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Simulation of Coherent Nonadiabatic Dynamics Using Classical Trajectories

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In this paper, we describe a trajectory-based implementation of the semiclassical-limit Liouville equation approach to molecular dynamics on multiple electronic surfaces. The formalism is briefly reviewed, and a realization of the general theory in the context of a classical trajectory-based molecular dynamics algorithm is described. The method is applied to a model problem consisting of one-dimensional motion on two coupled electronic surfaces, and the results are compared with coupled-state wave packet calculations. Excellent agreement is obtained, even for the detailed phase space structure of the nonclassical electronic coherences, demonstrating that electronic coherent effects can be included naturally in generalized classical molecular dynamics simulations.

I. Introduction

Chemical reactions occur by the rearrangement of atoms, breaking and remaking bonds to form the final product species from the initial reactant molecules. Whether in isolation in a dilute gas or under the influence of the surrounding solvent in a condensed phase, this chemical transformation is a *dynamical* process involving the mechanical motion of electrons and atomic nuclei. These underlying elementary dynamical steps occur on the ultrafast time scales of molecular translations, vibrations, rotations, and electronic transitions, most conveniently measured in femtoseconds. In this sense, all chemistry is *femtochemistry*.[1−4] Until recently, the details of elementary dynamical processes in chemical systems could only be inferred indirectly from measurements with time resolution many orders of magnitude longer than the intrinsic dynamical time scales. The rapidly advancing field of femtochemistry now allows us to watch chemical reactions unfold in real time.[1−4]

The interpretation of the wealth of detail provided by ultrafast experiments poses fascinating but challenging opportunities for theory. The highly nonequilibrium initial ensembles and subsequent nonlinear nonseparable dynamics induced by ultrafast laser excitation lead to conditions that can violate the limits of validity of the traditional equilibrium statistical mechanical or linear response-based theories of condensed-phase reaction rates and dynamics.[5−7] Direct computer simulation of many-body systems is an increasingly powerful tool for modeling condensed-phase ultrafast dynamics.[8] Still, a fully quantum mechanical treatment of the electronic and nuclear degrees of freedom for a many-body system is an intractable numerical problem and will probably remain so for the foreseeable future. It is thus necessary to turn to simplifying approximations and conceptual models in order for progress to be made.

A variety of approximate methods for simulating many-body chemical dynamics have been developed and applied to a range of physical problems. Some approaches strive to retain a fully quantum mechanical treatment of the atomic motion, at the expense of making rather severe dynamical approximations. An example of this philosophy is found in the array of methods based on the time-dependent mean-field approximation.[9−20] Other methods treat the fully correlated atomic motion without dynamical approximations using classical mechanical trajectories instead of quantum wave packets. This captures the full classical many-body nonlinear dynamics of the system, but at the expense of neglecting quantum effects. Despite the intrinsically quantum nature of molecular systems, classical trajectory integration often works surprisingly well. An illustrative example can be found in our recent work on photodissociation−recombination of I_2 in rare gas solids.[21−25] Here, excellent agreement between experiment and theory was achieved. A fully-correlated classical description of the many-body caging and recombination was essential for modeling the key dynamical processes responsible for the reformation of the I_2 molecule with the large degree of vibrational coherence observed experimentally. In particular, strongly correlated collisions between the atoms of the nascent I_2 and a collective cage oscillation were found to play an essential role in the creation of a localized I_2 phase space ensemble (the classical analogue of a localized wave packet) in a harmonic part of the I_2 potential, building in the long-lasting vibrational coherence.[24] This delicate phase matching of highly nonlinear system and bath oscillations would not be correctly modeled by, for instance, a time-dependent self-consistent field wave packet calculation, where a mean-field separation of these subsystems is performed.

For many problems of physical interest, however, the nuclear and electronic degrees of freedom cannot be uncoupled, and electronic transitions unavoidably accompany the motion of the nuclei. This introduces an intrinsically quantum mechanical feature into the dynamics. Numerous attempts have been made to develop methods that allow the intuitive and computational advantages of classical mechanics to be combined with the possibility of transitions between electronic states. Landau,[26] Zener,[27] and Stuckelberg[28] developed early theories of electronic transitions induced by scattering events described by simple *known* classical trajectories.[29] The classical motion of the nuclei was assumed to be independent of the electronic dynamics in these early studies, which is a good approximation in the limit of high kinetic energy collisions. In general, though, the coupled electronic−nuclear dynamics must be solved simultaneously and self-consistently, and several approaches to this problem have been proposed.[30,31] A significant amount of work has been based on the "mean trajectory approximation". Here, the classical and quantum dynamics are combined by assuming that

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a *single* classical trajectory describes the nuclear motion and evolves in a time-dependent potential given by the instantaneous quantum expectation value of the full potential energy operator. This trajectory, in turn, provides an explicit time dependence to the quantum Hamiltonian operator via its dependence on the nuclear coordinates, and the coupled Schrodinger and Hamilton's equations are solved simultaneously and self-consistently. This dynamical approach forms the basis of a number of methods, including the time-dependent mean field[9−20] and self-consistent eikonal[32] approximations and the classical electron model.[33−39] These methods share the mean trajectory equations of motion but differ in the details of their implementation.

The mean trajectory methods are quite useful for certain types of physical problems. However, they suffer from a fundamental dynamical inconsistency.[40] In asymptotic regions where electronic transitions become negligible, the full dynamics should partition into distinct trajectory ensembles on each populated electronic surface. The mean trajectory method instead leads to a single ensemble, each member of which is evolving on its own weighted average of the quantum state-dependent asymptotic potentials. In certain applications, this is acceptable, while in others, unacceptable nonphysical effects result. The classical electron model avoids this problem by binning the final electronic actions, leading to a well-defined asymptotic electronic state.[33−39] Phenomenological electronic damping is introduced in some implementations[17] in an effort to avoid these undesirable effects.

An alternative approach to coupled-state molecular dynamics that does not suffer from the above inconsistencies is the surface-hopping method, introduced by Tully and Preston[41] and still under active development.[40,42−44] In a surface-hopping calculation, an ensemble of trajectories is propagated using standard classical trajectory integration but with an important modification. At a given instant of time, each trajectory in the ensemble evolves under the influence of a single electronic surface but may undergo a sudden transition, or "hop", between the states, based on a transfer probability and hopping algorithm. A disadvantage of the standard surface-hopping approach is that it treats the electronic dynamics as *incoherent*, ignoring the phase relation between the electronic states. Recent implementations of the surface-hopping method couple a coherently evolving electronic wave function to *each* trajectory in an ensemble. This trajectory is found at every instant on a definite electronic surface but may "hop" at any time between these surfaces.[40,44] The absolute square of the instantaneous quantum-state amplitudes are used as input for the stochastic hopping algorithm. Quantum coherence is thus incorporated into the surface-hopping method *at some level*, but the fundamental justification for the manner in which it is treated is not well-established, and spurious effects, such as *too much* coherence in some cases, can result.[40] Despite this potential drawback, surface hopping has been employed successfully in a broad range of physical applications.

A formal theory of coupled electronic−nuclear dynamics was proposed by Pechukas,[45,46] based on a semiclassical analysis of the full Feynman path integral[47] expression for the electronic−nuclear propagator. Unfortunately, the resulting elegant formalism is difficult to implement in practice, owing to nonlocal time effects: the forces on the classical subsystem in the semiclassical limit depend on the complete time history of the quantum subsystem, which in turn depends on the complete history of the classical motion. Progress has recently been made by Webster et al.[48−50] in implementing the Pechukas formalism in numerical simulations, while Coker and co-workers have clarified the connection between this approach and the surface-hopping method in the limit of short electronic coherence time.[31,44]

In most of these previous attempts at combining classical and quantum elements into one consistent dynamical theory, the probabilistic description of the quantum subsystem in terms of its wave function or density matrix is coupled to a classical description formulated in terms of *independent classical trajectories*, either individually or as part of a final average over an ensemble. A lone classical trajectory does not have a natural quantum analogue, and the coupled trajectory-wave function description used in these methods can lead to significant problems and inconsistencies, as briefly described above.

Recently, we proposed an alternative approach to classical dynamics on coupled electronic surfaces, based on a semiclassical limit of the multistate quantum Liouville equation for the electronic−nuclear dynamics.[51] The resulting formalism yields equations of motion for coupled phase space distribution functions corresponding to both the electronic state-dependent nuclear probability distributions and the electronic coherence between states. These equations of motion have the form of a generalized nonequilibrium statistical mechanics, and the electronic coupling manifests itself as extra terms in the classical Liouville-like equations governing the distributions. These additional terms act as "sources" and "sinks" of probability flow between states and also control the generation, evolution, and decay of electronic coherences. In marked contrast with other approaches that introduce classical mechanics in terms of individual trajectories or classical paths, our formalism is developed from the outset in terms of the coupling between the distribution functions representing populations or coherences themselves. The ability to treat electronic coherences naturally within a classical-like context is a unique advantage of this approach.

In a previous publication,[51] we described in detail the general formalism of our coupled Liouville-like representation of classical molecular dynamics on coupled electronic states. In addition, we provided analytical results in simplifying limits and made comparisons with conventional descriptions of nonadiabatic dynamics, such as Landau−Zener theory.[26,27,29] We also presented a direct numerical solution of the generalized Liouville partial differential equations for a one-dimensional, two-state model system. The results were compared with coupled state wave packet calculations, and excellent agreement was observed, justifying a posteriori the approximations made in the derivation of the semiclassical equations of motion. However, the grid solution of the phase space partial differential equations we presented requires even more numerical effort than the exact quantum approach and, as it stands, does not constitute a practical method for treating many-body coupled-state dynamics. An efficient trajectory-based implementation is desirable, preferably in the form of a relatively minor modification of the standard classical molecular dynamics computer simulation. The challenge of developing such a method is to *use* classical trajectories as a numerical tool to solve equations of motion that are, at a fundamental level, more general than Hamilton's equations for orbits in phase space.

In this paper, we present a trajectory implementation of our coupled-surface semiclassical Liouville approach to nonadiabatic dynamics. Such an implementation is straightforward for dynamics on a *single* electronic surface: In that case, evolution of the phase space distribution function solving Liouville's equation is achieved simply by propagating an ensemble of trajectories sampled from the initial phase space density by the corresponding Hamilton's equations. A generalization of this Hamiltonian trajectory approach is required to incorporate the effect of the nonclassical coupling terms in the Liouville-like equations of motion. We present such a generalization below and compare the results of its application with numerically exact quantum results for a simple but nontrivial one-dimensional two-state model problem. We treat the same model problem as considered in our previous publication,[51] which allows a direct comparison of the accuracy of the trajectory implementation with the phase space grid solution of the underlying semiclassical Liouville-like equations.

The organization of this paper is as follows: In section II, we briefly review the formalism of the coupled-state semiclassical Liouville approach. In section III, we describe the realization of this formalism as a classical trajectory-based molecular dynamics algorithm. Section IV presents the results of applying the method to a model problem and gives a comparison of the trajectory results with the analogous exact quantum quantities. Finally, a discussion is given in section V.

II. Theory

Our theoretical development begins with the exact quantum mechanical Liouville equation for the density operator $\hat{\rho}(t)$, given by[52−54]

$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = [\hat{H}, \hat{\rho}] \tag{1}$$

where $\hat{H}$ is the Hamiltonian of the system and $[\hat{H}, \hat{\rho}]$ denotes the commutator of $\hat{H}$ and $\hat{\rho}$. In the case of vibrational dynamics on a single electronic surface, the classical analogue of eq 1 is the corresponding classical Liouville equation of nonequilibrium statistical mechanics[55−57]

$$\frac{\partial\rho}{\partial t} = \{H, \rho\} \tag{2}$$

where $\rho = \rho(q, p, t)$ and $H = H(q, p, t)$ are now *functions* of the classical phase space variables (q,p) and

$$\{A, B\} = \frac{\partial A}{\partial q}\frac{\partial B}{\partial p} - \frac{\partial B}{\partial q}\frac{\partial A}{\partial p} \tag{3}$$

is the Poisson bracket of the functions A and B. This result can be derived by performing a Wigner−Moyal expansion of the quantum mechanical Liouville equation in powers of $\hbar$.[54,58,59] To lowest order in $\hbar$, the commutator of two operators is related to the classical Poisson bracket of the corresponding phase space functions via

$$[\hat{A}, \hat{B}] \rightarrow i\hbar\{A, B\} + O(\hbar^3) \tag{4}$$

In practice, a numerical solution of eq 2 can be accomplished (to within statistical uncertainty) by integrating Hamilton's equations

$$\dot{q} = \partial H/\partial p$$
$$\dot{p} = -\partial H/\partial q \tag{5}$$

using a finite ensemble of initial conditions $\{(q_j(0), p_j(0))\}$ ($j = 1, 2, ..., N$) sampled from the probability distribution given by the initial phase space density $\rho(q, p, t = 0)$. The density of evolving trajectories $\{(q_j(t), p_j(t))\}$ in phase space then approximates $\rho(q, p, t)$, the exact solution of the Liouville equation, eq 2.

The classical limit in the more general case of a Hamiltonian that is a *matrix* of operators representing vibrational dynamics on multiple electronic states is not as straightforward. The coupling between the highly quantum mechanical electronic states introduces an intrinsically nonclassical component to the evolution of the full density ρ. Nonetheless, a consistent semiclassical limit can be derived.[51] Here, we briefly review the approach for the case of one-dimensional vibrational motion on two coupled electronic states; the method can be easily generalized to treat N coupled surfaces and n vibrational degrees of freedom.

The Hamiltonian and density operators for the two-state problem are given in the electronic basis $\{|1\rangle, |2\rangle\}$ by

$$\hat{H} = \begin{pmatrix} \hat{H}_{11} & \hat{H}_{12} \\ \hat{H}_{21} & \hat{H}_{22} \end{pmatrix} \tag{6}$$

and

$$\hat{\rho} = \begin{pmatrix} \hat{\rho}_{11} & \hat{\rho}_{12} \\ \hat{\rho}_{21} & \hat{\rho}_{22} \end{pmatrix} \tag{7}$$

respectively. (The electronic states $\{|1\rangle, |2\rangle\}$ can be chosen to be either adiabatic or diabatic basis functions.) Substituting eqs 6 and 7 into eq 1 gives the quantum mechanical Liouville equation

$$i\hbar\frac{\partial\hat{\rho}_{ij}}{\partial t} = \sum_{k=1}^{2} \hat{H}_{ik}\hat{\rho}_{kj} - \hat{\rho}_{ik}\hat{H}_{kj} \tag{8}$$

for i and $j = 1,2$. For simplicity, we assume in what follows that the off-diagonal elements of the Hamiltonian are individually Hermitian: $\hat{H}_{12} = \hat{H}_{21} \equiv \hat{V}$; see ref 51 for a development of the general case. Defining the operators

$$\hat{H}_o = \frac{1}{2}(\hat{H}_{11} + \hat{H}_{22})$$
$$\hat{H}' = \hat{H}_{11} - \hat{H}_{22} \tag{9}$$

and using the explicitly Hermitian combinations of the off-diagonal density operators

$$\mathrm{Re}\,\hat{\rho}_{12} = \frac{1}{2}(\hat{\rho}_{12} + \hat{\rho}_{21})$$
$$\mathrm{Im}\,\hat{\rho}_{12} = \frac{1}{2i}(\hat{\rho}_{12} - \hat{\rho}_{21}) \tag{10}$$

the Liouville equation can be written explicitly as

$$i\hbar\frac{\partial\hat{\rho}_{11}}{\partial t} = [\hat{H}_{11}, \hat{\rho}_{11}] + [\hat{V}, \mathrm{Re}\,\hat{\rho}_{12}] - i[\hat{V}, \mathrm{Im}\,\hat{\rho}_{12}]_+ \tag{11}$$

$$i\hbar\frac{\partial\hat{\rho}_{22}}{\partial t} = [\hat{H}_{22}, \hat{\rho}_{22}] + [\hat{V}, \mathrm{Re}\,\hat{\rho}_{12}] - i[\hat{V}, \mathrm{Im}\,\hat{\rho}_{12}]_+ \tag{12}$$

$$i\hbar\frac{\partial\hat{\rho}_{12}}{\partial t} = [\hat{H}_o, \hat{\rho}_{12}] + \frac{1}{2}[\hat{V}, \hat{\rho}_{11} + \hat{\rho}_{22}] + \frac{1}{2}[\hat{H}', \hat{\rho}_{12}]_+ - \frac{1}{2}[\hat{V}, \hat{\rho}_{11} - \hat{\rho}_{22}]_+ \tag{13}$$

where $[\hat{A}, \hat{B}]_+ \equiv \hat{A}\hat{B} + \hat{B}\hat{A}$ is the anticommutator of the operators $\hat{A}$ and $\hat{B}$.

We can now derive semiclassical equations of motion for the phase space functions corresponding to the density matrix element operators $\hat{\rho}_{ij}$. Equations 11−13 are written explicitly in terms of commutators and anticommutators of Hermitian operators, which have well-defined semiclassical limits. A systematic expansion in powers of $\hbar$ can be developed using the Wigner−Moyal approach.[54,58,59] For our present purposes, we keep only the leading terms and thus consider the semiclassical limit. For commutators, the transcription to the semiclassical limit is given by eq 4. For anticommutators, the correspondence is

$$[\hat{A}, \hat{B}]_+ \rightarrow 2A(q, p)\, B(q, p) + O(\hbar^2) \tag{14}$$

To lowest order in $\hbar$, the resulting classical-like equations of motion corresponding to eqs 11−13 are

$$\frac{\partial \rho_{11}}{\partial t} = \hat{L}_{11}\rho_{11} + \{V, \mathrm{Re}\, \rho_{12}\} - \frac{2V}{\hbar}\mathrm{Im}\, \rho_{12} \tag{15}$$

$$\frac{\partial \rho_{22}}{\partial t} = \hat{L}_{22}\rho_{22} + \{V, \mathrm{Re}\, \rho_{12}\} + \frac{2V}{\hbar}\mathrm{Im}\, \rho_{12} \tag{16}$$

$$\frac{\partial \rho_{12}}{\partial t} = (\hat{L}_{\mathrm{o}} - i\omega)\, \rho_{12} + \frac{1}{2}\{V, \rho_{11} + \rho_{22}\} + \frac{iV}{\hbar}(\rho_{11} - \rho_{22}) \tag{17}$$

Here, we have defined a set of Liouville operators $\hat{L}_\mu$ ($\mu = 0$, 11, 22) in terms of their action on a phase space function $f(q, p)$

$$\hat{L}_\mu f \equiv \{H_\mu, f\}\ (\mu = 0, 11, 22) \tag{18}$$

The frequency term $\omega(q)$ in eq 17 is given by

$$\omega(q) \equiv \frac{H'(q)}{\hbar} \tag{19}$$

where H' is the difference of the potential curves U_i on the two electronic states: $H'(q) = U_1(q) - U_2(q)$.

It should be noted that the semiclassical theory developed here is *more classical* than, for instance, alternatives based on coupled-state semiclassical wave packet dynamics.[60] The latter includes quantum effects, such as interference and nodal structure, for nuclear dynamics on noninteracting electronic states. In the absence of electronic coupling, our formalism reduces to purely *classical* dynamics on the individual potential surfaces.

III. Classical Trajectory Implementation

The semiclassical approach developed above is a generalization of conventional classical Liouville dynamics. The partial differential equations for the phase space distributions contain a term of the form $\partial\rho_\mu/\partial t = \{H_\mu, \rho_\mu\}$ ($\mu = 11, 22, 12$), which corresponds to the usual Hamiltonian flow of classical trajectories in phase space. In addition, there are nonclassical terms involving the coupling V and the difference potential $H'(q)$. In the absence of these additional terms, a trajectory implementation is straightforward: The phase space density $\rho_\mu(\Gamma, t)$ is approximated by an ensemble of trajectories

$$\tilde{\rho}_\mu(\Gamma, t) = \frac{1}{N_\mu}\sum_{j=1}^{N_\mu} \delta(\Gamma - \Gamma_j^{(\mu)}(t)) \tag{20}$$

where each δ-function in the sum is two-dimensional and is centered on a member of the ensemble at $\Gamma_j^{(\mu)}(t) \equiv (q_j^{(\mu)}(t), p_j^{(\mu)}(t))$ ($j = 1, 2, ..., N_\mu$). Here, N_μ is the number of trajectories in the μth ensemble. The tilde on the density signifies that this expression is not a smooth function but is instead a singular "generalized function",[61] owing to the discrete, finite underlying trajectory ensemble. A smooth representation of $\rho_\mu(\Gamma, t)$ is obtained by convoluting eq 20 with a test function $\phi(\Gamma)$

$$\rho_\mu(\Gamma, t) = \int\!\!\int \phi(\Gamma - \Gamma')\, \tilde{\rho}_\mu(\Gamma', t)\, d^2\Gamma' \tag{21}$$

We use a two-dimensional phase space Gaussian test function in the numerical calculations below, of the form

$$\phi(\Gamma - \Gamma_{\mathrm{o}}) \equiv \phi(q - q_{\mathrm{o}}, p - p_{\mathrm{o}}) = \frac{1}{2\pi\sigma_q\sigma_p}\exp\left[-\frac{(q - q_{\mathrm{o}})^2}{2\sigma_q^2} - \frac{(p - p_{\mathrm{o}})^2}{2\sigma_p^2}\right] \tag{22}$$

where σ_q and σ_p are the widths of the test function in q and p, respectively; these widths are determined by numerical considerations in practice. The function $\rho_\mu(\Gamma, t)$ then evolves by the motion of the underlying trajectory ensemble under Hamilton's equations. The shape of this function will change as the trajectories move through phase space. The total number of trajectories is constant, and so the phase space trace $\mathrm{Tr}\, \rho_\mu \equiv \int\!\int \rho_\mu(\Gamma, t)\, \mathrm{d}^2\Gamma = 1$ is manifestly conserved by this Hamiltonian implementation of Liouville dynamics.

We now consider the case of coupled multistate dynamics. Here, the off-diagonal elements of $\hat{H}$ induce transfer of probability between states 1 and 2, and so the individual phase space traces of ρ_{11} and ρ_{22} are *not* separately conserved; only the total trace is constant: $\mathrm{Tr}\, \rho = \mathrm{Tr}\, \rho_{11} + \mathrm{Tr}\, \rho_{22} = 1$. The coupled-state motion is composed of two underlying dynamical processes. One component is "conventional" classical dynamics *on* the respective electronic surfaces (or in the coherence phase space for ρ_{12}), governed by the Liouville equations $\partial\rho_\mu/\partial t = \{H_\mu, \rho_\mu\}$; this is the same as in the uncoupled case. The additional inhomogeneous terms not present in the conventional classical Liouville equation both affect the dynamics on the surfaces and induce flow of probability (or, more correctly, classical *amplitude* for the possibly complex off-diagonal terms) between states.

The ansatz of eq 20 must be generalized in order to allow this extended Liouville-like dynamics to be modeled with classical trajectories. A number of possible implementations can be contemplated, including a surface-hopping approach, where the number of trajectories in the 11, 22, and 12 ensembles are allowed to vary. We instead choose to generalize eq 20 by introducing a new set of dynamical variables $\{a_j^{(\mu)}(t)\}$ ($j = 1, 2, ..., N_\mu$), which, together with the $\{\Gamma_j^{(\mu)}(t)\}$, characterize the ensembles of trajectories. The variables $\{a_j^{(\mu)}(t)\}$ correspond to the relative weights of each member of the ensemble, and probability flow between electronic states manifests itself in the time variations of these weights. For the off-diagonal coherence ρ_{12}, these coefficients are complex numbers and incorporate the nonclassical phase resulting from the term involving the difference potential (see eq 17]. The coupled-state generalization of $\tilde{\rho}_\mu(\Gamma, t)$ can thus be written

$$\tilde{\rho}_\mu(\Gamma, t) = \sum_{j=1}^{N_\mu} a_j^{(\mu)}(t)\, \delta(\Gamma - \Gamma_j^{(\mu)}(t)) \tag{23}$$

The smoothing process used to obtain $\rho_\mu(\Gamma, t)$ from eq 23 is, again, given by eqs 21 and 22.

In order to use eq 23 as a way of propagating the coupled-phase space functions $\rho_\mu(\Gamma, t)$, equations of motion must be derived for the $\{a_j^{(\mu)}(t)\}$. These are then combined with conventional Hamiltonian dynamics for the phase space variables $\{\Gamma_j^{(\mu)}(t)\}$. We derive these equations of motion by considering the short-time limit of the integrated form of the inhomogeneous coupled linear partial differential equations given in eqs 15−17. To first order in Δt, these short-time propagations can be written as:

$$\rho_{11}(\Gamma, t + \Delta t) = \mathrm{e}^{\Delta t\hat{L}_{11}}[\rho_{11}(\Gamma, t) + b_{11}(\Gamma, t)\Delta t + O(\Delta t^2)] \qquad (24)$$

$$\rho_{22}(\Gamma, t + \Delta t) = \mathrm{e}^{\Delta t\hat{L}_{22}}[\rho_{22}(\Gamma, t) + b_{22}(\Gamma, t)\Delta t + O(\Delta t^2)] \qquad (25)$$

$$\rho_{12}(\Gamma, t + \Delta t) = \mathrm{e}^{\Delta t\hat{L}_0}\,\mathrm{e}^{-i\omega(\Gamma)\Delta t}[\rho_{12}(\Gamma, t) + b_{12}(\Gamma, t)\Delta t + O(\Delta t^2)] \qquad (26)$$

where

$$b_{11}(\Gamma, t) = \{V(\Gamma), \mathrm{Re}\,\rho_{12}(\Gamma, t)\} - \frac{2V(\Gamma)}{\hbar}\,\mathrm{Im}\,\rho_{12}(\Gamma, t) \qquad (27)$$

$$b_{22}(\Gamma, t) = \{V(\Gamma), \mathrm{Re}\,\rho_{12}(\Gamma, t)\} + \frac{2V(\Gamma)}{\hbar}\,\mathrm{Im}\,\rho_{12}(\Gamma, t) \qquad (28)$$

$$b_{12}(\Gamma, t) = \frac{1}{2}\{V(\Gamma), \rho_{11}(\Gamma, t) + \rho_{22}(\Gamma, t)\} + \frac{iV(\Gamma)}{\hbar}[\rho_{11}(\Gamma, t) - \rho_{22}(\Gamma, t)] \qquad (29)$$

and in eq 26 we have made the short-time approximation

$$\mathrm{e}^{\Delta t(\hat{L}_0 - i\omega)} \cong \mathrm{e}^{\Delta t\hat{L}_0}\,\mathrm{e}^{-i\omega\Delta t} \qquad (30)$$

Equations 24−26 form the basis of our numerical propagation of the densities $\rho_\mu(\Gamma, t)$ for a time step Δt at time t. The structure of the equations suggest that each time step Δt be split into two parts: an update of the coefficients $\{a_j^{(\mu)}(t)\}$, which depends on the inhomogeneous terms $b_\mu(\Gamma, t)$ (and the phase ω for ρ_{12}), followed by the action of $\exp(\Delta t\hat{L}_\mu)$, which induces the trajectories in the ensemble to be propagated in phase space under Hamilton's equations with Hamiltonian H_μ.

For the (11) density, the propagation of the coefficients involves solving the equation

$$\sum_{j=1}^{N_1} a_j^{(11)}(t + \Delta t)\,\delta(\Gamma - \Gamma_j^{(11)}(t)) = \sum_{j=1}^{N_1} a_j^{(11)}(t)\,\delta(\Gamma - \Gamma_j^{(11)}(t)) + \Delta t\sum_{k=1}^{N_o}\left\{\mathrm{Re}\,a_k^{(0)}(t)\,V'[\Gamma_k^{(0)}(t)]\,\delta'(\Gamma - \Gamma_k^{(0)}(t)) - \frac{2}{\hbar}\,\mathrm{Im}\,a_k^{(0)}(t)\,V[\Gamma_k^{(0)}(t)]\,\delta(\Gamma - \Gamma_k^{(0)}(t))\right\} \qquad (31)$$

where

$$V'(\Gamma) \equiv \frac{\mathrm{d}V(q)}{\mathrm{d}q} \qquad (32)$$

and

$$\delta'(\Gamma - \Gamma_0) \equiv \frac{\partial}{\partial p}\,\delta(\Gamma - \Gamma_0) \equiv \delta(q - q_0)\,\frac{\mathrm{d}}{dp}\,\delta(p - p_0) \qquad (33)$$

These expressions result from substituting the appropriate $\tilde{\rho}_\mu(\Gamma, t)$ into eq 27 and evaluating the Poisson brackets. The entire quantity in the square brackets of eq 24 is then interpreted as being equivalent to a sum over the trajectories of ensemble (11), but with updated coefficients. Note that all the trajectory positions $\Gamma_j^{(\mu)}(t)$ are evaluated at time t in this phase of the propagation. In the following expressions, we will suppress their time dependence in the interest of notational simplicity.

The coefficients $\{a_j^{(\mu)}(t)\}$ in eq 31 are known, whereas the $\{a_j^{(11)}(t + \Delta t)\}$ are the unknowns that need to be determined. The criterion for determining the new coefficients is that the smoothed representation of the function on the left-hand side of eq 31 is as close as possible to the smoothed representation of the function on the right-hand side. Smoothing eq 31 with the function ϕ gives

$$\sum_{j=1}^{N_1} a_j^{(11)}(t + \Delta t)\,\phi(\Gamma - \Gamma_j^{(11)}) = \sum_{j=1}^{N_1} a_j^{(11)}(t)\,\phi(\Gamma - \Gamma_j^{(11)}) + \Delta t\sum_{k=1}^{N_o}\left\{\mathrm{Re}\,a_k^{(0)}(t)\,V'(\Gamma_k^{(0)})\,\phi'(\Gamma - \Gamma_k^{(0)}) - \frac{2}{\hbar}\,\mathrm{Im}\,a_k^{(0)}(t)\,V(\Gamma_k^{(0)})\,\phi(\Gamma - \Gamma_k^{(0)})\right\} \qquad (34)$$

where

$$\phi'(\Gamma - \Gamma_o) \equiv \frac{\partial}{\partial p}\phi(q - q_o, p - p_o) \qquad (35)$$

Taking the quantities at time t as known, we find the coefficients at time $t + \Delta t$ by minimizing the phase space norm of the difference between the two representations of the intermediate phase space function. Defining

$$f(\Gamma) \equiv \sum_{j=1}^{N_1} a_j^{(11)}(t)\,\phi(\Gamma - \Gamma_j^{(11)}) + \Delta t\sum_{k=1}^{N_o}\left\{\mathrm{Re}\,a_k^{(0)}(t)\,V'(\Gamma_k^{(0)})\,\phi'(\Gamma - \Gamma_k^{(0)}) - \frac{2}{\hbar}\,\mathrm{Im}\,a_k^{(0)}(t)\,V(\Gamma_k^{(0)})\,\phi(\Gamma - \Gamma_k^{(0)})\right\} \qquad (36)$$

and $\alpha_j \equiv a_j^{(11)}(t + \Delta t)$, we minimize the phase space integral

$$\mathrm{error} = \int\!\!\int d^2\Gamma|f(\Gamma) - \sum_{j=1}^{N_1}\alpha_j\phi(\Gamma - \Gamma_j^{(11)})|^2 \qquad (37)$$

with respect to the coefficients $\{\alpha_j\}$

$$\frac{\partial}{\partial\alpha_m}\int\!\!\int d^2\Gamma|f(\Gamma) - \sum_{j=1}^{N_1}\alpha_j\phi(\Gamma - \Gamma_j^{(11)})|^2 = 0 \qquad (m = 1, 2, ..., N_1) \quad (38)$$

This gives

$$\int\!\!\int \mathrm{d}^2\Gamma\,\phi(\Gamma - \Gamma_m^{(11)})[f(\Gamma) - \sum_{j=1}^{N_1}\alpha_j\phi(\Gamma - \Gamma_j^{(11)})] = 0 \qquad (m = 1, 2, ..., N_1) \quad (39)$$

or

$$\int\!\!\int d^2\Gamma\, f(\Gamma)\, \phi(\Gamma - \Gamma^{(11)}_m) = \sum_{j=1}^{N_1} \alpha_j \int\!\!\int d^2\Gamma\, \phi(\Gamma - \Gamma^{(11)}_m)\, \phi(\Gamma - \Gamma^{(11)}_j) \quad (m = 1, 2, ..., N_1) \tag{40}$$

We now define the following matrices

$$\mathbf{S}^{(\mu\nu)}_{mj} = \int\!\!\int \phi(\Gamma - \Gamma^{(\mu)}_m)\, \phi(\Gamma - \Gamma^{(\nu)}_j)\, d^2\Gamma \tag{41}$$

$$\mathbf{D}^{(\mu\nu)}_{mj} = \int\!\!\int \phi(\Gamma - \Gamma^{(\mu)}_m) \frac{\partial}{\partial p} \phi(\Gamma - \Gamma^{(\nu)}_j)\, d^2\Gamma \tag{42}$$

The elements of these matrices can be evaluated analytically for the case of a Gaussian ϕ. The equations for the unknown coefficients at time $t + \Delta t$ become

$$\sum_{j=1}^{N_1} \mathbf{S}^{(11)}_{mj} a^{(11)}_j (t + \Delta t) = \sum_{j=1}^{N_1} \mathbf{S}^{(11)}_{mj} a^{(11)}_j (t) + \Delta t \sum_{k=1}^{N_0} \left\{ \mathbf{D}^{(10)}_{mk} V'(\Gamma^{(0)}_k)\, \mathrm{Re}\, a^{(0)}_k(t) - \frac{2}{\hbar} \mathbf{S}^{(10)}_{mk}(\Gamma^{(0)}_k)\, \mathrm{Im}\, a^{(0)}_k(t) \right\} \tag{43}$$

for $m = 1, 2, ..., N_1$, or, in matrix-vector notation

$$\mathbf{S}^{(11)}\mathbf{a}^{(11)}(t + \Delta t) = \mathbf{S}^{(11)}\mathbf{a}^{(11)}(t) + \Delta t \left\{ \mathbf{D}^{(10)}\mathbf{V}'^{(0)}\, \mathrm{Re}\, \mathbf{a}^{(0)}(t) - \frac{2}{\hbar} \mathbf{S}^{(10)}\mathbf{V}^{(0)}\, \mathrm{Im}\, \mathbf{a}^{(0)}(t) \right\} \tag{44}$$

A parallel analysis gives the result for the (22) coefficients

$$\mathbf{S}^{(22)}\mathbf{a}^{(22)}(t + \Delta t) = \mathbf{S}^{(22)}\mathbf{a}^{(22)}(t) + \Delta t \left\{ \mathbf{D}^{(20)}\mathbf{V}'^{(0)}\, \mathrm{Re}\, \mathbf{a}^{(0)}(t) + \frac{2}{\hbar} \mathbf{S}^{(20)}\mathbf{V}^{(0)}\, \mathrm{Im}\, \mathbf{a}^{(0)}(t) \right\} \tag{45}$$

Here, we have defined the following diagonal matrices

$$\mathbf{V}^{(0)}{}_{ij} = V(\Gamma^{(0)}_i)\delta_{ij}$$

$$\mathbf{V}'{}^{(0)}_{ij} = V'(\Gamma^{(0)}_i)\delta_{ij} \tag{46}$$

A similar procedure is followed for the (12) coefficients for the electronic coherence. Here, the additional factor of the time-dependent phase must be included. The result is

$$\mathbf{S}^{(00)}\mathbf{a}^{(0)}(t + \Delta t) = \mathbf{S}^{(00)}\mathbf{\Phi}^{(0)}\mathbf{a}^{(0)}(t) + \Delta t \left\{ \frac{1}{2} \mathbf{D}^{(01)}\mathbf{V}'^{(1)} + \frac{i}{\hbar} \mathbf{S}^{(01)}\mathbf{V}^{(1)} \right\} \mathbf{\Phi}^{(1)}\mathbf{a}^{(1)}(t) + \Delta t \left\{ \frac{1}{2} \mathbf{D}^{(02)}\, \mathbf{V}'^{(2)} - \frac{i}{\hbar} \mathbf{S}^{(02)}\mathbf{V}^{(2)} \right\} \mathbf{\Phi}^{(2)}\mathbf{a}^{(2)}(t) \tag{47}$$

where the superscript $\mu = 0$ signifies the (12) ensemble. The diagonal matrix of phase factors is given by

$$\Phi^{(\mu)}_{nm} = e^{-i\Delta t\omega(\Gamma^{(\mu)}_m)}\delta_{mn} \tag{48}$$

The updated coefficients $\{a^{(\mu)}_j(t + \Delta t)\}$ are then determined by solving the linear equations of eqs 44, 45, and 47.[62]

After the coefficients are updated, the second part of the time step consists of conventional Hamiltonian dynamics, which results in a new set of phase space coordinates $\{\Gamma^{(\mu)}_j(t + \Delta t)\}$. This process is repeated for the number of desired total time steps.

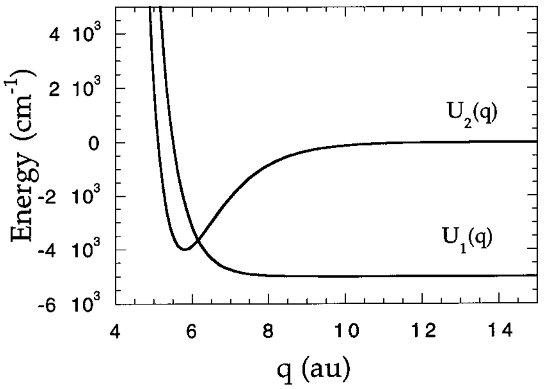

Figure 1. Potential curves used in numerical calculations.

IV. Numerical Test of Method

In this section, we test our trajectory implementation by treating a one-dimensional problem and comparing the results of our molecular dynamics simulation with those of a (numerically) exact coupled state wave packet calculation. We consider a model one-dimensional system consisting of motion of a particle with mass m on two coupled excited electronic surfaces. The model chosen is identical to that considered in ref 51, allowing a direct comparison between the trajectory implementation presented here and the numerical grid solution of the semiclassical partial differential equations given in eqs 15−17. The system is excited at $t = 0$ by a sudden optical excitation from a harmonic ground electronic state. The two excited states treated explicitly in the simulation consist of a repulsive exponential potential

$$U_1(q) = A\, e^{-\alpha(q-q_1)} - B \tag{49}$$

which is initially populated by the optical excitation and which is crossed by a bound Morse potential

$$U_2(q) = D(e^{-2\beta(q-q_2)} - 2e^{-\beta(q-q_2)}) \tag{50}$$

The potential curves are shown in Figure 1. These two diabatic curves are coupled by an off-diagonal term $H_{12} = V(q)$, which is taken to be a Gaussian function centered at the crossing point q_c

$$V(q) = V_o\, e^{-c(q-q_c)^2} \tag{51}$$

The numerical values of the potential parameters are given in Table 1.

The initial quantum state of the system is a localized Gaussian wave packet on the repulsive surface, centered at the ground-state equilibrium bond length q_e

$$\psi(q, t = 0) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \exp\left[-\frac{m\omega}{2\hbar}(q - q_e)^2\right] \tag{52}$$

The parameters m, q_e, and ω are also given in Table 1. In our model, the laser pulse couples the ground state exclusively to the repulsive state 1, and thus the initial population on the bound state 2 is zero. As the system evolves, the coupling term V_{12} will induce population transfer from state 1 to state 2.

TABLE 1: Numerical Values of Parameters, in atomic units

A	2.2782×10^{-2}	V_0	1.2×10^{-3}
B	2.2782×10^{-2}	c	4.0
α	2.0	q_c	6.15315
q_1	5.5	m	1×10^4
D	1.8225×10^{-2}	ω	4×10^{-3}
β	1.0	q_e	5.7
q_2	5.8		

Exact quantum mechanical calculations were performed using the standard FFT-based grid method of Kosloff,[63] generalized to treat coupled wave packet dynamics on multiple electronic surfaces.

The initial conditions for the classical trajectory simulations were determined from the Wigner transform[58,59] of the initial quantum wave packet, eq 52, which gives a two-dimensional phase space Gaussian function; we take this Wigner function to be identical to the classical $\rho_{11}(\Gamma, 0)$. A number of possibilities exist for the calculation of the initial conditions for the corresponding ensembles. One natural alternative would be to sample the initial phase space variables $\{\Gamma_j^{(11)}(0)\}$ of the initially populated (11) state using the corresponding probability distribution $\rho_{11}(\Gamma, 0)$. In this case, all of the coefficients $\{a_j^{(11)}(0)\}$ would be equal to unity, and the value of ρ_{11} would be reflected by the resulting density of initial conditions in phase space. In the calculations reported here, we chose instead to use a simple grid of initial conditions in phase space. With this choice, the coefficients $\{a_j^{(11)}(0)\}$ for the (11) ensemble are not all unity but are chosen to fit the initial distribution. The (22) and (12) ensembles are also placed on identical grids, but with zero coefficients initially. As a practical consideration, the size and shape of the grids must be chosen to be large enough in extent so that there is an overlap of the evolving grids in the electronic coupling region for all ensembles throughout the simulation. In the calculations presented here, we generated 900 trajectories for each of the three [(11), (22), and (12)] ensembles. The trajectories and coefficients were then propagated as described in the previous section. We employed a large number of trajectories in this first report to allow the intrinsic accuracy of the method to be assessed.

In Figure 2, we show the populations of the states 1 and 2 as a function of time for both the exact and semiclassical molecular dynamics. In our trajectory implementation, the population of the μth electronic state is given by

$$P_\mu(t) \equiv \mathrm{Tr}\,\rho_\mu(\Gamma, t) = \sum_{j=1}^{N_\mu} a_j^{(\mu)}(t) \quad (\mu = 11, 22) \qquad (53)$$

The results of our trajectory-based implementation are compared with the corresponding numerically exact quantum mechanical quantities. The figure shows that the state 2 population increases rapidly around $t = 500$ au, as the state 1 wave packet passes through the crossing region on its way to dissociation on the repulsive surface. Approximately 25% of the total population is transferred to the bound diabatic state 2 during this passage. The classical trajectory results are in nearly quantitative agreement with the quantum wave packet dynamics.

A more demanding test of the accuracy of our method is an examination of the time-dependent semiclassical phase space probabilities and coherences themselves. In parts b of Figures 3−6, we show the evolution of reduced semiclassical configuration space densities $P_{ij}^{\mathrm{SC}}(q, t) = \int \rho_{ij}(q, p, t)\, \mathrm{d}p$, In parts a of Figures 3−6, the analogous quantum mechanical quantities $P_{ij}^{\mathrm{Q}}(q, t) = \psi_i^*(q,t)\, \psi_j(q, t)$ are shown. (The real and imaginary parts of $P_{12}(q, t)$ are shown in Figures 5 and 6, respectively.)

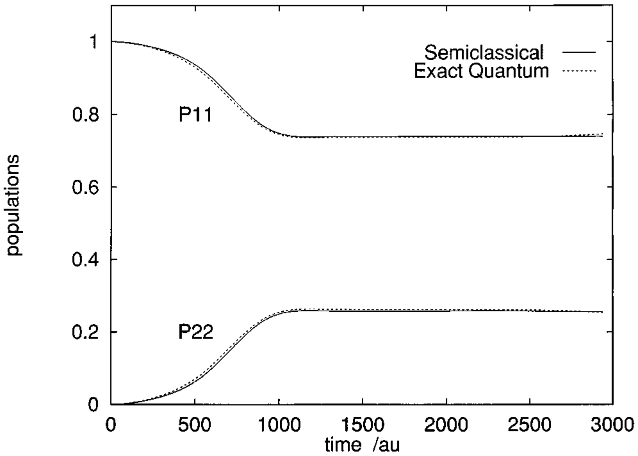

Figure 2. Comparison of semiclassical trajectory and exact quantum populations of states 1 and 2 as functions of time.

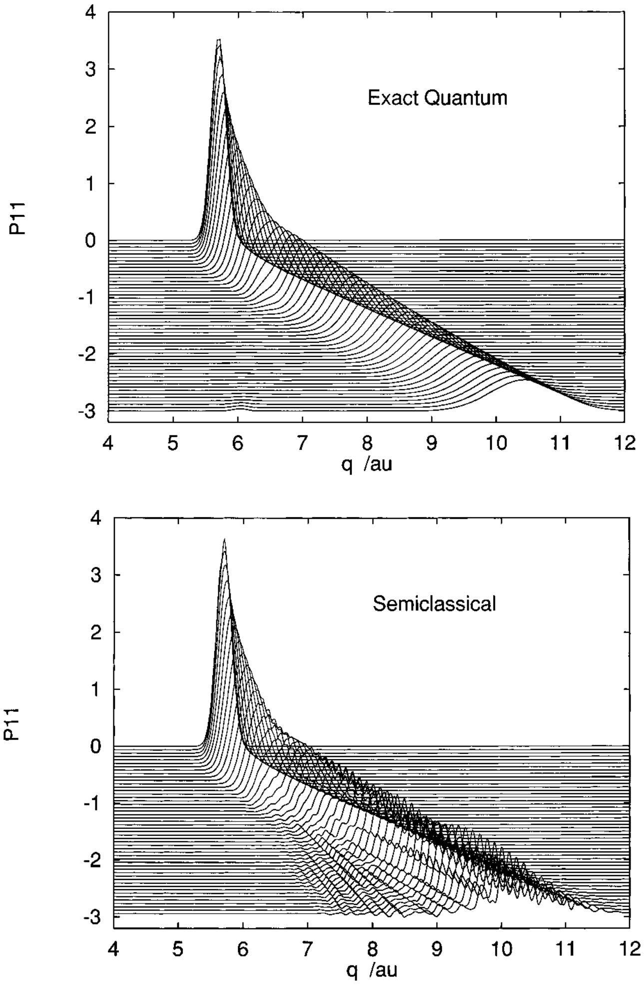

Figure 3. Comparison of semiclassical generalized distribution functions and exact quantum mechanical results. The figure shows 50 curves representing the reduced configuration space probability distribution $P_{11}(q)$ as a function of q, as defined in the text. The top curve is the $t = 0$ result, and each successive curve below it is displaced down by 60 au in time relative to the previous curve, yielding a total simulation time of 3000 au. The result is a space−time (q, t) representation of the evolution of P_{11}. (a, top) Exact quantum mechanical results. (b, bottom) Semiclassical trajectory results.

The figures summarize the entire simulation in a space−time (q, t) diagram, with $P_{ij}(q, t)$ as the dependent variable.

Inspection of these figures reveals that the classical trajectory ensembles, generalized by the evolving coefficients $\{a_j^{(\mu)}(t)\}$,

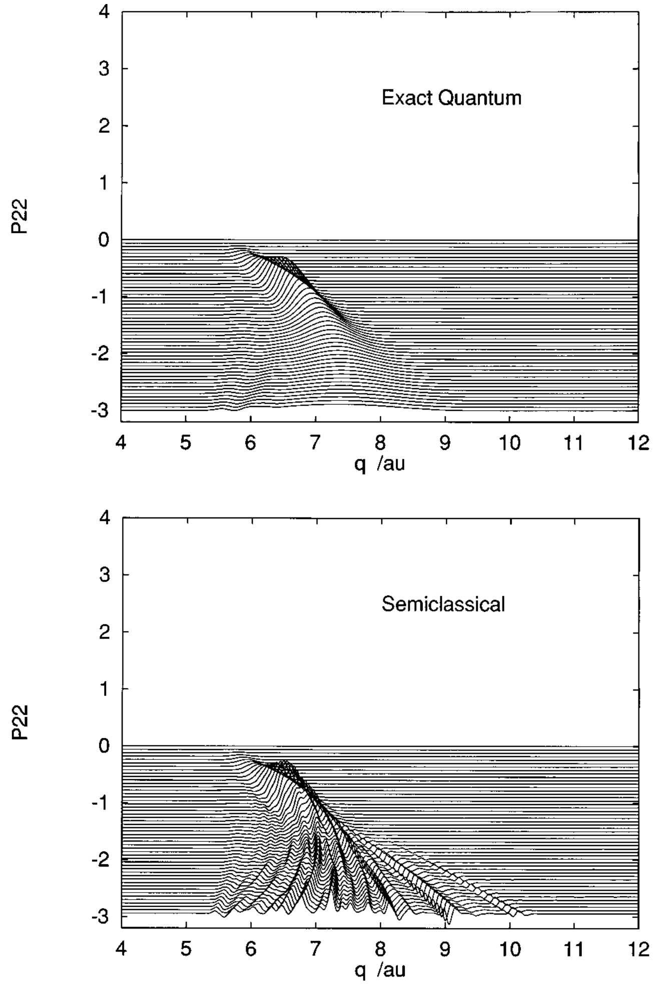

Figure 4. Same as Figure 3, for P_{22}.

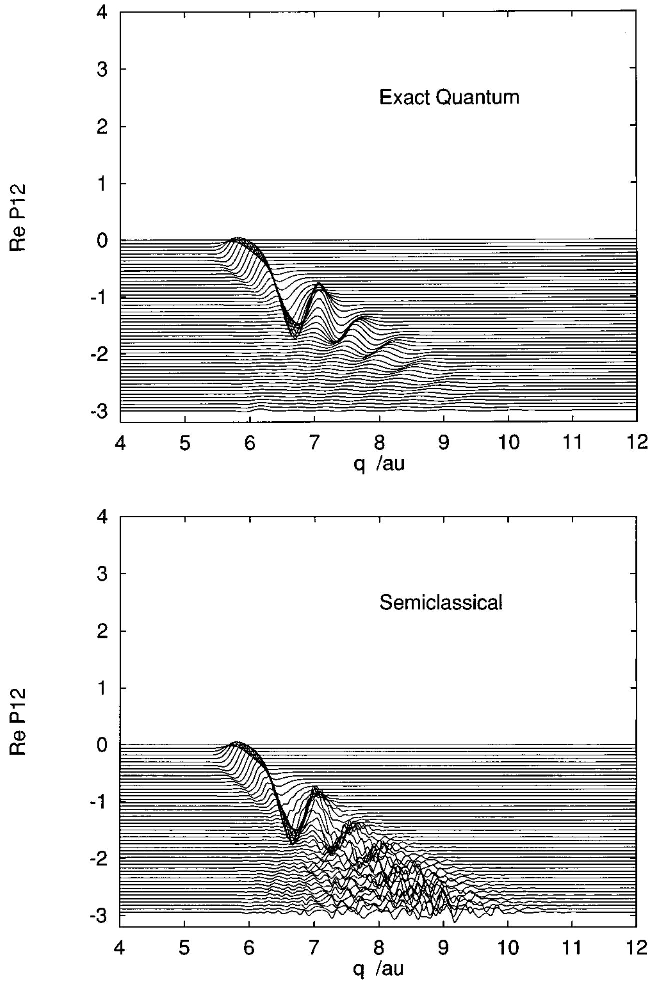

Figure 5. Same as Figure 3, for Re P_{12}.

give an excellent representation of the corresponding quantum mechanical density matrix elements at a fine level of detail. This agreement is nearly perfect at early times. The close agreement is obtained even for the "nonclassical" electronic coherence $\rho_{12}(\Gamma,\ t)$. This quantity is a complex valued, oscillatory function of the phase space variables $\Gamma = (q, p)$. In the exact calculations, its structure results from the interplay of the product of the quantum amplitudes ψ_1 and ψ_2. In our semiclassical trajectory formulation, this comes about instead by a coherent superposition of the (12) ensemble trajectories, each weighted by a complex amplitude $a_j^{(12)}(t)$. This coherent superposition of *classical* trajectories, evolving under Hamiltonian dynamics with the averaged Hamiltonian H_0, accumulating a phase that is a time integral of the difference potential (divided by Planck's constant) and, with additional nonclassical coupling terms, does a remarkable job of faithfully capturing the quantum mechanical structure of the electronic coherence and its dependence on the nuclear phase space variables. The level of agreement obtained here, particularly at early times, is comparable to the agreement between numerically exact quantum wavepacket dynamics and a corresponding direct numerical grid solution of the semiclassical phase space partial differential equations, eqs 15−17. (See ref 51 for comparison.)

Near the end of the simulation, numerical noise begin to appear in the trajectory results. We believe that these occur owing to instabilities in our simple numerical implementation, and we are currently developing and testing more efficient and stable algorithms.

V. Discussion

In this paper, we have described a trajectory-based implementation of our recently proposed semiclassical-limit approach to molecular dynamics on coupled electronic surfaces.[51] Building on the conventional method of modeling single surface dynamical processes in the classical limit using trajectory integration and ensemble averaging, we presented an augmented dynamical description of multistate classical dynamics, based on adding additional time-dependent coefficients to each member of the coupled ensembles. Physically, these new dynamical variables represent the evolving weights (and phases for the electronic coherence) of the trajectories. All of the nonclassical effects of electronic coupling and coherence are described by the equations of motion for these coefficients, while the phase space trajectories themselves obey conventional Hamilton's equations, just as in the classical single-state case.

Despite the use of classical trajectories in our numerical implementation, we stress that our approach is explicitly a theory of the evolution of the distribution functions $\rho_{ij}(\Gamma,\ t)$ themselves—*not* of individual, independent trajectories. This is an important point, and at the heart of the description of nonclassical processes. Electronic coherence in our theory is not a property of any individual trajectory but results from the "interference" of a whole ensemble of trajectories modeling an evolving *function*. This function, in turn, both controls and is influenced by the evolution of other functions—the probability distributions on the two surfaces—and thus influences the generalized dynamics of many other trajectories.

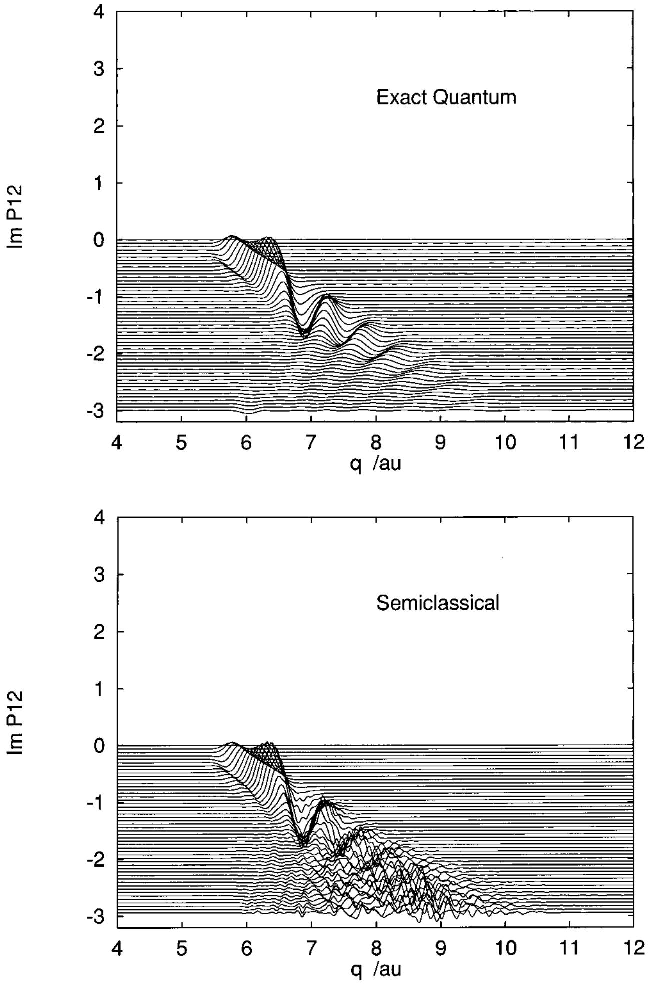

Figure 6. Same as Figure 3, for Im P_{12}.

When used as a numerical method for solving the coupled-state partial differential equations for the $\rho_{ij}(\Gamma, t)$, the members of all the ensembles become entwined in a web of mutual interactions that is quite different from their rigorous independence in a conventional single-surface molecular dynamics simulation. We conjecture that many of the fundamental problems associated with previous approaches to modeling electronic transitions with classical trajectories, such as problems with the treatment of electronic coherence in surface hopping,[31,40] unphysical mixed electronic states in mean trajectory methods,[40] and nonlocal time difficulties in the path integral-based work,[44,49] are due to their focus on *single independent* trajectories coupled to quantum degrees of freedom. In the *exact* quantum mechanical description of multistate dynamics are the evolving wave packets on each state that couple to each other. This roughly translates in the classical limit to interactions between the entire evolving ensembles. Quantum mechanics is a theory of the evolution of probability distributions (derived from underlying amplitudes), and a correct treatment of dynamics at the ensemble level is built explicitly into our classical limit approach. We will explore this fundamental issue of classical-quantum correspondence more fully in a future publication.[64]

The work presented in this paper constitutes a first successful attempt at building a classical trajectory-based implementation of our general semiclassical approach to nonadiabatic dynamics. We have shown that an augmentation of a standard molecular dynamics program can be made which allows certain intrinsically quantum mechanical properties, such as electronic population transfer and the evolution of electronic coherence, to be modeled with excellent accuracy, at least in principle. More work needs to be done, however, before this approach becomes an efficient numerical method for modeling many-body systems. Refinements currently under development include methods for incorporating birth, death, and “retirement” of trajectories to allow the total number of *interacting* members of the ensembles to be minimized while keeping the ensembles overlapping in phase space regions where coupling is operative; the use of more elaborate higher-order representations of the short-time propagator, allowing larger time steps to be employed; and the incorporation of dynamical approximations into the trajectory equations of motion, permitting an explicit and detailed calculation of the full electronic coherence to be avoided for applications where it is not required. These will be discussed in future publications.

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