

Decoherence and Its Role in Electronically Nonadiabatic Dynamics

Yinan Shu and Donald G. Truhlar*



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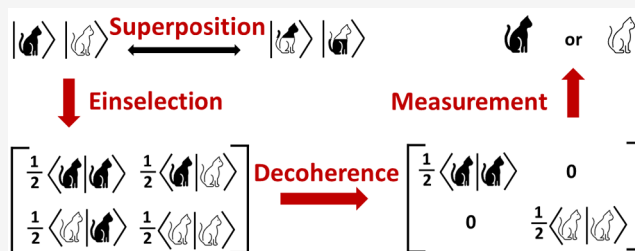
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ABSTRACT: Decoherence is the tendency of a time-evolved reduced density matrix for a subsystem to assume a form corresponding to a statistical ensemble of states rather than a coherent combination of pure-state wave functions. When a molecular process involves changes in the electronic state and the coordinates of the nuclei, as in ultraviolet or visible light photochemistry or electronically inelastic collisions, the reduced density matrix of the electronic subsystem suffers decoherence, due to its interaction with the nuclear subsystem. We present the background necessary to conceptualize this decoherence; in particular, we discuss the density matrix description of pure states and mixed states, and we discuss pointer states and decoherence time. We then discuss how decoherence is treated in the coherent switching with decay of mixing algorithm and the trajectory surface hopping method for semiclassical calculations of electronically nonadiabatic processes.



1. INTRODUCTION

Many chemical processes may be understood in terms of a single electronic state that evolves adiabatically, adjusting essentially instantaneously to changing nuclear positions. This is often called the Born–Oppenheimer approximation, and, for many problems, such as the vibrational spectroscopy of most closed-shell molecules or the reaction kinetics of most thermally activated chemical reactions, it is an excellent approximation. However, there are also many processes where we must consider two or more electronic states;^{1–3} this includes photochemical reactions promoted by visible light (vis) or ultraviolet (UV) photons, many electron transfer reactions, quenching and chemical reaction of electronically excited species, electronic energy transfer, Penning ionization, dissociative attachment, excitation of electron–hole pairs, and many other processes. These processes are called electronically nonadiabatic processes or non-Born–Oppenheimer processes, and they are the subject field of this article. (“Electronically nonadiabatic” simply means that the electronic quantum numbers are not conserved, i.e., that the electronic state changes.) More specifically, we will consider the role and treatment of decoherence in such processes since this is critical for understanding them.

Although the present article is focused on fundamental issues and many of the references pertain to gas-phase molecular dynamics, we note that reduced density matrices, electronic decoherence, and mixed states, which are all discussed here, also play a role in more complex phenomena, for example, exciton transport^{4,5} and the distinction between Bloch wave transport of electrons and diffusive electrical conduction.^{6,7} Interest in the density matrix treatment of mixed states has also increased in recent years because of the use of magnetic resonance

spectroscopy for quantum information processing and quantum computing.^{8,9}

The treatment of decoherence involves aspects of quantum mechanics that are not well covered in most textbooks; therefore, we begin with a brief introduction to some of the concepts needed to discuss it.

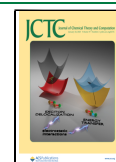
2. THEORETICAL CONCEPTS

Decoherence is often discussed in the context of measurements, in which one considers a system interacting with an apparatus that measures it. We take a broader perspective in which any interaction of a system with its environment may be interpreted as the system being measured by its environment; one may say that the environment is continuously “witnessing” or “monitoring” the system. Furthermore, we view decoherence as a continuous process, not as a sudden collapse of a wave function. The perspective of the present article is nicely summarized in the following quotations:

*The environment surrounding a quantum system can, in effect, monitor some of the system’s observables. As a result, the eigenstates of those observables continuously decohere and can behave like classical states.*¹⁰

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Instead of describing the quantum measurement process as a discontinuous change of the state of the system—the decoherence model is based on the application of the Schrödinger equation to the system and the environment with which it interacts.¹¹

This perspective evolves from the seminal work of von Neumann,¹² Zeh,¹³ and Zurek.¹⁰ The rest of Section 2 reviews the theoretical concepts needed to make the meaning of this Perspective more precise.

2.1. Pure States. At the beginning, it is important to clarify the meaning of the state of a system. An isolated system may be in a pure state, which is described by a wave function. The 1954 Nobel Prize in Physics was given to Max Born for “fundamental research in quantum mechanics, especially in the statistical interpretation of the wave function”. Born’s seminal work¹⁴ in the interpretation of a wave function was based on examining what quantum mechanics tells us about the state of a particle after a collision. He wrote, “One gets no answer to the question, ‘What is the state after the collision,’ but only to the question ‘how probable is a specified outcome of the collision’”.¹⁴ We may conclude that “The state [i.e., wave function] of a system is not a description of the system itself. [It is] a statement about the probabilities of obtaining, for any given dynamical variable, certain results upon their measurement.”¹⁵

“Systems in the real world are rarely in pure states.”¹⁶ As we shall discuss below, this is because systems in the real world are not isolated, i.e., a system of interest, call it \mathcal{S} , is invariably a subsystem of a larger system consisting of \mathcal{S} plus an interacting environment, which we may call \mathcal{E} . As mentioned above, this is often discussed in the context of measurement theory, where the environment is a measuring apparatus,¹² but here we are interested in environments more broadly.

2.2. Density Matrices and Mixed States. If a system is described by wave function Ψ , the expectation value for the measurement of a physical observable X (e.g., position, momentum, angular momentum, energy, etc.) is

$$\langle X \rangle = \langle \Psi | X | \Psi \rangle \quad (1)$$

More generally, the wave function may be expressed in terms of a basis $\{\psi_I\}$:

$$\Psi = \sum_I c_I \psi_I \quad (2)$$

which leads to

$$\langle X \rangle = \sum_{IJ} c_I c_J^* \langle \psi_I | X | \psi_J \rangle \quad (3)$$

It is convenient to define the matrix element of a “density matrix” ρ as

$$\rho_{IJ} = c_I c_J^* \quad (4)$$

We then may write eq 3 as

$$\langle X \rangle = \sum_{IJ} \rho_{IJ} X_{JI} = \text{Tr}(\rho \mathbf{X}) \quad (5)$$

where $\text{Tr}(\mathbf{M})$ or $\text{Tr } \mathbf{M}$ denotes the trace of a matrix \mathbf{M} , where the trace is the sum of the diagonal elements of the matrix. Just as the matrix \mathbf{X} with elements X_{IJ} is a representation of the operator X in basis $\{\psi_I\}$, the density matrix ρ with elements ρ_{IJ} is a representation of operator $\hat{\rho}$ in basis $\{\psi_I\}$. This operator is variously called the density operator, the statistical operator,¹⁷ or the state operator. Unfortunately, it is also deeply ingrained in

the literature to call it the density matrix, and the unwary might easily get confused by naming an operator as if it were a matrix. To distinguish the operator from the matrix, we call the operator the density operator and denote it as $\hat{\rho}$. (As usual in nonelementary discussions of quantum mechanics, we do not display the caret symbol (^) for other operators.)

The diagonal elements of a density matrix are called populations; the off-diagonal elements are called coherences. The populations may also be called probabilities, because they are normalized to sum to unity.

A useful representation of the density operator for a pure state Ψ as defined in eq 2 is¹⁸

$$\hat{\rho} = |\Psi\rangle\langle\Psi| = \sum_{IJ} c_I c_J^* |\psi_I\rangle\langle\psi_J| \quad (6)$$

That is, the density operator is the projection operator onto the wave function. Clearly, a pure state may be specified either by giving its wave function or by giving its density operator.

We mentioned above that most real systems are not in a pure state. Systems that are not in a pure state are said to be in a mixed state; alternatively, one can say that the system is in an impure or nonpure state. A mixed state cannot be described by a wave function, but it can be described by a density matrix. For a mixed state composed a statistical mixture of pure states Ψ_L , the density operator is

$$\hat{\rho} = \sum_L p_L |\Psi_L\rangle\langle\Psi_L| \quad (7)$$

where p_L is the classical probability (not amplitude) of finding the system in state L . Notice that this is an incoherent combination of states, in contrast to the coherent superposition in eq 2. In other words, we have a classical mixture of quantum states.

Although much of the literature is written in terms of the density operator, we will give our discussion mainly in terms of the density matrix in an orthonormal basis; this will be denoted by bold ρ with matrix elements ρ_{IJ} . Notice in the following that the density matrix depends on the choice of basis, although the density operator does not.

One basic reason for defining mixed states is to describe an ensemble of similarly prepared systems, such as the particle of a dilute gas in thermal equilibrium. More generally, mixed states provide a quantum description when the exact state is not known but one still wants to construct a probability distribution. For example, despite the fact that it is thermally equilibrated, if a molecule in a very dilute gas is regarded as an isolated system (not part of larger system), we know there is a classical Boltzmann distribution of states (determining p_L), but we do not know which state a particular molecule is in; therefore, in keeping with perspective expressed above, in which a state is associated with the probabilities expected for measurements, the appearance of classical probabilities in eq 7 is necessary to properly describe our knowledge of the probabilities of measuring physical observables.¹⁸ We shall see below that the concept of a mixed state also is needed to describe states of a subsystem, and that is the main reason for introducing them in the present article.

Notice that there are two types of statistical probabilities implicit in the previous paragraph. Even if a system were in a pure quantum state and we knew which state, there would be a quantum mechanical probability distribution of measuring certain outcomes. Furthermore, sometimes we do not know

the exact state, or the system is not a pure state; then there is an additional classical probability distribution on top of the quantum mechanical probability distribution.

Recall that we only consider orthonormal bases. One may show that a density matrix is Hermitian and has a trace of unity and that its eigenvalues are non-negative numbers between 0 and 1. For a pure state, one eigenvalue is 1 and the rest are zero; the eigenvector associated with the unit eigenvalue is the state vector (wave function). If there are two nonzero eigenvalues, the density matrix represents a mixed state. One can show that

$$\text{Tr}(\rho^2) \leq \text{Tr}(\rho) \quad (8)$$

where the equality holds for a pure state, and the inequality holds for a mixed state; $\text{Tr}(\rho^2)$ is sometimes called the purity of the quantum state.¹⁹ Equation 8 is true in any orthonormal basis.

For either a pure state or a mixed state of an isolated system (i.e., an entire system), the time dependences of the density matrix can be derived from the time-dependent Schrödinger equation, which yields^{16,18–22}

$$i\hbar \frac{\partial}{\partial t} \rho = [\mathbf{H}, \rho] \quad (9)$$

where \mathbf{H} is the Hamiltonian matrix, and $[\cdot, \cdot]$ denotes a commutator. This is similar in form to the classical Liouville theorem,^{21,23}

$$\frac{\partial}{\partial t} \rho = \{H, \rho\} \quad (10)$$

where t is time, ρ is the density in phase space, H is the Hamiltonian, and $\{\cdot, \cdot\}$ denotes a Poisson bracket. Equation 9 is called the Liouville–von Neumann (LvN) equation or the quantum Liouville equation. The quantum analogue of the classical conservation of phase space volume is discussed elsewhere²² but is not needed here.

Evolution of the state vector according to the time-dependent Schrödinger equation is equivalent to a unitary transformation of the state vector at one time to a different state vector at a later time.^{16,18,19} This also corresponds to a unitary transformation of the density operator. For this reason, evolution of the density matrix according to eq 9 is often referred to as unitary evolution. Unitary evolution maintains purity and coherence.

Note that the pure state content of a mixed state is not uniquely definable,^{18,24} and, in this sense, the language “mixed state” is somewhat unfortunate. Therefore, some workers call such states nonpure states, but the mixed state language pervades the literature, and so we shall usually use this language.

2.3. Composite Systems: Separable and Entangled. To explain entanglement, we consider a system composed of two two-level subsystems: A and B.¹⁹ Let the states (wave functions) of A be a_1 and a_2 and the states of B be b_1 and b_2 . A direct product basis for the composite system has four elements:

$$\psi_1 \equiv |a_1\rangle|b_1\rangle \equiv |11\rangle \quad (11)$$

$$\psi_2 \equiv |a_1\rangle|b_2\rangle \equiv |12\rangle \quad (12)$$

$$\psi_3 \equiv |a_2\rangle|b_1\rangle \equiv |21\rangle \quad (13)$$

$$\psi_4 \equiv |a_2\rangle|b_2\rangle \equiv |22\rangle \quad (14)$$

Such a basis is sometimes denoted using direct product notation as $\{|a_i\rangle \otimes |b_j\rangle\}$. We now prepare system A in state

$$\phi = \alpha_1 a_1 + \alpha_2 a_2 \quad (15)$$

and system B in state

$$\chi = \beta_1 b_1 + \beta_2 b_2 \quad (16)$$

and consider these two systems to be noninteracting subsystems of a composite system AB. The state of the composite system is

$$\Psi = \phi\chi = \alpha_1\beta_1|11\rangle + \alpha_1\beta_2|12\rangle + \alpha_2\beta_1|21\rangle + \alpha_2\beta_2|22\rangle \quad (17)$$

Now consider a general state of the composite system:

$$\Psi = \gamma_{11}|11\rangle + \gamma_{12}|12\rangle + \gamma_{21}|21\rangle + \gamma_{22}|22\rangle \quad (18)$$

with no special relation among the coefficients γ_{IJ} except for the normalization constraint, which is

$$\sum_{IJ} |\gamma_{IJ}|^2 = 1 \quad (19)$$

In general, the coefficients in eq 18 cannot be written in the product form of eq 17. (This can be done only if $\gamma_{11}/\gamma_{21} = \gamma_{12}/\gamma_{22}$ and $\gamma_{11}/\gamma_{12} = \gamma_{21}/\gamma_{22}$.) A state of the form of eq 17 is called separable or unentangled, and a state of the form of eq 18 that cannot be written as eq 17 is called nonseparable or entangled. If we create the composite system in such a way that A and B do not interact, we may obtain the separable state of eq 17, but usually A and B will interact, and AB will become entangled (we will briefly discuss the entanglement process at the start of subsection 2.6 on the decoherence process).

2.4. Subsystems and Reduced Density Matrices. In order to discuss subsystems, we need the concept of a reduced density matrix. Let us call the system A and the environment B; then we will consider A and B as subsystems of the composite system AB. The key observation is that an entangled wave function for the entire system is a pure state in the state space of the entire system, but usually it corresponds to a mixed state in the state space of the subsystem. “If a composite system is in a pure state, its subsystems are in general in mixed states.”¹⁶

Just as the state of an entire system is specified by the density matrix of the entire system, the state of a subsystem is specific by the reduced density matrix of the subsystem. The reduced density matrix of the subsystem can be calculated from the density matrix of the entire system. Therefore, we can translate the above observation as follows: the reduced density matrix of a subsystem is generally impure, even when calculated from a pure density matrix for the entire system.

As an example, we next calculate the reduced density matrix of subsystem A when the entire system is described by eq 18. The density operator of combined system AB is obtained by applying the operator of eq 6 to eq 18. In the basis of eqs 11–14, this yields

$$\hat{\rho} = \sum_{IL \in A, JM \in B} \gamma_{IJ} \gamma_{LM}^* |a_I\rangle|b_J\rangle \langle a_L| \langle b_M| \quad (20)$$

Now the reduced density operator $\hat{\rho}^{(A)}$ for subsystem A is obtained by tracing $\hat{\rho}$ over the space of subsystem B, which yields

$$\begin{aligned} \hat{\rho}^{(A)} &= \text{Tr}_B(\hat{\rho}) = \sum_{K \in B} \langle b_K | \hat{\rho} | b_K \rangle \\ &= \sum_{K \in B} \left\langle b_K \left| \sum_{IL \in A, JM \in B} \gamma_{IJ} \gamma_{LM}^* |a_I\rangle|b_J\rangle \langle a_L| \langle b_M| \right| b_K \right\rangle \end{aligned} \quad (22)$$

Since here we assume the basis $\{|b_j\rangle\}$ is orthonormal, the reduced density operator for subsystem A becomes

$$\hat{\rho}^{(A)} = \sum_{IL \in A, K \in B} \gamma_{IK} \gamma_{LK}^* |a_I\rangle \langle a_L| \quad (23)$$

Therefore, the reduced density matrix $\rho^{(A)}$ for subsystem A in basis $\{|a_i\rangle\}$ is

$$\rho_{IL}^{(A)} = \sum_{K \in B} \gamma_{IK} \gamma_{LK}^* \quad (24)$$

which leads to

$$\rho_{11}^{(A)} = |\gamma_{11}|^2 + |\gamma_{12}|^2 \quad (25)$$

$$\rho_{22}^{(A)} = |\gamma_{21}|^2 + |\gamma_{22}|^2 \quad (26)$$

$$\rho_{12}^{(A)} = \gamma_{11} \gamma_{21}^* + \gamma_{12} \gamma_{22}^* \quad (27)$$

$$\rho_{21}^{(A)} = (\rho_{12}^{(A)})^* \quad (28)$$

It can be shown that the eigenvalues, λ_{\pm} , of reduced density matrix $\rho^{(A)}$ are generally neither 0 nor 1:

$$\lambda_{\pm} = \frac{1}{2} \left(1 \pm \sqrt{1 - 4|\gamma_{11}\gamma_{22} - \gamma_{12}\gamma_{21}|^2} \right) \quad (29)$$

from which we conclude that the subsystem is in a mixed state. This is confirmed by

$$\text{Tr}(\rho^{(A)})^2 = 1 - 2|\gamma_{11}\gamma_{22} - \gamma_{12}\gamma_{21}|^2 < \text{Tr}(\rho^{(A)}) = 1 \quad (30)$$

2.5. Dynamics of a Mixed State. As already mentioned, a subsystem is not usually in a pure state. Applying the Schrödinger equation to the evolution of a system that is not in a pure state is an approximation. Therefore, we need a new equation of motion (EOM), not the time-dependent Schrödinger equation and not eq 9, for the evolution of a subsystem. This can be accomplished by adding another term to the right-hand side of the LvN equation; this term involves the system–environment interaction Hamiltonian. In particular, if we call the primary subsystem A and the environment B, we must replace eq 9 by^{5,25,26}

$$i\hbar \frac{\partial}{\partial t} \rho^{(A)} = [\mathbf{H}^{(A)}, \rho^{(A)}] + \text{Tr}_B([\mathbf{H}^{(AB)}, \rho]) \quad (31)$$

where we have written the total Hamiltonian matrix as

$$\mathbf{H} = \mathbf{H}^{(A)} + \mathbf{H}^{(B)} + \mathbf{H}^{(AB)} \quad (32)$$

Equation 31 will be called a nonunitary LvN. It is not a closed equation, because it still contains the entire system's density operator in the final term.⁵ In the general case, the final term of eq 31 must account for dissipation and decoherence. For a system in equilibrium with a thermal reservoir, the time evolution of the reduced density matrix can be written in terms of the dynamics in the primary subsystem and time-correlation functions of bath operators that appear in the system–bath interactions;^{5,24,27,28} however, our focus here is on nonequilibrium, nonstationary systems. The mathematical physics literature of nonunitary evolution contains many attempts to develop practical approximations to the final term of eq 31 and to determine constraints on its behavior and functional form.^{19,29–43} In some cases, the approximations lead to a master equation involving only populations without coherences.⁴⁴ We will consider the more general case, which we will call a nonunitary LvN equation even when approximations are made.

Another name for a nonunitary LvN is a generalized master equation. In the literature, what we call a nonunitary LvN equation is sometimes called a master equation, although we and many others, especially in the statistical mechanics field, prefer to save the term “master equation” for an equation involving only populations. Thus, a nonunitary LvN involves the entire reduced density matrix of the primary system, whereas a master equation (in our notation) involves only the populations. The solutions of a nonunitary LvN equation tend toward those of a master equation at long times. Note that the master equation is sometimes called the Pauli master equation.⁴⁵

A wide variety of approximate nonunitary LvN equations have been proposed. The literature is large, and it is beyond the scope of the present article to review it in a comprehensive fashion, although it is worthwhile to mention two well-known approaches. One widely used approximation for the last term of eq 31 is the Lindblad approximation,^{27,31,46,47} which is suitable for weak, Markovian system–environment interactions in which the environmental time scale is much faster than the system time scale. Another commonly used approximation is the Redfield equation,^{29,30,48} originally proposed for a nuclear spin system weakly coupled to a thermal environment. We do not use the Lindblad approximation or the Redfield equations, and we will not discuss them further.

2.6. Decoherence. When we introduced a mixed state above, we postulated a situation where full knowledge of the state of the system is not available. However, mixed states also arise as a result of time evolution, even when the system is initially in a known pure state. Even if we start with a coherent state, when the system interacts with an environment, it will undergo nonunitary evolution that will lead to a mixed state. Decoherence refers to this process and also to the process of the evolution of a mixed state, because a mixed state may have nonzero coherences, and its evolution can diminish or destroy the remaining coherence.

Consider a system or subsystem described by the coherent pure state

$$\Psi = c_1 \psi_1 + c_2 \psi_2 \quad (33)$$

where ψ_j is an eigenfunction of the physical observable X with eigenvalue X_j , and c_j is a coefficient. The expectation value of X is given by eqs 3–5. But a basic postulate of quantum mechanics is that, if the measurement did not perturb X , the measured average value of X will be

$$\langle X \rangle = |c_1|^2 X_1 + |c_2|^2 X_2 \quad (34)$$

where

$$X_j \equiv X_{jj} \equiv \langle \psi_j | X | \psi_j \rangle \quad (35)$$

We expect eq 34 because the probability X_j will be equal to $|c_j|^2$. More generally, the measurement might perturb X , and then the measured average value of X will be

$$\langle X \rangle = p_1 X_1 + p_2 X_2 \quad (36)$$

where p_j is a probability.

Equations 34 and 36 differ from eq 5 in that the off-diagonal elements of the density matrix are not present. Therefore, either prior to the measurement of X or during the measurement of X , the off-diagonal elements of the density matrix (in the representation of eigenstates of X) must have decayed to zero. This is the central fact of decoherence; a coherent superposition

of state vectors decays into a mixed state characterized by classical probabilities:

$$\begin{pmatrix} |c_1|^2 & c_1^*c_2 \\ c_1c_2^* & |c_2|^2 \end{pmatrix} \rightarrow \begin{pmatrix} p_1 & 0 \\ 0 & p_2 \end{pmatrix} \quad (37)$$

2.7. Pointer State. The above discussion shows that the coherences must decay, either continuously due to continuous monitoring of the primary system by the environment or rapidly during a measurement, or both. But in what basis do they decay? In the case of a well-designed measurement, the answer is clear. A measurement of property X should cause the coherences to vanish in a basis of the eigenstates of X . But the problem is much harder for continuous environmental monitoring.

Our own approach follows the original work of Zeh¹³ and Zurek.^{10,49–52} This leads to the concept of a pointer basis:

*Interaction with the environment will typically single out a preferred set of states [basis]. These pointer states [pointer basis] remain untouched in spite of the environment, while their superpositions lose phase coherence and decohere. Their name—pointer states—originates from the context of quantum measurements.... They are the preferred states of the pointer of the apparatus.*¹⁰

Thus, each case of subsystem–environment interaction selects its own preferred basis, called the pointer basis, and this selection is called environment-induced superselection (einselection).⁴⁹ The pointer basis of a given subsystem–environment combination remains stable in the presence of that combination.

In summary, the nature of the measurement (or, more generally, the nature of the subsystem–environment interaction) selects a preferred basis, called the pointer basis, and the subsystem decoheres into an effectively classical mixture in the pointer basis.¹⁰

2.8. Decoherence Process. We showed in eq 24 that the reduced density matrix of subsystem A is generally a mixed state. Next, we discuss how the entangled state of eq 18 arises. Let A be the primary system and B be the environment. The Hilbert spaces of A and B are $\{|r_j\rangle\}$ and $\{|s_{\mathcal{K}}\rangle\}$, respectively. Any environment state J can be expressed in the basis $\{|s_{\mathcal{K}}\rangle\}$:

$$\phi_j \equiv \phi_j^{(B)} = \sum_{\mathcal{K} \in B} \alpha_{j\mathcal{K}} |s_{\mathcal{K}}\rangle \quad (38)$$

where $\alpha_{j\mathcal{K}}$ is a coefficient. We consider a process where subsystem A is initially a pure state,

$$\Psi^{(A)} = \sum_{I \in A} c_I |r_I\rangle \quad (39)$$

where c_I is a coefficient. When any state of A interacts with the environment B, the environment state will adjust according to the subsystem state.^{10,12,49} If the subsystem is in state $\Psi^{(A)} = |r_1\rangle$, the environment state will adjust to a state that we will call ϕ_1 . Therefore, the combined system–environment state becomes

$$\Psi^{(AB)} = \sum_{I \in A} c_I |r_I\rangle |\phi_I\rangle \quad (40)$$

The states $\{|\phi_I\rangle\}$ are not necessarily orthogonal. Expanding eq 40 according to eq 38, we arrive at

$$\Psi^{(AB)} = \sum_{I \in A} c_I |r_I\rangle \sum_{\mathcal{K} \in B} \alpha_{I\mathcal{K}} |s_{\mathcal{K}}\rangle = \sum_{I \in A, \mathcal{K} \in B} \gamma_{I\mathcal{K}} |r_I\rangle |s_{\mathcal{K}}\rangle \quad (41)$$

where

$$\gamma_{I\mathcal{K}} = c_I \alpha_{I\mathcal{K}} \quad (42)$$

As in eqs 11–14, we consider two states each for the subsystem A and the environment B:

$$\psi_1 = |r_1\rangle |s_1\rangle \quad (43)$$

$$\psi_2 = |r_1\rangle |s_2\rangle \quad (44)$$

$$\psi_3 = |r_2\rangle |s_1\rangle \quad (45)$$

$$\psi_4 = |r_2\rangle |s_2\rangle \quad (46)$$

Equation 41 is equivalent to eq 18 with

$$\gamma_{11} = c_1 \alpha_{11} \quad (47)$$

$$\gamma_{12} = c_1 \alpha_{12} \quad (48)$$

$$\gamma_{21} = c_2 \alpha_{21} \quad (49)$$

$$\gamma_{22} = c_2 \alpha_{22} \quad (50)$$

But, generally, eq 41 is not equivalent to eq 17, i.e., $\gamma_{11}/\gamma_{21} \neq \gamma_{12}/\gamma_{22}$.

Equation 40 is critical for understanding coherence decay. The density operator for the entire system AB with state $\Psi^{(AB)}$ shown in eq 40 is

$$\hat{\rho} = \sum_{IJ \in A} c_I c_J^* |r_I\rangle \langle r_J| \langle \phi_I| \langle \phi_J| \quad (51)$$

The reduced density operator for the primary subsystem A is then given by

$$\hat{\rho}^{(A)} = \sum_{IJ \in A} c_I c_J^* \langle \phi_I | \phi_J \rangle |r_I\rangle \langle r_J| \quad (52)$$

Therefore, the coherences (off-diagonal elements) of the reduced density matrix include factors proportional to the overlaps of environment states, and the density matrix elements become

$$\rho_{IJ}^{(A)} = c_I c_J^* \langle \phi_I | \phi_J \rangle \quad (53)$$

Equation 53 is identical to eq 24, which can be shown by using eq 42. However, eq 53 gives a clear physical picture about how the coherence decays to zero. In particular, as the overlaps of the environmental states decay, the superposition of states is continuously reduced to a classical mixture with off-diagonal elements equal to zero.

Equation 53 also illustrates the transition to a classical world. From eq 38, we have

$$\langle \phi_I | \phi_J \rangle = \sum_{\mathcal{K} \in B} \alpha_{I\mathcal{K}}^* \alpha_{J\mathcal{K}} \quad (54)$$

When the number of degrees of freedom is very high (macroscopic), the state vectors of the environment have a high probability to be orthogonal,⁵³ so that the coherence decays almost instantaneously on a macroscopic time scale.

2.9. Decoherence Time. Generally, initial conditions should be chosen according to the experiment one is simulating, and decoherence may show a short-time induction period where it has no simple functional form, but eventually it can conform to a decay law. At these longer times, it includes an exponentially decaying contribution, which can be seen in model systems.^{54–59} In other cases, the theory yields Gaussian

decay.^{60–68} Yan and Zurek⁶⁹ have emphasized that, generally, the decay function is a convolution $f * g$ of exponential decay $f(t)$ and Gaussian decay $g(t)$,

$$f(t) = \exp\left(-\frac{t}{\tau_{1,IK}}\right) \quad (55)$$

$$g(t) = \exp\left(-\frac{t^2}{\tau_{2,IK}^2}\right) \quad (56)$$

$$(f * g)(t) = \int_{-\infty}^{\infty} dt' f(t') g(t - t') \quad (57)$$

where t and t' are time, and $\tau_{1,IK}$ and $\tau_{2,IK}$ are, respectively, exponential and Gaussian decay parameters with units of time. Therefore, coherences decay as

$$\rho_{IK}^{(A)}(t) = \rho_{IK}^{(A)}(0)(f * g)(t) \quad (58)$$

Yan and Zurek⁶⁹ noted that the suppression of coherence involves contributions both from decay of overlap (i.e., ϕ_I and ϕ_J in eq 54 becoming more and more different) and from spreading out of spectral density (i.e., the increase of the number of significant nonzero coefficients α_{JK} in eqs 38 and 54); the overlap decay follows an exponential decay law, while spreading of spectral density causes a Gaussian decay. Therefore, the Gaussian decay may potentially contribute significantly for condensed-phase systems with many degrees of freedom. However, for molecular systems in the gas phase, the number of degrees of freedom over which the environmental amplitude may spread is limited, and overlap decay may dominate. These are just general considerations; further research is needed to better understand the nature of the decay, but our models assume exponential decay of mixing as a way to mimic decay of coherence.

With that rationale, we seek to model the decay of the coherence between state I and state K with the following form for gas-phase systems:

$$\rho_{IK}^{(A)}(t) = \rho_{IK}^{(A)}(0) \exp\left(-\frac{k_{IK}}{t}\right) \equiv \rho_{IK}^{(A)}(0) \exp\left(-\frac{t}{\tau_{IK}}\right) \quad (59)$$

where t is the time, k_{IK} is the first-order rate constant, and τ_{IK} is called the decoherence time. At small t ,

$$\exp(-k_{IK}t) \xrightarrow{\text{small } t} (1 - k_{IK}t) \quad (60)$$

i.e., the initial decay of the decay law is linear in t .

3. QUANTAL AND QUASICLASSICAL DYNAMICS

Systems with only a very few atoms may be treated fully quantum mechanically, with a quantum mechanical treatment of the electrons producing a potential energy surface or a set of potential energy surfaces and their couplings, and with quantum mechanical scattering theory for the nuclear motion. The accurate quantum mechanical scattering theory may be either time-independent^{70–74} or time-dependent.^{72,75–77}

When the dynamics is calculated by a converged quantum mechanical algorithm, coherence and decoherence are automatically treated properly. However, when one uses a mixed quantum mechanical–classical method for a system with more than one electronic state, we must include the coherence of the

electronic subsystem and its decoherence by the nuclear subsystem as explicit parts of the algorithm.

A converged quantum mechanical treatment of the nuclear motion is impractical for most problems of interest, and, instead, one uses a semiclassical method—also called a mixed quantum mechanical–classical method—in which the potential energy surface or a set of potential energy surfaces and their couplings is produced by a quantum mechanical treatment of the electrons, and the nuclear motion is treated classically,⁷⁸ quasiclassically,^{79,80} or semiclassically.^{81,82} In this context, the word “semiclassical” means that we contend with the intrinsically nonclassical feature that each electronic state provides a different potential energy function for nuclear motion. In most of the chemical dynamics literature, the word “quasiclassical” has a different meaning; in particular, it is usually used to refer to trajectory calculation that involves an average over a classical ensemble of classical trajectories, with the only nonclassical element (the reason why we say “quasi”) being that—for each trajectory—the initial energy in one or more than one of the vibrational modes is restricted to be a quantum mechanically allowed value determined by a previous (accurate or approximate) calculation. Our considerations for single-surface trajectory calculations will apply to both purely classical calculations and quasiclassical trajectory calculations. In both types of calculations, one computes trajectories for an ensemble of initial conditions and then averages the results over the ensemble.

Molecular dynamics on a single potential energy surface requires (1) a potential energy function, usually obtained by electronic structure calculations (although for nonreactive electronically adiabatic processes, the potential energy function can be modeled by molecular mechanics), and (2) a calculation of nuclear dynamics. The Born–Oppenheimer approximation states that the total electronic energy in a given electronic state plus the nuclear repulsion provides a potential energy surface for nuclear motion. The electronic structure calculations needed for this purpose can be performed in advance, and the quantities needed for dynamics may be fitted to analytic functions, or the electronic structure calculations can be performed as needed by the dynamics algorithm; the latter is called “direct dynamics”.

How Quasiclassical Trajectory Calculations Simulate Quantum Dynamics. Let us first review the method for calculating quantum mechanical vibrational-state-to-vibrational-state quantum mechanical transition probabilities for a Born–Oppenheimer process (i.e., a process involving only a single electronically adiabatic potential energy surface) by localized time-dependent wave packets. We do this because a localized wave packet method provides a good way to understand the approximations involved in trajectory calculations.^{83–85} The quantum mechanical method is as follows:

- (1) Express the initial wave function for vibrational state j as a linear combination of basis functions that are localized multidimensional, many-particle Gaussian wave packets.
- (2) Propagate the coupled motion of the wave packets using the time-dependent Schrödinger equation.
- (3) When the process is complete, project the coherent linear combination of Gaussian packets onto an accurate final-state vibrational wave function for state k to calculate the $j \rightarrow k$ transition probability.
- (4) Increase the number of Gaussians in step 1 until the results of step 3 converge.

To make a connection of such quantum mechanical calculation to a quasiclassical trajectory calculation, we make the following changes:

- Choose a frozen Gaussian basis so that each time-dependent Gaussian basis function has a classical energy (i.e., an energy computed from its mean momentum $\langle p \rangle$ and mean position $\langle x \rangle$) equal to the total energy of the process under consideration.
- In propagating the wave function in step (2), propagate each Gaussian separately using a local quadratic approximation to the potential (a multidimensional Taylor series centered at $\langle x \rangle$, so there is a new Taylor series at every time step). Because of this approximation, the coordinate and momentum parameters of each Gaussian wave packet become a classical trajectory.
- In step (3), average the results over the ensemble of independent trajectories instead of adding Gaussian wave packets coherently. The initial conditions of these trajectories should, in some way, represent the initial state of the system to be simulated; for example, if a system has two vibrations, we should average over the initial relative (classical) phases of these vibrations.

These three approximations reduce the quantum mechanical calculation to a trajectory calculation. A widely used convention is to call this a quasiclassical trajectory if the initial conditions simulate a definite quantum state of the system (for example, if the initial energy is one of the quantized energies of the system) and to call it a classical trajectory if the initial conditions ignore quantization.

Mixed quantum–classical dynamics has been discussed in the context of the LvN equation by Kapral and Ciccotti.²⁵

4. MULTISURFACE SEMICLASSICAL DYNAMICS

With the background provided above, we are now ready to discuss multisurface semiclassical trajectories. According to the generalized Born–Oppenheimer approximation, each electronic state of the system is associated with its own potential energy surface. As compared to the single-surface trajectories briefly discussed in Section 3, an algorithm for the multisurface case needs five new ingredients:

- We must propagate the electronic density matrix as well as the trajectory, because the effective potential energy for the trajectory depends on the time evolution of the electronic density matrix.
- We must decide on what potential energy surface or what weighted average of all the available potential energy surfaces to use for the trajectory.
- We must decide which basis to treat as the pointer basis.
- We need a practical algorithm that mimics eq 37.
- We need a model for the decoherence time.

Next, we consider these five ingredients in turn.

4.1. Unitary Propagation of the Electronic Density Matrix. Here, we consider propagation of the electronic density matrix without decoherence; we will add decoherence in ingredient (4).

We consider independent trajectories whose results will be averaged, as discussed in section 3 and in the previous paragraph. Although semiclassical trajectory calculations may be performed in either the electronically adiabatic basis (electronic wave functions determined in the usual way with fixed nuclei) or a diabatic basis,⁸⁶ we restrict the present treatment to the adiabatic basis. Note that when spin–orbit coupling is included,

the adiabatic basis is sometimes called the diagonal basis⁸⁷ or the fully adiabatic basis,⁸⁸ but we will simply refer to it as the adiabatic basis. (Note that spin–orbit coupling is relativistic, and the label “adiabatic” is sometimes used for diagonalizing only the nonrelativistic part of the electronic Hamiltonian, but here, we use it to mean diagonalizing the entire electronic Hamiltonian, even when spin–orbit coupling is included.)

Let \mathbf{R} denote nuclear Cartesian coordinates of the $3N_{\text{atoms}}$, and let \mathbf{r} denote the electronic coordinates. Write the total molecular Hamiltonian as

$$H = T^{\text{nuc}} + H^{\text{elec}} \quad (61)$$

where H^{elec} is the electronic Hamiltonian including nuclear repulsion, and T^{nuc} is the nuclear kinetic energy, which is given by

$$T^{\text{nuc}} = \sum_{\eta}^{N_{\text{atoms}}} -\frac{\hbar^2}{2M_{\eta}} \nabla_{\mathbf{R},\eta}^2 \quad (62)$$

where η is the index of an atom, N_{atoms} is the number of atoms, and $\nabla_{\mathbf{R},\eta}$ is a three-dimensional gradient operator. The electronic basis functions $\{\phi_I^{\text{elec}}\}$ satisfy the relation

$$\langle \phi_I^{\text{elec}}(\mathbf{r}; \mathbf{R}) | H^{\text{elec}} | \phi_J^{\text{elec}}(\mathbf{r}; \mathbf{R}) \rangle_{\mathbf{r}} = \delta_{IJ} V_J(\mathbf{R}) \quad (63)$$

where $\langle \dots | \dots \rangle_{\mathbf{r}}$ denotes a matrix element in electronic state space, and $V_J(\mathbf{R})$ is the potential energy function for nuclear motion when the electronic state is J . We also define the nonadiabatic coupling vector, which will be required below, as

$$\mathbf{d}_{IJ} = \langle \phi_I^{\text{elec}} | \nabla_{\mathbf{R}} | \phi_J^{\text{elec}} \rangle_{\mathbf{r}} \quad (64)$$

where $\nabla_{\mathbf{R}}$ is a $(3N_{\text{atoms}})$ -dimensional gradient. The nonadiabatic coupling vector is often called the NAC. It is an element of an $N_{\text{states}} \times N_{\text{states}}$ matrix \mathbf{d} , each of whose elements is a $3N_{\text{atoms}}$ -dimensional vector. We will also find it convenient to define the real part of any complex variable z as

$$\text{Re}(z) = \frac{1}{2}(z + z^*) \quad (65)$$

We start with a molecular wave function that can be factorized into a product form of electronic and nuclear parts:⁸⁹

$$\Psi = \Phi^{\text{elec}}(\mathbf{r}; \mathbf{R}(t)) \chi^{\text{nuc}}(\mathbf{R}(t)) \quad (66)$$

where t is the time, $\mathbf{R}(t)$ is a trajectory, and χ^{nuc} is a nuclear-motion wave packet centered (as discussed in Section 3) on the trajectory. By substituting eq 66 into the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \Psi}{\partial t} = H \Psi \quad (67)$$

one obtains the electronic mean-field equation,

$$i\hbar \frac{\partial}{\partial t} \Phi^{\text{elec}} = \langle \chi^{\text{nuc}} | H | \chi^{\text{nuc}} \rangle_{\mathbf{R}} \Phi^{\text{elec}} \quad (68)$$

and the nuclear mean-field equation,

$$i\hbar \frac{\partial}{\partial t} \chi^{\text{nuc}} = \langle \Phi^{\text{elec}} | H | \Phi^{\text{elec}} \rangle_{\mathbf{r}} \chi^{\text{nuc}} \quad (69)$$

The combination of eqs 68 and 69 is called “time-dependent self-consistent field theory”. Next, we replace the wave packet with the trajectory, so that only the electronic wave system is treated quantum mechanically. This reduces eq 68 to

$$i\hbar \frac{\partial}{\partial t} \Phi^{\text{elec}} = H^{\text{elec}}(\mathbf{r}; \mathbf{R}(t)) \Phi^{\text{elec}} \quad (70)$$

where the electronic Hamiltonian $H^{\text{elec}}(\mathbf{r}; \mathbf{R}(t))$ becomes parametrically dependent on the nuclear coordinates and, therefore, it changes along a trajectory. Expanding the electronic wave function in the adiabatic space gives

$$\Phi^{\text{elec}} = \sum_{I=1}^{N_{\text{states}}} c_I(t) \phi_I^{\text{elec}}(\mathbf{r}; \mathbf{R}(t)) \quad (71)$$

where N_{states} is the number of electronic states. In the following discussion, we will always employ capital letters I, J, K, L, M as electronic state indices, and ignore the N_{states} in the summation operator for simplicity.

Next, we substitute eq 71 into the electronic mean-field equation; we make the substitution

$$\frac{\partial \phi_I^{\text{elec}}}{\partial t} = (\nabla_{\mathbf{R}} \phi_I^{\text{elec}}) \cdot \frac{d\mathbf{R}}{dt} \equiv \dot{\mathbf{R}} \cdot \nabla_{\mathbf{R}} \phi_I^{\text{elec}} \quad (72)$$

Projecting with $\langle \phi_I^{\text{elec}} |$, we notice that the diagonal elements of the \mathbf{d} matrix are null vectors, we redefine $c_I(t)$ by removing a time-dependent phase factor (as in eq 6 of the Tully–Preston paper⁸¹), and we use eq 4. These steps yield the following time dependence for the elements of the reduced density matrix:⁹⁰

$$\dot{\rho}_{II} = -2 \sum_{J \neq I} \text{Re}(\rho_{IJ} \dot{\mathbf{R}} \cdot \mathbf{d}_{IJ}) \quad (73)$$

and

$$\dot{\rho}_{IJ} = \frac{i}{\hbar} \rho_{IJ} (V_J - V_I) - \sum_L (\rho_{LJ} \dot{\mathbf{R}} \cdot \mathbf{d}_{IL} + \rho_{IL} \dot{\mathbf{R}} \cdot (\mathbf{d}_{LJ})^*) \quad (I \neq J) \quad (74)$$

When spin–orbit coupling is neglected, the adiabatic basis functions can be taken as real, which makes \mathbf{d}_{IJ} real; in such a case, eq 73 can be reduced to

$$\dot{\rho}_{II} = -2 \sum_{J \neq I} \text{Re}(\rho_{IJ}) \dot{\mathbf{R}} \cdot \mathbf{d}_{IJ} \quad (75)$$

Notice that, although eqs 73 and 74 involve a reduced density matrix for the electronic subsystem, we simplified $\rho^{(\text{elec})}$ to ρ , and we will simply refer to this as the density matrix in the rest of the article. Notice also that the diagonal elements of the density matrix are real, which is consistent with them being treated as populations, and the off-diagonal elements are complex.

4.2. The Effective Potential Energy Surface. In Section 4.1, we presented the EOM for electronic density matrix. Equation 69 involves the nuclear wave packet propagating on a mean-field potential that is generated by the electrons. Replacing the wave packet by a trajectory then reduces the problem to a classical particle propagating on an effective potential given by

$$V_{\text{eff}} = \langle \Phi^{\text{elec}} | H^{\text{elec}} | \Phi^{\text{elec}} \rangle_{\mathbf{r}} \quad (76)$$

This is called the Ehrenfest approximation, and the effective potential is called the self-consistent potential (SCP).¹⁰⁸ A general form of the nuclear EOM that conserves energy is given by

$$\dot{\mathbf{P}} = - \sum_I \left(\rho_{II} \frac{\partial V_I}{\partial \mathbf{R}} \right) + \sum_{IJ} \text{Re} \left(\frac{\rho_{IJ} (V_I - V_J) \dot{\mathbf{R}} \cdot \mathbf{d}_{IJ}}{\dot{\mathbf{R}} \cdot \mathbf{G}_{IJ}} \mathbf{G}_{IJ} \right) \quad (77)$$

where $\dot{\mathbf{P}}$ is the time derivative of the $(3N_{\text{atoms}})$ -dimensional nuclear momentum, and \mathbf{G}_{IJ} can be any nonzero vector that is not perpendicular to the velocity vector $\dot{\mathbf{R}}$.⁹¹ The combination of eqs 75 and 77 is called the generalized semiclassical Ehrenfest method. Usually \mathbf{G}_{IJ} is taken to be \mathbf{d}_{IJ} , and this reduces eq 77 to the following widely used nuclear EOM:

$$\dot{\mathbf{P}} = - \sum_I \left(\rho_{II} \frac{\partial V_I}{\partial \mathbf{R}} \right) + \sum_{IJ} \text{Re}(\rho_{IJ} (V_I - V_J) \mathbf{d}_{IJ}) \quad (78)$$

One can also write eq 78 as

$$\dot{\mathbf{P}} = - \sum_I \left(\rho_{II} \frac{\partial V_I}{\partial \mathbf{R}} \right) + \sum_{I \neq J} 2 \text{Re}(\rho_{IJ} V_I \mathbf{d}_{IJ}) \quad (79)$$

Equations 74 and 79 constitute the semiclassical Ehrenfest method.

The semiclassical Ehrenfest method or generalized semiclassical Ehrenfest method is the starting point for our preferred method for including decoherence, but we note that much of the literature is based on a simpler method called “trajectory surface hopping” (TSH).⁸¹ The TSH method employs the same electronic equation of motion as the semiclassical Ehrenfest method, and this equation of motion is overcoherent, because decoherence is neglected. (The original surface hopping calculations^{81,92} employed the Landau–Zener approximation^{93,94} rather than the electronic EOM, but the electronic EOM was introduced⁹⁵ into surface hopping calculations in subsequent work and is the preferred method for most TSH calculations today, although some calculations use an algorithm⁹⁶ based on the Zhu–Nakamura extension of the Landau–Zener approximation.) Before discussing the incorporation of decoherence in surface hopping and in semiclassical Ehrenfest, we here give a brief introduction to TSH.

In TSH, the trajectory propagates on a single adiabatic potential energy surface (PES),

$$\dot{\mathbf{P}}_{\text{TSH}} = - \frac{\partial V_K}{\partial \mathbf{R}} \quad (80)$$

where K is called the active state in TSH, and the electronic density matrix propagates in the same way as that of semiclassical Ehrenfest, i.e., by eqs 70–75. To allow for electronic nonadiabaticity, a TSH trajectory can hop to a different state along the trajectory. The most widely used algorithm for this is the fewest-switches algorithm,⁹⁷ based on the electronic EOM. In the fewest-switches algorithm, the number of switches of the active state is minimized with the objective that, in an ensemble of trajectories where switching is performed stochastically, the number of trajectories propagating on surface K is proportional to the electron population (ρ_{KK}) of state K . In practice, this goal is strictly achieved only for the case where the surfaces are degenerate^{98,99} and when no hops are frustrated (frustration is discussed in the next paragraph). Although propagating on a single surface is ad hoc, and although the surfaces are often far from degenerate, TSH has been used successfully in many applications, and it is popular because of its ease of implementation. The method can be made more accurate by introducing time uncertainty into the positions of the surface switches,¹⁰⁰ yielding a method called fewest switches with time uncertainty (FSTU); however, even with this improvement, it is less accurate than our preferred method, which, as explained in section 4.4, is obtained by introducing decoherence into the generalized semiclassical Ehrenfest

method. For this evaluation, accuracy is ascertained by comparison to accurate quantum dynamics for electronically nonadiabatic atom–diatom collisions, where accurate quantum dynamics is achievable.^{39,101}

An especially troublesome aspect of the fewest switches TSH method is that sometimes the trajectory tries to make a hop that is forbidden by local conservation of energy or local conservation of the component of momentum in the direction coupled to the surface hop. This is not possible since nuclear motion is classical in this semiclassical method (and, hence, does not penetrate tunneling regions); such attempted hops are called “frustrated hops”. Although strategies have been developed for dealing with frustrated hops,¹⁰² they are still a cause for concern, because they destroy the self-consistency of the electronic and nuclear motion. One of the advantages of employing an SCP instead of a single PES is that the nuclear and electronic EOMs are always self-consistent. And therefore, when decoherence is introduced into electronic density matrix, as will be discussed in the next subsection, it influences the nuclear EOM as well. A direct consequence of this consistency is that the approaches based on the decoherence-corrected semiclassical Ehrenfest method or generalized semiclassical Ehrenfest method do not suffer from the problem of frustrated hops.

4.3. The Pointer Basis. In general, the pointer basis is unknown, although in cases where the adiabatic approximation is valid, i.e., where the primary system adjusts adiabatically to changes in the environment, the adiabatic basis is the pointer basis.¹⁰³ As we will discuss below, decoherence is expected to be fastest where the potential energy surfaces are widely separated. In these regions, the Born–Oppenheimer electronically adiabatic approximation is often a good approximation. This implies that it is usually best to take the pointer basis to be adiabatic basis, and we shall assume that is being done in the rest of this article.

4.4. Decoherence. A very clear (and pedagogically elucidating) example of the importance of including decoherence in the intervals between strong coupling regions was provided by Thachuk et al.¹⁰⁴ A practical example of how decoherence can make a qualitative change in the outcome of a photochemical example is provided by recent study of thioformaldehyde.¹⁰⁵

The earliest semiclassical treatments of electronically nonadiabatic dynamics ignored decoherence. The first introduction of noninstantaneous decoherence into multistate semiclassical calculations is due to Bittner and Rossky.¹⁰⁶ They considered a liquid-phase system, where the primary subsystem consists of the electronic degrees of freedom of the solute, and the environmental bath is a macroscopic liquid. They concluded that “even for weakly interacting baths, the effect of quantum decoherence must be considered in order to make realistic predictions of condensed-phase phenomena.” Prezhdó later emphasized the importance of decoherence in large systems and condensed phases.¹⁰⁷

A key difference of the treatment in the previous paragraph from the treatment used in our work and here is that we recognize that even a small gas-phase molecule shows significant decoherence of the electronic degrees of freedom.^{99,108} A key conclusion⁹⁹ in one of our early papers treating electronic decoherence by the nuclear environment is that electronic decoherence “plays a critical role even in small-molecule gas-phase systems”. A later analysis by Hwang and Rossky,¹⁰⁹ showed that intramolecular decoherence contributions tend to be dominant in nonadiabatic dynamics, compared to solvent

effects. For an electronically excited molecule in the gas phase, the primary subsystem consists of the electronic degrees of freedom of the molecule, and the environmental subsystem consists of the nuclear degrees of freedom of the molecule. For an electronically excited molecule in a liquid-phase solvent, the environment would be a combination of the nuclear degrees of freedom of the solute and all the degrees of freedom of the solvent.

Section 2 presented the concepts necessary to explain decoherence. In this subsection, we discuss the application of these concepts to electronically nonadiabatic dynamics of molecules. A direct consequence of decoherence discussed in section 2 is that the off-diagonal matrix elements of density matrix represented in the pointer basis should decay to zero exponentially with a rate constant that is the reciprocal of the decoherence time. Therefore, incorporating decoherence into the electronically nonadiabatic dynamics should involve three pieces of information: pointer basis, decoherence time, and an algorithmic representation of the decay of coherence. We have already discussed the preferred choice of pointer basis in section 4.3, and we will focus on algorithms in this subsection. Decoherence time will be discussed in detail in the next subsection.

Equations 74 and 75 govern unitary (i.e., coherent) propagation of the electronic density matrix. However, it is important to recognize that state changing is primarily promoted in regions where the electronic states are strongly coupled. In a polyatomic system, one can pass through strong coupling regions more than once (which is typical in many processes, for example, most photochemical reactions), and it is important to recognize that decoherence occurs between such strong coupling regions. Incorporating decoherence requires propagating the electronic density matrix according to a nonunitary LvN equation, as shown in eq 31. We distinguish three types of methods to mimic the decay of coherence, namely, (i) decay of mixing, (ii) decay to a block, and (iii) decay of off-diagonal density matrix elements.

- (i) The decay of mixing algorithms^{36,39,99,101,110–115} decay all the coefficients in eq 71 to zero except one, which we denote as $c_k(t)$. And, therefore, when decay of mixing is finished, only one diagonal element of the density matrix ρ_{kk} survives as unity; all the rest of the density matrix elements decay to zero. At the end of semiclassical nonadiabatic dynamics simulations, the ensemble involves a classical mixture of quantum electronic states in the pointer basis. This is the origin of the name “decay of mixing”; each trajectory not only involves a decay of coherence, but also a decay from a classical mixture. In semiclassical nonadiabatic dynamics employing methods of type (i), we employ a large ensemble of initial conditions with the goal that the final ensemble-averaged result is comparable to the reduced electronic density matrix computed from quantum simulation of the entire molecular system. Thus, we do not explicitly treat the decay of coherence in a single trajectory but rather our treatment has the goal that the results averaged over an ensemble should mimic full quantum dynamics; that is, averaging over an ensemble of trajectories reconstructs the classical probabilities in a mixed-state electronic density matrix.
- (ii) In decay to a block,¹¹⁶ only the coherence between the states inside and outside of a subset of the N_{states} is

decayed. This has been shown to have certain advantages in simulations of systems with a dense manifold of states.

- (iii) Enforcing the decay of the off-diagonal matrix elements of the density matrix but not the non-pointer-state diagonal ones would attempt to mimic the quantal results with a single trajectory. Combining this method with the semiclassical Ehrenfest method would not eliminate the problem of the trajectory ending in a nonphysical state. Therefore, we do not recommend this, and we will not consider it further.

4.4.1. Decay-of-Mixing Methods. We next focus on the decay-of-mixing methods for adding decoherence to the semiclassical Ehrenfest method. We first discuss the self-consistent decay of mixing (SCDM) method that incorporates decay of mixing by strategy (i) into eqs 74 and 75.^{99,110,115,117} In particular, this method assumes that

$$\dot{\rho}_{IJ} = [\dot{\rho}_{IJ}]_C + [\dot{\rho}_{IJ}]_D \quad (81)$$

where $[\cdot]_C$ and $[\cdot]_D$ respectively denote the coherence contribution to the time evolution and the decay-of-mixing contribution. Notice that the two terms in eq 81 correspond to the two terms in eq 31. Therefore, $[\dot{\rho}_{IJ}]_C$ is given in eqs 74 and 75, and for $[\dot{\rho}_{IJ}]_D$, we write

$$[\dot{\rho}_{IJ}]_D = \begin{cases} -\frac{1}{2} \left(\frac{1}{\tau_{IK}} + \frac{1}{\tau_{JK}} \right) \rho_{IJ} & \text{for } I \neq K, J \neq K, I \neq J \\ \frac{1}{2} \left(\frac{1}{\rho_{KK}} \sum_{L \neq K} \frac{\rho_{LL}}{\tau_{LK}} - \frac{1}{\tau_{JK}} \right) \rho_{IJ} & \text{for } I = K, J \neq K, I \neq J \\ \frac{1}{2} \left(\frac{1}{\rho_{KK}} \sum_{L \neq K} \frac{\rho_{LL}}{\tau_{LK}} - \frac{1}{\tau_{IK}} \right) \rho_{IJ} & \text{for } I \neq K, J = K, I \neq J \end{cases} \quad (82)$$

and

$$[\dot{\rho}_{II}]_D = \begin{cases} -\frac{\rho_{II}}{\tau_{IK}} & \text{for } I \neq K \\ \sum_{L \neq K} \frac{\rho_{LL}}{\tau_{LK}} & \text{for } I = K \end{cases} \quad (83)$$

where state K is the pointer state, and τ_{IK} is the decay-of-mixing time (our algorithmic substitute for the decoherence time) from state I to state K . In the following discussion, we will always employ K to denote the pointer state.

The overall effect of eqs 82 and 83 is to increase the population ρ_{KK} of the pointer state and reduce all the other elements. One can show that this decay-of-mixing algorithm is unitary, i.e., the electronic density matrix is propagated according to the time-dependent Schrödinger equation plus an additional decay-of-mixing term, but the total propagator is still a unitary propagator. It is the ensemble averaging that makes the final result nonunitary. Because the algorithm is unitary, the electronic density matrix of a single trajectory maintains the status of a pure-state density matrix; therefore, one can equivalently write the EOM in terms of the coefficients of eq 71, and the resulting equations are

$$\dot{c}_I = [\dot{c}_I]_C + [\dot{c}_I]_D \quad (84)$$

and

$$[\dot{c}_I]_C = \frac{i}{\hbar} \left(c_I V_I - i\hbar \sum_{I \neq J} c_J \hat{\mathbf{R}} \cdot \mathbf{d}_{IJ} \right) \quad (85)$$

$$[\dot{c}_I]_D = \begin{cases} -\frac{1}{2\tau_{IK}} c_I & \text{for } I \neq K \\ \sum_{J \neq K} \frac{1}{2\tau_{JK}} \frac{\rho_{JJ}}{\rho_{KK}} c_I & \text{for } I = K \end{cases} \quad (86)$$

Because the nuclear and electronic density matrix equations of motion should be consistent, the additional decay-of-mixing term imposes an additional decay-of-mixing force on the nuclear motion, which maintains conservation of energy, momentum, and angular momentum of the entire molecular system:

$$\dot{\mathbf{P}} = [\dot{\mathbf{P}}]_C + [\dot{\mathbf{P}}]_D \quad (87)$$

where the decay-of-mixing force is

$$[\dot{\mathbf{P}}]_D = \sum_{I \neq K} \frac{\rho_{II}}{\tau_{IK}} \frac{(V_I - V_K)}{(\mathbf{s}_{IK} \cdot \hat{\mathbf{R}})} \mathbf{s}_{IK} \quad (88)$$

where \mathbf{s}_{IK} is called the decay-of-mixing vector. From a purely mathematical point of view, \mathbf{s}_{IK} can be any real vector that is not perpendicular to $\hat{\mathbf{R}}$. In our methods, \mathbf{s}_{IK} is defined as

$$\mathbf{s}_{IK} = \text{Re} \left(\frac{a_0 \mathbf{P}_{\text{vib}} \mathbf{d}_{IK}}{|\mathbf{d}_{IK}|} \right) + \mathbf{P}_{\text{vib}} \quad (89)$$

where $a_0 = 1$ bohr ≈ 0.529 Å, and \mathbf{P}_{vib} is the vibrational momentum (computed by removing the overall angular and center-of-mass motion of the molecule).

So far, we have specified the pointer basis, but we have not specified the pointer state. We start with the pointer state being the initial state, but then we stochastically switch the pointer state with the objective that the ensemble average of populations will agree as well as possible with accurate quantum dynamics. The method we chose to accomplish this is to switch the pointer state with the fewest-switches algorithm⁹⁷ that is used to determine the hopping probability in TSH.

The above equations in which the electronic density matrix is propagated according to eq 81, and the nuclear EOM that is defined in eq 87 describe the SCDM method.¹¹⁷ In this method, decoherence is always present. This works well, but our experience¹¹³ shows that it is even more accurate to base the switching probabilities on a completely coherent passage through each region of strong coupling of the potential energy surfaces. Therefore, in our most successful method, which is called “coherent switching with decay of mixing” (CSDM).^{101,112,113,115} we modify SCDM such that the electronic density matrix controlling the switching of the pointer state is treated fully coherently in the electronic EOM for each complete passage through a strong interaction region, while the trajectory follows the path based on including decoherence. This involves propagating two density matrices. The SCDM density matrix still controls the trajectory, but the switching is controlled by a separately propagated coherent density matrix. At every point of minimum state coupling between strong coupling regions, the coherent density matrix is synched to the SCDM density matrix.⁹⁰

SCDM and CSDM are included in the ANI¹¹⁸ and SHARC-MN¹¹⁵ computer programs. SHARC-MN also includes two versions of CSDM that are more convenient because they do not

require NACs, namely, time-derivative CSDM¹¹⁹ (tCSDM) and curvature-driven CSDM¹²⁰ (κ CSDM).

4.4.2. Trajectory Surface Hopping (TSH) Methods. One may also incorporate decoherence into TSH methods, although the practical formulation varies.^{121–125}

A straightforward way to include decoherence in TSH was proposed by Granucci et al.;¹²² this method is included in the SHARC⁸⁷ and SHARC-MN¹¹⁵ programs, in which it is called trajectory surface hopping with energy-based decoherence (TSH-EDC). In this method, the coefficients of all the nonactive electronic states are caused to decay exponentially at every time step.

A different strategy for adding decoherence to TSH has also been proposed¹²³ in which it is added to the FSTU method, yielding FSTU with stochastic decoherence (FSTU/SD); FSTU/SD is available in the ANT¹¹⁸ program. The FSTU/SD method involves stochastic reinitialization of the density matrix based on exponential decay of coherence.

One can also add EDC-type decoherence to FSTU, yielding FSTU-EDC, which is in SHARC-MN.

4.4.3. Comparison of Methods. Important differences between CSDM and decoherence-adapted TSH include the following:

- (1) CSDM involves consistent nuclear and electronic EOMs, and therefore it does not suffer the frustrated hop problem; in fact, there are no hops, and the momentum changes continuously.
- (2) Because CSDM is based on the semiclassical Ehrenfest approximation, it is robust on the choice of representation, i.e., CSDM results do not depend significantly on the electronic representation involved, and therefore one can obtain similar results when the trajectory is propagated in adiabatic, diabatic, or other representations. However, unlike the semiclassical Ehrenfest approximation, each CSDM trajectory yields a unit probability for producing a pure state if the trajectory proceeds to a region where the states are no longer strongly coupled.

We recommend CSDM, tCSDM, or κ CSDM as the preferred methods, but if, for some reason, TSH is chosen, we recommend that one should always add decoherence, and the FSTU-EDC method is recommended, because of its simplicity and broad applicability.

4.5. Decoherence Time. The CSDM, tCSDM, κ CSDM, TSH-EDC, FSTU/SD, and FSTU-EDC methods all involve a decoherence time parameter that governs the exponential decay of coherence as in eq 59. An important difference among methods including decoherence is the formula used for the decoherence time. Note that we label the time parameter as the decoherence time, even when it governs both decoherence and decay of mixing. A more precise name might be algorithmic decoherence time, because, as explained in section 4.4, the decay of mixing algorithm is an algorithmic way to model decoherence with the objective that the ensemble average of the populations agrees well with the expected quantum mechanical result.

Two classes of methods have been used to model the decoherence time for electronically nonadiabatic processes. One class is based on a wave packet derivation with various assumptions, and this usually leads to a result that depends on the forces on the two surfaces, as well as other variables. The other is based on energies and does not involve forces.

4.5.1. Approaches Based on Wave Packets. The key ingredient in deriving a decoherence time is the insight extracted

from eqs 52 and 53. These equations show that coherence decays in a reduced density matrix, because the overlaps of environment wave functions decay. Our derivation starts with the assumption that nuclear wave packets on different potential energy surfaces are frozen Gaussians; then, we compute how fast the overlap integral of the frozen Gaussians will decay.

The early approaches by Bittner and Rossky,¹⁰⁶ Schwartz, Bittner, Prezhdo, and Rossky,¹²⁶ and Prezhdo and Rossky,⁶¹ derived the decoherence time by computing the decay of overlap of two frozen Gaussians that start on two different potential energy surfaces but with the same position and momentum, and their derivations yield a Gaussian shape for the time dependence of the decoherence, where the Gaussian exponent depends on the difference in forces on the two potential energy surfaces and on the temperature. The force on the trajectory on surface *I* is given as

$$\mathbf{F}_I = -\frac{\partial V_I}{\partial \mathbf{R}} \quad (90)$$

This result is not useful for general photochemical simulations, because photochemical processes are not usually described by a temperature. Furthermore, wave packets on different potential energy surfaces have different momenta (except when the system passes through an intersection where the surfaces are degenerate); therefore, the assumption that the two wave packets start with the same momentum is wrong. The wave packets will get out of phase not only because of different forces on the two surfaces but also because of different initial momenta. Neglecting the difference of initial momenta may be appropriate when considering the full ensemble of trajectories; therefore, it is possible that it might be appropriate in some methods to approximate decoherence time. However, we want to emphasize that, here, we are interested in decay of mixing time, which is an algorithmic replacement for decoherence time, and only the final population distribution of the full ensemble is physically meaningful. Decay of mixing time is employed as a simulation tool for individual trajectories.

The analytic decay derived by analytically computing the overlaps of nuclear frozen Gaussian wave packets with the assumption of neglecting the difference in initial momenta follows a Gaussian law, but this should not be confused with the Gaussian-law decay discussed in subsection 2.9 that arises from the spreading of spectral density.

Note that when the decoherence is Gaussian, the initial decay is quadratic in time, which differs from the linear time dependence anticipated at the end of Section 2. We will see in the following that allowing the initial momenta to be different gives an exponential (which has a linear term). Hence, the equal-initial-momenta assumption loses the leading term in the decay.

A derivation that (i) incorporates more of the physics by releasing the constraint that the initial momenta of the frozen Gaussians are the same and (ii) is not limited to systems described by a temperature yields an exponential decay of coherence.¹²⁷ The derivation was performed for systems with only one nuclear degree of freedom, and it yields

$$\tau_{IK} = \left(k_{IK}^{\Delta F} + \sqrt{(k_{IK}^{\Delta P})^2 + (k_{IK}^{\Delta F})^2} \right)^{-1} \quad (91)$$

where

$$k_{IK}^{\Delta F} = \frac{\pi(F_I - F_K)}{P_I + P_K} \quad (92)$$

$$(k_{IK}^{\Delta P})^2 = \frac{(\dot{R}_I - \dot{R}_K)(P_I - P_K)|V_I - V_K|}{4\hbar^2\pi^2} \quad (93)$$

where \dot{R}_I and P_I are velocity and momentum of the nuclear wave packet on the I th potential energy surface (associated with the I th electronic state). For applications, one needs a multidimensional generalization of this formula. Then, the decoherence time may depend on $P_{I,\eta}$, $F_{I,\eta}$, $\dot{R}_{I,\eta}$ and $R_{I,\eta}$ which are the η th components of momentum, force, velocity, and position (where η is the index of the nuclear degrees of freedom of the primary subsystem) of the nuclear wave packet on the I th potential energy surface (associated with the I th electronic state). In practice, since semiclassical nonadiabatic trajectory calculations involve a single trajectory, one does not know what velocities and momenta the nuclear wave packets have on different surfaces, and this gives some flexibility in the generalization. For example, the difference in momentum on two surfaces may be approximated as in a surface hop.¹²³ Depending on the system and initial conditions of the trajectories, either the force-change term or the momentum-change term may dominate.

A similar approach to the above wave packet derivation is the overlap decoherence correction of Granucci, Persico, and Zocante.¹²⁸ These authors explicitly compute the overlap matrix in real time by spawning frozen Gaussians to different states (although they propagate these spawned Gaussians in an approximated way).¹²⁸

Subotnik and Shenvi also proposed a way to estimate the decoherence time based on explicitly modeling the decoherence of wave packets; in their case, this was accomplished by propagating additional variables along with the trajectories.¹²⁹

To cut down on the expense, a simplified version was proposed,¹³⁰ and it has also been used by Plasser et al.¹³¹

Some models in the literature assume that there is no decoherence on parallel surfaces, but that neglects decoherence due to wave packets getting out of overlap (see eqs 52 and 53), because they have different momenta. Therefore, we recommend that such models should not be used.

4.5.2. Energy-Based Decoherence. The second class of formulas for the decoherence time is based on energies without involving forces. Although not derived from wave packets, these energy-based decoherence time formulas have been used in several successful applications, and they are probably more widely used than the wave packet-derived formulas. The first such formula was developed as an ingredient in the natural decay of mixing (NDM) method:⁹⁹

$$\tau_{IK}^{\text{NDM}} = \left| \frac{\hbar}{V_I - V_K} \frac{E}{T_{\text{vib}}} \right| \quad (94)$$

where T_{vib} is vibrational kinetic energy, and E is the total energy of the system, i.e., nuclear kinetic energy plus relative potential energy. The motivation was as follows:⁹⁹

“Wave packets in degenerate electronic states will not separate in space, and therefore no decoherence will occur; the relaxation time is infinite. The relaxation time should also become infinite if the internal vibrational energy becomes zero, since it is the relative movement of the particles through space that causes decoherence. We note that in the absence of Coriolis coupling, which vanishes for zero total angular momentum and which is often small even when it does not vanish, rotation of the system as a whole does not result in decoherence; hence T_{vib} is used instead of the total kinetic energy, T ”.

In the later versions of the decay of mixing methods, eq 94 was modified.^{111,112,114} In the SCDM method, we used

$$\tau_{IK}^{\text{SCDM}} = C \left(\frac{\hbar}{V_I - V_K} + \frac{\hbar}{4T_{\text{vib}}} \right) \quad (95)$$

where C is a user-defined parameter. We considered the first term (with $C = 1$) to be a physical lower limit for the decoherence time. This term also ensures that the decoherence time is large when the system is in a region where the electronic states are strongly coupled, so that passage through such a region is reasonably coherent. The second term makes the decoherence time tend to ∞ as the speed of internuclear motions decreases toward zero, which is reasonable, since it is the internuclear motion that is causing the decoherence. The constant C is assumed to be greater than or equal to 1, which allows the system to be more coherent during passages through strong coupling regions. Empirically, it was found that C values in the range of 6–9 worked best, although in the adiabatic representation, the accuracy was only slightly dependent on C .

In the CSDM method, we again enforced $\hbar/(V_I - V_K)$ as the shortest possible decoherence time, and we also required that decay of mixing cannot occur when the momentum in the direction that couples electronic and nuclear motion is insufficient to support the required accompanying energy transfer. These considerations yielded

$$\tau_{IK}^{\text{CSDM}} = \frac{\hbar}{V_I - V_K} \left(1 + \frac{E_0}{T_{\text{DM}}} \right) \quad (96)$$

where E_0 is 1 hartree ≈ 27.2 eV, and

$$T_{\text{DM}} = \sum_{\eta} \frac{(P_{\eta} \cdot \hat{s}_{IK,\eta})^2}{2M_{\eta}} \quad (97)$$

where P_{η} is the η th component of nuclear momentum, $\hat{s}_{IK,\eta}$ is the η th component of the decoherence direction, and M_{η} is the atomic mass corresponding to the η th component of the nuclear degrees of freedom.

A similar formula was used by Granucci and Persico¹²² for TSH-EDC:

$$\tau_{IK}^{\text{EDC}} = \frac{\hbar}{V_I - V_K} \left(1 + \frac{C}{T} \right) \quad (98)$$

where T is the full kinetic energy, and C is a parameter, usually set as 0.1 hartree ≈ 2.72 eV.

Although the formulas for the wave packet-based decoherence time and the energy-based decoherence time look very different, some studies have shown that they can yield similar results, because one can change the parameters in eqs 94–98.^{128,132}

5. CONCLUDING REMARKS

In this Perspective, we have pedagogically introduced the theoretical concepts that are essential to understand decoherence in electronically nonadiabatic molecular events. Specifically, we emphasize that the reduced density matrix of a subsystem will evolve according to a nonunitary Liouville–von Neumann (LvN) equation, even if the full density matrix of the combined subsystem and environment remains pure. Therefore, it is incorrect to describe the evolution of a subsystem by the time-dependent Schrödinger equation. When governed by a nonunitary LvN equation, the off-diagonal elements of the

subsystem reduced density matrix decay to zero. This is the central fact of decoherence, and this decay of coherence is caused by the decay of the overlaps of environmental states. The parameter controlling the time scale of this decay is called the “decoherence time”.

Decoherence is essential in understanding the propagation of the electronic reduced density matrix in chemical and physical systems, not just in a condensed phase due to the solvent but even in a small molecule in the gas phase, where the electronic subsystem is decohered by the nuclei, which act as an environment. The continuous monitoring of electrons by the nuclei causes decoherence of the reduced electronic density matrix.

Simulations of the decoherence effect in nonadiabatic dynamics are achieved by a combination of a decay-of-mixing algorithm and an ensemble average over initial conditions. We recommend an approach called “coherent switching with decay of mixing” (CSDM). Finally, we discuss the methods used to approximate the decoherence time.

■ APPENDIX

Classical Coherence

Note that “coherence” is a word with multiple meanings. In the present article, we are discussing quantum mechanical coherence, but the reader should be aware that the literature is replete with discussions of classical coherence, which is a different phenomenon, as discussed elsewhere.^{133–136} An example of classical coherence is a classical harmonic oscillator that continues oscillating with a given amplitude and given frequency because it is not interacting with an environment that damps (one might say “decoheres”, although that word is not usually used in a classical context) the oscillations.

Classical Entanglement

A warning about a second possible source of confusion may also be useful. A commonly used example of quantum entanglement is the dissociation of singlet H_2 . If we let the two hydrogen atoms (A and B) continue to separate, they will eventually be a mile apart. Before we do a measurement, the probability that the spin of B is up is 50%, and the probability that it is down is also 50%. If we now measure the spin of A and find that it is up, this measurement event immediately changes the probability that the spin of faraway B is “down” to 100%; that is because subsystems A and B are entangled in the total wave function of singlet AB. If we regard the wave function as expressing our knowledge of the probabilities of observing various results upon measurements of a system (a point of view espoused in the discussion in Section 2 of Born’s interpretation of the wave function), this change in our knowledge of the probability of measurements on B may be considered to be a change in the wave function of B. Now consider a situation that we might call classical entanglement.¹⁵ We have a black marble and a white one. We give Jack and Jill closed containers that each contain one marble, but we do it in an uncontrolled fashion with our eyes closed so we do not know who has the black marble. Jack and Jill now walk a mile in opposite directions. The probability that Jill has the black marble is 50%. But Jack now opens his container and finds the black marble. This measurement (witnessing event, monitoring event) immediately changes the probability that faraway Jill has a white marble to 100%. This classical entanglement should not be confused with quantum entanglement.

■ AUTHOR INFORMATION

Corresponding Author

Donald G. Truhlar – Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States; orcid.org/0000-0002-7742-7294; Phone: 612-624-7555; Email: truhlar@umn.edu

Author

Yinan Shu – Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States; orcid.org/0000-0002-8371-0221

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.jctc.2c00988>

Notes

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