Simulation of molecular transitions using classical trajectories

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In the present work, we describe the implementation of a semiclassical method to study physical-chemical processes in molecular systems where electronic state transitions and quantum coherences play a dominant role. The method is based on classical trajectory propagation on the underlying coupled electronic surfaces and is derived from the semiclassical limit of the quantum Liouville equation. Unlike previous classical trajectory-based methods, quantum electronic coherences are treated naturally within this approach as complex weighted trajectory ensembles propagating on the average electronic surfaces. The method is tested on a model problem consisting of one-dimensional motion on two crossing electronic surfaces. Excellent agreement is obtained when compared to the exact results obtained by wavepacket propagation. The method is applied to model quantum wavepacket interferometry, where two wavepackets, differing only in a relative phase, collide in the region where the two electronic surfaces cross. The dependence of the resulting population transfer on the initial relative phase of the wavepackets is perfectly captured by our classical trajectory method. Comparison with an alternative method, surface hopping, shows that our approach is appropriate for modeling quantum interference phenomena.

Keywords: Electronic coherence, molecular physics

1. Introduction

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 slower than the intrinsic dynamical time scales. The rapidly advancing field of femtochemistry now allows us to watch chemical reactions unfold in real time [1]. 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 [2-4]. Direct computer simulation of many-body systems is an increasingly powerful tool for modeling condensed phase ultrafast dynamics [5]. 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. Despite the intrinsically quantum nature of molecular systems, classical trajectory integration often works surprisingly well. 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 which allow the intuitive and computational advantages of classical mechanics to be combined with the possibility of transitions between electronic states. Landau [6], Zener [7], and Stuckelberg [8] developed early theories of electronic transitions induced by scattering events described by simple known classical trajectories [9]. 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 gene-
ral, though, the coupled electronic-nuclear dynamics must be solved simultaneously and self-consistently, and several approaches to this problem have been proposed [10], including time-dependent mean field, self-consistent eikonal [11] approximations, the classical electron model, and the very popular surface hopping method, introduced by Tully and Preston [12] and still under active development. 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 wavefunction 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. Recently, Martens et al. 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 [13]. 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 to other approaches which introduce classical mechanics in terms of individual trajectories or classical paths, the 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 [13], Martens et al. described in detail the general formalism of our coupled Liouville-like representation of classical molecular dynamics on coupled electronic states. In addition, they provided analytical results in simplifying limits and made comparisons with conventional descriptions of nonadiabatic dynamics, such as Landau-Zener theory [6, 7, 9]. They 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 wavepacket 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 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 the 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. In Sec. 2, we present such a generalization and compare the results of its application with numerically exact quantum results for a simple but nontrivial one-dimensional two-state model problem in the diabatic representation. In Sec. 3, the classical trajectory-method is applied to model quantum wavepacket interferometry, where two wavepackets, differing only in a relative phase, collide in the region where the two electronic surfaces cross. A discussion is presented in Sec. 4.

2. Simple two-state system

Our development begins with the exact quantum mechanical Liouville equation for the density operator, given by [15–17]

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

(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 (1) is the corresponding classical Liouville equation of nonequilibrium statistical mechanics $\partial \rho / \partial t = \{H, \rho\}$ where $\rho = \rho(q, p, t)$ and $H = H(q, p, t)$ are now functions of the classical phase space variables. To lowest order in $\hbar$, the commutator of two operators is related to the classical Poisson bracket of the corresponding phase space functions via $[A, B] \rightarrow i\hbar \{A, B\} + O(\hbar^2)$. In practice, a numerical solution of the classical Liouville equation can be accomplished (to within statistical uncertainty) by integrating Hamilton’s equations $\dot{q} = \partial H/\partial p$ and $\dot{p} = -\partial H/\partial q$ using a finite ensemble of initial conditions $\{(q_j(0), p_j(0))\}$ ($j = 1, 2, \ldots, N$) 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. 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 $\rho$. Nonetheless, a consistent semiclassical limit can be derived [13]. Here, we briefly review the approach for the case of one dimensional vibrational motion on two coupled electronic sta-
tes; 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 \{|1\rangle, |2\rangle\} basis by
\begin{align}
\hat{H} &= \begin{pmatrix} \hat{H}_{11} & \hat{H}_{12} \\
\hat{H}_{21} & \hat{H}_{22} \end{pmatrix} \\
\hat{\rho} &= \begin{pmatrix} \hat{\rho}_{11} & \hat{\rho}_{12} \\
\hat{\rho}_{21} & \hat{\rho}_{22} \end{pmatrix},
\end{align}
respectively. In this section, the electronic states \{|1\rangle, |2\rangle\} are chosen to be diabatic basis functions, the adiabatic representation has been used in Ref. 14. Substituting Eqs. (2) and (3) into Eq. (1) gives the quantum mechanical Liouville equation
\begin{align}
\frac{i\hbar}{\hbar} \frac{\partial \hat{\rho}_{ij}}{\partial t} &= \sum_{k=1}^{2} \hat{H}_{ik} \hat{\rho}_{kj} - \hat{\rho}_{ik} \hat{H}_{kj} \\
&= \sum_{k=1}^{2} \hat{H}_{ik} \hat{\rho}_{kj} - \hat{\rho}_{ik} \hat{H}_{kj} \\
&= \sum_{k=1}^{2} \hat{H}_{ik} \hat{\rho}_{kj} - \hat{\rho}_{ik} \hat{H}_{kj}
\end{align}
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. 13 for a development of the general case. We can now derive semiclassical equations of motion for the phase space functions corresponding to the density matrix element operators $\hat{\rho}_{ij}$. Each of the terms of Eqs. (4) is 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 [17–19]. For our present purposes, we keep only the leading terms, and thus consider the semiclassical limit. For anticommutators, the transcription to the semiclassical limit is given by $[A, B]_+ \rightarrow 2A(q, p)B(q, p) + O(\hbar^2)$. To lowest order in $\hbar$, the resulting classical-like equations of motion corresponding to Eqs. (4) are
\begin{align}
\frac{\partial \rho_{11}}{\partial t} &= \dot{\rho}_{11} + \{V, \text{Re} \rho_{11}\} - \frac{2V}{\hbar} \text{Im} \rho_{12}, \\
\frac{\partial \rho_{22}}{\partial t} &= \dot{\rho}_{22} + \{V, \text{Re} \rho_{12}\} + \frac{2V}{\hbar} \text{Im} \rho_{12}, \\
\frac{\partial \rho_{12}}{\partial t} &= \left(\dot{\rho}_{0} - i\omega\right) \rho_{12} + \frac{1}{2} \{V, \rho_{11} + \rho_{22}\} + \frac{iV}{\hbar} \left(\rho_{11} - \rho_{22}\right).
\end{align}
Here, we have defined a set of Liouville operators $\dot{\rho}_{i}, f \equiv \{H_{ii}, f\} (i = 1, 2)$ and $\dot{L}_{0}f \equiv \{\frac{1}{2}(H_{11} + H_{22}), f\}$; and the frequency term $\omega$ in Eq. (7) is given by $\omega(q) \equiv (H_{11} - H_{22})/\hbar$. The phase space density $\rho_{ii}(\Gamma, t)$ is approximated by an ensemble of trajectories
\begin{align}
\rho_{ii}(\Gamma, t) &= \sum_{j=1}^{N_{e}} a_{ij}^{(n)}(t) \delta(\Gamma - \Gamma_{j}^{(n)}(t))
\end{align}
where each $\delta$-function in the sum is two-dimensional, and is centered on a member of the ensemble at $\Gamma_{j}^{(n)}(t) \equiv [q_{j}^{(n)}(t), p_{j}^{(n)}(t)]$. The variables $\{a_{ij}^{(n)}(t)\}$ 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 $\rho_{12}$, these coefficients are complex numbers, and incorporate the nonclassical phase resulting from the term involving the difference potential [see Eq. (7)]. A smooth representation of $\rho_{ii}(\Gamma, t)$ is obtained by convoluting Eq. (8) with a test function $\phi(\Gamma)$: $\rho_{ii}(\Gamma, t) = \int d\Gamma' \phi(\Gamma - \Gamma') \rho_{ii}(\Gamma, t)$. We use a two-dimensional phase space Gaussian test function in the numerical calculations below, of the form
\begin{align}
\phi(\Gamma - \Gamma_{0}) &= \phi(q - q_{0}, p - p_{0}) \\
&= \frac{1}{2\pi \sigma_{q} \sigma_{p}} \exp \left[ -\frac{(q - q_{0})^{2}}{2\sigma_{q}^{2}} - \frac{(p - p_{0})^{2}}{2\sigma_{p}^{2}} \right]
\end{align}
where $\sigma_{q}$ and $\sigma_{p}$ are the widths of the test function in $q$ and $p$, respectively; these widths are determined by numerical considerations in practice. The evolution of $\rho_{ii}$ arises through the flow of the corresponding trajectories of the $ij$th ensemble, $\{\Gamma_{i}^{(n)}(t)\}$, and the coefficients of the trajectories, $\{a_{ij}^{(n)}(t)\}$.

The time evolution of the $\{\Gamma_{i}^{(n)}(t)\}$ is governed by conventional Hamilton’s equations, generated by the $ij$th Hamiltonian with initial conditions $\{\Gamma_{i}^{(n)}(0)\}$ and $\{a_{ij}^{(n)}(0)\}$. The time dependence of the weights $\{a_{ij}^{(n)}(t)\}$ is induced by the nonclassical electronic coupling. In practice, the numerical integration of the equations of motion for the full set of dynamical variables $\{\Gamma_{i}^{(n)}(t), a_{ij}^{(n)}(t)\}$ is accomplished by combining, within a given time step, the conventional classical molecular dynamics propagation of the phase space variables with a linear algebraic calculation of the updated coefficients. The details of these calculations can be found in Ref. 22.

We tested our trajectory implementation by treating a model one-dimensional system consisting of motion of a particle with mass $m$ on two coupled excited electronic surfaces. 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, $U_{1}(q) = Ae^{-2(q-q_{1})} - B$ which is initially populated by the optical excitation, and which is crossed by a bound Morse potential, $U_{2}(q) = \frac{D}{2}e^{-2(q-q_{2})} - 2e^{-(q-q_{2})}$]. The potential curves are shown in Fig. 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 $q_{c}$, $V(q) = V_{0}e^{-4(q-q_{c})^{2}}$.

The initial quantum state of the system is a localized Gaussian wavepacket on the repulsive surface, centered at the ground state equilibrium bond length $q_{g}$.
\begin{align}
\psi(q, t = 0) &= \frac{m\omega}{\pi\hbar}^{1/4} \exp \left[ -\frac{m\omega}{2\hbar}(q - q_{e})^{2} \right]
\end{align}
SIMULATION OF MOLECULAR TRANSITIONS USING CLASSICAL TRAJECTORIES

The numerical values of the parameters are 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 $V(q)$ will induce population transfer between the states.

<table>
<thead>
<tr>
<th>Table I. Numerical values of parameters, in atomic units</th>
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<tr>
<td>$A$</td>
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<td>$q_1$</td>
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<td>$q_2$</td>
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Exact quantum mechanical calculations were performed using the standard FFT-based grid method of Kosloff [20], generalized to treat coupled wavepacket dynamics on multiple electronic surfaces.

In Fig. 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 $\mu$th electronic state is given by $P_\mu(t) = \text{Tr} \rho_\mu(t) = \sum_j \rho_\mu^{j(j)}(t) \quad (\mu = 1, 2)$. The results of our trajectory-based implementation are compared with the corresponding numerically exact quantum mechanical quantities. The classical trajectory results are in nearly quantitative agreement with the quantum wavepacket dynamics.

3. Wavepacket Interferometry

In this section, we consider in more detail the treatment of electronic coherence in the context of our semiclassical Liouville approach. We focus on an idealized ultrafast experiment, which we call nonadiabatic wavepacket interferometry, in which the coherent phase relation between two initially populated electronic states plays a dominant role in the subsequent nonadiabatic dynamics. This manifestly coherent case is an important and challenging test for approximate methods for modeling nonadiabatic dynamics. An experimental realization of this general scenario is being pursued in ongoing work [23]. We consider an idealized pump-probe experiment consisting of a coherent ultrafast excitation from the lowest-lying ground electronic state to a coherent superposition of two excited electronic states |1⟩ and |2⟩ using a pair of laser pulses with a well-defined and controllable phase relation $\phi$. A diabatic representation [21, 24] is adopted for the description of the electronic states. For simplicity, we assume in our analysis that the laser pulses creating the initial coherent superposition are very short, and that each couples the ground state to a single upper surface. Each of the pulses then prepares a copy of the initial vibrational state $|\psi\rangle$ of the ground electronic state on the appropriate excited surface. As they evolve subsequently, the two components overlap in the region of crossing potential curves, and the dynamics is dominated by quantum interference of the possible pathways available to the moving wavepackets. The resulting effect is large if both initial components are comparable in magnitude, and if the relative phase of the two components is well-defined. Further, the sign and magnitude of the effect can be controlled externally by manipulating the phase $\phi$.

The two excited states treated explicitly in the simulation and the coupling term are chosen to be the same as those used in the previous section. We simulate the coupled state nuclear dynamics of this system using our trajectory implementation of the semiclassical Liouville method [22], and compare the results with those of numerically exact coupled-state wavepacket propagation. Following the development of the previous section, we select initial wavepackets of the form

$$
\Psi(q, 0) = \begin{bmatrix} \psi_1(q, 0) \\ \psi_2(q, 0) \end{bmatrix} = \begin{bmatrix} \sqrt{P_1(0)} \Psi(q - q_e) \\ \sqrt{1 - P_1(0)} \Psi(q - q_e) e^{i\phi} \end{bmatrix}
$$

(11)

where $\psi(q - q_e)$ is a real-valued minimum uncertainty configuration space Gaussian given by Eq. (10) centered at $q_e = 4.8$ (atomic units), $P_1(0)$ is the initial state 1 population, normalized such that $P_1(0) + P_2(0) = 1$, and $\phi$ is the relative phase of the initial wavepackets. The same value of $q_e$ is chosen for both wavepackets, to model a sudden vertical transition from a lower-lying harmonic ground state with equilibrium distance $q = q_e$. The initial expectation value of the momentum is zero for each component of $\Psi(q, 0)$.

Exact quantum mechanical results are obtained using the standard numerical methods developed for wavepacket propagation by Kosloff [20]. The semiclassical trajectory calculations are performed using the numerical algorithms described in the previous section and, in more detail, in Ref. 22.

In Fig. 3, we present composite results for several calculations performed with equal initial populations on states 1 and 2 ($P_1(0) = P_2(0) = 0.5$), and with a number of values of the initial relative phase $\phi$. We note that the results are strongly dependent on $\phi$, the relative phase of the initial wavepackets. In Fig. 4, we show the $\phi$ dependence of the final state 1 and state 2 populations, $P_1(T)$ and $P_2(T)$, respectively, where $T = 1100$ au corresponds to the final time of the numerical simulations.

It is found that the method yields excellent agreement for both the time-dependent populations and the detailed evolving states. This demonstrates that our semiclassical approach is capable of capturing the intrinsically quantum mechanical phenomenon of electronic coherence, even when the coherence plays a central and dominant role in the dynamics of electronic transition.

We compared our semiclassical method with the widely used surface hopping algorithm, which has proven to be an accurate and efficient tool for modeling coupled electronic-nuclear dynamics in a wide range of physical settings. While for the case of incoherent dynamics both methods produced similar results in about the same CPU time (roughly, 1/2 hour in a 533 MHz 164 LX Alpha processor), in the case of wavepacket interferometry, surface hopping failed to properly capture the interferometric quantum transition dynamics. For these one dimensional systems, the CPU time for both the exact and semiclassical calculations are quite modest. Nonetheless, we should note that the semiclassical calculation (and the surface hopping version) are actually slower than the exact wavepacket calculations for the results presented here. The promise of the method is that it will allow many-body systems that can not be tackled with exact quantum methods to be treated. We have indeed very recently applied the full implementation of the method successfully to model electronic relaxation of a model diatomic in a liquid, a several hundred atom system, in about 5 hours on a 533 MHz Alpha processor. For coherent processes such as the one described here, approximate but qualitatively accurate results can, in fact, be obtained with about the same effort as a conventional classical molecular dynamics simulation. A publication on this subject is in preparation. The origin of the shortcomings of the fewest-switches surface hopping method is the independent nature of the trajectory ensembles underlying surface hopping. Each trajectory determines its own fate using a stochastic algorithm and perhaps its individual representation of the evolving electronic degrees of freedom. Interference between distinct trajectories is not a part of the theory, and the decision of one trajectory to undergo a transition, or not, is unaffected by the rest of the ensemble. This is often a good approximation for the commonly encountered problem of electronic population relaxation. Here, the electronic coherence $\rho_{12}$ is absent initially, and must be created by the evolving populations. When created, $\rho_{12}$ is localized around the regions of crossing (or avoided crossing in the adiabatic re-
presentation) of the potential surfaces. This region becomes infinitesimally small as $\hbar \to 0$. The probability of electronic transition can be incorporated accurately into the method in this classical limit, as done in surface hopping, without resorting to a fully coherent theory. If the electronic coherence is large initially, such as is the case in the nonadiabatic wavepacket interferometry process, the approximation that individual trajectories undergo localized, independent transitions breaks down. Interference between various paths and processes can play an important role, and thus interdependence of trajectories within and between ensembles must be included. The semiclassical Liouville method employed here allows this quantum effect to be incorporated into a classical molecular dynamics simulation.

4. Conclusions

In this review, we have described a trajectory-based implementation of our recently proposed semiclassical-limit approach to molecular dynamics on coupled electronic surfaces. 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 multi-state 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. 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, are due to their focus on single independent trajectories coupled to quantum degrees of freedom. In the exact quantum mechanical description of multi-state dynamics, is the evolving wavepackets on each state that couple to each other. This roughly translates in the classical limit to interactions between the entire evolving ensembles. The work presented here constitutes a first successful attempt at building a classical trajectory-based implementation of the 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.