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Machine Learning Decoherence Time Formulas with Force-Projected Kinetic Energies for Nonadiabatic Scattering Dynamics

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Abstract: The framework of mixed quantum-classical dynamics is promising for realizing efficient and reliable simulations of general nonadiabatic dynamics processes. In particular, the surface hopping method based on independent trajectories has attracted extensive interest over the past decades. In practical applications, however, its accuracy is often limited by the overcoherence problem. To address this limitation, we here utilize a machine learning approach to reveal the optimal decoherence time formula for high-dimensional systems and consider the kinetic energy projected along various force directions as the feature inputs. Remarkably, the obtained formula consistently distinguishes itself within the training set across four distinct descriptor spaces. The systematic benchmark confirms the high reliability of the formula based on the kinetic energy projected along the force direction of the nonactive potential energy surface. In fact, the vast majority of average population errors achieved by surface hopping with the new formula are below 0.01 and 0.02 in the investigated one- and two-dimensional systems, respectively. These results thus highlight the high performance of the new decoherence time formula in nonadiabatic scattering dynamics and demonstrate the feasibility of projecting the total kinetic energy onto a proper force direction to uncover the intricate decoherence effect in high-dimensional applications.

Key words: nonadiabatic dynamics, surface hopping, overcoherence problem, decoherence time formula, machine learning.

In chemistry, physics, biology, and materials science, many important dynamical processes (e.g., photochemical reactions [1-7] photosynthesis in plants [8-11] as well as the various electron/exciton dynamics in optoelectronic materials [12-19]) all involve the participation of multiple electronic states and exhibit strong nonadiabatic effects. As a representative mixed quantum-classical dynamics method, trajectory surface hopping is supposed to achieve a good balance between simulation accuracy and computational efficiency, making it widely used in the theoretical investigation of nonadiabatic dynamics [20-23]. One of the key advantages of trajectory surface hopping lies in its seamless integration with first-principles electronic structure calculations, thus enabling real-time and real-space simulation of complex realistic systems [24,25]. In particular, a series of related software packages have been developed and widely utilized in different application scenarios [26-33]. However, the traditional fewest switches surface hopping (FSSH) [34] still suffers from some theoretical limitations, particularly in handling the overcoherence problem of high-dimensional systems due to the classical treatment of nuclear motion [35-37].

In the past decades, extensive efforts have been devoted to addressing the challenge of overcoherence in the framework of mixed quantum-classical dynamics [35-49]. In principle, by incorporating the coupling between trajectories, robust density matrix formulations can be developed to properly describe the dynamical evolution [37,43]. However, considering the strong requirement for *ab initio* nonadiabatic dynamics simulations and complex large-scale applications, independent-trajectory-based approaches offer a more efficient and accessible alternative [21-23,44]. In the standard methodology of traditional surface hopping [34], the time evolution of each trajectory comprises four main procedures: classical nuclear dynamics, electronic wavefunction propagation, calculation of hopping probabilities, and velocity adjustment after successful surface hops. At each time step, decoherence correction can be approximately introduced through a decoherence time formula, which serves as an effective strategy to improve the accuracy

while maintaining the computational efficiency [45-47]. Namely, the wavefunction coefficient of any nonactive state i (i.e., w_i) is corrected by

$$w'_{i(\neq\alpha)} = w_i \exp(-\Delta t/\tau_{ai}), \quad (1)$$

where Δt is the time-step size and τ_{ai} is the decoherence time between the active state a and a nonactive state i. Accordingly, the wavefunction coefficient of the active state a (i.e., w_a) is then reset through

$$w'_a = \frac{w_a}{|w_a|}\sqrt{1-\sum_{i\neq a}|w'_i|^2}. \quad (2)$$

In this study, we identify the optimal decoherence time formulas through a general machine learning-assisted approach, which leverages the benchmark data from fully quantum dynamics and utilizes a discrete-space optimization algorithm to adaptively tune the corresponding parameters in a large set of iteratively generated decoherence time expressions [48]. Ultimately, the decoherence time can be calculated by the descriptors and the related parameters during the nonadiabatic dynamics simulation. In our recent study, we have found a novel decoherence time formula in the form of [49]

$$\tau_{ai} = C_0 + C_1\frac{\Delta E_i}{E^{\boldsymbol{D}}_{kin}(E^{\boldsymbol{D}}_{kin}-\Delta E_i)}, \quad (3)$$

where $E^{\boldsymbol{D}}_{kin}$ represents the kinetic energy based on the nuclear momenta projected along a certain direction $\boldsymbol{D}$. Specifically, for the feature input $E^{\boldsymbol{d}_{ai}}_{kin}$, $\boldsymbol{d}_{ai}$ corresponds to the nonadiabatic coupling (NAC) vector and the parameters in Eq. (3) are calculated as C_0 = 1.0×10^5 and C_1 = 20. This machine learning decoherence time formula has demonstrated high performance in both one- and two-dimensional scattering systems. Note that phase correction [50] has been employed in all surface hopping simulations and atomic units are used throughout the present study unless otherwise specified. Besides, instantaneous decoherence correction is applied when the decoherence time is negative.

In general, one may expect whether other feature input $E^{\boldsymbol{D}}_{kin}$ with different $\boldsymbol{D}$ could also give good performance. Therefore, we study the force-projected kinetic energies here. For each trajectory, the nuclear motion is solved by the Newton equation

$$\frac{d\boldsymbol{P}}{dt} = -\nabla_{\boldsymbol{R}}E_a(\boldsymbol{R}), \quad (4)$$

where $\boldsymbol{P}$ and $E_a(\boldsymbol{R})$ are the nuclear momenta and the eigenenergy of the active state a, respectively. We may first consider $\boldsymbol{D}$ as the force on the active potential energy surface (PES) in Eq. (4), $\boldsymbol{F}_a$, which is calculated during the dynamics simulation even without adding any decoherence correction. Similarly, the force acting on a nonactive state reads

$$\boldsymbol{F}_i = -\nabla_{\boldsymbol{R}}E_i(\boldsymbol{R}). \quad (5)$$

Besides $\boldsymbol{F}_a$ and $\boldsymbol{F}_i$, we also explore the force difference, which incorporates information from both the active PES a and the nonactive PES i,

$$\Delta\boldsymbol{F}_{i(\neq a)} = -\nabla_{\boldsymbol{R}}[E_i(\boldsymbol{R}) - E_a(\boldsymbol{R})]. \quad (6)$$

Similar to those in the surface hopping method, the electronic evolution in the Ehrenfest mean field (EMF) [51] approach also follows the time-dependent Schrödinger equation, and the nuclear motion is governed by the Newton equation. The difference lies in the fact that the nuclear motion in EMF is described by

$$\frac{\partial\boldsymbol{P}}{\partial t} = -\langle\psi(\boldsymbol{r},t)|\nabla_{\boldsymbol{R}}\hat{H}_0(\boldsymbol{r},\boldsymbol{R}(t))|\psi(\boldsymbol{r},t)\rangle, \quad (7)$$

where $\boldsymbol{P}$ is the nuclear momenta on the average PES, $\hat{H}_0(\boldsymbol{r},\boldsymbol{R}(t))$ is the electronic Hamiltonian at the specified nuclear coordinates $\boldsymbol{R}(t)$, and $\psi(\boldsymbol{r},t)$ is the electronic wavefunction at time t. By substituting the adiabatic expansion of the wavefunction into Eq. (7), we can derive the equation for the nuclear motion in the adiabatic representation,

$$\frac{\partial\boldsymbol{P}}{\partial t} = -\sum_i(w_i w_i^*\nabla_{\boldsymbol{R}}E_i) + \sum_{i,k}\boldsymbol{d}_{ik}\,w_k w_i^*(E_i - E_k). \quad (8)$$

In the following study, we denote the force of the average PES in Eq. (8) as $\boldsymbol{F}_{MF}$, which also uses information from both active and nonactive PESs.

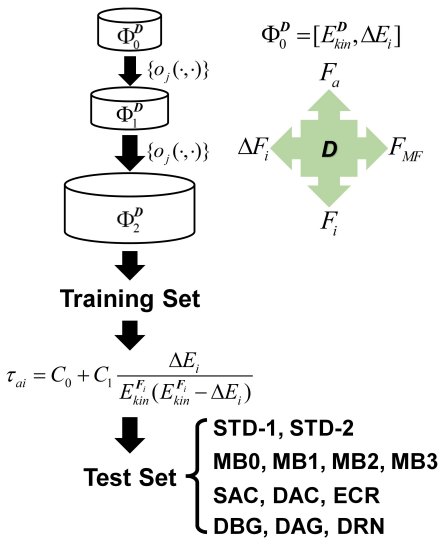

Figure 1. Schematic workflow of the screening processes for decoherence time formulas assisted by machine learning. The initial descriptor space is defined as $\Phi_0^{\boldsymbol{D}} = [E_{kin}^{\boldsymbol{D}}, \Delta E_i]$, where $\Delta E_i = E_i - E_a$ and $\boldsymbol{D}$ is a chosen force direction which has four different options (i.e., $\boldsymbol{F}_a$, $\boldsymbol{F}_i$, $\Delta\boldsymbol{F}_i$, and $\boldsymbol{F}_{MF}$). Through iterative generation with a series of binary operations $\{o_j(\cdot,\cdot)\}$, we can obtain four different second-order descriptor spaces (i.e., $\Phi_2^{\boldsymbol{F}_a}$, $\Phi_2^{\boldsymbol{F}_i}$, $\Phi_2^{\Delta\boldsymbol{F}_i}$, and $\Phi_2^{\boldsymbol{F}_{MF}}$) with a total number of 1,484 descriptors. After screening with the training set, we obtain the optimal decoherence time formula and benchmark it against a test set with a wide array of one-dimensional and two-dimensional model systems.

As the detailed machine learning algorithms to obtain the optimal decoherence time formula have been described elsewhere [48,49], we here only give a brief introduction and the workflow in **Figure 1**. A large number of candidate descriptors are generated in an iterative manner. Namely, the initial descriptor space is defined as $\Phi_0^{\boldsymbol{D}} = [E_{kin}^{\boldsymbol{D}}, \Delta E_i]$, where $\Delta E_i = E_i - E_a$ and $\boldsymbol{D}$ is a chosen force direction. We then obtain the descriptor space $\Phi_1^{\boldsymbol{D}}$ by applying a series of selected binary