoherence rates:

\[
\tau_{ij} = \frac{\hbar}{|E_{i} - E_{j}|} \left( 1 + \frac{C}{E_{\text{kin}}} \right),
\]

(8)

where \( E_{i} \) are the energies of the electronic states, \( E_{\text{kin}} \) is the kinetic energy of nuclei, and \( C \) is an empirical parameter, typically set to 0.1 Hartree.

In general, an approximation describing decoherence by a single parameter should become more accurate in large systems and with fast decoherence. Strong motivation for the decoherence correction arose from NAMD applications of this type.\(^{39,40,79,93}\) In such cases, decoherence arises due to the combined effect of fluctuations in many degrees of freedom, and the decoherence rate can be evaluated by the optical response theory.\(^{94,95}\) which gives reliable results and can be benchmarked against optical measurements of homogeneous linewidths.\(^{96,97}\)

\[
\lambda_{ij} t^{2} = \left( \frac{t}{\tau_{ij}} \right)^{2} = \frac{\hbar}{2 C_{ij}} \int_{0}^{t} dt' \int_{0}^{t'} dt'' C_{ij} \left( t'' \right)
\]

\[
= \frac{\langle \delta E_{ij} \rangle^{2}}{\hbar^{2}} \int_{0}^{t} dt' \int_{0}^{t'} dt'' \tilde{C}_{ij} \left( t' \right),
\]

(9a)

\[
\tilde{C}_{ij} \left( t \right) = \frac{C_{ij}}{\langle \delta E_{ij} \rangle^{2}} \frac{\langle \delta E_{ij} (t) \delta E_{ij} (0) \rangle}{\langle \delta E_{ij} \rangle}.
\]

(9b)

\[
C_{ij} \left( t \right) = \langle \delta E_{ij} (t) \delta E_{ij} (0) \rangle.
\]

(9c)

The approach does not require adjustable parameters and is actively utilized by Prezhdo and co-workers to study quantum dynamics in nanoscale systems.\(^{75,95,98-102}\)

In the present work, we utilize the optical response formalism, Eqs. (9), for the realistic system and the modified wavepacket result, Eq. (5), for the model. The modification is as follows:

\[
\lambda_{ij} = f \frac{1}{\tau_{ij}} = f \frac{|E_{i}(t) - E_{j}(t)|}{2\hbar \sqrt{a_{0}}},
\]

(10)

The function \( f \) is a proportionality factor between the decoherence rate, \( \frac{1}{\tau_{ij}} \), and the strength of decoherence control, \( \lambda_{ij} \).

We found empirically that with the parameter \( a_{0} \) set to the constant value \( a_{0} = 1 \) Bohr, the optimal choice for the proportionality factor, \( f \), is

\[
f = \frac{100}{p_{0}},
\]

(11)

where \( p_{0} \) is the initial nuclear momentum. The constant 100 in Eq. (11) was found empirically and produces reasonable results for different model systems. By choosing the fixed value for all systems, we pursue the goal of transferability of the factor \( f \). A functional dependence of the factor \( f \) on the initial momentum and other system parameters can be considered.

Keeping in mind the discussed elaborations in the form of Eq. (11), the physical meaning of the choice given by Eq. (11) is straightforward to rationalize. It represents a linear dependence of the nuclear wavepacket width on system temperature, which can be related to the (initial) nuclear kinetic energy. Using Eq. (11), the factor \( \frac{f}{\sqrt{a_{0}}} \) can be rewritten as

\[
\frac{f}{\sqrt{a_{0}}} = \frac{1}{\sqrt{p_{0}^{2}/100}} = \frac{1}{\sqrt{a_{0} \left( \frac{p_{0}}{100} \right)^{2}}} \sim \frac{1}{\sqrt{a_{0} E_{\text{kin},0}}} \sim \frac{1}{\sqrt{a_{0} T}} \sim \frac{1}{a(T)},
\]

(12)

which is consistent with Eq. (6). Note that for the nuclear mass \( m = 2000 \) a.u. used in the model calculations, the first proportionality in Eq. (12) is close to the equality, because \( \left( \frac{p_{0}}{100} \right)^{2} = \frac{p_{0}^{2}}{2m^{5/2}} = \frac{7}{5} E_{\text{kin}} \).

D. Analysis of the CPF method

It is illustrative to analyze the limiting behavior of the decoherence control parameters, \( \lambda_{ij} \). In the high-temperature limit, \( T \to \infty \), the parameter \( a \to \infty \), which is equivalent to \( f \to 0 \), and \( \lambda_{ij} \to 0 \).\(^{92}\) Therefore, the coherence penalty term vanishes, and the original Ehrenfest dynamics is recovered. It is known that in the high-temperature limit the results of the FSSH and Ehrenfest dynamics coincide. Hence, our scheme is well behaved in the high-temperature limit.

Let us show how decoherence arises from the penalty term in the modified Hamiltonian, Eq. (4). The dynamics of the phase space variables \( z = \{(q_{i}, p_{i})\}, i = 1, \ldots, N \) is governed by the propagator \( \exp(iL_{\tilde{H}} \cdot dt) \), where \( iL_{\tilde{H}} = \frac{\hbar}{2} \). The Hamiltonian \( \tilde{H} \) can be split into two parts:

\[
\tilde{H} = H + H',
\]

(13)

where \( H \) is the original (closed) system Hamiltonian, Eq. (3), and \( H' = \sum_{i,j} \lambda_{ij}(q_{i}^{2} + p_{i}^{2})(q_{j}^{2} + p_{j}^{2}) \) is the penalty functional. The Liouvillian can be split in a similar way:

\[
\exp(iL_{\tilde{H}} \cdot dt) = \exp \left( iL_{H} \cdot \frac{dt}{2} \right) \exp \left( iL_{H'} \cdot \frac{dt}{2} \right).
\]

(14)
Expression (14) is a composition of two Hamiltonian flows maps. Because Hamiltonian flow maps are symplectic, and because the compositions of Hamiltonian flow maps are also Hamiltonian, the overall flow map is symplectic. This is an important property for numerical integration of Eq. (2).

From the physical point of view, the picture is clear – the operator exp (i $L_H \cdot dt$) corresponds to dynamics of the closed system, which is described by the Hamiltonian $H$. The action of this operator generates the standard Ehrenfest dynamics. The action of the operator $exp (i L_H \cdot dt / 2)$ deserves a closer examination. Writing $i L_H$ explicitly, we obtain

$$i L_H = \sum_i \left( \frac{\partial \phi_i}{\partial q_i} \dot{q}_i + \frac{\partial \phi_i}{\partial p_i} \dot{p}_i \right) = \sum_i \phi_i \left( \frac{\partial \phi_i}{\partial q_i} - q_i \frac{\partial \phi_i}{\partial p_i} \right),$$

where

$$\phi_i = 2 \sum_{j \neq i} (\lambda_{ij} + \lambda_{ji}) \left( q_j^2 + p_j^2 \right).$$

Equation (16) has a great similarity with the expression for the inverse of the decoherence time intervals used in the Lindblad formulation.75, 104, 105 According to this formulation, the average of the inverse decoherence time, $\langle \frac{1}{\tau_j} \rangle$, for state $i$ is given by the microscopic decoherence rates between state $i$ and other states, $r_{i \sim j}$, weighted by the populations of the other states, $|c_j|^2$, $j \neq i$:

$$\langle \frac{1}{\tau_j} \rangle = \sum_{j \neq i} r_{i \sim j} \langle |c_j|^2 \rangle = \sum_{j \neq i} r_{i \sim j} (q_j^2 + p_j^2).$$

The close similarity of Eqs. (16) and (17) reinforces the earlier hypothesis on the physical meaning of parameters $\lambda_{ij}$.

Further application of the Trotter factorization gives

$$\exp (i L_H \cdot dt) = \prod_{i=1}^{N} \exp \left( \phi_i \left( \frac{\partial \phi_i}{\partial q_i} - q_i \frac{\partial \phi_i}{\partial p_i} \right) \frac{dt}{2} \right) \times \prod_{i=N}^{1} \exp \left( \phi_i \left( \frac{\partial \phi_i}{\partial q_i} - q_i \frac{\partial \phi_i}{\partial p_i} \right) \frac{dt}{2} \right).$$

The quantum state of a system is altered by a series of operators of the type

$$\exp \left( \phi_i \left( \frac{\partial \phi_i}{\partial q_i} - q_i \frac{\partial \phi_i}{\partial p_i} \right) dt \right).$$

The action of such operator is well known – it propagates the phase of state $i$:

$$q_i (t + dt) = \cos (\phi_i dt) q_i (t) - \sin (\phi_i dt) p_i (t), \quad \text{(20a)}$$

$$p_i (t + dt) = \sin (\phi_i dt) q_i (t) + \cos (\phi_i dt) p_i (t), \quad \text{(20b)}$$

or

$$c_i (t + dt) = q_i (t + dt) + ip_i (t + dt) = \exp (\phi_i dt) (q_i (t) + ip_i (t)) = \exp (\phi_i dt) c_i (t).$$

An operator of a similar type is encountered in the Trotter decomposition of $i L_H$, in which the standard dynamical phase is used: $\phi_i = E_i / 2$. In the above derivation, we assume that $\phi_i$ is constant during any given infinitesimal period of time. This approximation can further be supported by noting that the solution given by Eqs. (20) and (21) preserves the norm of the wavefunction. The operator equation (18) causes no population transfer between the pair of states $i$ and $j$. The phase shift $\phi_i$ of a given electronic state $i$ does not depend on the electronic degrees of freedom of the same electronic state $i$. It depends only on the variables corresponding to all other states $j \neq i$.

The main effect of the coherence penalty term defined in Eq. (4) is to include additional phase shifts to phases of all quantum states. Because the phase shifts are different and time-dependent, the total phase of each adiabatic state diverges from that of all other states – the states dephase, decohere. It should be emphasized that the effects included via the coherence penalty term constitute only a partial correction of the Ehrenfest dynamics – no spatial redistribution or state collapse of wavefunctions is included, all effects arise solely due to the dynamic phase shifts. Therefore, the method can fail in some cases. Still, it is expected that the CPF approach can outperform the standard Ehrenfest and even FSSH techniques.

It is illustrative to analyze the proposed method from the point of view of the mapped QHD theory.106-108 Specifically, one can utilize the Ehrenfest Hamiltonian, Eq. (3), to derive a hierarchy of Heisenberg equations of motion, similar to the one leading to the QHD-2 Hamiltonian.106, 109, 110 Under certain approximations, the equations of motion can be derived from the classically mapped QHD-2 Hamiltonian. In such an extension, quantum effects of nuclei, including decoherence, arise via the wavepacket width variable, $s$, and its conjugate momentum, $p_s$. The QHD-2 Hamiltonian can also be obtained effectively via the following substitution:

$$E_i (\vec{R}) \rightarrow E_i (\vec{R}) + E_i ^{(2)} (\vec{R}) s_i^2 + \ldots,$$

$$d_{ij} (\vec{R}) \rightarrow d_{ij} (\vec{R}) + d_{ij} ^{(2)} (\vec{R}) s_i s_j + \ldots.$$ 

In the simplest case, we truncate the Taylor expansions at the second order of energy and at the zeroth order of non-adiabatic coupling. We also add the corresponding conjugate momenta and width kinetic energy to express the final model Hamiltonian:

$$\tilde{H} = \sum_i \left( \frac{E_i + E_i ^{(2)} s_i^2}{2h} \right) (q_i^2 + p_i^2) - \frac{P}{m} \sum_{i,j} d_{ij} p_i p_j$$

$$+ \sum_i \left( \frac{P_i^2}{2m} + \frac{\hbar^2}{8ms_i^2} \right)$$

$$= H + E_i ^{(2)} s_i^2 \left( q_i^2 + p_i^2 \right)$$

$$+ \sum_i \left( \frac{P_i^2}{2m} + \frac{\hbar^2}{8ms_i^2} \right) = H + H',$$
\[ H' = \sum_i \frac{E_i^{(2)} s_i^2}{2\hbar} (q_i^2 + p_i^2) + \sum_i \left( \frac{p_i^2}{2m} + \frac{\hbar^2}{8m s_i^2} \right). \]  

The equations of motion generated by the Hamiltonian \( H' \) are

\[ \dot{q}_i = -\frac{\partial H'}{\partial p_i} = \frac{E_i^{(2)} s_i^2}{\hbar} p_i, \]  

\[ \dot{p}_i = -\frac{\partial H'}{\partial q_i} = -\frac{E_i^{(2)} s_i^2}{\hbar} q_i, \]

\[ \dot{s}_i = -\frac{\partial H'}{\partial p_{s,i}} = \frac{p_{s,i}}{m}, \]

\[ \dot{p}_{s,i} = -\frac{\partial H'}{\partial s_i} = \frac{\hbar^2}{8m s_i^2} - \frac{E_i^{(2)}}{\hbar} (q_i^2 + p_i^2) s_i. \]

The term \( \sum \frac{E_i^{(2)} s_i^2}{2\hbar} (q_i^2 + p_i^2) \) contributes to dephasing of wavepackets, as it is clear from Eqs. (24a) and (24b). The variable \( s_i \) changes in time and is different for each electronic state, but its derivative depends on the state population. In the case when the population of the state is 0, the wavepacket monotonically spreads out, since \( \dot{p}_{s,i} > 0 \) and at some point \( \dot{s}_i > 0 \).

The QHD-2 dynamics is similar to the Ehrenfest dynamics in the sense that the expectation values are propagated directly. Performing calculations according to Eqs. (24) constitutes one option, but it may be rather elaborate, especially for realistic multi-dimensional systems. At the same time, the physics of Eqs. (24) is clear – the phase of each electronic state is corrected by an additional time-dependent term that, in turn, depends on populations of electronic states. This same physics is modeled by the CPF dynamics, but the latter is computationally more tractable for realistic systems. In the present work, we only point out to the similarity of the two approaches, as the QHD-2 dynamics may be somewhat more rigorous and can be thought of as a basis for and an extension of the CPF method.

III. RESULTS AND DISCUSSION

In this section, we demonstrate performance of the CPF method with two types of systems. First, we apply it to two model 1D systems – the famous Tully’s double avoided crossing (DAC) and extended coupling with reflection (ECWR) problems.\textsuperscript{25} We utilize slightly modified parameters for the first model, in order to enhance the effects of quantum interference and decoherence. In the second type of application, we study electronic energy relaxation dynamics in two realistic nanoscale systems.

A. Model systems

We apply the CPF method to study the scattering probabilities for Tully’s DAC and ECWR potentials. The potentials are defined by

\[ V_{00} = A \exp(-B x^2), \]  

\[ V_{11} = E - V_{00}, \]

\[ V_{01} = V_{10} = C \exp(-D x^2) \]

with parameters \( A = 0.1, B = 0.028, C = 0.015, D = 0.06, E = 0.05 \) for DAC, and

\[ V_{00} = A, \]

\[ V_{11} = -A, \]

\[ V_{01} = V_{10} = \begin{cases} B \exp(C x), & x \leq 0 \\ B \exp(-C x), & x > 0 \end{cases} \]

with parameters \( A = 0.0006, B = 0.1, C = 0.9, D = 1.0 \) for ECWR. Atomic units of energy and length are adopted in all cases. The potentials are depicted in Fig. 1. In our studies we modify the original DAC potential, to increase the effective size of the potential well and enhance decoherence effects. The parameters for the ECWR potential are the same as in the original Tully’s prescription.

Because the CPF approach has a lot in common with the Ehrenfest method and does not include stochastic trajectory branching, it cannot be expected to resolve accurately reflection vs. transmission. Further, in multi-dimensional potentials, which can correspond to realistic systems, the terms “reflection” and “transition” may be not well defined. One is often interested in total populations of different quantum states rather than directionally resolved scattering probabilities. Therefore, in the present work we focus on description of total populations.

In all our simulations, the system starts in a pure state 0 (lower energy state), at coordinate \( x = -20 \) a.u., in the region of negligible non-adiabatic coupling between the states. An initial positive momentum is assigned to the classical degree of freedom. The magnitude of the initial momentum is varied as the initial condition parameter. Integration of the equations of motion is performed over a sufficiently long time interval, to allow the classical trajectory to escape the region of strong coupling by the end of the evolution. Typically, 10 000 integration time steps of 10 a.u. (\( \sim 0.5 \) fs) satisfy this requirement. The mass of the classical particle is set to \( m = 2000 \) a.u., which is close to the mass of the hydrogen atom.

In order to understand the improvements and possible pitfalls of the new method, we compare its performance with FSSH, Ehrenfest, and exact numerical solutions. The latter is obtained using the split-operator technique combined with the fast Fourier transform, similar to the procedure of Kosloff \textit{et al.}\textsuperscript{35}

For the CPF calculations we utilize the decoherence rates, \( \lambda_{ij} \), given by Eq. (10). The parameters entering Eq. (10) are defined as \( a = a_0 p_0 \) and \( f = \frac{a}{p_0} \), where \( p_0 \) is the initial wavepacket momentum, \( a_0 \) is the reference width of the wavepacket, set to 1 a.u., and \( K \) is the empirical proportionality factor, set to 100 a.u. of momentum. Only a single trajectory is needed for the CPF method, similar to the Ehrenfest
method. For the FSSH calculations, a swarm of 2000 trajectories was used to calculate statistical properties (observable probabilities).

The total population of the initial quantum state is shown in Fig. 2 as a function of the initial nuclear momentum, \( p_0 \). The CPF method yields notable improvements over the standard Ehrenfest technique for the DAC potential (Fig. 2(a)). It is known that in the limit of large kinetic energies, solutions given by the Ehrenfest and FSSH methods become indistinguishable. One can, therefore, expect that the CPF high-temperature limit also coincides with the Ehrenfest result. This is partially satisfied, but one can still observe a slight shift of the exact numerical solution with respect to the Ehrenfest/FSSH. The CPF method perfectly matches the exact solution, asymptotically approaching the Ehrenfest/FSSH results in the high-energy/high-temperature limit.

Although the high-temperature/high-energy limit is rather straightforward to describe, the intermediate range of kinetic energies presents a bigger challenge. One can observe that positions of the maxima of the Stueckelberg oscillations obtained with the FSSH and Ehrenfest methods are shifted toward higher kinetic energies, in contrast to the exact numerical solution. For the range of initial momenta \( p_0 > 15 \) a.u., the CPF method yields solutions that are much closer to the exact numerical results. The solutions generated by the other two methods show notable deviation with respect to the exact result. Starting at \( p_0 > 25 \) a.u., the CPF and numerical solutions practically coincide. Therefore, it can be concluded that the CPF method successfully reproduces the expected “lower-energy” shift of the maxima.

In the region of low kinetic energies, \( p_0 < 12 \) a.u., in which the Ehrenfest method breaks down as manifested by large-amplitude oscillations, the CPF method works especially well, approaching both the FSSH and exact solutions. Because of the inverse dependence on the initial momentum via factor \( f \), Eq. (11), the coherence penalty is larger in the low-energy region. As a result, the dephasing is fast. On the other hand, fast dephasing often leads to the quantum Zeno effect – frequent observations of the system by external means lead to projection of the quantum state onto the dominant eigenstate, slowing down interstate transitions.\(^{100,111-115}\) This mechanism explains the decreased transition rates between the quantum states and the smaller magnitude of fluctuations observed in the low kinetic energy region. From the entire range of the initial momenta, perhaps only the region with \( 12 < p_0 < 15 \) is the most problematic – the CPF results deviate notably from the exact numerical results. At the same time, the solutions are close to those obtained with the FSSH method.

Performance of the CPF method for the ECWR potential is illustrated in Fig. 2(b). As expected, in the high-energy limit (\( p_0 > 30 \) a.u.) all methods produce identical results. For lower kinetic energies, the CPF results show no artificial oscillation of FSSH and are intermediate between the Ehrenfest and exact solutions. Because the CPF method is a correction to the Ehrenfest dynamics, the shape of the CPF curve in Fig. 2(b) is similar to the one obtained with the original Ehrenfest method. The CPF results show an improvement in on average sense. For small initial momenta, the total population of the lower energy state is systematically larger than the one obtained with the plain MF description, and corresponds to the FSSH results if they are averaged over the period of the artificial oscillation.

Comparison of the panels in Fig. 2 provides additional information on the prerequisites for successful application of the CPF method. Most notably, CPF provides an important correction in cases when complex interference patterns of wavefunctions can develop. The two avoided crossing re-
regions provide the mean for developing such interference patterns in the DAC problem. In the ECWR problem there is only one point of strong non-adiabatic coupling, thus, the interference effects are less pronounced. Hence, corrections provided by CPF are less essential. Second, being an extension of the Ehrenfest approach, the CPF method breaks down when the wavefunction scatters and loses its localization, as in the ECWR problem. The above analysis has important implication to realistic systems, in which the number of avoided crossing regions can be large, while the nuclear wavepacket often remains localized. Under these circumstances, the CPF method is likely to be applicable, rendering itself a useful practical approximation for studies of realistic systems.

In order to understand better the mechanics of the CPF method, we study in detail representative trajectories for each model – at high and low initial nuclear momenta. Figure 3 presents the coherence measure (CM), defined by $|c_i^* c_j|^2$, as a function of the nuclear coordinate. The CM trajectories are superimposed with the profiles of the adiabatic energy levels. The CM changes very rapidly in regions of strong non-adiabatic coupling – at each of the two avoided crossing points for the DAC potential and at the maximum of the non-adiabatic coupling for the ECWR potential. The CMs remain practically constant away from these points. In the vicinity of the avoided crossing points the CM exhibits decaying oscillations. CPF contributes the most of its effect in these regions by decreasing coherences, as clearly illustrated in Fig. 3. Coherences in the Ehrenfest method are notably larger, or, at least, not smaller than in the CPF method.

The FSSH and Ehrenfest methods are often called overcoherent. After a stochastic hop is made in FSSH, the coherences developed in the solution of the semiclassical TD-SE remain unchanged, even though the population of the quantum levels is changed. The CPF method provides a mean of correcting for overcoherence. The penalty terms suppress development of coherence in the solution of the semiclassical TD-SE.

**B. Realistic systems**

To demonstrate applicability of the CPF method to realistic systems, we compute relaxation time scales for two interfacial systems involving a quantum dot (QD) and a substrate. We consider the Au(QD)/TiO$_2$ and PbSe(QD)/TiO$_2$ heterojunctions (Fig. 4). The interfacial electron transfer dynamics in these systems is studied experimentally.$^{116–118}$ The electron-hole recombination is considered for the Au(QD)/TiO$_2$ system. The measured time-scales span a relatively wide range due to charge diffusion. The fastest component corresponding to the recombination of charges that already reached the interface is of the order of 10 ps for large nanoparticles and is faster for smaller particles.$^{116}$ The nanoparticle used in the present calculations is small, and the extrapolated timescale of 1 ps is expected.$^{119}$ The quantum transition leads to recombination of the electron from the lowest unoccupied molecular orbital (LUMO), localized on the TiO$_2$ surface, with the hole in the highest unoccupied molecular orbital (HOMO), localized on the gold nanoparticle. For
the PbSe(QD)/TiO$_2$ system, the experimentally studied process is electron transfer from LUMO+1, which is localized on the TiO$_2$ substrate, to LUMO, which is localized on the PbSe QD. The reported timescale for this process is 1.6 ps.\cite{117,118}

The simulation cells and \textit{ab initio} calculations are set up as follows. The stoichiometric rutile (110) surface is created to represent the substrate material. A bigger ($6 \times 2$) surface and a smaller ($5 \times 2$) surface are used for the PbSe(QD)/TiO$_2$ and Au(QD)/TiO$_2$ systems, respectively, as motivated by the size of the adsorbed QDs–Pb$_{16}$Se$_{16}$ bigger than Au$_{20}$. Each TiO$_2$ (110) surface comprises six atomic layers of TiO$_2$, with the bottom three layers frozen in the bulk configuration. To model the interfacial systems, slab geometry is utilized with 20 Å of vacuum added in the direction normal to the surface. The PbSe QD binds strongly to the TiO$_2$ surface via two O-Pb bonds between the QD and the surface, while the gold nanoparticle interacts weakly with the TiO$_2$ surface without covalent bonding.

Geometry optimization, electronic structure, and adiabatic molecular dynamics calculations are carried out using the Vienna \textit{ab initio} simulation package (VASP).\cite{120,121} Valence electrons are treated explicitly, while the core electrons are accounted for via pseudopotentials generated with the projector augment wave method.\cite{120} The Perdew–Burke–Ernzerhof (PBE) functional\cite{122,123} is used to describe the exchange and correlation terms in electronic energy. The DFT+$U$\cite{124} approach is utilized to improve accuracy of the electronic structure calculations. The on-site Coulomb terms $U = 6.0$ eV and $J = 0.5$ eV are applied to the 3d orbitals of Ti atoms. These parameters are known to reproduce the electronic structure and properties of bulk TiO$_2$.\cite{125} The initially optimized structures are thermalized by MD with velocity rescaling to temperatures of 300 K for the Au(QD)/TiO$_2$ system and 100 K for the PbSe(QD)/TiO$_2$ system, the temperatures used in the corresponding experiments.\cite{116,118} 3 ps and 2 ps Born–Oppenheimer MD trajectories are computed within the microcanonical ensemble for Au(QD)/TiO$_2$ and PbSe(QD)/TiO$_2$, respectively. The velocity Verlet scheme with 1 fs integration time-step is utilized to integrate the equations of motion. Additional details of simulations can be found elsewhere.\cite{119,127}

The NA-MD calculations have been performed with the PYXAID package.\cite{98,128} The dynamics is computed with the Ehrenfest\cite{29,130} and FSSH\cite{25} schemes. We also consider two semiclassical schemes that account for decoherence effects – the recently developed decoherence-induced surface hopping (DISH)\cite{75} technique and FSSH with decoherence (D-FSSH).\cite{38,131}

The computational schemes that account for decoherence (CPF, DISH, and D-FSSH) utilize the microscopic decoherence rates computed using the optical response formula, Eq. (9). The calculated energy gaps are adjusted to match the experimental values, by utilizing a constant shift – the scissor-operator\cite{132,134} approach. Specifically, the average HOMO–LUMO gap in the Au(QD)/TiO$_2$ system is adjusted to 1.1 eV reported in the experiment.\cite{116} The average energy gap between the LUMO and LUMO+1 levels of the PbSe(QD)/TiO$_2$ system is adjusted to the experimental value of 0.3 eV.\cite{117,118}

The time-scales for the interfacial electron transfer computed with the different methods are summarized in Table I. It can be observed that in all cases the plain Ehrenfest method yields longer relaxation times in comparison to those obtained with FSSH. The DISH scheme increases these timescales even further. One can also observe that the DISH scheme tends to overestimate the relaxation timescales. This discrepancy is especially pronounced in the case of the PbSe(QD)/TiO$_2$ system.

The CPF method shows the results that do not obey such a monotonic relationship. On the one hand, in the case of Au(QD)/TiO$_2$ system the CPF method slows down the relaxation, relative to the Ehrenfest dynamics. On the other hand, it accelerates the relaxation with respect to the plain Ehrenfest dynamics for the PbSe(QD)/TiO$_2$ system. In all cases, the resulting timescales are in much better agreement with the experimental values.

The D-FSSH method provides results in reasonable agreement with the experiments. This is a well-established semiclassical scheme that accounts for decoherence effects. Therefore, it can serve as an internal reference for assessment of accuracy of the new CPF scheme. D-FSSH and CPF show the best agreement with each other and with the experimental values.

<table>
<thead>
<tr>
<th></th>
<th>Ehrenfest</th>
<th>FSSH</th>
<th>D-FSSH</th>
<th>DISH</th>
<th>CPF</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(QD)/TiO$_2$</td>
<td>324 fs</td>
<td>133 fs</td>
<td>1.2 ps</td>
<td>1.6 ps</td>
<td>890 fs</td>
<td>~1.0 ps</td>
</tr>
<tr>
<td>PbSe(QD)/TiO$_2$</td>
<td>3.8 ps</td>
<td>622 fs</td>
<td>1.3 ps</td>
<td>8.4 ps</td>
<td>1.8 ps</td>
<td>1.6 ps</td>
</tr>
</tbody>
</table>
results. Thus, the CPF method is sufficiently accurate and can be easily applied to realistic systems.

The distinctive features of the CPF method are worth mentioning explicitly. Unlike the FSSH, D-FSSH, or DISH schemes, the present approach is based on a simple Ehrenfest-like dynamics, and hence, it is continuous and preserves Hamiltonian structure. No stochastic processes that describe hopping are required. Moreover, since the TD-SE is solved for the averaged quantities (distributions), only one trajectory is required, as opposed to the hundreds of stochastic trajectories required in the surface hopping schemes, such as FSSH, D-FSSH, or DISH. Thus, the method is computationally very efficient. Being an extension of the original Ehrenfest dynamics, the CPF approach is easy to implement and, hence, it can be added into any ab initio code with very little effort.

IV. CONCLUSIONS

We have presented the coherence penalty functional method, CPF, for incorporating decoherence effects into NA-MD simulations. The method is based on a simple idea to dynamically penalize development of coherences during evolution of quantum degrees of freedom. The methodology is formulated on the grounds of the Ehrenfest method for semiclassical dynamics. Decoherence effects are introduced via an additional term in the classically mapped Hamiltonian, thus preserving the overall Hamiltonian structure of the equations of motion. The CPF is analogous to exchange-correlation functionals in DFT. It provides an effective way for introducing dynamical correlation effects, such as decoherence, on top of the mean-field Ehrenfest approach.

We illustrate the applicability of the method by performing calculations on model and realistic systems. For the model problems, we showed that the development of coherences is suppressed in the regions of strong non-adiabatic coupling, leading to oscillatory decay of coherences to some saturation value. The coherences do not completely decay to zero – the effect that can be understood from the on average interpretation of the Ehrenfest dynamics. In all cases, the CPF method leads to smaller coherences than the original Ehrenfest approach, affecting quantum state transition rates. Our simulations demonstrate clearly the accuracy improvement for the DAC transition probabilities, leading to better agreement of the peaks of the Stuckelberg oscillations with the exact numerical results. For the ECWR problem, an on average improvement is observed. For the realistic Au(QD)/TiO2 and PbSe(QD)/TiO2 systems the CPF approach shows a notable improvement of the computed electron transfer time scales. The results agree with the decoherence corrected FSSH method.

The CPF methodology has a certain relation to the quantized Hamiltonian dynamics. The method can be enhanced by allowing some of the variables entering the penalty functional to depend on time. For example, the quantities $\lambda_{ij}$ can be mapped on the QHD variables $s$ and $p_s$, thus providing additional dynamical coupling between the nuclear and electronic degrees of freedom. Alternatively, the quantities $\lambda_{ij}$ may be varied in time according to a specifically designed protocol or can simply be approximated by a certain functional form. The dependence of the penalty functional on coherences can be rather arbitrary, in principle, and other functional forms may prove more accurate, more general, or both. In the present work, we considered the simplest possible CPF of the form of Eq. (4), which provides good results.

It is straightforward to combine the CPF scheme with FSSH and related approaches. In FSSH one solves the TD-SE first, and then uses the coefficients of the evolving wave-function to determine the hopping probabilities. CPF includes decoherence into the TD-SE. Using the modified TD-SE to determine the hopping probabilities will include decoherence effects into FSSH. These opportunities certainly require additional exploration in the future.

To recapitulate, the presented method provides a fully Hamiltonian formulation of semiclassical non-adiabatic dynamics. It is simple in implementation and computationally efficient. The functional form of CPF is flexible; it can be generalized and adjusted to study various classes of systems. The technique is easy to use with any ab initio code or a model potential, as has been demonstrated with both model and realistic systems. It does not require large ensembles of stochastic trajectories, which makes it appropriate for calculations on large systems.

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