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Cite as: J. Chem. Phys. 137, 22A545 (2012); https://doi.org/10.1063/1.4757100
Submitted: 08 June 2012 . Accepted: 19 September 2012 . Published Online: 15 October 2012

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Decoherence-induced surface hopping

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(Received 8 June 2012; accepted 19 September 2012; published online 15 October 2012)

A simple surface hopping method for nonadiabatic molecular dynamics is developed. The method derives from a stochastic modeling of the time-dependent Schrödinger and master equations for open systems and accounts simultaneously for quantum mechanical branching in the otherwise classical (nuclear) degrees of freedom and loss of coherence within the quantum (electronic) subsystem due to coupling to nuclei. Electronic dynamics in the Hilbert space takes the form of a unitary evolution, intermittent with stochastic decoherence events that are manifested as a localization toward (adiabatic) basis states. Classical particles evolve along a single potential energy surface and can switch surfaces only at the decoherence events. Thus, decoherence provides physical justification of surface hopping, obviating the need for ad hoc surface hopping rules. The method is tested with model problems, showing good agreement with the exact quantum mechanical results and providing an improvement over the most popular surface hopping technique. The method is implemented within real-time time-dependent density functional theory formulated in the Kohn-Sham representation and is applied to carbon nanotubes and graphene nanoribbons. The calculated time scales of non-radiative quenching of luminescence in these systems agree with the experimental data and earlier calculations.

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I. INTRODUCTION

Mixed quantum-classical methodologies provide an intuitive approach to real-time dynamic simulations of physical and chemical processes in condensed phases.1 Quantum-classical simulations of solution chemistry,2–4 surface chemistry,5–9 and excitons in polymers10 and nano-sized structures11–13 prove valuable toward understanding quantum systems in a macroscopic environment. Classical equations of motion are applied to a large number of degrees of freedom, avoiding intractable quantum mechanical basis set calculations. Dynamics of a small quantum subsystem can be treated utilizing a reduced description of the total system. Quantum-classical models are widely used despite fundamental obstacles in the interaction between quantum and classical regimes.14, 15 The Ehrenfest method16–18 approximates quantum-classical coupling through expectation values of quantum variables. An improved treatment of the quantum-classical interaction introduces the quantum backreaction through a distribution of classical variables individually correlated to quantum basis states.19 Renowned surface hopping methods20, 21 stochastically sample the dynamic evolution of this quasi-classical distribution. As the system size grows, however, the quantum subsystem responds with increasing measure to subtle quantum effects in the classically treated degrees of freedom.

A quantum mechanical wave packet of the total system, accounting for all quantum effects of the bath, splits into uncorrelated branches and loses coherence over time. The resulting decoherence can be viewed as an environment-induced destruction of superpositioned quantum states of the microscopic system.22, 21 In more detail, the microscopic system evolves quantum mechanically as a superposition of fluctuating system states in contact with a bath. Concomitantly, through the quantum backreaction, the macroscopic bath follows an array of (non-classical) trajectories associated with individual components of the quantum state. Divergence among the bath trajectories leads to a loss of phase relationship among the states of the total system. When the divergence is slow relative to transitions within the quantum subsystem, standard quantum-classical approaches model dynamic evolution quite well. However, when the opposite is true and the divergence is fast relative to the rates of transitions, quantum-classical approaches must be corrected for decoherence. Coherence loss is facilitated by a lack of phase-space structure,24 and furthermore, becomes an irreversible phenomenon in systems with many degrees of freedom. Modeling the dynamic evolution of condensed phase systems requires a theoretical account of decoherence as either an inherent quantum effect of the bath or a phenomenological consequence of the system-bath interaction.

The importance of decoherence in condensed-phase chemical reactions has long been appreciated.25, 26 Reaction rates carry an explicit dependence on decoherence.27, 28 The environment acts as a source of friction that damps nonadiabatic effects and, accordingly, reaction probabilities. Mini-
decoherence.\textsuperscript{40-42} In quantum dots, nano-wires, and nanotubes, exciton dephasing\textsuperscript{43-45} is pervasive as the wave packet evolves nonadiabatically throughout a large number of quantum states.

Modifications of quantum-classical surface hopping approaches treat the effect of decoherence on the evolution of the quantum subsystem. Decoherence corrections have been designed and applied to electronic\textsuperscript{,46} and vibrational\textsuperscript{47,48} excited state dynamics. Interestingly, inclusion of decoherence strengthens the quantum-classical correspondence, and, in the context of trajectory surface hopping simulations, is most readily seen as an increase in the internal stability.\textsuperscript{49,50} Many decoherence-corrected approaches utilize information about the excited state potential surfaces to estimate the effect of trajectory divergence on the transition probability.\textsuperscript{51} A computationally simple approach assumes the classical environment establishes an open system in which diffusive, coherence-destroying, dynamics can be described by Markovian evolution.\textsuperscript{52} Combining wave packet collapse with the time-dependent Schrödinger equation (TDSE) provides a complete description of electron dynamics subject to quantum decoherence. Previous work on the stochastic Schrödinger equation along a mean-field trajectory\textsuperscript{53} sets the stage for the current work, in which decoherence induces stochastic surface hopping.

Decoherence-induced surface hopping (DISH) relies on a simple picture of quantum state diffusion, that is applicable to large, condensed-phase systems. The system-bath interaction is treated within a semiclassical approximation, and appears in both the dynamics of the quantum system coupled to an explicit classical bath and the model for decoherence. Theoretical background on the TDSE, dissipative dynamics with explicit connections to DISH, and electronic dephasing is presented in Sec. II. Section III contains the DISH algorithm, and Sec. IV offers an analysis of the method with regard to established effectiveness criteria.\textsuperscript{21} Next, DISH is tested with model problems and compared to the exact quantum mechanical solutions and fewest switches surface hopping (FSSH). Finally, DISH is implemented within time-domain density functional theory in the Kohn-Sham representation and is applied to electron-phonon relaxation in carbon nanotubes (CNT) and graphene nanoribbons (GNR). The latter calculations are compared to available experimental data and results obtained with decoherence-corrected fewest FSSH.

II. THEORETICAL BACKGROUND

The quantum-classical approximation alleviates computational requirements on the evaluation of the TDSE by eliminating terms in the Hamiltonian associated with nuclear degrees of freedom and introducing a convenient dependence on classical nuclear trajectories. Nuclei evolve according to the classical equations of motion,

\begin{equation}
\mathbf{M}\dot{\mathbf{R}}(t) = -\nabla_{\mathbf{R}} V_{\text{e}}(\mathbf{R}(t)) + \mathbf{F}_{\text{Q}}(t),
\end{equation}

where \(\mathbf{M}\) is a diagonal matrix of individual particle masses, \(V_{\text{e}}\) is the interaction potential between classical particles, and \(\mathbf{F}_{\text{Q}}\) is the quantum force. Classical paths of the nuclei, \(\mathbf{R}(t)\), are determined through the quantum force, which can be computed as an adiabatic Hellmann-Feynman force or a mean-field force.\textsuperscript{54,55} Alternatively, the Pechukas method\textsuperscript{56} offers a self-consistent solution for the nuclear path under the influence of quantum transitions. As coherences are quenched, quantum transition probabilities approach zero, and the “best” classical path is determined by the Hellmann-Feynman force associated with a single adiabatic state. Environment-induced decoherence leads to a conceptually and computationally simple procedure for switching potential energy surfaces.

Introducing decoherence at the microscopic level for condensed phases can be achieved by an approximate solution to the Nakajima-Zwanzig generalized quantum master equation,\textsuperscript{57-62} quantum correction factors to classical reaction rates,\textsuperscript{63-65} numerical formulations of path integral methods,\textsuperscript{66-68} or phenomenological equations of motion for the reduced density matrix.\textsuperscript{69-72} Phenomenological approaches aim to generate quantum Langevin-like dynamics, in which the dynamics become dissipative due to a “friction” generated by quantum fluctuations in the environment. We follow a distinct, yet parallel, procedure toward modeling decoherence by applying a dissipative extension to the TDSE. Drawing from the methodology of stochastic Schrödinger and master equations,\textsuperscript{73-78} solutions to the modified equations of motion are found through a computationally efficient, “quantum-jump” procedure. Hence, decoherence results in surface hopping, and, in DISH, quantum transitions only occur at the time of decoherence.

The primary task is to employ a time-evolution operator that evolves the initial electronic state according to interactions between the electronic subsystem and nuclear bath,

\begin{equation}
|\Psi(t)\rangle = \hat{U}(t, t_{0})|\Psi(t_{0})\rangle,
\end{equation}

\begin{equation}
\hat{U}(t, t_{0}) = \prod_{\alpha} \left[ \hat{L}_{\alpha}(t) \right] \hat{U}(t, t_{0}).
\end{equation}

The unitary part, \(\hat{U}(t, t_{0})\), of the evolution operator results from solving the TDSE, generating a coherent superposition of quantum states. The \(L\) operator introduces a stochastic localization of the quantum state, destroying coherences and ultimately damping the dynamics. Adiabatic states serve as both a representation for the TDSE as well as a localization basis. Our treatment of decoherence extends the TDSE through a stochastic adaptation of the time-evolution operator for quantum systems coupled to an environment, \(\hat{U}\), and provides a mechanism for surface hopping that models diverging evolutions of the environment.

A. Time-dependent Schrödinger equation

Applying the unitary part of the time-evolution operator, \(\hat{U}(t, t_{0})\), is equivalent to solving the TDSE,

\begin{equation}
i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, \mathbf{R}, t) = \hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R}(t))\psi(\mathbf{r}, \mathbf{R}, t),
\end{equation}

where \(\hat{H}_{\text{el}}\) is the electronic Hamiltonian,

\begin{equation}
\hat{H}_{\text{el}} = -\frac{\hbar^{2}}{2} \sum_{i} \frac{1}{m_{i}} \nabla_{i}^{2} + V(\mathbf{r}, \mathbf{R}(t)).
\end{equation}
prize the time-dependent quantum state vector. Equivalently, the Schrödinger time-evolution operator, $\hat{U}(t, t_0)$, when applied to the quantum state vector at $t = t_0$, generates a coherent superposition of the adiabatic basis states. In Subsection II B, we define an operator, $\hat{L}$, that extends $\hat{U}(t, t_0)$ in order to incorporate quantum decoherence into the dynamics.

### B. Quantum dissipative dynamics

Quantum dissipation can be described by a number of different schemes.\cite{Jaeger2012} We follow most closely the approach associated with the stochastic Schrödinger equation and related quantum-jump procedures.\cite{DiStasio2014,Popescu2015,Popescu2016} The quantum jumps in the electronic subsystem due to interaction with the nuclei is the source of surface hopping in DISH. The idea of using quantum dissipation in order to achieve surface hopping was originally proposed in Ref. 53 in the context of the stochastic Schrödinger equation.

The form of the $\hat{L}_\alpha(t)$ operators in Eq. (3) follows from the quantum mechanics with spontaneous localization (QMSL)\cite{Zurek1981,Popescu2016} model of environment-induced decoherence. Similar to Lindblad theory,\cite{Lindblad1975} the QMSL model applies to the Born-Markov limit of condensed phase dynamics, which is characterized by weak system-bath coupling and memory-independent processes. In a Markovian environment, we assume that the time-dependent wave function spontaneously localizes under the influence of the decoherence operators, $\hat{L}_\alpha(t)$.

$$|\psi_{\text{red}}(r, t)\rangle = \hat{L}_\alpha(t) |\psi(r, t)\rangle.$$  \hspace{1cm} (9)

Upon localization, a reduced state vector, $|\psi_{\text{red}}(r, t)\rangle$, is generated. $\hat{L}_\alpha(t)$ is a nonlinear, norm-conserving operator, which depends on the specific times, $\tau_\alpha$, at which the adiabatic basis state, $\phi_\alpha(r, R)$, decoheres from the electronic wave packet. Stochastic application of the operator, $\hat{L}_\alpha(t)$, bypasses the need for mixed-state densities in the equations of motion for dynamic systems undergoing decoherence\cite{Zurek1981} and introduces decoherence effects directly at the level of the wave function.

Similar to QMSL, stochastic Schrödinger equations describe the evolution of pure quantum states subject to dissipation induced by a quantum environment. A probability is associated with each resulting, reduced state vector, $|\psi_{\text{red}}(r, t)\rangle^2$, such that the ensemble average over many realizations recovers the reduced density matrix. A stochastic Schrödinger equation can be expressed using the stochastic Itô calculus as

$$d|\psi(z(t))\rangle = [-iHdt + \hat{\mathbf{L}} \cdot d\mathbf{z}]|\psi(z(t))\rangle.$$ \hspace{1cm} (10)

It contains a deterministic element, $-iHdt$ that evolves the quantum subsystem subjected to the classical fields generated by the environment and a randomized element, $\hat{\mathbf{L}} \cdot d\mathbf{z}$, that depends on specific realizations of the Wiener process, $\mathbf{z}(t)$, reflecting the influence of quantum fluctuations in the environment. Ensuring that the probability distribution generated by $\mathbf{z}(t)$ reproduces quantum mechanical norms requires additional modification to Eq. (10).\cite{Jaeger2012} DISH utilizes a numerical surface hopping procedure, in which each realization, $\psi(z(t))$, is renormalized following state reduction. With proper normalization, the “raw” processes (Eq. (10)) are representative of a mixed-state density matrix, and reduction, or
localization, of the state vector becomes synonymous with decoherence and provides a physical mechanism for surface hopping.

The stochastic differential equation (10) is one route toward unraveling the Lindblad master equation for the reduced density matrix of the electronic subsystem. It is unique, if the evolution of the wave function is required to be continuous. If the continuity requirement is not imposed, a family of stochastic processes can be generated that produce identical ensemble averaged results. An equation describing discontinuous processes is the ordinary TDSE, whose solution is given by the projection operators, \( \langle \phi_\alpha | \langle \psi_1 | \rangle \sum_{i \neq \alpha} c_i(t) | c_i(t) \rangle r_{ai} \). The stochastic mean-field approximation developed earlier uses the stochastic Schrödinger equation (10) directly. The DISH approach formulated here is as a discontinuous jump process, leading to a more typical surface hopping, in which deterministic nuclear trajectories associated with electronic basis states are interrupted by occasional stochastic events.

The Markovian approximation involved in QMSL and Lindblad theory can be lifted by using generalized Lindblad master equations and their stochastic wave function unraveling. Highly non-Markovian quantum dynamics can be achieved by considering several parallel random processes for the wave function.

The process of localization depends on the amount of time each adiabatic basis state remains part of the coherent superposition, or the decoherence interval for each state. Following the QMSL methodology, environment-induced localization is coarse-grained in time along the coherence intervals. The DISH algorithm defines coherence intervals by either the decoherence time, \( \tau_\alpha \), or a Poisson process with the characteristic time \( \tau_\alpha \). The decoherence times for each component state depend on the Schrödinger evolution of the quantum state and are given by the following equation:

\[
\frac{1}{\tau_\alpha}(t) = \sum_{i \neq \alpha} | c_i(t) |^2 r_{ai}. \tag{11}
\]

Here, the sum is computed over all adiabatic states except the state under consideration. The coefficients, \( c_i(t) \), are found by solving the quantum-classical TDSE (Eq. (7)). Decoherence rates for each pair of states, \( r_{ai} \), can be determined by a number of methods discussed in Subsection II C. This expression applies to a multi-state system and is directly related to Eq. (2.29) of Ref. 82. Thus, our multi-state definition of decoherence time corresponds closely to one of the most standard models of decoherence. In DISH, each state can decohere from the rest of the wave function on the time scale determined by Eq. (11). Any pair of states can lose coherence due to interaction with the environment, and therefore, the decoherence rate for each pair of states should be determined. As shown in the Appendix, the decoherence time of a two-state system becomes the inverse of the decoherence rate, \( r_{ai} \). As a result of Eq. (11), wave functions that are localized have longer coherence intervals than wave functions delocalized over a large number of basis states, coinciding with the physical intuition that stronger delocalization results in faster decoherence. Equation (11) also demonstrates that the stochastic or diffusive nature of the quantum coefficients vanishes as the wave function approaches the adiabatic eigenstates, \( \tau_\alpha \to \infty \) as \( c_{ai} \to 1 \), and, accordingly, dissipative dynamics can be described as irreversible localization in the Hilbert space.

A distribution of decoherence events sets the framework for dynamic reduction of the wave function in DISH. At each decoherence event, the wave function reduces according to one of two projections. With the probability of \( | c_{ai} |^2 \), the wave function is projected onto the decohering state, \( \phi_\alpha \). Alternatively, the decohering state is projected out. At the time of a decoherence event, \( \hat{L}_\alpha(t) \) takes on the form of the corresponding projection operators,

\[
\hat{L}_\alpha(t) = \begin{cases} \frac{1}{N}(\hat{P}_\alpha) & \xi \leq |c_{ai}|^2, \\ \frac{1}{1-\xi}(\hat{I} - \hat{P}_\alpha) & \xi > |c_{ai}|^2. \end{cases} \tag{12}
\]

\[ P_\alpha = |\phi_\alpha \rangle \langle \phi_\alpha | \] is the projection operator, and \( (\hat{I} - \hat{P}_\alpha) \) is its complement. \( \xi \) is a random number between 0 and 1. The normalization constant, \( N \), is \( |c_{ai}|^2 \). The stochastic treatment of coherence loss defined by Eqs. (11) and (12) is a form of surface hopping, in which surface hops coincide with decoherence events.

Decoherence, and hence surface hopping, can occur for any basis state and are not limited by the particular surface on which the nuclei are propagating. This unique feature of DISH arises from the fact that environment-induced decoherence affects the entire quantum wave packet. However, surface hops are still regulated by quantum probabilities, and, as a result, Eq. (12) generates low probabilities for surface hops between weakly coupled surfaces.

Designation of the possible outcomes follows from measurement theory, where the measuring apparatus is the environment. The system-environment interaction projects the quantum subsystem onto the eigenstates of the interaction operator, \( \hat{L} \). At the decoherence time, the environment “detects” either a quantum state that has localized to the decohering state or a quantum state in which the decohering state is absent. Equivalently, progression of the wave function through the coherence intervals of each adiabatic basis state generates coarse-grained quantum probabilities that reflect quantum evolution in the presence of decoherence.

C. Electronic dephasing and quantum decoherence

Quantum decoherence can be succinctly described by the decay of the overlap function,

\[
J_{ij}(t) = \langle \Psi_i(t) | \Psi_j(t) \rangle . \tag{13}
\]

\( \Psi(t) \) is a wave function for the total system, and \( J_{ij}(t) \) represents an off-diagonal element of the total density matrix. The decay rate of the norm of \( J(t) \) gives the rate of coherence loss. Determination of the overlap function typically involves semiclassical approximations, in which coherence information can be extracted from classical trajectory simulations. In these scenarios, \( J_{ij} \) is associated with the bath contribution to an off-diagonal matrix element of the reduced density matrix of the electronic subsystem. In the following, a number of approaches to the computation of dephasing rates are presented. Any one of these formulas may be applied to the DISH algorithm. The DISH simulation can be performed with
the dephasing rates between all pairs of states determined \textit{a priori} or evaluated on-the-fly in conjunction with the DISH simulation.

\( J(t) \) plays the role of the response function in nonlinear optical spectroscopy, and the decay of \( J(t) \) provides a measure of the pure dephasing contribution to the single particle spectral linewidths resulting from interactions between quantum system and the environment. The response function can be determined from quantum-classical simulations and can be expressed by the following:

\[
J_{ij}(t) \approx \langle J_{ij}(\mathbf{R}(t)) \rangle_T = \exp(i \omega_{ij} t) \left( \exp \left[ -\frac{i}{\hbar} \int_0^t \Delta E_{ij}(\tau) \, d\tau \right] \right)_T.
\]

(Eq. (14))

The average energy difference between the optically coupled states divided by \( \hbar \) is given by \( \omega_{ij} \). \( \Delta E_{ij}(\tau) \) is the energy difference evaluated along a classical trajectory, and \( \langle \ldots \rangle_T \) indicates canonical averaging. The optical response function describes the dissolution of photo-induced superpositions of electronic levels (coherences) due to interactions with a disordered environment, providing a quantitative measure of electronic dephasing.

The canonical averaging in the above expression can be approximated with a second-order cumulant expansion\textsuperscript{84, 85} resulting in

\[
\langle J_{ij}(\mathbf{R}(t)) \rangle_T \approx \exp \left[ -\frac{\langle \delta U(t)^2 \rangle_T}{\hbar^2} \int_0^t dt_1 \int_0^{t_1} dt_2 \tau_1 C(\tau_1) \right].
\]

(Eq. (15))

The energy gap correlation function, \( C(t) \), characterizes the rate of linear response of the environment to electronic transitions and is expressed through the classical distribution of energy fluctuations,

\[
C(t) = \frac{\langle \delta U(t) \cdot \delta U(t_0) \rangle_T}{\langle \delta U(t_0)^2 \rangle_T}.
\]

(Eq. (16))

\( \delta U \) is the deviation of the energy gap from the average value,

\[
\delta U(t) = \Delta E_{ij}(\mathbf{R}(t)) - \langle \Delta E_{ij}(\mathbf{R}(t)) \rangle_T.
\]

(Eq. (17))

Equations (14) and (15) are directly amenable to quantum-classical simulations and describe pure dephasing as a result of classical fluctuations in the environment. Dephasing rates for a pair of states are determined by the time constant of the decay of \( J_{ij}(t) \). These formulas provide an excellent estimate of the time scale for quantum decoherence and can be tested directly against spectral linewidths in single particle experiments when pure dephasing is fast compared to nonadiabatic relaxation processes.

The prototypical view of decoherence as diverging wave packets can be captured by frozen Gaussians in the short-time limit.\textsuperscript{86, 87} Schwartz and co-workers employ the frozen Gaussian approximation to define a quantum decoherence rate attainable by quantum-classical simulations,\textsuperscript{88, 89}

\[
\tau_{ij}^{-2} = \frac{\sum_n \left| \mathbf{F}^n(0) - \mathbf{F}^n_i(0) \right|^2}{4a_n \hbar^2}.
\]

(Eq. (18))

The sum is over nuclear coordinates, \( \mathbf{F}^n(0) - \mathbf{F}^n_i(0) \) is the difference between the Hellmann-Feynman forces associated with the dephering state, \( i \), and the mean-field force, and \( a_n \) is a parameter that depends on the width of the Gaussian associated with a particular nuclear coordinate \( n \). The decoherence time can also be related to the difference between instantaneous quantum forces, using the expression\textsuperscript{40}

\[
\tau_{ij}^{-1} = \sum_n \frac{\left| \mathbf{F}_i(t) - \mathbf{F}_j(t) \right|^2}{2\hbar \sqrt{a_n}}.
\]

(Eq. (19))

Equation (19) provides a rough estimate of the decoherence time by evaluating the difference between forces on diverging classical trajectories, \( \mathbf{F}_i - \mathbf{F}_j \). The Gaussian width parameter for the nuclear coordinate \( n \) is \( a_n \). Within the Gaussian approximation, the decoherence time is proportional to the short-time solvent response. In the high-temperature limit, the decoherence time can then be estimated from \( C(t) \) (Eq. (16)) and experimentally accessible Stokes shifts,\textsuperscript{40}

\[
\left[ \frac{\tau_D}{\tau_e} \right]^2 = \frac{6k_B T}{\lambda}.
\]

(Eq. (20))

\( \tau_D \) is the decoherence time, and \( \tau_e \) is short-time, Gaussian decay component of \( C(t) \). The Stokes shift is \( 2\lambda \) and is measured between the absorption and emission maxima in equilibrium solvent configurations.

The decoherence time employed in the decay of mixing approaches by Truhlar and co-workers\textsuperscript{91, 92} is

\[
\tau_{ij} = \left| \frac{\hbar E}{\Delta E_{ij} T_{\text{ vib}}} \right|.
\]

(Eq. (21))

\( \Delta E_{ij} \) is the potential energy difference associated with states \( i \) and \( j \) in the diabatic representation. \( E \) is the total energy of the system, and \( T_{\text{ vib}} \) is the kinetic energy of the nuclei. Decoherence relies on diverging classical trajectories. If either the diabatic states are degenerate or the nuclei stop moving, the decoherence time becomes infinite.

Treating electronic wave packets as Gaussians, Yang and co-workers developed an expression for the decoherence rate by directly associating electronic momenta with energy differences between adiabatic states;\textsuperscript{46}

\[
\frac{1}{\tau_{ij}} \approx \text{Re} \left[ \alpha_{ij} \Delta x_{ij} \Delta \dot{x}_{ij} \right].
\]

(Eq. (22))

Here, decoherence depends on Gaussian width parameters, \( \alpha_{ij} \), the spatial separation between Gaussians, \( \Delta x_{ij} \), and the rate of separation between Gaussian centers, \( \Delta \dot{x}_{ij} \). Gaussian widths enter the expression through \( \alpha_{ij} = \alpha \alpha_j / (\alpha_i + \alpha_j) \).

In DISH, stochastic reductions in the Hilbert space are a consequence of quantum decoherence. The time scale for decoherence of a given electronic state from the electronic wave packet is determined by the pure dephasing rates between the given state and all other states (Eq. (11)). Each pair-wise dephasing rate is weighted by the electronic population of the complementary state. DISH can employ, and is not limited to any one of the dephasing rates presented here. Specifically, application of DISH to carbon nanotubes and graphene nanoribbons uses the pure dephasing formulas from optical response theory (Eq. (15)) in order to define the decoherence time. One-dimensional model systems made use of a Gaussian approach (Eq. (19)) to estimate pair-wise dephasing.
rates. The decoherence time determined within DISH defines the time at which electronic coherences have dissolved due to interaction with the environment. The physical picture of condensed-phase dynamics generated by DISH is that electronic coherences fade resulting from diverging nuclear trajectories, and quantum jumps reflect the probabilities of observing distinct states associated with diverging pathways.

III. DISH ALGORITHM

The state vector, \([c_1(t), c_2(t), \ldots, c_N(t)]\), comprised of the time-dependent coefficients of the (adiabatic) basis states contains all the dynamic information of the quantum subsystem. \(\hat{L}(t_m)\hat{U}(\Delta t)\) operates directly on the state vector during the simulation. \(\hat{U}(\Delta t)\) continuously evolves the state along the nuclear trajectory according to the TDSE, and \(\hat{L}(t_m)\) stochastically projects the coherent quantum state onto the states comprising the mixed-state density matrix. Evolution of the state vector deviates from traditional quantum-classical methods by application of \(\hat{L}(t_m)\), which induces surface hopping at decoherence events. A block scheme of the DISH method is shown in Figure 1.

1. Set the state vector for \(t = t_0\). The initial state can be defined as the adiabatic state that results from photo-excitation. For example,

\[
\psi(t_0) = \begin{bmatrix} 0 \\ \vdots \\ 1 \end{bmatrix} \tag{23}
\]

sets the initial state to the \(N\)th adiabatic basis state. Alternatively, one can initially evolve the wave function with the TDSE from the ground state while including the interaction with a laser pulse that creates the photo-excitation.

2. Propagate the classical particles on the initial (adiabatic) potential energy surface, Eq. (1). In the case that \(\psi(t_0)\) is a superposition of adiabatic states, the adiabatic surface is chosen according to the quantum mechanical probabilities, \(|c_1|^2\).

3. Integrate the Schrödinger equation (7) to compute the coefficients of the time-evolved state vector, \([|c_1(t_m)|, |c_2(t_m)|, \ldots, |c_N(t_m)|]\). \(t_m\) is the time at the \(n\)th time step within the current coherence interval. The wave function evolves according to

\[
\psi(t_m) = \hat{U}(t_{m-1} + \Delta t; t_{m-1})\psi(t_{m-1}). \tag{24}
\]

Integration over the time step describes coherent evolution. In order to obtain physically meaningful results, the time step cannot be larger than the smallest coherence interval.

4. Evaluate the coherence of each basis state. The decoherence time for state \(\phi_a\) is determined by weighting pure dephasing rates, \(\tau_{\text{adi}}\), by quantum coefficients, given by Eq. (11). Dephasing rates are determined by one of the formulas presented in Sec. II C. They may or may not depend on time, depending on the model chosen to represent the dephasing process. Decoherence times, \(\tau_a(t_m)\), are computed from either \(t_0\) or the time of the previous decoherence event, in which case \(m\) indexes the time steps of the current coherence interval for state \(\phi_a\).

5. Determine if the current time step is within the coherence interval for each basis state. A random number having a Poisson distribution with parameter \(\tau_a(t_m)\) is generated. If the random number is larger than the time since the previous decoherence event, the state vector is reduced. If more than one state undergoes decoherence at the same time step, a random number is generated to select one of the decohered states. Alternatively, one can reduce the time step in order to achieve a better time-resolution of decoherence events.

The following steps are conditional. If one or more of the basis states at the given time step decohere from the evolving quantum state, then the wave function undergoes a stochastic reduction, and the nuclear trajectory can experience a surface hop. If evolution does not result in decoherence, the simulation continues with Schrödinger evolution (step 2).

6. Compute the reduced wave function corresponding to the decoherence of \(\phi_a\). \(\hat{L}_a\) is applied to the state vector (Eq. (12)). A random number with a uniform distribution is compared to the quantum probability of observing adiabatic state \(\phi_a\) at time \(t_m\) given by \(|c_a(t_m)|^2\). If the random number is less than or equal to the quantum probability, then the nuclear trajectory hops to the potential surface of \(\phi_a\), and the wave function is reset to \(\psi(t_m) = \phi_a\). If the random number is greater than \(|c_a(t_m)|^2\), \(\phi_a\) is projected out from the current state vector, the wave function is renormalized, and the simulation continues with step 2. If the projected out state corresponds to the potential energy surface occupied by the nuclear trajectory, the trajectory hops to one of the remaining surfaces.

![FIG. 1. A block scheme of the DISH algorithm.](image-url)
that is chosen according to the probabilities given by the squares of the coefficients for the remaining states.

7. Reset nuclear velocities. The change in electronic energy resulting from the hop is accommodated by the nuclear velocity component that lies in the direction of the nonadiabatic coupling vector at the time of the hop.21,93 Trajectory hops that increase electronic energy are rejected if insufficient nuclear kinetic energy is available. Return to step 2.

IV. DISCUSSION

Nonadiabatic dynamics of large systems involves a non-trivial redistribution of energy between the quantum subsystem and its environment. Energy is exchanged across the system-environment interface and dissipated throughout the many, diverging degrees of freedom of the bath. As a result, the quantum subsystem undergoes decoherence, becoming resolved into macroscopically distinct states that cannot be described by Schrödinger dynamics. In order to capture decoherence, quantum properties of the bath must be taken into account. Unlike quantum Liouvillian approaches94,95 that can simulate dynamics of mixed-state densities resulting from quantum decoherence, DISH builds decoherence effects directly into the wave function. Decoherence effects are realized through stochastic reductions of the quantum subsystem, yielding a surface hopping approach for quantum evolution in condensed-phase systems. Many surface hopping approaches, including FSSH, rely on physically motivated models for hopping probabilities, whereas DISH utilizes standard quantum probabilities, $|c_i|^2$, to predict hopping dynamics. A conceptual advantage of DISH, as compared to FSSH and its decoherence-corrected variants, is that branching appears due to decoherence rather than ad hoc transition probabilities, which have been later corrected for decoherence effects.

A number of surface hopping approaches with decoherence have been developed. Decoherence corrections have been suggested for FSSH.99,96,97 Introducing the Liouville-von Neumann equations, Rossky and co-workers have modified mean field surface hopping98 by damping off-diagonal elements of the reduced density matrix according to the decoherence time scale.89,99 Pioneered by the stochastic mean-field approximation,53 other approaches including coherent switching with decay of mixing,92 mean-field with stochastic decoherence,88,100 and simultaneous-trajectory surface hopping101 induce surface hops through wave function collapse. Similar to the stochastic mean field approach,53 DISH is built upon the standard model of decoherence and system-bath interaction. By evolving classical trajectories in pure states and using the standard quantum mechanical expression to determine surface hopping probabilities, DISH is, arguably, the simplest and most physically justified surface hopping technique that includes decoherence.

A. Internal consistency and detailed balance

For an ensemble of independent surface-hopping trajectories, the fraction of trajectories evolving on a given potential energy surface must equal the quantum probability of observing the associated basis state. Evolving trajectories self-consistently with the quantum state through either a mean-field or Pechukas force56 eliminates the internal consistency issue, since each evolution of the wave function gives a single nuclear trajectory. In these cases, there are no surface hops, and trajectory ensembles are not generated. FSSH benefits from a proof, showing that the surface hopping prescription is consistent with the standard quantum probability rules.21 However, rejecting hops to higher energy electronic states due to insufficient nuclear kinetic energy needed to accommodate the electronic energy gain causes the rift between quantum probabilities and surface hopping statistics.49,93,102 Compared to FSSH, DISH uses the standard quantum mechanical rules to determine hopping probabilities, and therefore, DISH is internally consistent. At the same time, similar to FSSH, DISH uses velocity rescaling and encounters hop rejection that perturbs internal consistency. Additional studies of the internal consistency violation due to hop rejection in DISH are required. One would expect the violation to be smaller in DISH than FSSH, since in DISH the occupied surface is determined at each hopping event directly by the quantum mechanical occupation of the corresponding state, while in FSSH the state occupation and surface hopping probability are connected in a less direct way.

Even though hop rejection violates the principle of internal consistency, it leads to the principle of detailed balance103–105 by making transitions upward in energy less likely than transition downward in energy. Assuming that energy rapidly equilibrates within the classical subsystem, the velocity-rescaling/hop-rejection scheme is equivalent to a Boltzmann factor biasing the probability to hop to a higher energy potential surface.106,107 In the long-time limit, the difference in the rates of transitions upward and downward in energy leads to the Boltzmann distribution of state populations, maintaining the canonical ensemble under the surface hopping dynamics. Note that detailed balance cannot be satisfied in the quantum Zeno regime of infinitely fast decoherence, when quantum transitions cease to occur.40–42 The principle of detailed balance is particularly important for simulation of electron-phonon relaxation processes.13,79,106,108,109

B. Physical observables

In mixed quantum-classical simulations, physical observables are computed over the course of a (nonadiabatic) trajectory to generate time-dependent properties of the quantum system. Both classical phase-space variables and quantum wave functions factor into the computation of physical observables. Classical equations of motion introduce a dependence on initial positions and momenta of the environment, requiring that averages be taken with respect to a set of classical trajectories with distinct initial coordinates. Unlike FSSH, which constructs a distribution of surface hopping populations to represent the quantum density, DISH employs quantum probabilities directly, and expectation values are determined by the wave function rather than a statistical construction. At every time-step, stationary-state observables, $O_i$,
are weighted by DISH coefficients, yielding a quasi-classical expression for time-dependent expectation values,

\[
(\Psi(r; R)|\hat{O}(t)|\Psi(r; R))_T = \frac{1}{N_{\text{traj}}} \sum_{R=1}^{N_{\text{traj}}} \sum_{i} |c_i^R(t)|^2 O_i.
\]  

(25)

The sum over \(N_{\text{traj}}\) builds an average over nuclear trajectories. Coefficients, \(c_i^R(t)\), result from DISHs equation of motion (3) and reflect the distribution of quantum states due to decoherence. Electronic decoherence and trajectory branching are simultaneously ingrained into the computation of observables.

C. Favorable attributes

DISH preserves the sought-after computational facility afforded by traditional surface hopping approaches. DISH requires only a single trajectory for each member of the classical ensemble. In comparison to the stochastic mean field approach, which pioneered the use of decoherence to achieve trajectory branching and employed a mean-field trajectory continuously modified for decoherence effects, DISH trajectories evolve according to Hellmann-Feynman forces due to a coarse-grained account of decoherence. The use of Hellmann-Feynman rather than mean-field forces is particularly advantageous with \textit{ab initio} electronic structure calculations, in which the force evaluation often constitutes the most time consuming step. Similar to FSSH, computation of decoherence-induced transition probabilities does not encumber the simulations. In contrast to FSSH, transition probabilities in DISH are determined by \(|c_i|^2\), according to the standard quantum mechanical prescription.

DISH can be applied to systems in which the dynamics is described by a large number of strongly coupled quantum states and a large number of classical degrees of freedom. Decoherence is treated as an inherent trait of a single adiabatic state, and, consequently, decoherence-induced transitions are pertinent for as long as the adiabatic state carries non-zero population. DISH does not rely on pre-defined regions, in which decoherence interactions are turned either on or off. Regions of extremely high density of states, where the adiabatic representation is questionable, coincides with frequent decoherence events and surface hops, producing a mean-field type of evolution. Because decoherence-induced localization is an irreversible process, DISH results in adiabatic molecular dynamics in the limit of small nonadiabatic coupling.

V. TWO-STATE MODEL SYSTEMS

In systems with many classical degrees of freedom, decoherence occurs rapidly and has a large impact on scattering probabilities. The effects of decoherence, however, can be observed in two-state, one-dimensional systems, in which decoherence events are facilitated by non-parallel surfaces. The dual avoided crossing (DAC) and extended coupling with reflection (ECWR) models\(^\text{21}\) are particularly challenging for mixed quantum-classical approaches due to regions of strong nonadiabatic coupling followed by diverging surfaces. Individual surface hopping in trajectories in FSSH evolve coherently, and the ensemble of FSSH trajectories, collectively, approximates divergence of the wave packet. In DISH, individual trajectories experience decoherence through application of the decoherence operator, \(L\).

In the DAC model system, low energy quantum particles (wave packets) are rigorously 100% transmitted, yet overly coherent approaches introduce finite reflection probabilities. Coherence loss precludes the generation of upper state transients,\(^\text{46}\) which appear as reflected trajectories. With the ECWR potential, the wave packet evolves coherently in the region of strong coupling and, immediately following, branches into non-interacting reflected and transmitted components. DISH accounts for decoherence on a per-trajectory basis, and, consequently, the ensemble of quantum-classical trajectories does not generate artificial reflection probabilities with the DAC potential nor undue interference effects with the ECWR potential. DISH predicts scattering probabilities to greater accuracy than FSSH and does not require ad hoc hopping prescriptions, while maintaining the computational benefit of traditional surface hopping approaches.

In each system, a particle having 2000 a.u. of mass evolves on two coupled potential energy surfaces corresponding to upper and lower quantum states. DISH is compared with FSSH and quantum wave packet propagation. Scattering probabilities from DISH are determined from the squares of the quantum trajectory amplitudes resulting from Eq. (3) averaged over a spread of momenta (Eq. (25)). In both DAC and ECWR, the spread of momenta is defined as \(20/k_0\), corresponding to the width of a Gaussian with \(k_0\) a.u. of momentum. The classical position coordinate is set to \(-10\) bohr and initially evolves on the lower state potential energy surface. The initial quantum state vector is set to the lower state, and the adiabatic representation is employed. Classical equations of motion are integrated using the velocity Verlet algorithm with a time step of 0.1 a.u. The quantum subsystem is propagated numerically using a Trotter expansion of the quantum propagator at every classical time step.

DISH requires the computation of pure dephasing rates either \textit{a priori} or concurrently with the simulation. Pure dephasing rates for DAC and ECWR systems are determined by Eq. (19), which is a concurrent approach. Instantaneous adiabatic forces as well as the width of a diverging Gaussian wave packet contribute to the dephasing rate. The expression for the Gaussian width parameter, \(a_w\), is the same as that used in the approach developed by Schwartz and co-workers.\(^\text{88}\) In total, one phenomenological parameter, \(w\), is employed, and resulting scattering probabilities are shown to be insensitive to modest differences in \(w\).

A. Dual avoided crossing

Quantum potentials and state coupling in the diabatic representation of the DAC model are given by the following:

\[
V_{11}(x) = 0,
\]

\[
V_{22}(x) = -A \exp(-Bx^2) + E,
\]

(26)
\[ V_{12}(x) = V_{21}(x) = C \exp(-Dx^2). \]

The adiabatic potentials are shown in Figure 2, with \( A = 0.10, B = 0.28, C = 0.0015, D = 0.06, \) and \( E = 0.05. \) The width parameter, \( w, \) is understood to be the width of the nonadiabatic coupling region, \( w = 1/\sqrt{D}. \) As the quantum wave packet evolves through the DAC potential, interference between upper and lower states cause Stueckelberg oscillations in the transmission probabilities, and the probability for reflection is zero for quantum particles with \( \log_e(E) > -3. \)

The quantum mechanical interference pattern is reproduced by mixed quantum-classical simulations, including DISH and FSSH, most accurately at high energy (Figure 3). In the top panel of Figure 3, reflection probabilities of DISH are compared to FSSH and the quantum mechanical solution. Quantum results are obtained from solution of the TDSE on a grid. FSSH simulations involve the same integration techniques as described above for DISH. DISH accurately produces the ratio of reflected to transmitted components, and, similar to FSSH, deviates from the quantum interference pattern at low energy. For incident momentum \( k_0 < 14.1 \) a.u., classical trajectories can evolve on the upper surface temporarily but not asymptotically. Deviations between quantum-classical and purely quantum transmission probabilities is attributed to strong quantum mechanical effects stemming from long lived resonance states. DISH shows an improvement over FSSH in the low-energy reflection probabilities. Here, decoherence effectively shuts down quantum transitions resulting in reflection and can be understood as correcting the classical trajectories for quantum effects.

In the DAC model, decoherence events are very rare, and, as a consequence, surface hops do not occur. Figure 4 contains representative DISH trajectories of different initial momentum, \( k_0. \) Only the trajectory with \( k_0 = 2 \) a.u. undergoes a decoherence event, which causes the upper state to be projected out of the state vector. This feature of DISH essentially resets the quantum state such that propagation through avoided crossing are independent processes, yielding equally sized peaks in the transition probabilities centered on the avoided crossings. For trajectories with larger incident momenta, the DISH solution is identical to the TDSE evaluated along the classical coordinates. DISH trajectories do not necessarily hop between upper and lower surfaces but, through quantum probabilities, reproduce the correct branching ratio of upper and lower state transmission. FSSH, on the other hand, provides hopping probabilities that can underestimate transmission on the lower state, Figure 3.
**B. Extended coupling with reflection**

Diabatic potentials and the coupling matrix elements of the ECWR model system are given by

\[
\begin{align*}
V_{11}(x) &= A, \\
V_{22}(x) &= -A, \\
V_{12}(x) &= V_{21}(x) = B \exp(Cx), & x < 0, \\
V_{12}(x) &= V_{21}(x) = B [2 - \exp(-Cx)], & x > 0,
\end{align*}
\]

where \(A = 6 \times 10^{-4}\), \(B = 0.1\), and \(C = 0.9\). Corresponding adiabatic potentials are shown in Figure 2. The width parameter, \(w\), is taken to be \(1/C\) in units of bohr. Strong nonadiabatic coupling extends over a large region (negative \(x\)), abruptly followed by a region, in which upper and lower surfaces are widely separated. Consequently, a wave packet splits (decoheres) into a component that is transmitted on the lower surface and a component that is reflected back onto the pair of quasi-degenerated states at negative \(x\). For energies \(>28\) a.u., part of the wave packet is transmitted on the upper surface.

Unlike the DAC model, which features Stueckelberg oscillations, quantum interference between upper and lower states is absent in the ECWR model, as wave packets readily and permanently diverge. A comparison of reflection probabilities obtained with DISH, FSSH, and the numerical quantum results is given in Figure 5. FSSH reflection probabilities incorrectly exhibit large oscillations, resulting from residual, artificial coherence effects, i.e., surface hops after coherence loss. DISH trajectories that encounter a reflective potential (upper state) subsequently undergo a large number of decoherence events after the quantum state reverses direction and re-enters the region of strong coupling. Each of these decoherence events results in projecting out one of the quasi-degenerate states, hopping is quenched, and DISH probabilities, \(|c(t)|^2\), reproduce the non-oscillating quantum results.

FIG. 4. Representative trajectories from the dual avoided crossing simulation for low incident momentum, 2, 14, and 30 a.u. are shown. Decoherence yields independent transition events, as seen by the two equally sized peaks in the \(k_0 = 2\) a.u. trajectory. At \(k_0 = 14\) a.u. \((\log_{10}(E) = -3)\), DISH underestimates lower state transmission by 10% and is an improvement over FSSH, which underestimates this value by 20%, Figure 3.

With initial momenta greater than \(\sim 28\) a.u., the quantum wave packet has enough energy to overcome the reflective potential and transmit on upper and lower states. In DISH, branching between upper and lower state transmission stems from a single decoherence-induced hop as the surfaces diverge, \(-5.0 < x < 0.0\). Following the hop, surfaces become parallel once again, and states do not mix further. On-average DISH trajectories displayed in Figure 6 show the progression from coherent state to a decohered mixture. For positive \(x\), population is not exchanged between upper and lower states. In order to reproduce the quantum mechanical branching ratio, the singular decoherence event must incur a hop according to quantum probabilities. Hopping probabilities in DISH are precisely quantum probabilities. Testing the dependence of the branching ratio on dephasing rate, Figure 6 displays DISH trajectories for \(w = 0.1, 0.5, 1.0,\) and 10.0. Trajectories for \(w = 0.1\) significantly deviate from the other

FIG. 5. Probability of reflection in the lower state is shown for the extended coupling with reflection model. For momenta \(<28\) a.u., FSSH generates large oscillations in the reflection probabilities due to unphysical interference with the transmitting part of the wave packet. By explicitly treating decoherence in the dynamics, DISH follows the quantum mechanical reflection in this regime.

FIG. 6. Ensemble-averaged DISH trajectories with initial group momentum of 30 a.u. As the surfaces diverge, the branching ratios generated by DISH are entirely dictated by a single decoherence induced hopping event and, for \(w \neq 0.1\), accurately reproduce the quantum mechanical result. For \(w = 0.5\) and greater, transmission probabilities are largely independent of phenomenological parameter, \(w\).
simulations shown. For such narrow $w$, decoherence occurs too rapidly, not allowing quantum transitions probabilities to build up. Longer coherence intervals, from $w = 0.1$ on, reproduce correct quantum mechanical results.

VI. EXCITON DYNAMICS IN CARBON NANOTUBES AND GRAPHENE NANORIBBONS

Carbon nanotubes and GNR exhibit extremely large electron mobilities.\textsuperscript{110, 111} In a photo-excited state, electron transport properties of these nano-materials are affected by diffusive processes, in which exciton energy converts to heat and dissipates. Excitons in semi-conducting GNRs and CNTs annihilate as a result of both radiative and nonradiative decay mechanisms. Radiative processes are competitive in CNTs but not predominant, as demonstrated by low fluorescence yields.\textsuperscript{112-114} The rate of nonradiative relaxation to the ground electronic state in GNRs predicates its unique photophysical properties.\textsuperscript{115-117}

Nonradiative exciton decay is a direct consequence of the exchange of energy between electrons and phonons. The electron-phonon interaction mediates the rate at which excited electrons lose energy to lattice vibrations. Quantum-classical simulations treat phonons, or lattice vibrations, classically, and downward transitions in the quantum subspace coincide with increases in the classical kinetic energy. Application of DISH to exciton annihilation in CNTs and GNRs demonstrates that decoherence is an important contribution for nonradiative processes. Relaxation rates calculated from DISH simulations agree with those determined by experiment and decoherence-corrected FSSH.

The surface hopping simulations employed here, DISH and decoherence-corrected FSSH,\textsuperscript{51, 108} are based on a two-state model for ground state recovery. Two adiabatic states and their nonadiabatic coupling are computed within the time-dependent Kohn-Sham formalism\textsuperscript{79} and represent the ground and first excited states. A standard decoherence correction is applied to FSSH,\textsuperscript{108} in which the wave function is modified by resetting the excited state coefficient in accordance with the pure dephasing rate, which is computed from optical response functions, Eqs. (14) and (15). Employing a two-state model in DISH simplifies the algorithm, such that decoherence events equate to state switching at the pure dephasing time. Details on the two-state limit of DISH are reported in the Appendix. The primary distinction between DISH and decoherence-corrected FSSH is that DISH introduces surface hopping only at decoherence events, while FSSH treats decoherence and surface hopping as two independent processes.

Surface hopping simulations are carried out for three CNTs with (6,4) chirality, including one without atomic defects and two systems with different bond-rearrangement defects (Figure 7). Two (16,16) GNR systems are considered, including one system with the same 7557 bond-insertion defect present in the CNT. The GNR is also displayed in Figure 7. These systems are representative of those investigated by time-resolved spectroscopy under experimental conditions. Monitoring exciton dynamics from DISH in comparison to FSSH for different systems provides a diagnostic on the reliability of DISH.

Investigation of electron-hole recombination in CNTs by photoluminescence spectroscopy gives evidence of a relaxation time scale on the order of 10s of picoseconds to nanoseconds.\textsuperscript{112} Relaxation times of CNTs determined through decoherence-corrected FSSH, are 147 ps, 67 ps, and 42 ps, for the ideal, Stone-Wales, and 7557 systems, respectively.\textsuperscript{108} Figure 8 compares the population recovery in
FIG. 9. Ground state recovery of GNRs from the first excited state takes place within 100 s of ps. (Top) Surface hopping populations of the ground electronic state from decoherence-corrected TDKS-FSSH simulations. (Bottom) Quantum probabilities of the ground state determined by DISH.

the ground state, which determines the exciton annihilation rates, from both FSSH and DISH simulations. DISH results show good agreement with the FSSH data. The DISH relaxation times are determined to be 200 ps, 107 ps, and 22 ps. DISH reproduces the enhancement of nonradiative recombination by atomic defects. Radiative lifetimes of CNTs are 1–2 orders of magnitude larger, and both DISH and FSSH describe relatively fast nonradiative pathways that account for the low photoluminescence yields.\textsuperscript{112–114}

Direct experimental evidence on the exciton dynamics has yet to be attained for substrate free GNRs. Figure 9 displays the interband relaxation of ideal and defect-containing GNRs. Similar to CNTs, nonradiative recombination occurs on a relatively short time scale of 100 s of picoseconds. Decoherence-corrected FSSH results in relaxation times of 309 ps and 124 ps for the ideal and 7557 defect systems, respectively.\textsuperscript{109} Similar to CNTs, defects increase exciton relaxation rates. DISH simulations produce relaxation times of 231 ps and 143 ps, in agreement with decoherence-corrected FSSH. Both DISH and FSSH simulations show that defects open nonradiative decay channels, increasing relaxation rates.

Similar ground state recovery rates between DISH and FSSH indicates that the stochastic DISH trajectory closely follows the dynamics of the decoherence-corrected FSSH ensemble. In the context of DISH formalism, the electronic wave function evolves toward the ground state in the presence of decoherence-inducing interactions with a phonon environment. Stochastic hopping in DISH and decoherence-corrected FSSH are both governed simultaneously by coherences and quantum probabilities, but, only in DISH, are quantum transitions directly related to coherence intervals. Accuracy in the electron-phonon relaxation rates in CNTs and GNRs depends on a number of factors, particularly, decoherence rate.\textsuperscript{108} DISH provides a unified treatment of decoherence and quantum transitions without computational expense beyond standard surface hopping approaches.

VII. CONCLUDING REMARKS

By combining the computational simplicity of quantum-classical nonadiabatic molecular dynamics with a formal treatment of quantum decoherence, DISH provides a straightforward and physically justified trajectory surface hopping scheme, in which transitions between surfaces occur during decoherence events. The transition probabilities and observables are computed according to standard quantum mechanical rules. On one hand, DISH can be viewed as a surface hopping approach to quantum dynamics in dissipative environments. And, in another sense, DISH unifies decoherence and nonadiabatic transitions, providing a non-phenomenological account of quantum transitions in condensed-phases. Evolution of the quantum subsystem in DISH is affected by a series of decoherence events that converts the wave function into a statistical mixture of quantum states, justifiable through the fundamental nature of decoherence and the quantum-classical correspondence.

The importance of decoherence in chemical and physical processes in the condensed phase cannot be understated. A considerable amount of attention has been given to small quantum systems in macroscopic environments. DISH extends the feasibility of quantum-classical simulations to large quantum systems in macroscopic environments. Investigation of charge-transfer through crystals or solutions, exciton dynamics in biological macromolecules, long-range electron transfer, and photo-induced dynamics in condensed phases all require a theoretical approach that can simultaneously treat many quantum degrees of freedom undergoing irreversible, dissipative evolution. As demonstrated with the non-radiative relaxation of CNTs and GNRs, the DISH approach achieves this goal.

ACKNOWLEDGMENTS

Financial support of the National Science Foundation (NSF) Grant No. CHE-1050405 is gratefully acknowledged.

APPENDIX: TWO-STATE LIMIT OF DISH

Consider an arbitrary wave function in a two-state basis at time, \(t\),

\[ \psi(t) = c_i \phi_i + c_f \phi_f. \]  

(A1)

Initial and final states are designated as, \(\phi_i\) and \(\phi_f\), respectively. According to the general equation (11), the decoherence times for initial and final states are determined by the
Because the dephasing rate, $\tau f$, between states $i$ and $f$ is not double counted. The sum of the decoherence rates $1/\tau_i$ and $1/\tau_f$ for states $i$ and $f$ is equal to $\tau_f$. For example, state $i$ decoheres from the superposition at the rate of $1/\tau_i$, state $f$ decoheres from the superposition at the rate of $1/\tau_f$, and overall, the pair of states loses coherence with the rate of $\tau_f$. In the limit that $\xi_2$ approaches 1, $\tau_1$ approaches infinity and $\tau_f$ approaches $\tau_2$, and vice versa. Consequently, decoherence events occur on the time scale determined by the pure dephasing rate, $\tau_f$.

The projection operator acts on the wave function during the decoherence events to isolate the quantum system to an adiabatic state and according to the following a special case of Eq. (12):

$$\hat{L}\psi(t) = \begin{cases} 
\phi_f, & \xi \leq |c_f(t)|^2 \\
\phi_i, & \xi > |c_f(t)|^2
\end{cases}. \quad (A4)$$

Evolution of the quantum system introduces non-zero quantum probabilities for state switching. At every decoherence event, the quantum probabilities are reset to 0 and 1. The transition probabilities for state switching. At every decoherence event, the quantum probabilities are reset to 0 and 1. The state-switching probabilities are large, and the information, the state coefficients deviate significantly from the following expressions:

$$\frac{1}{\tau_i} = |c_f|^2 r_{if}, \quad (A2)$$

$$\frac{1}{\tau_f} = |c_i|^2 r_{if}. \quad (A3)$$

For systems that undergo slow loss of phase coherence, the quantum probabilities are reset to 0 and 1. The tum probabilities for state switching. At every decoherence event, the quantum probabilities are reset to 0 and 1. The state-switching probabilities are large, and the information, the state coefficients deviate significantly from the following expressions:

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