Electronically Nonadiabatic Dynamics in Complex Molecular Systems: An Efficient and Accurate Semiclassical Solution

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ABSTRACT: Chemical reaction dynamics is always a central theme in chemistry research. In many important chemical processes, reaction dynamics is electronically nonadiabatic, i.e., dynamics involves coupled multiple electronic states. We demonstrate in this paper that a semiclassical (SC) treatment based on an initial value representation methodology and a classical mapping formalism for the electronic degrees of freedom is now able to provide a rigorous and practical solution to electronically nonadiabatic dynamics in complex molecular systems. The key component of this treatment is to incorporate a correlated importance sampling protocol in nonadiabatic SC calculations, which results in a speedup factor of 100 or more in comparison with that using the standard sampling approach. This is illustrated by application to a two-state model coupled with up to 10 nuclear bath modes for a benchmark nonadiabatic excitation energy transfer problem. This work provides great opportunities for the effectively theoretical investigations on reaction mechanisms in complex molecular systems, in which electronically nonadiabatic dynamics plays an importance role.

INTRODUCTION

The well-known Bohn–Oppenheimer (BO) approximation, which assumes that nuclei evolve along a single potential energy surface that is defined by fast-moving electrons, is a milestone in the roadmap for understanding chemical reactions at a molecular level. However, in many fields such as photochemical reactions, nanoscale electronics, and chemical dynamics in biological systems, BO approximation breaks down and nonadiabatic transitions occur between different electronic states, or different BO potential energy surfaces. Non-adiabatic effects here play a crucial role in characterizing many important features in chemical reactions, such as reaction rates and branching ratios. An ideal general theoretical method for treating electronically nonadiabatic chemical dynamics should be able to treat both electronic and nuclear dynamics consistently. However, in prevalent mixed quantum-classical simulations, only a few degrees of freedom (DOF) are treated quantum mechanically while nuclear dynamics is usually treated classically. The inconsistency between the quantum and classical treatments may results in unphysical or inaccurate description of the dynamics, e.g., Ehrenfest dynamics may predict a wrong asymptotic behavior, and a priori knowledge of the quantum decay time is normally needed in the surface hopping algorithms. Alternatively the classical mapping formalism, i.e., the Meyer–Miller–Stock–Thoss (MMST) theory, exactly maps discrete quantum electronic states into continuous classical degrees of freedom, i.e., each electronic state is mapped into a classical harmonic oscillator. Combined with the MMST theory, a semiclassical (SC) approach based on an initial value representation (IVR) methodology integrates both electronic and nuclear motions into a consistent dynamical framework, and quantum coherent dynamics is inherently incorporated. The main challenge is how this SC methodology can be implemented efficiently to electronically nonadiabatic dynamics in complex molecular systems.

In this paper we report how the recently developed correlated importance sampling method makes this SC solution to high-dimensional nonadiabatic dynamics practical. In comparison with the standard sampling method, a speedup factor of 100 or more has been achieved in the new nonadiabatic SC calculations for a benchmark two-state model coupled with up to 10 nuclear DOF to model the excitation energy transfer in photosynthesis systems. This model photosynthetic system has been studied by a variety of theoretical methods including the reduced hierarchy equation method, linearized SC-IVR (LSC-IVR), partial linearized density matrix approach, and other methods which are mostly derived from density matrix formalism.

THEORETICAL METHODS

To proceed, we start from the theoretical foundation of the MMST and SC-IVR methods. In terms of Cartesian coordinates and momenta, the MMST nuclear-electronic Hamiltonian is given by

\[ H = \sum_i \frac{p_i^2}{2m_i} + V_N(x) + \sum_e \left( \frac{p_e^2}{2m_e} + V_e(x) \right) \]

where \( i \) and \( e \) denote nuclear and electronic degrees of freedom, respectively. The nuclear potential \( V_N(x) \) typically includes long-range forces and many-body interactions, while the electronic potential \( V_e(x) \) depends on the electronic wavefunction and is determined by solving the Schrödinger equation. The classical mapping formalism maps the electronic states into classical harmonic oscillators, with the Hamiltonian taking the form

\[ H = \sum_i \frac{p_i^2}{2m_i} + \sum_e \left( \frac{p_e^2}{2m_e} + \omega_e^2 q_e^2 \right) \]

where \( \omega_e \) is the classical harmonic oscillator frequency associated with the electronic state. The classical mapping is achieved by solving the coupled equations of motion for the nuclear and electronic coordinates and momenta, with the classical trajectories being updated at each time step.

The semiclassical approach based on an initial value representation (IVR) method integrates both electronic and nuclear motions into a consistent dynamical framework, with quantum coherent dynamics inherently incorporated. The key component of this treatment is to incorporate a correlated importance sampling protocol in nonadiabatic SC calculations, which results in a speedup factor of 100 or more in comparison with that using the standard sampling approach. This is illustrated by application to a two-state model coupled with up to 10 nuclear bath modes for a benchmark nonadiabatic excitation energy transfer problem. This work provides great opportunities for the effectively theoretical investigations on reaction mechanisms in complex molecular systems, in which electronically nonadiabatic dynamics plays an importance role.

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\[ H(x, p, Q, P) = \sum_{i=1}^{n} \left( \frac{1}{2} (x_i^2 + p_i^2) - 1 \right) H_i(P, Q) + \sum_{i=1}^{n} \sum_{j=i+1}^{n} (x_ix_j + p_ip_j) H_{ij}(P, Q) \]  
(1)

where \( n \) is the number of electronic states, \( H_i \) and \( H_{ij} \) are the diabatic Hamiltonian matrix elements (which are in general functions of nuclear coordinates and momenta \( Q, P \)), and \( x_i \) and \( p_i \) are the Cartesian variables for the \( i \)th electronic DOF, respectively. Classical trajectories for the nuclear and electronic DOF are generated, as usual, by Hamilton’s equations

\[ \dot{Q} = \frac{\partial H}{\partial P}, \quad \dot{P} = -\frac{\partial H}{\partial Q}, \quad \ddot{x} = -\frac{\partial H}{\partial x}, \quad \ddot{p} = -\frac{\partial H}{\partial p} \]  
(2)

with the Hamiltonian given by eq 1. These are the equations of motion in the SC-IVR calculations of dynamical properties.

The dynamical properties of complex molecular systems can be evaluated, in principle, by the corresponding quantum mechanical time correlation function

\[ C_{QM}(t) = \text{tr} \left[ \hat{A} e^{iHt/\hbar} \hat{B} e^{-iHt/\hbar} \right] \]  
(3)

here \( \hat{A} \) and \( \hat{B} \) are operators for general quantities of interest. Considering the extreme difficulty in the exact quantum calculations for complex systems, approximations are normally made to eq 3. The SC-IVR theory approximates the time evolution operators by a phase space average over the initial phase points of classical paths (trajectories); e.g., the coherent state IVR due to Herman and Kluk is

\[ e^{-iHt/\hbar} = (2\pi\hbar)^{-F} \int dq_0 \int dp_0 C(p_0, q_0)e^{i(S(p_0, q_0)/\hbar)} |p_0, q_0\rangle \langle p_0, q_0| \]  
(4a)

where \( F \) is the DOF of the system, \( |p_0, q_0\rangle \) and \( |p_0, q_0\rangle \) are the coherently transformed initial and final state IVR due to the path correlation between the two initial phase points for the bath DOF is incorporated in \( \langle p_0, q_0| \hat{A}|p_0, q_0\rangle \). In a separate paper, we show that how this time-independent correlated importance sampling approach performs in comparison with the previously proposed time-dependent importance sampling method. We now generalize the correlated importance sampling to electronically nonadiabatic dynamics, by treating the electronic-nuclear coupling as a system-bath model. The correlated importance sampling function for the SC-IVR calculations of nonadiabatic dynamics is therefore given by

\[ \rho_{MC}(p_0, q_0, p_0', q_0') \propto \langle p_0, q_0| \hat{A}|p_0', q_0'\rangle \langle p_0, q_0| \hat{A}_b|p_0, q_0\rangle \]  
(7)

\[ C_{LSC}(t) = (2\pi\hbar)^{-F} \int dq_0 \int dp_0 A^\prime(p_0, p_0') B^\prime(p_0, p_0') \]  
(6a)

\[ O^\prime(p_0, p_0') = \int d\Delta q e^{-i\Delta q\hat{A}_b(p_0 + \Delta q/2)|\hat{A} - \Delta q/2} \]  
(6b)

where \( O = A, B \).

Although LSC-IVR has been applied to systems with hundreds of DOF, the more accurate SC-IVR was previously thought to work only for a few DOF in practice. To facilitate the implementation of SC-IVR, we proposed a very efficient correlated importance sampling approach, which introduces a correlated importance sampling approach,18 which introduces the path correlation in the sampling function of the initial phase points:

\[ \rho_{MC}(p_0, q_0, p_0', q_0') \propto \langle p_0, q_0| \hat{A}_b|p_0', q_0'\rangle \langle p_0, q_0| \hat{A}_b|p_0, q_0\rangle \]  
(8)

where \( \hat{A}_b \) is the factorized electronic and nuclear part of operator \( \hat{A} \), the phase point \( (p_0, q_0) \) includes both electronic and nuclear DOF.

We demonstrate in the following how this correlated importance sampling protocol provides an efficient and accurate SC solution to high-dimensional nonadiabatic dynamics by considering a benchmark photosynthetic model system. The Frenkel exciton Hamiltonian for this model is given by

\[ H_e = \epsilon_0 + \sum_{i=1}^{N} \left[ \frac{P_{ki}^2}{2m_{ki}} + \frac{1}{2} m_{ki} \omega_{ki}^2 \left( Q_{ki} - \frac{\epsilon_{ki}}{m_{ki} \omega_{ki}^2} \right)^2 \right] + \sum_{j=1}^{N} \sum_{k=1}^{N} \left[ \frac{P_{kj}^2}{2m_{kj}} + \frac{1}{2} m_{kj} \omega_{kj}^2 Q_{kj} \right] \]  
(9)

where \( n \) and \( N \) are the total number of bacteriochlorophyll sites and the number of the bath modes coupled with each site, respectively; \( m_{ki}, P_{ki}, Q_{ki}, \omega_{ki}, \epsilon_{ki} \) are the mass, momentum, coordinate, frequency, and coupling strength, respectively, for
the kth harmonic phonon bath mode coupled with ith site. Note here each electronic state couples with independent nuclear bath, and we only consider a two-site model in this work. The energy levels of the two sites are $\varepsilon_1^0 = 100 \text{ cm}^{-1}$, $\varepsilon_2^0 = 0 \text{ cm}^{-1}$, the site—site electronic coupling $J_{12} = 100 \text{ cm}^{-1}$, and the bath temperature is 300 K. The spectra density of phonon modes (for all sites) takes the Debye form,

$$
\rho(\omega) = \frac{2\lambda}{\omega^2 + \tau_c^2} \omega 
$$

where the reorganization energy $\lambda$ represents the electronic-nuclear coupling strength, and $\tau_c = 500 \text{ fs}$ is the characteristic time of the phonon bath. We discretize the continuous phonon spectra density eq 10a as done in ref 32. In brief, we have

$$
\omega_j = \omega_0 \tan\left(\frac{\arctan(\omega_m/\omega_0)}{N}\right) 
$$

$$
\lambda_j = \frac{4\lambda\arctan(-\omega_m/\omega_0)}{\pi N} 
$$

where $N$ is the number of bath modes, $\omega_0$ is the characteristic frequency of the bath, and $\omega_m = 100\omega_0$ is the maximum frequency.

The electronic excitation population functions for each site can be evaluated in terms of time correlation function by eqs 3–6,

$$
P_i(t) = \text{tr}[\hat{\rho}(0)e^{-i\hat{H}_c t/\hbar} \hat{\rho}_e e^{-i\hat{\Delta}t/\hbar}] 
$$

with the operators $\hat{A} = \hat{\rho}(0)e^{-i\hat{\Delta}t/\hbar}$, $\hat{B} = \hat{\rho}_e$. Here the density matrix element is

$$
\hat{\rho}_e = |\Phi_i\rangle\langle\Phi_i| 
$$

where the electronic-oscillator wave function for electronic state $i$ is given by

$$
\Phi_i(x) = \langle x|\Phi_i\rangle = \left(\frac{1}{\pi}\right)^{n/4} (2\pi)^{n} \prod_{j=1}^{n} \epsilon^{-1/2}\xi_j^{2n} 
$$

and the corresponding coherent state wave function is

$$
\Phi_i(x, p) = \langle x, p|\Phi_i\rangle = \sqrt{\frac{2}{\epsilon}} (x_i - ip_i) \prod_{j=1}^{n} \epsilon^{-1/4}(x_j^{2} + p_j^{2})^{-2\epsilon/2} 
$$

The nonadiabatic dynamics is integrated by using the fourth order Runge–Kutta method with a time step $\Delta t = 50.0 \text{ au}$. Monodromy matrices are also integrated in the same way, from which the SC prefactor is calculated by using eq 4.

**RESULTS AND DISCUSSIONS**

Figure 1 illustrates the excitation energy transfer calculated by SC-IVR with use of different sampling methods. For comparison, we also show in panel a the results for the pure electronic two-state model, i.e., with no bath, by using the SC-IVR (SC), and the quantum discrete variable representation method (QM). Both methods provide identical transfer dynamics. In the SC-IVR calculations, $10^8$ trajectories are used for the correlated importance sampling protocol and $10^9$ for the standard sampling method ($10^7$ for the no bath case). The electronic-nuclear coupling strength $\lambda = J_{12}$. As more bath modes are introduced, the Rabi oscillation (coherent dynamics) becomes less pronounced. In panel b there are 2 bath modes coupled to each electronic state, the correlated importance sampling approach provides nicely converged results, while even with 10 times more trajectories used, the standard sampling method performs poor at longer times.

By examining the standard deviations of these calculations in Figure 2, it appears that $10^8$ trajectories in the standard sampling protocol result in a comparable standard deviation with that from $10^7$ trajectories with use of the correlated sampling method, which indicates that 2 orders of more
trajectories are required for the standard sampling to reach a comparable convergence with the correlated sampling. As the system becomes more complex, for the 5 bath modes per state case, the advantages of using the correlated sampling approach are more appreciated: the results from the standard sampling method with use of even $10^9$ trajectories are far from converged. The corresponding standard deviation calculations in Figure 2 imply that the speedup factor of using the correlated sampling is about 1000.

The high-dimensional nonadiabatic calculations were also performed for a variety of reorganization energies (electronic-nuclear coupling strength). Figure 3 illustrates the effect of electronic-nuclear coupling strength on the transfer dynamics for the 5 bath modes per state case. As the electronic-nuclear coupling increases, it shows a greater degree of quantum decoherence (the magnitude of Rabi oscillation becomes smaller). At the same time, the coupled Hamiltonian dynamics becomes highly nonlinear therefore the performance of the SC-IVR calculations degrades a bit, especially at long times, as shown in Figure 4 by comparing the standard deviations of the correlation function for different coupling strength parameters in the SC-IVR calculations. Figure 4 demonstrates clearly again the advantage of using the correlated importance sampling over the standard one.

**CONCLUSIONS**

Electronically nonadiabatic dynamics involves the evolution of nuclear motions on coupled multiple BO potential energy surfaces. In this work we show that with the aid of a correlated importance sampling approach, the SC-IVR in the MMST framework provides an efficient and accurate solution to electronically nonadiabatic dynamics in complex molecular systems. The inclusion of path correlation in the bath DOF in the sampling protocol requires 100 or more times fewer trajectories than that using the standard sampling method to obtain converged results in nonadiabatic SC calculations. The effect of electronic-nuclear coupling strength on the computational efficiency is also investigated. The success of this SC treatment for a benchmark two-state model coupled with up to 10 nuclear DOF paves the way for future work on exploring chemical reaction mechanisms in complex molecular systems, i.e., in clusters, solutions, or even materials and biological systems.

**ASSOCIATED CONTENT**

Supporting Information

The results of the standard deviation of the population functions for site 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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