Implementation of Coherent Switching with Decay of Mixing into the SHARC Program

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Cite This: J. Chem. Theory Comput. 2020, 16, 3464–3475		Read Online		
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ABSTRACT: Simulation of electronically nonadiabatic dynamics is an important tool for understanding the mechanisms of photochemical and photophysical processes. Two contrasting methods in which the electrons are treated quantum mechanically while the nuclei are treated classically are semiclassical Ehrenfest dynamics and trajectory surface hopping; neither method in its original form includes decoherence. Decoherence in the context of electronically nonadiabatic dynamics refers to the gradual collapse of a coherent quantum mechanical electronic state under the scrutiny of nuclear motion into a mixture of stable pointer states. This is modeled in the coherent switches with decay of mixing (CSDM) method by the decay of the off-diagonal elements of the electronic density matrix. Here, we present an implementation of CSDM in the SHARC program; a key element of the



new implementation is the use of a different propagator than that used previously in the ANT program.

1. INTRODUCTION

Theoretical simulation of electronically nonadiabatic processes such as those that occur in photochemistry and photocatalysis is challenging. Modeling these phenomena requires knowledge of both ground-state and excited-state potential energy surfaces (PESs) and of the couplings between these surfaces. In the electronically adiabatic representation, the couplings are due to nuclear momentum and kinetic energy operators acting on electronic wave functions and are nonadiabatic couplings (NACs); in a diabatic representation, the important couplings are scalar off-diagonal matrix elements of the electronic Hamiltonian.¹ Accordingly diabatic representations are defined here as those in which the coupling of electronic states due to nuclear momenta and nuclear kinetic energy is negligible compared to the coupling due to off-diagonal elements of the electronic Hamiltonian.² When one considers nonadiabatic processes between different spin states, one can employ a blocked molecular-Coulomb-Hamiltonian (MCH) representation or a diagonal representation. For the MCH representation, the diagonal blocks contain electronic Hamiltonian matrix elements states of the same spin, and the off-diagonal blocks are spin-orbit couplings that drive the population transfer between different spin states. The diagonal representation has a fully diagonalized Hamiltonian, including both Coulomb and spin-orbit terms. With the potential surfaces and couplings in hand, one can then simulate the dynamics, which is the subject of this paper.

Many electronically nonadiabatic processes occur on time scales of femtoseconds to picoseconds,³⁻¹² and they are often faster than intramolecular vibrational relaxation; hence they must be treated nonstatistically. Electronically nonadiabatic

molecular dynamics is required for this purpose,¹³⁻³⁰ and we are concerned here with methods employing mixed quantumclassical dynamics, which in the present article refers to algorithms in which the electrons are treated quantum mechanically and the nuclei are treated classically or semiclassically. In such methods, the nuclei propagate on an effective potential, which may be a self-consistent potential, as in the semiclassical Ehrenfest method $^{31-33}$ or the coherent switches with decay of mixing (CSDM) method,³⁴ or it may be an unaveraged adiabatic or diabatic PES; in the unaveraged case the dynamics is punctuated by switches to other PESs, as in the trajectory surface hopping (TSH) method.^{13–16,21} The use of a self-consistent potential is particularly appropriate in regions with closely coupled electronic states, e.g., in a region near a conical intersection seam, where propagation on a single potential energy surface is not justified by the Born-Oppenheimer approximation. Most electronically nonadiabatic processes are controlled by such regions.³⁵

Although plausible justifications are available,³⁶⁻⁴² TSH has an *ad hoc* character motivated in large part by computational simplicity. The results obtained with the TSH method depend strongly on the electronic representation (adiabatic or diabatic), and TSH lacks a balanced treatment of coherence

Received: February 4, 2020 Published: April 6, 2020



Journal of Chemical Theory and Computation

and decoherence in the electronic density matrix. In contrast, the semiclassical Ehrenfest method can be derived from the time-dependent Schrödinger equation by combining the timedependent self-consistent field approximation and the independent-trajectory approximation, and an advantage of the semiclassical Ehrenfest method is that the results are independent of the electronic representation (adiabatic or diabatic) that is employed. However, the semiclassical Ehrenfest method predicts an unphysical final state in that it yields a coherent mixture of electronic states, whereas the physical final state is a classical mixture of pure electronic states produced by decoherence. Since the nuclear kinetic energy equals the total energy minus the electronic energy (following the usual convention, we always define the "electronic energy" to include the nuclear repulsion), the incorrect prediction of the electronic state also leads to an incorrect prediction of the nuclear kinetic energy. In the CSDM method, this deficiency of the semiclassical Ehrenfest method is eliminated by introducing decoherence into the semiclassical Ehrenfest method. In addition to CSDM, recent work has suggested other ways to balance coherence and decoherence in simulations of nonadiabatic processes, and we refer the reader to a recent review for detailed coverage of these other methods.⁴³

Section 2 presents a discussion of coherence and decoherence. Section 3 presents the equations of motion for the semiclassical Ehrenfest method and for the CSDM method, in which decoherence is added to the semiclassical Ehrenfest method in a way that can be understood in terms of the Liouville-von Neumann equation.⁴⁴ The CSDM method has previously been implemented in the ANT (<u>A</u>diabatic and Nonadiabatic Trajectories) program,⁴⁵ and the main purpose of the present article is to describe its implementation in the SHARC (Surface <u>H</u>opping including <u>Ar</u>bitrary <u>C</u>ouplings) program.^{28,46,47} This combines the strengths of CSDM with the capabilities of SHARC to deal with different kinds of couplings on the same footing and with the trajectory management and analysis toolset of the SHARC suite. Section 4 explains how the quantum-classical methods are implemented in the SHARC program. Section 5 presents an application of the photodynamics of ethylene. Section 6 is the conclusion.

2. DECOHERENCE

Decoherence is a basic feature of the quantum dynamics of a subsystem interacting with an environment. In the present context, we are concerned with the electronic subsystem evolving in the environment of nuclear motion. In such a case, electronic decoherence is caused by the "bath" of nuclei. In general, decoherence occurs to a state in the pointer basis, which is a set of states that survives under the scrutiny of the environment.⁴⁸ In regions where the Born-Oppenheimer adiabatic approximation is valid, the pointer basis is the electronically adiabatic basis,⁴⁹ and for weakly damped harmonic chains, the pointer basis belongs to the class of coherent states, 50,51 but in general the pointer basis is unknown, and it is determined by the type of information transfer that occurs when a subsystem interacts with its environment.^{48,52,53} This means the system may decohere to adiabatic states, diabatic states, or even states in other representations. In our work we usually assume that the pointer basis is the electronically adiabatic one, which may be justified in part by the idea that decoherence is most important in regions where the electronic states are not strongly coupled,

but the formalism allows decoherence to any other basis, and, for example, there may be problems where it is more appropriate to assume that the pointer basis is a diabatic one that is identical to the adiabatic approximation in asymptotic regions where the Born–Oppenheimer approximation is valid, but not everywhere.

A mixed quantum-classical treatment should allow for decoherence in which the environment (i.e., the nuclei) destroys coherence between the states of the quantum subsystem (which is the subsystem of electrons). Decoherence induces two effects in mixed quantum-classical dynamics. (1) It causes the environment-induced superselection of the pointer basis (called einselection for short),⁵³ which means all superpositions of electronic quantum states decay into a classical mixture of pointer states. For example, if one expands the electronic wave function as

$$\varphi^{\text{elec}}(t) = \sum_{I=1}^{N} c_I(t)\phi_I(t)$$
(1)

where $\{\phi_I(t)\}\$ is the pointer basis at time *t*, and *N* is the number of basis functions retained in the calculation, the offdiagonal electronic density matrix element

$$\rho_{II} = c_I c_J^*, \ I \neq J \tag{2}$$

(which are called coherences) should decay with a time constant called the decoherence time, which, for the processes of interest here, is typically on the order of magnitude of 2-50 fs. (2) The einselection reacts back on the nuclei and influences the further propagation of the nuclei. Neither semiclassical Ehrenfest nor TSH describes these effects correctly.

From the electronic wave function perspective, the pointer basis is einselected because this is the only basis that survives under the scrutiny of the nuclei; other bases are unstable. From the nuclear wave function perspective, in which the coefficients in eq 1 are interpreted in terms of nuclear wave functions, ρ_{II} can be interpreted in terms of the overlap of nuclear wave packets associated with different electronic states. Unless the two PESs on which nuclei propagate are degenerate, such that the nuclear wave packets of the coupled electronic states have the same velocities, their spatial overlap will decay (and also they will get out of phase). In fact, the spatial separation of the nuclear wave packets after traversing a strong interaction region can be very fast. This causes TSH and semiclassical Ehrenfest to be overcoherent because the equations of motion for the density matrices employed in TSH and semiclassical Ehrenfest are derived (or approximately derived in the case of TSH) from the time-dependent Schrödinger equation, which is inadequate for any subsystem and in particular is inadequate for the electronic subsystem of a molecule, which is better described by the Liouville-von Neumann equation.⁴⁴ Overcoherence is also an artifact of the classical localization of the nuclear trajectories in semiclassical Ehrenfest and TSH. The overcoherence may cause serious inaccuracies in simulations, for example, a too short excited-state lifetime 5^{54-56} or incorrect partitioning of flux into possible product states.^{57,58}

Robustness with Respect to Representation. In semiclassical Ehrenfest, the nuclei propagate on a self-consistent potential given by⁵⁹

$$V = \sum_{I,J}^{N} \operatorname{Re}(\rho_{IJ} \langle \varphi_{I} | H^{\text{elec}} | \varphi_{J} \rangle)$$
(3)

where $\operatorname{Re}(f)$ denotes the real part of f, H^{elec} is the electronic Hamiltonian, which—as usual—includes the nuclear repulsion, and φ_I is electronic wave function of state I. Employing the self-consistent potential makes the effective potential independent of a change in representation provided the transformed states span the same space. A diabatic basis that spans the same space as the *N*-state adiabatic basis is called adiabatic equivalent, and we restrict ourselves to representations obtained by a unitary transformation from the adiabatic one so that we are always working in an adiabatic-equivalent one with an invariant self-consistent potential. Such invariance of the self-consistent potential with respect to the chosen basis is very important in regions of space where the electronic states are strongly coupled, such as near a conical intersection or when the density of electronic states is high.

In TSH, the classical particles (nuclei) propagate locally on a single-state potential, U_{II} , which is a diagonal element of H^{elec} and is not invariant to the choice of representation. It is usually calculated in the adiabatic representation, in which case it is called V_I .

Decoherence Added to Trajectory Surface Hopping. One can add decoherence to trajectory surface hopping, and that does indeed improve the method, ^{57,60–68} but one cannot add decoherence completely consistently in the context of propagating on individual surfaces (as surface hopping does) rather than on effective surfaces determined by the density matrix.

Decoherence Added to Semiclassical Ehrenfest. A more consistent way to add decoherence to electronically nonadiabatic dynamics is the CSDM method, which may be considered an implementation of the Liouville-von Neumann equation,⁴⁴ which is the correct equation for describing the quantum mechanical propagation of the density matrix of a subsystem. The state to which the system decoheres in this approach (i.e., the algorithmic choice for the pointer state) has been called the decoherent state in previous work, but here it is simply called the pointer state. Whereas TSH involves coherent propagation of a trajectory on a single potential energy surface, which is stochastically switched, CSDM involves a combination of coherent and incoherent propagation of a trajectory on the self-consistent potential while the pointer state is switched. The CSDM algorithm incorporates advantages from both semiclassical Ehrenfest and TSH. Specifically, like TSH, it predicts an observable asymptotic behavior, and like semiclassical Ehrenfest, it propagates the trajectory continuously (i.e., without hops) in the strong interaction region and is robust with regard to the choice of the representation.

In the present article, we discuss the details of the implementation of CSDM in the SHARC program.

3. EQUATIONS OF MOTION

3.1. Semiclassical Ehrenfest. The semiclassical Ehrenfest method³¹⁻³³ is a version of the time-dependent Hartree approximation (time-dependent self-consistent field approximation) in which the nuclear coordinates evolve classically governed by a mean-field treatment of the quantal electronic motion. This involves the factorization of the molecular wave

function as a product of wave functions for slow (nuclear) and fast (electronic) motions:

$$\psi(\mathbf{R}, \mathbf{r}, t) = \chi^{\text{nuc}}(\mathbf{R}, t)\varphi^{\text{elec}}(\mathbf{r}, t)$$
(4)

where *t* is time; **r** and **R** are electronic and nuclear coordinates (**R** is a $3N_{\text{atoms}}$ -dimensional vector, where N_{atoms} is the number of atoms); and ψ , χ^{nuc} , and φ^{elec} are molecular, nuclear-motion, and electronic wave functions, respectively. Inserting eq 4 into the time-dependent Schrödinger equation, we get the electronic mean-field equation:

$$i\hbar \frac{\partial}{\partial t} \varphi^{\text{elec}}(\mathbf{r}, t)$$
$$= \langle \chi^{\text{nuc}}(\mathbf{R}, t) | H(\mathbf{r}, \mathbf{R}) | \chi^{\text{nuc}}(\mathbf{R}, t) \rangle_{\mathbf{R}} \varphi^{\text{elec}}(\mathbf{r}, t)$$
(5)

and the nuclear mean-field equation:

$$i\hbar \frac{\partial}{\partial t} \chi^{\text{nuc}}(\mathbf{R}, t)$$

= $\langle \varphi^{\text{elec}}(\mathbf{r}, t) | H(\mathbf{r}, \mathbf{R}) | \varphi^{\text{elec}}(\mathbf{r}, t) \rangle_{\mathbf{r}} \chi^{\text{nuc}}(\mathbf{R}, t)$ (6)

where H is the molecular Hamiltonian.

If one used Gaussian wave packets for the nuclear motion, and if the initial quantized nuclear wave functions were represented as a superposition of Gaussians, one would have interference between the individual wave packets, and one could only obtain accurate results by treating them coherently.⁶⁹ In practical wave packet methods, this interference is usually neglected, which may be called the independent wave packet assumption (or-in some contexts-the independent first-generation approximation).⁷⁰ In the present treatment, we will make this approximation, and we will replace the ensemble of nuclear wave packets with an ensemble of trajectories, so we will have an independent-trajectory approximation. The initial state of the nuclei will be simulated by picking the trajectory initial conditions in phase space such that averaging over the distribution in phase space mimics the initial quantum state, and the results will be averaged over the independent trajectories. The electronic wave function, in contrast will be initialized to mimic the experiment being simulated.

First, we consider the electronic mean-field equation. Replacing the nuclear wave packets by trajectories reduces eq 5 to

$$i\hbar \frac{\partial}{\partial t} \varphi^{\text{elec}}(\mathbf{r}; \mathbf{R}(t)) = H(\mathbf{r}, \mathbf{R}(t)) \varphi^{\text{elec}}(\mathbf{r}; \mathbf{R}(t))$$
(7)

where $\mathbf{R}(t)$ is a trajectory. By expanding the electronic wave function as a linear combination of *N* electronically adiabatic states ϕ_p we get

$$\varphi^{\text{elec}}(\mathbf{r}; \mathbf{R}(t)) = \sum_{J=1}^{N} c_J(t) \phi_J(\mathbf{r}; \mathbf{R}(t))$$
(8)

where *J* indexes the electronic states in the basis used for propagation, and c_J is a time-dependent configuration state coefficient. Inserting eq 8 into eq 7, projecting on the left with ϕ_I , and making the usual semiclassical approximation⁷¹ of neglecting the second-derivative nonadiabatic term leads to the following equation of motion for the time-dependent coefficients:

 $\frac{dc_I}{dt} = -\frac{i}{\hbar} \left(c_I(t) V_I - i\hbar \sum_{J \neq I}^N c_J(t) \mathbf{d}_{IJ} \cdot \mathbf{v} \right)$ (9)

where

$$V_I = \langle \phi_I | H^{\text{elec}} | \phi_I \rangle \tag{10}$$

is the adiabatic electronic state energy (i.e., the Born-Oppenheimer potential energy surface) and

$$\mathbf{d}_{IJ} = \left\langle \phi_{I} \middle| \frac{\partial \phi_{J}}{\partial \mathbf{R}} \right\rangle \tag{11}$$

is the nonadiabatic coupling vector, and **v** is the classical nuclear velocity vector. Note that **d** is an $N \times N$ matrix, each of whose elements is a $3N_{\text{atoms}}$ -dimensional vector.

For the nuclear motion, we write the nuclear wave function as

$$\chi^{\text{nuc}} = A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right)$$
(12)

When eq 12 is substituted in the nuclear mean-field eq 6 and the classical limit is taken,³⁸ one gets Newton's equation by focusing on the equation of motion for $S(\mathbf{R},t)$ and recognizing that it is a Hamilton–Jacobi equation:

$$\mathbf{F} = \sum_{i=1}^{N_{\text{atoms}}} M_i \frac{d\mathbf{v}_i}{dt}$$
(13)

where M_i and \mathbf{v}_i are the mass and velocity of atom *i*, with the force given by

$$\mathbf{F} = -\sum_{I}^{N} \rho_{II} \frac{\partial V_{I}}{\partial \mathbf{R}} + \sum_{I}^{N} \sum_{J}^{N} \operatorname{Re}(\rho_{IJ}(V_{I} - V_{J})\mathbf{d}_{IJ})$$
(14)

Hence, for semiclassical Ehrenfest dynamics in the adiabatic approximation, the electronic and nuclear equations of motion are eqs 9 and 14.

A similar derivation may be carried out for diabatic representation. In this case, eqs 9 and 14 are replaced by

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$$\frac{\partial c_I}{dt} = -\frac{i}{\hbar} \sum_{J}^{N} \langle \phi_I | H^{\text{elec}} | \phi_J \rangle(t) c_I(t)$$
(15)

$$\mathbf{F} = -\sum_{I}^{N} \sum_{J}^{N} \operatorname{Re}\left(\rho_{IJ}(t) \frac{\partial}{\partial \mathbf{R}} \langle \phi_{I} | H^{\text{elec}} | \phi_{J} \rangle(t)\right)$$
(16)

3.2. Coherent Switching with Decay of Mixing. In this section, we assume that the calculations are carried out in the adiabatic approximation. The treatment in the previous section is fully coherent. However, the quantum subsystem is coupled to an environment of nuclei, so the equation of motion for the electronic coefficients needs an additional term to account for decoherence:

$$\frac{dc_I}{dt} = \left[\frac{dc_I(t)}{dt}\right]_{co} + \left[\frac{dc_I(t)}{dt}\right]_{de}$$
(17)

where the subscripts co and de denote the coherent and decoherent contributions, with the coherent contribution being given by eq 9. The decoherent contribution drives the diagonal density matrix element of the pointer state K to unity and all the other density matrix elements to zero in a relaxation

time that is called the decoherence time. The assumption of first order decay gives

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$$\left[\frac{dc_I}{dt}\right]_{de} = \begin{cases} -\frac{1}{2\tau_{IK}}c_I(t) & I \neq K\\ \sum_{\substack{J \neq K}}^N \frac{1}{2\tau_{JK}(t)}\frac{\rho_{JJ}(t)}{\rho_{KK}(t)}c_I(t) & I = K \end{cases}$$
(18)

where τ_{IK} is the decoherence time for state *I* and the second index *K* is the index of the pointer state. From eq 18, one can see that

$$\left[\frac{d\rho_{KK}(t)}{dt}\right]_{de} = \sum_{J \neq K}^{N} \frac{\rho_{JJ}}{\tau_{JK}} > 0$$
(19)

$$\left[\frac{d\rho_{II}(t)}{dt}\right]_{de} = -\frac{\rho_{II}}{\tau_{IK}} < 0, I \neq K$$
(20)

and

$$\sum_{I=1}^{N} \left[\frac{d\rho_{II}(t)}{dt} \right]_{de} = 0$$
(21)

The decoherent term contributes a decoherent force in the equation of motion for the nuclei such that the total energy is conserved. We have

$$\mathbf{F} = [\mathbf{F}]_{co} + [\mathbf{F}]_{de} \tag{22}$$

where $[\mathbf{F}]_{co}$ is given by eq 14. The decoherent force:

$$[\mathbf{F}]_{de} = \sum_{I \neq K}^{N} \frac{\rho_{II}(t)}{\tau_{IK}} \frac{(V_I - V_K)}{\mathbf{s}_{IK} \cdot \mathbf{v}} \mathbf{s}_{IK}$$
(23)

where \mathbf{s}_{IK} is the decoherence vector given by

$$\mathbf{s}_{IK} = \operatorname{Re}\left(\frac{a_0 \mathbf{P}_{\text{vib}} \cdot \mathbf{d}_{IK}}{|\mathbf{d}_{IK}|} \mathbf{d}_{IK}\right) + \mathbf{P}_{\text{vib}}$$
(24)

where \mathbf{P}_{vib} is the internal vibrational momentum (computed by removing the overall angular motion from the total momentum of the molecule), and $a_0 = 1$ bohr. In specifying the decoherence time below, we will find it useful to break the $3N_{\text{atoms}}$ -dimensional vector \mathbf{s}_{IK} into N_{atoms} three-dimensional vectors $\mathbf{s}_{i,IK}$ each associated with a given atom *i*. The decoherence vector is derived by considering the conservation of total angular momentum; the appendices give a detailed discussion of the decoherent force, the conservation of energy and angular momentum, and the choice of decoherent direction in CSDM.

In CSDM, the decoherence time is approximated as⁷²

$$\tau_{IK} = \frac{\hbar}{|V_I - V_K|} \left(C + \frac{2E_0}{\sum_i^{N_{\text{atoms}}} \frac{M_i}{2} |\mathbf{v}_i \cdot \hat{\mathbf{s}}_{i,IK}|^2} \right)$$
(25)

with

$$\hat{\mathbf{s}}_{i,IK} = \frac{\mathbf{s}_{i,IK}}{|\mathbf{s}_{i,IK}|} \tag{26}$$

where *C* and E_0 are parameters, and M_i and \mathbf{v}_i are the mass and velocity of atom *i*. The default values of the parameters are *C* = 1 (unitless) and $E_0 = 0.1$ hartree; it has been shown that the

CSDM results are reasonably insensitive to these two parameters.⁷³ The decoherence time of the pointer state (state *K*) is infinity, and hence $\frac{1}{\tau_{KK}} = 0$.

A key element of the CSDM method is that we propagate two electronic amplitudes, the true amplitude, $c_I(t)$, propagated by eq 17, which includes decoherence, and another called the coherent amplitude $[c_I(t)]_{co}$, propagated by eq 9, which does not. The true amplitude controls the effective potential and is continuous throughout the trajectory. The only use made of the coherent amplitude is to switch the pointer state. The density matrix associated with $[c_I(t)]_{co}$ has elements labeled $\tilde{\rho}_{IJ}$ to distinguish it from the true density matrix, with elements ρ_{IJ} . The amplitudes $[c_I(t)]_{co}$ and density matrix elements $\tilde{\rho}_{IJ}$ are initialized to $c_I(t)$ and ρ_{IJ} , respectively, and they are reinitialized to these quantities at each local minimum of the coupling strength defined by

$$D_{K}(t) = \sum_{I \neq K}^{N} |\mathbf{d}_{IK}|$$
(27)

The reinitialization of coherent amplitudes after each passage through a strong interaction region was introduced into TSH by Parlant and Gislason¹⁸ and Parlant and Alexander,¹⁹ and its importance was emphasized by Thachuk and Wardlaw.⁷⁴ The pointer state K is stochastically switched along the trajectory with a switching probability computed as

$$P_{K \to I}^{\text{CSDM}} = \max\left(-\frac{(d\tilde{\rho}_{KI}/dt)dt}{\tilde{\rho}_{KK}}, 0\right)$$
(28)

where

$$\frac{d\tilde{\rho}_{KI}}{dt} = 2\left(\left[\frac{dc_K(t)}{dt}\right]_{\rm co}[c_I^*(t)]_{\rm co}\right)$$
(29)

The use of coherent quantities to switch the pointer state is the main element distinguishing CSDM from earlier decay-ofmixing methods. Previous comparisons to accurate quantum dynamics³⁴ have shown that combining eqs 28 and 29 with reinitialization between complete passages through a strong interaction region, as done in CSDM, yields more accurate results than previous^{75,76} decay-of-mixing schemes.

Thus, in CSDM the electronic coefficients and nuclear equations of motion are given by eqs 17 and 22; the pointer state K is stochastically switched based on eq 28.

4. IMPLEMENTATION IN SHARC

Transitions between states of the same spin are called internal conversion. When spin—orbit coupling is included, one can also have transitions between states with different spin, and this is called intersystem crossing. SHARC is applicable to either kind of transition, and it uses the following nomenclature for the electronic representations in which propagation is carried out. An MCH representation is one in which the Hamiltonian includes blocks for each of the sets of states with the same spin and off-diagonal blocks connecting these blocks. (The singlet blocks are diagonal with only Coulomb terms. The nonsinglet blocks have diagonal Coulomb terms and off-diagonal spin—orbit terms, and the off-diagonal blocks have only spin—orbit terms.) A diagonal representation is one in which the Hamiltonian is fully diagonalized. (Alternative names that have been used⁷⁷ for these representations are valence

adiabatic for MCH and fully adiabatic for diagonal.) In SHARC, the configuration state coefficients are propagated in the MCH basis and then transformed to the diagonal basis by

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$$\mathbf{c}^{\text{diag}} = \mathbf{U}^{\dagger} \mathbf{c}^{\text{MCH}} \tag{30}$$

where **U** is the matrix containing the eigenvectors of \mathbf{H}^{MCH} , which is the Hamiltonian matrix in the MCH representation. Propagating and transforming separately avoids the estimation of $d\mathbf{U}(t)/dt$,⁴⁷ which is numerically unstable for two reasons. First, requiring that **U** diagonalizes the Hamiltonian matrix does not uniquely define the transformation matrix **U** because each eigenvector can be multiplied by a complex phase factor without changing its eigenvalue. Second, $d\mathbf{U}(t)/dt$ becomes large and difficult to treat numerically near the seams where spin states cross. If there is no spin–orbit coupling, then **U** is the unit matrix.

The configuration state coefficients are propagated by a time-ordered product of matrix exponentials.⁴⁷ The equation of motion for the coefficients in CSDM is reformulated as

$$\mathbf{c}^{\text{diag}}(t + \Delta t) = \mathbf{U}^{\dagger}(t + \Delta t)[\mathbf{P}_{\mathbf{C}}^{\text{MCH}}(t + \Delta t, t)]$$
$$\mathbf{P}_{\mathbf{D}}^{\text{MCH}}(t + \Delta t, t)]\mathbf{U}(t)\mathbf{c}^{\text{diag}}(t)$$
(31)

where

$$\mathbf{P}_{\mathbf{C}}^{\mathrm{MCH}}(t + \Delta t, t) = \exp(-(i\mathbf{H}^{\mathrm{MCH}} + \mathbf{v} \cdot \mathbf{d}^{\mathrm{MCH}})\Delta t) \qquad (32)$$

is the coherent propagator matrix, \mathbf{H}^{MCH} and \mathbf{d}^{MCH} are the Hamiltonian and nonadiabatic coupling matrix in the MCH basis, \mathbf{v} is the velocity, and $\mathbf{P}_{D}^{\text{MCH}}(t + \Delta t, t)$ is the decoherent propagator matrix. The decoherent propagator matrix is diagonal with diagonal elements

$$[P_D^{\text{MCH}}(t + \Delta t, t)]_{II} = \begin{cases} \exp\left(-\frac{\Delta t}{2\tau_{IK}^{\text{MCH}}(t)}\right) & I \neq K \\ \exp\left(\sum_{J \neq K}^{N} \frac{\Delta t}{2\tau_{JK}^{\text{MCH}}(t)} \frac{\rho_{JJ}^{\text{MCH}}(t)}{\rho_{KK}^{\text{MCH}}(t)}\right) & I = K \end{cases}$$
(33)

where

$$\rho_{II}^{\text{MCH}}(t) = c_{I}^{\text{MCH}}(t)c_{I}^{\text{MCH}*}(t)$$
(34)

and where *N* is the number of states, *K* is the pointer state, the state index *I* runs from 1 to *N*, and Δt is the time step used for nuclear equations of motion.

For propagation of electronic coefficients, it is preferred to use a much smaller time step; this is especially important for steps where the pointer state switches. Hence, within a nuclear propagation time step Δt , the electronic motion is propagated with *n* substeps, with each substep equal to $\Delta t/n$. Hence, eq 31 is rewritten as,

$$\mathbf{c}(t+\Delta t) = \mathbf{U}^{\dagger}(t+\Delta t) (\prod_{l=1}^{n} \mathbf{P}_{l}) \mathbf{U}(t) \mathbf{c}(t)$$
(35)

The propagator \mathbf{P}_l is computed by linear interpolation of the Hamiltonian, nonadiabatic coupling matrix, and velocity. The electronic coefficients (and hence the densities) are updated after each substep. Hence,

$$\mathbf{P}_{l} = \mathbf{P}_{\mathbf{C},l} \mathbf{P}_{\mathbf{D},l} \tag{36}$$

$$\mathbf{P}_{l} = \underbrace{\exp\left(-(i\mathbf{H}_{l} + \mathbf{T}_{l})\frac{\Delta t}{n}\right)}_{\mathbf{P}_{\mathbf{C},l}} \underbrace{\exp\left(\mathbf{D}_{l}\frac{\Delta t}{n}\right)}_{\mathbf{P}_{\mathbf{D},l}}$$
(37)

$$\mathbf{H}_{l} = \mathbf{H}^{\mathrm{MCH}}(t) + \frac{l}{n} (\mathbf{H}^{\mathrm{MCH}}(t + \Delta t) - \mathbf{H}^{\mathrm{MCH}}(t))$$
(38)

$$\mathbf{T}_{l} = \mathbf{v}(t) \cdot \mathbf{d}^{\text{MCH}}(t) + \frac{1}{n} (\mathbf{v}(t + \Delta t) \cdot \mathbf{d}^{\text{MCH}}(t + \Delta t) - \mathbf{v}(t) \cdot \mathbf{d}^{\text{MCH}}(t))$$
(39)

The matrix \mathbf{D}_l is diagonal, with the following diagonal elements

$$D_{l,II} = \begin{cases} -\frac{1}{2\tau_{IK}^{\text{MCH}}} & I \neq K \\ \sum_{J \neq K}^{N} \frac{1}{2\tau_{JK}^{\text{MCH}}} \frac{\rho_{JJ}^{\text{MCH}}(t + \frac{l}{n}\Delta t)}{\rho_{KK}^{\text{MCH}}(t + \frac{l}{n}\Delta t)} & I = K \end{cases}$$

$$(40)$$

Notice that the substep decoherent propagator $\mathbf{P}_{\mathbf{D},l}$ is diagonal, and \mathbf{T}_l is a matrix with 0 on diagonal. By using a large number of substeps, for example 100 or 200, the matrix elements of $(-(i\mathbf{H}_l + \mathbf{T}_l)(\Delta t/n))$ in eq 36 are on the order of 10^{-2} to 10^{-3} in atomic units for processes at typical chemical energies (eV, not hundreds of eV). Hence $\mathbf{P}_{\mathbf{C},l}$ is close to an identity matrix. Therefore

$$[\mathbf{P}_{\mathbf{C},l}, \mathbf{P}_{\mathbf{D},l}] \approx 0 \tag{41}$$

This ensures that, within the linear interpolation approximation for the matrices and vectors in eq 37 and 38, the substep propagation is closely equivalent to whole step propagation.

From eq 31, one sees that in current implementation the decoherence propagator for CSDM is calculated directly in the MCH representation and transformed back to the diagonal representation after a full nuclear propagation time step Δt . An alternative approach would be to use

$$\mathbf{c}^{\text{diag}}(t + \Delta t) = \mathbf{P}_{\mathbf{D}}^{\text{diag}}(t + \Delta t)\mathbf{U}^{\dagger}(t + \Delta t)$$
$$[\mathbf{P}_{\mathbf{C}}^{\text{MCH}}(t + \Delta t, t)]\mathbf{U}(t)\mathbf{c}^{\text{diag}}(t)$$
(42)

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In this way, $\mathbf{c}^{\text{diag}}(t)$ is first transformed to $\mathbf{c}^{\text{MCH}}(t)$, then it is propagated coherently to $\mathbf{c}^{\text{MCH}}(t + \Delta t)$ and transformed to $\mathbf{c}^{\text{diag}}(t + \Delta t)$, and finally the decoherent propagator $\mathbf{P}_{\text{D}}^{\text{diag}}(t + \Delta t)$ is applied. This raises the question of whether—when spin—orbit coupling is included—the diagonal basis or the MCH basis should be treated as the pointer basis, and in general one does not know the answer to this. A previous study of processes with conserved spin shows that CSDM is robust with respect to the choice of adiabatic and diabatic representations as the pointer basis. This suggests that CSDM might be robust with respect to the choice between diagonal and MCH representations, but this is a subject that deserves further study.

In CSDM the switching probability for the pointer state is estimated based on the coherent densities. Hence along the trajectory, we also propagate the coherent coefficients; this is done by

$$[\mathbf{c}^{\text{diag}}(t+\Delta t)]_{\text{co}} = \mathbf{P}_{\mathbf{C}}^{\text{diag}}(t+\Delta t, t)[\mathbf{c}^{\text{diag}}(t)]_{\text{co}}$$
(43)

Notice that

$$\mathbf{P}_{\mathbf{C}}^{\text{diag}}(t + \Delta t, t) = \mathbf{U}^{\dagger}(t + \Delta t) \lfloor \mathbf{P}_{\mathbf{C}}^{\text{MCH}}(t + \Delta t, t) \rfloor \mathbf{U}(t)$$
(44)

The coherent coefficients are initialized the same as the true coefficients, but their propagation is done with eq 43. Along the CSDM trajectory, the $D_K(t)$ of eq 27 is computed in a diagonal basis and recorded for the previous two time steps, $D_K(t - \Delta t)$ and $D_K(t - 2\Delta t)$. If $D_K(t - \Delta t)$ is the local minimum among the three steps, the coherent coefficients $[\mathbf{c}^{\text{diag}}(t - \Delta t)]_{\text{co}}$ will first be reinitialized as $\mathbf{c}^{\text{diag}}(t - \Delta t)$ and will then be propagated to $[\mathbf{c}^{\text{diag}}(t)]_{\text{co}}$ according to eq 43. The physical picture of this reinitialization process is that the coherent coefficients relax to the true coefficients (to which decoherence has been introduced) after every passage of a strong interaction region. To be compatible with the Magnus integrator, the switching probabilities are computed as^{47,78}

$$P_{K \to I} = \left(1 - \frac{|[c_K^{\text{diag}}(t + \Delta t)]_{\text{co}}|^2}{|[c_K^{\text{diag}}(t)]_{\text{co}}|^2}\right) \times \frac{\text{Re}[[c_I^{\text{diag}}(t + \Delta t)]_{\text{co}}(\mathbf{P}_{\mathbf{C}}^{\text{diag}}(t + \Delta t, t)_{IK})^*[c_K^{\text{diag}}(t)^*]_{\text{co}}]}{|[c_K^{\text{diag}}(t)]_{\text{co}}|^2 - \text{Re}[[c_K^{\text{diag}}(t + \Delta t)]_{\text{co}}(\mathbf{P}_{\mathbf{C}}^{\text{diag}}(t + \Delta t, t)_{KK})^*[c_K^{\text{diag}}(t)^*]_{\text{co}}]}$$
(45)

The negative switching probabilities are set to zero and

$$P_{K \to K} = 1 - \sum_{I \neq K}^{N} P_{K \to I}$$

$$\tag{46}$$

Then eq 45 can be used to compute the switching probability.

The gradients for propagation of the nuclei are computed from the coherent force and the decoherent force in the diagonal representation. The coherent force is formulated as

$$[\mathbf{F}]_{co} = -\left(\sum_{I}^{N} \rho_{II}^{diag} \mathbf{G}_{II}^{diag} + \sum_{I}^{N} \sum_{J \neq I}^{N} \operatorname{Re}\left(\rho_{IJ}^{diag} \mathbf{G}_{IJ}^{diag}\right)\right)$$
(47)

where

$$\mathbf{G}_{IJ}^{\mathrm{MCH}} = \nabla_{\mathbf{R}} H_{II}^{\mathrm{MCH}} \delta_{IJ} - (H_{II}^{\mathrm{MCH}} - H_{JJ}^{\mathrm{MCH}}) \mathbf{d}_{IJ}^{\mathrm{MCH}}$$
(48)

$$\mathbf{G}^{\text{diag}} = \mathbf{U}^{\dagger} \mathbf{G}^{\text{MCH}} \mathbf{U}$$
(49)

Notice that \mathbf{H}^{MCH} and $\mathbf{d}_{IJ}^{\text{MCH}}$ are directly computed from ab initio electronic structure codes. The decoherent force is formulated as

$$[\mathbf{F}]_{de} = \sum_{I \neq K}^{N} \frac{c_{I}^{diag} c_{I}^{diag^{*}} (H_{II}^{diag} - H_{KK}^{diag})}{\tau_{IK}^{diag} (\mathbf{v} \cdot \mathbf{s}_{IK}^{diag})} \mathbf{s}_{IK}^{diag}$$
(50)

where

$$\mathbf{s}_{IK}^{\text{diag}} = \text{Re}\left(\frac{a_0 \mathbf{P}_{\text{vib}} \cdot \mathbf{d}_{IK}^{\text{diag}}}{|\mathbf{d}_{IK}^{\text{diag}}|} \mathbf{d}_{IK}^{\text{diag}}\right) + \mathbf{P}_{\text{vib}}$$
(51)

$$\mathbf{d}_{IJ}^{\text{diag}} = \mathbf{U}^{\dagger} \mathbf{d}_{IJ}^{\text{MCH}} \mathbf{U}$$
(52)

The nuclear position and momentum are updated based on the velocity-Verlet algorithm: 79

$$\mathbf{a}(t) = \frac{\mathbf{F}(t)}{M} \tag{53}$$

$$\mathbf{R}(t + \Delta t) = \mathbf{R}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^{2}$$
(54)

$$\mathbf{a}(t+\Delta t) = \frac{\mathbf{F}(t+\Delta t)}{M}$$
(55)

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{1}{2}[\mathbf{a}(t) + \mathbf{a}(t + \Delta t)]\Delta t$$
(56)

Figure 1 shows a flowchart for the current implementation of semiclassical Ehrenfest and CSDM in SHARC.



Figure 1. Flowchart of semiclassical Ehrenfest and CSDM methods in the SHARC program.

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When performing nonadiabatic direct dynamics with NACs obtained from electronic structure calculations, the NACs are calculated by eq 11 by varying one nuclear Cartesian coordinate with the others fixed. This produces the NAC in a three-dimensional space-frame (SF) coordinate system, and we can emphasize this by calling them SF-NACs. The variation of the nuclear coordinates that is used moves the center of mass, and this variation is also not orthogonal to an infinitesimal rotation. Therefore, using the SF-NAC does not conserve the center-of-mass motion, and it does not conserve angular momentum in nonadiabatic direct dynamics.⁸⁰ This problem can be overcome by using a projected NAC, which is obtained by applying a projection operator on the SF-NAC to project out its translational and rotational components.⁸⁰ In the present implementation and the following application with semiclassical Ehrenfest and CSDM, the projected NAC is used in the propagation, and the direction of projected NAC is used to adjust kinetic energy after a surface hop in TSH.

5. APPLICATION OF DIRECT DYNAMICS TO EXCITED ETHYLENE

In this section, we illustrate the new implementation of CSDM by applying it to electronically nonadiabatic dynamics of ethylene, which has previously been widely studied.^{78,81,82} For comparison, we also calculate dynamics for ethylene using TSH with energy-difference based decoherence correction.⁵⁷ (EDC), with TSH without any decoherence correction,²⁰ and with semiclassical Ehrenfest^{31–33,83} (SE). Two of these methods (CSDM and TSH-EDC) include deoherence, and the other two do not. Two of these methods (CSDM and SE) are based on a continuous self-consistent potential, and the other two involve hops.

For each of the four dynamics methods, we calculated 100 trajectories with the same set of initial conditions. To set up the initial conditions, the ground-electronic-state minimumenergy geometry and frequencies were calculated with MP2/6- $31G^{**}$, and the initial geometries and velocities were randomly sampled from the ground-vibrational-state Wigner distribution;⁸⁴ the molecule was then vertically excited to S₁. The electronic wave function for the nonadiabatic dynamics was computed with state-averaged complete-active-space selfconsistent-field theory (SA-CASSCF/6-31G^{**})⁸⁵ by averaging three states with two active electrons in two active orbitals using the MOLPRO⁸⁶ software package. The time step for nuclear propagation was set to 0.1 fs, and the number of substeps for CSDM and SE (*n* in eq 37) was set to 200. The



Figure 2. Ensemble-average time evolution of the electronic state probability for the adiabatic S_0 , S_1 , and S_2 states of ethylene, averaged over 100 trajectories, calculated by (a) CSDM (solid) and SE (dotted), (b) TSH-EDC (solid) and TSH (dotted). The population of the ground state is shown in blue, and the populations of the excited states are in red and pink.

projected NAC⁸⁰ was employed to ensure the convergence of angular momentum. Although the low-lying excited states of ethylene have some Rydberg character, the basis set and active space used here have been previously validated for studying the nonadiabatic dynamics of the $\pi \rightarrow \pi^*$ excitation.⁸² We do not need spin—orbit coupling so the MCH and diagonal representations are the same for singlet states, and they will just be called the adiabatic representation.

In the present implementation for ethylene, the average computational cost for a CSDM trajectory is about 2.5 times higher than that of a TSH trajectory; we would expect the timings to be more similar for an application to intersystem crossing.

Examination of the individual trajectories shows that neither TSH nor SE increases or decays the population vector to a kronecker delta (with elements unity or zero) after visiting the strong interaction region. This unphysical⁷⁴ result is the expected result for methods without decoherence. Figure 2 shows the populations of the three states averaged over the 100-trajectory ensemble, as computed by CSDM, TSH-EDC, TSH, and SE. Figure 2 shows that both CSDM and TSH-EDC physically decay the excited state population to zero after a sufficiently long time. The observed half-lives $\tau_{1/2}$ of the S₁ excited state are 47, 67, 67, and 57 fs for CSDM, TSH-EDC, TSH, and SE, respectively. If the population of the S_1 state is fitted to $\exp(-t/\tau)$ (the data before 15 fs is not used in this fit because the initial decay corresponds to an induction period in which the decay is not yet first order), the lifetimes τ are 60 and 73 fs for CSDM and TSH-EDC dynamics, respectively.

Both the half-life (47 fs) and the lifetime calculated from the single-exponential fit (60 fs) of the CSDM dynamics are close to the experimentally observed lifetime (10-40 fs).⁸⁷ Similar results were found by previous calculations based on TSH with semiempirical electronic wave functions, yielding an S₁ lifetime of around 50 fs.⁷⁸ Both the present CSDM and TSH calculations and those previous semiempirical TSH calculations agree better with experiment than previous calculations with ab initio multiple spawning (AIMS),^{82,88} although one should be cautious about comparing to experiment at the present stage since the CASSCF energetics are certainly not quantitatively accurate. (The calculations in this section are presented mainly to illustrate the use of the new implementation and provide a comparison of four methods applied to the same problem with the same program, not primarily for comparison to experiment. In addition we note that the differences between methods may be larger for some other systems.)

Two possible pathways are available for the ethylene nonadiabatic dynamics: (1) If the ethylene molecule twists the C=C bond and pyramidalizes one of the $-CH_2$ groups, the excited-state population decays to the ground state by passage close to the so-called pyramidalized conical intersection. (2) Due to the high excitation energy of the $\pi \to \pi^*$ excitation, it provides a pathway along which one of the H atoms migrates from one C atom to the to the other by passage close to an ethylidene-like conical intersection. Figure 3 shows two representative trajectories from CSDM dynamics that go near (a) a pyramidalized conical intersection and (b) an ethylidene-like conical intersection. For the pyramidalized conical intersection, one would observe the change of the pyramidalization angle, which is defined in panel a. For ethylidene-like conical intersection one can see one of the C-H bond changes after forming the ethylidene-like structure.



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Figure 3. Representative trajectories of CSDM dynamics for quenching of ethylene via the two types of conical intersections: (a) twisted-pyramidalized conical intersection, (b) ethylidene-like conical intersections.

6. CONCLUSION

In previous work, the coherent switching with decay of mixing (CSDM) algorithm was developed to include decoherence in the semiclassical Ehrenfest method, and it has been validated against accurate quantum dynamics^{22,89} as well as being used in practical simulations.^{4–6,60,90–93} The CSDM algorithm employs a self-consistent potential as in the semiclassical Ehrenfest method but with decoherence introduced, and it combines the advantages of the semiclassical Ehrenfest method with those of the fewest switches algorithm of TSH. In the present work, we have discussed the incorporation of decoherence in semiclassical nonadiabatic dynamics simulations, and we report its implementation in the SHARC program. In addition, we have presented a simulation of the excited state nonadiabatic dynamics of ethylene as an example to show the usage of the current CSDM implementation, and we have also compared the results with semiclassical Ehrenfest and TSH with and without a decoherence correction. The comparisons show the success of the current CSDM implementation and the importance of appropriate treatment of decoherence in mixed quantum-classical nonadiabatic dynamics.

APPENDIX A. CONSERVATION OF ENERGY AND DERIVATION OF THE DECOHERENT FORCE

We will only consider the diagonal (adiabatic) representation in the appendices. The molecular Hamiltonian can be written as

$$H = T_{\rm N} + V \tag{A-1}$$

where

$$T_{\rm N} = \sum_{i=1}^{N_{\rm atoms}} \frac{\mathbf{P}_i \cdot \mathbf{P}_i}{2M_i} \tag{A-2}$$

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is the nuclear kinetic energy, N_{atoms} is the number of atoms, \mathbf{P}_i and M_i are the momentum and mass of atom i

$$V = \sum_{I=1}^{N} \rho_{II} V_I \tag{A-3}$$

is the self-consistent potential (SCP), and V_I is the adiabatic potential energy surface defined in eq 10. The time derivative of the molecular Hamiltonian is

$$\dot{H} = \frac{d}{dt}(T_{\rm N} + V) = \sum_{i}^{N_{\rm atoms}} \mathbf{v}_i \cdot \dot{\mathbf{P}}_i + \dot{V}$$
(A-4)

where \mathbf{v}_i and $\dot{\mathbf{P}}_i$ are the velocity and time derivative of momentum of atom *i* and \dot{V} is the time derivative of SCP given by

$$\dot{V} = \sum_{I=1}^{N} \dot{\rho}_{II} V_{I} + \sum_{I=1}^{N} \rho_{II} \dot{V}_{I}$$
(A-5)

where

$$\dot{\rho}_{II} = [\dot{\rho}_{II}]_{co} + [\dot{\rho}_{II}]_{de}$$
 (A-6)

Therefore, the time derivative of the potential can be written as a sum of three terms

$$\dot{V} = \underbrace{\sum_{I=1}^{N} [\dot{\rho}_{II}]_{co} V_{I}}_{[\dot{V}]_{co}} + \underbrace{\sum_{I=1}^{N} \rho_{II} \dot{V}_{I}}_{[\dot{V}]_{co}} + \underbrace{\sum_{I=1}^{N} [\dot{\rho}_{II}]_{de} V_{I}}_{[\dot{V}]_{de}}$$
(A-7)

The sum of the first two terms defines the time derivative $[\dot{V}]_{co}$ of the coherent potential, and the last term of defines the time derivative $[\dot{V}]_{de}$ of the decoherent potential. Furthermore, after taking the real part, the term associated with Hamiltonian in time derivative of density vanishes and one has

$$[\dot{\rho}_{II}]_{co} = 2\operatorname{Re}([\dot{c}_{I}]_{co}^{*}c_{I}) = -2\sum_{J\neq I}^{N}\operatorname{Re}(\rho_{JI}\mathbf{d}_{IJ})\cdot\mathbf{v}$$
(A-8)

$$[\dot{\rho}_{II}]_{de} = 2\operatorname{Re}([\dot{c}_{I}]^{*}_{de}c_{I}) = \begin{cases} -\frac{\tau_{II}}{\tau_{IK}} & I \neq K \\ \sum_{J \neq K}^{N} \frac{\rho_{JJ}}{\tau_{JK}} & I = K \end{cases}$$
(A-9)

where $[\dot{c}_I]_{co}$ and $[\dot{c}_I]_{de}$ are defined by eqs 10 and 19, respectively. The time derivative of the electronic Hamiltonian matrix element may be written as

$$\dot{V}_I = \frac{\partial V_I}{\partial \mathbf{R}} \cdot \mathbf{v} \tag{A-10}$$

The conservation of the total energy requires the time derivative of the molecular Hamiltonian to equal zero:

$$\dot{H} = \mathbf{v} \cdot [\dot{\mathbf{P}}]_{co} + \mathbf{v} \cdot [\dot{\mathbf{P}}]_{de} + [\dot{V}]_{co} + [\dot{V}]_{de} = 0$$
(A-11)

where we have used the following definitions:

$$\dot{\mathbf{P}} = \left[\dot{\mathbf{P}}\right]_{co} + \left[\dot{\mathbf{P}}\right]_{de} \tag{A-12}$$

 $\mathbf{v} \cdot [\dot{\mathbf{P}}]_{co} = \mathbf{v} \cdot [\mathbf{F}]_{co} = -[\dot{V}]_{co}$ (A-13)

$$\mathbf{v} \cdot [\dot{\mathbf{P}}]_{de} = \mathbf{v} \cdot [\mathbf{F}]_{de} = -[\dot{V}]_{de}$$
(A-14)

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eqs A-13 and A-14 ensure the conservation of total energy. Eq A-13 involves the coherent force, which is the same as the force in the semiclassical Ehrenfest method. Therefore

$$\mathbf{v} \cdot [\mathbf{F}]_{co} = -\mathbf{v} \cdot \left(-\sum_{I=1}^{N} \sum_{J \neq I}^{N} 2\operatorname{Re}(\rho_{JI} V_{I} \mathbf{d}_{IJ}) + \sum_{I=1}^{N} \rho_{II} \frac{\partial V_{I}}{\partial \mathbf{R}} \right)$$
(A-15)

with

$$[\mathbf{F}]_{co} = -\sum_{I}^{N} \rho_{II} \frac{\partial V_{I}}{\partial \mathbf{R}} + \sum_{I}^{N} \sum_{J}^{N} \operatorname{Re}(\rho_{IJ}(V_{I} - V_{J})\mathbf{d}_{IJ})$$
(A-16)

Similarly eq A-14 involves the decoherent force

$$\mathbf{v} \cdot [\mathbf{F}]_{de} = -\sum_{I=1}^{N} [\dot{\rho}_{II}]_{de} V_{I}$$
(A-17)

By inserting eq A-9 into eq A-17, we get

$$\mathbf{v} \cdot [\mathbf{F}]_{de} = \sum_{I \neq K}^{N} \frac{\rho_{II}}{\tau_{IK}} (V_I - V_K)$$
(A-18)

where, as always, we use *K* to denote the pointer state. One can further decompose $[\mathbf{F}]_{de}$ as

$$\left[\mathbf{F}\right]_{de} = \sum_{I \neq K}^{N} \left[\mathbf{F}_{I}\right]_{de}$$
(A-19)

such that

$$\mathbf{v} \cdot [\mathbf{F}_I]_{de} = \frac{\rho_{II}}{\tau_{IK}} (V_I - V_K), I \neq K$$
(A-20)

Equations A-17, A-18, and A-20 do not fully define the direction of the decoherent force; they just constrain the component along the velocity vector. By multiplying both sides of eq A-18 by the unit vector $[\hat{\mathbf{F}}]_{de}$, which corresponds to the direction of the decoherent force, we get

$$(\mathbf{v} \cdot [\mathbf{F}]_{de})[\hat{\mathbf{F}}_{de}] = \sum_{I \neq K}^{N} \frac{\rho_{II}}{\tau_{IK}} (V_I - V_K)[\hat{\mathbf{F}}]_{de}$$
(A-21)

which may be rewritten as

$$(|\mathbf{v}||[\mathbf{F}]_{de}|\cos(\theta_{\mathbf{v}[\mathbf{F}]_{de}}))[\hat{\mathbf{F}}]_{de} = \sum_{I \neq K}^{N} \frac{\rho_{II}}{\tau_{IK}} (V_{I} - V_{K})[\hat{\mathbf{F}}]_{de}$$
(A-22)

where $|\mathbf{v}|$ and $|[\mathbf{F}]_{de}|$ are the norms of the vectors \mathbf{v} and $[\mathbf{F}]_{de}$, respectively, and $\theta_{\mathbf{v}[\mathbf{F}]_{de}}$ is the angle between the vectors \mathbf{v} and $[\mathbf{F}]_{de}$. eq A-21 can be rewritten as

$$(\mathbf{v} \cdot [\hat{\mathbf{F}}]_{de})[\mathbf{F}]_{de} = \sum_{I \neq K}^{N} \frac{\rho_{II}}{\tau_{IK}} (V_I - V_K) [\hat{\mathbf{F}}]_{de}$$
(A-23)

Thus, the decoherent force can be written as

$$[\mathbf{F}]_{de} = \sum_{I \neq K}^{N} \frac{\rho_{II}}{\tau_{IK}} \frac{(V_I - V_K)}{([\hat{\mathbf{F}}]_{de} \cdot \mathbf{v})} [\hat{\mathbf{F}}]_{de}$$
(A-24)

eq A-24 is equivalent to eq 16 in ref 34. Then, we divide the direction of the decoherent force as in eq A-19 and associate a decoherent direction \hat{s}_{IK} to each nonpointer state to get

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$$[\mathbf{F}]_{de} = \sum_{I \neq K}^{N} \frac{\rho_{II}}{\tau_{IK}} \frac{(V_I - V_k)}{\hat{\mathbf{s}}_{IK} \cdot \mathbf{v}} \hat{\mathbf{s}}_{IK}$$
(A-25)

which is the result in eq 24. This will provide a starting point for choosing \hat{s}_{IK} in Appendix B.

APPENDIX B. CONSERVATION OF ANGULAR MOMENTUM AND DIRECTION OF THE DECOHERENT FORCE

The total angular momentum is

$$\mathbf{J} = \mathbf{R} \times \mathbf{P} \tag{B-1}$$

and its time derivative is

$$\dot{\mathbf{J}} = \dot{\mathbf{R}} \times \mathbf{P} + \mathbf{R} \times \dot{\mathbf{P}}$$

$$= \dot{\mathbf{R}} \times \mathbf{P} + \mathbf{R} \times [\dot{\mathbf{P}}]_{co} + \mathbf{R} \times [\dot{\mathbf{P}}]_{de}$$
(B-2)

The sum of the first two terms corresponds to semiclassical Ehrenfest dynamics, and it has been previously shown that semiclassical Ehrenfest dynamics conserves the total angular momentum.³¹ Therefore, in order to conserve total angular momentum in CSDM, we must have

$$\mathbf{R} \times \left[\dot{\mathbf{P}}\right]_{de} = 0 \tag{B-3}$$

Combining this with Newton's second law and eq A-25 gives the following equation that \hat{s}_{IK} must satisfy:

$$\mathbf{R} \times \left(\sum_{I \neq K}^{N} f_{IK} \hat{\mathbf{s}}_{IK}\right) = 0 \tag{B-5}$$

where

$$f_{IK} = \frac{\rho_{II}}{\tau_{IK}} \frac{(V_I - V_K)}{(\hat{\mathbf{s}}_{IK} \cdot \mathbf{v})}$$
(B-6)

is a scalar function. Following ref 76, we choose

$$\mathbf{s}_{IK} = \operatorname{Re}(a_0(\mathbf{P}_{\operatorname{vib}} \cdot \mathbf{d}_{IK}) \mathbf{d}_{IK}) + \mathbf{P}_{\operatorname{vib}}$$
(B-7)

where a_0 is a bohr and \mathbf{P}_{vib} is the internal vibrational momentum⁹⁴ computed by removing the translational and rotational component of **P**.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DE-SC0015997, by the National Natural Science Foundation of China under grant No. 51536002.

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