

Molecular dynamics with electronic transitions

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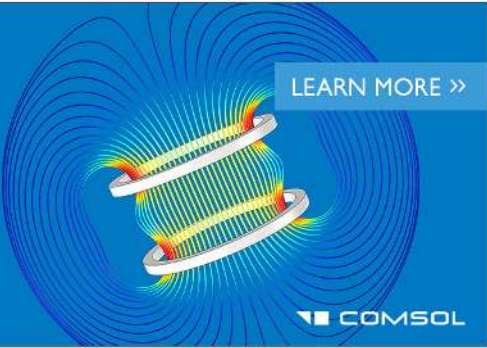
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Molecular dynamics with electronic transitions

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A method is proposed for carrying out molecular dynamics simulations of processes that involve electronic transitions. The time dependent electronic Schrödinger equation is solved self-consistently with the classical mechanical equations of motion of the atoms. At each integration time step a decision is made whether to switch electronic states, according to probabilistic "fewest switches" algorithm. If a switch occurs, the component of velocity in the direction of the nonadiabatic coupling vector is adjusted to conserve energy. The procedure allows electronic transitions to occur anywhere among any number of coupled states, governed by the quantum mechanical probabilities. The method is tested against accurate quantal calculations for three one-dimensional, two-state models, two of which have been specifically designed to challenge any such mixed classical-quantal dynamical theory. Although there are some discrepancies, initial indications are encouraging. The model should be applicable to a wide variety of gas-phase and condensed-phase phenomena occurring even down to thermal energies.

I. INTRODUCTION

The molecular dynamics technique has proved to be a very powerful tool for elucidating gas-phase and condensed-phase dynamical processes. The method is founded on the assumption that atomic motions are governed by classical mechanics subject to some appropriate multidimensional force field. Limitations of the method are well known. There may be practical difficulties with constructing accurate force fields, including large numbers of atoms, integrating for long times, or achieving accurate statistical samplings. There are also fundamental limitations that result from the basic assumptions of the method; quantum mechanical behavior is neglected and a single potential energy surface governs the motion. Quantal effects such as tunneling, interference and level quantization can be significant, particularly in low-energy processes involving hydrogen atom motion. Of at least comparable importance is the restriction to motion on a single potential energy surface. To each nondegenerate electronic state of a many atom system there corresponds a distinct Born-Oppenheimer potential energy surface. When a transition between electronic states occurs, the forces experienced by the atoms therefore change, often drastically. Proper incorporation of these effects can be crucial for describing a host of dynamical processes, including carrier recombination at surfaces or in condensed phases, photochemistry, radiationless transitions, laser or electron induced chemistry, dynamics at metal surfaces, and electron transfer in molecular, biological, interfacial, or electrochemical systems. In addition, the same considerations apply to other mixed quantal-classical situations not involving electronic transitions, e.g., vibrational relaxation in liquids.¹

The objective of this paper is to introduce a practical molecular dynamics method that accurately incorporates the effects of electronic transitions. The greatest advantage of the molecular dynamics approach is its ability to treat complicated many atom systems in full dimensionality. This practicality arises from the assumption that atoms obey clas-

sical mechanical equations of motion. We demand that this advantage be retained in the extended approach. Thus we require that atomic motions be described by classical-like trajectories. We make no attempt at incorporating quantum effects such as tunneling or zero-point motion, since current methods for doing this, even for motion on a single potential energy surface, require an enormous increase in computational effort over standard molecular dynamics. On the other hand, electronic transitions are inherently quantum mechanical and must be treated as such. Since the atomic trajectories determine the probabilities of electronic transitions and electronic transitions, in turn, strongly influence the forces governing the trajectories, the theory must treat self-consistently the classical and quantal degrees of freedom.

The treatment of nonadiabatic effects in molecular dynamics has a long history, with development of a host of classical, semiclassical, and quantum mechanical approaches.¹⁻³⁹ The most widely applied method and that which is most closely related to the current approach is the "surface-hopping" method with its many variants.^{7-10,23-28} However, with the method proposed in this paper transitions can occur anywhere, not just at localized avoided crossings. Furthermore, any number of coupled electronic states can be included, and quantum coherences between different "state switches" are maintained.

The objective of this work, to incorporate one kind of quantum effect (electronic transitions) while ignoring others (tunneling, zero-point motion, etc.) may appear inconsistent. But, to the extent that the Born-Oppenheimer separation of electronic and atomic motions is valid, the prominence of the two kinds of quantum effects are controlled by independent "small parameters" and there is no inconsistency in addressing either separately. The importance of tunneling and level quantization effects depends on the ratio of the atomic wavelength to the characteristic range of the potential. Thus these quantum effects are diminished in systems involving large atomic masses and large veloc-

ities. On the other hand, electronic transitions are controlled primarily by the separation between electronic energy levels, a property that is independent of atomic masses. For example, for a simple two-state avoided crossing, electronic transitions are probable if the so-called Massey parameter⁴⁰ ζ is of order unity

$$\zeta = \left| \frac{\hbar \mathbf{z} \cdot \mathbf{d}_{12}}{V_1 - V_2} \right| \gtrsim 1, \quad (1)$$

where V_1 and V_2 are the energies of the two adiabatic states at the position of the avoided crossing, \mathbf{z} is the atomic velocity vector, and \mathbf{d}_{12} is the nonadiabatic coupling vector to be defined below. Mass does not appear in this expression, and transitions are more probable at high velocities \mathbf{z} in contrast to the other quantum effects. Thus, it is proper to construct a theory which treats atomic motion in the short wavelength (classical) limit, while retaining effects of electronic transitions. Of course, any theory which attempts to combine quantal and classical degrees of freedom will ultimately encounter limits in which it fails. Our hope is to develop a method for which the range of useful accuracy will encompass most realistic systems of interest.

In the next section we present a list of attributes that are desirable, if not essential, for any approach that incorporates electronic transitions into molecular dynamics. We then propose a specific method, possibly the simplest that displays most of these attributes. In Sec. IV we test the proposed method against accurate quantum mechanical solutions of three model problems. We discuss the promise and limitations of the method in the final section.

II. DESIRED ATTRIBUTES OF THE METHOD

We list below some properties that are desirable in any extension of molecular dynamics to processes involving electronic transitions. We characterize these attributes as desirable rather than essential because there may be certain limits in which each may not be critical. Even such obvious criteria as unitarity and conservation of energy need not be exactly satisfied to be useful in all situations. Nevertheless, we view the majority of attributes listed here as almost essential.

(1) The method must be practical. As discussed, this appears to restrict us at present to methods in which the short wavelength limit is invoked for atomic motion, i.e., atoms follow trajectories. Furthermore, it is desirable that the trajectories be real valued, satisfy equations of motion that are not much more complicated than ordinary classical equations, need not be obtained iteratively, and need not be selected to satisfy "double-ended" boundary conditions.¹⁰ Calculation of electronic transition probabilities must not greatly increase the computational effort. Our insistence on a classical mechanical description of atomic motion is for practical reasons only. Considerable progress has been made in developing semiclassical and quantal theories of dynamical processes involving electronic transitions, and work in this area should definitely continue.^{1,4-6,9,10,13,18-21,41} In the present work we have more limited goals.

(2) Trajectories must split into branches. A variety of trajectory based methods have been developed which define

a "best" trajectory subject to the influence of electronic transitions. Among these methods are the "classical electron" model of Miller and co-workers¹¹ and the self-consistent eikonal approximation of Micha.¹⁴ Probably the most frequently employed of these methods is the so-called "Ehrenfest" or "time dependent Hartree" approach.²⁹⁻³⁹ With this method the atomic motions evolve classically on an effective potential $\bar{V}(\mathbf{R})$ given by

$$\bar{V}(\mathbf{R}) = \langle \psi_{\text{el}}(\mathbf{r}; \mathbf{R}) | H_{\text{el}}(\mathbf{r}; \mathbf{R}) | \psi_{\text{el}}(\mathbf{r}; \mathbf{R}) \rangle, \quad (2)$$

where \mathbf{r} and \mathbf{R} denote electronic and atomic positions, respectively, and brackets denote integration over electronic coordinates only. $H_{\text{el}}(\mathbf{r}; \mathbf{R})$ is the electronic Hamiltonian, i.e., the total Hamiltonian minus the atomic kinetic energy operator. $\psi_{\text{el}}(\mathbf{r}; \mathbf{R})$ is the electronic wave function which, in general, will be a linear combination of Born-Oppenheimer functions. Thus, the effective potential is the expectation value of the electronic Hamiltonian. The electronic wave function is determined self-consistently with the trajectory. In some situations these single trajectory methods can be quite accurate. But they cannot be satisfactory for a great many of the situations we wish to address. The basic problem is that, after it leaves a region of strong electronic coupling, the single trajectory evolves on a potential which is a weighted average of those corresponding to each electronic state. The physics of the situation demands that the trajectory be on one state or another, not somewhere in between. This argument is illustrated in Fig. 1. Consider an atom colliding with a metal surface. The atom may scatter from the surface or, if it can dissipate enough of its energy, it may remain trapped on the surface. Thus, if an electron-hole pair is excited the atom is more likely to remain trapped (trajectory branch 2), whereas if no electronic transition occurs it is more likely to scatter (branch 1). No weighted average path can accurately

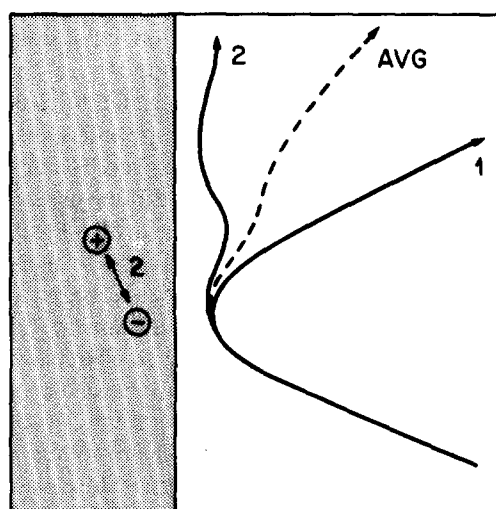


FIG. 1. Schematic illustration of a gas-surface scattering event showing two possible paths. If no electron-hole pair is excited in the solid (path 1), the gas scatters directly. If an electron-hole pair is excited (path 2), the loss of energy results in the gas remaining trapped on the surface. No average or best trajectory approach can adequately describe this situation.

ly represent both outcomes. Thus, a single trajectory method cannot describe electronically induced trapping of this sort. Many other important examples of the inadequacy of single trajectory methods can be cited. Frequently, in chemically reactive systems, one electronic state may have a low barrier and therefore lead to reaction with high probability, while another electronic state exhibits a high barrier that prohibits reaction. A single weighted average trajectory cannot correctly account for both pathways.⁴² Alternatively, a transition between two electronic states of relatively large energetic separation, although improbable, when it occurs can deposit a large amount of energy that can promote bond breakage. A single average trajectory will correspond to deposition of only a small fraction of the available energy, thus again failing to describe the essential physics. Herman¹ has emphasized the analog of this in vibrational relaxation, with the same conclusion: a single average or effective trajectory cannot properly describe the quantum transition.

A generally applicable molecular dynamics with electronic transitions must therefore include a mechanism for splitting a trajectory into two or more branches, each assigned to a particular electronic state and at least in regions of weak electronic coupling, each evolving on the potential energy surface corresponding to its electronic state. There are a number of ways to accomplish this. One possibility is to determine every possible path, and assign each a weight consistent with the electronic occupation number. An alternative is, at every branching point, to select one branch at random according to a sampling algorithm that achieves the correct statistical distribution of state populations. This latter "stochastic" approach is the one pursued in this work.

(3) The method should obey energy conservation, momentum conservation microscopic reversibility and unitarity.

(4) The method should be applicable to any number of coupled states and any number of entries into and exits from regions of strong electronic coupling.

(5) The method should be applicable to any kind of electronic coupling, not just localized avoided crossings. Thus, transitions should be allowed to occur at any place that the electronic coupling is significant. This is a major limitation of the conventional surface-hopping technique.

(6) Any electronic representation should be acceptable. It may be advantageous in some situations to employ a so-called "adiabatic" electronic representation⁸ instead of the usual adiabatic (Born–Oppenheimer) electronic basis.

(7) Electronic coherence should be described correctly. Accurate inclusion of quantum coherence associated with the electronic wave function is essential, and it has proved difficult to achieve in a classical-like theory based on probabilities rather than amplitudes. Electronic coherence effects can be very important. One example is the occurrence of "Stueckelberg oscillations"^{2,3} that occur due to interference between two or more pathways to the same final state. Of perhaps more importance, at least in condensed phase applications, is the proper inclusion of the washing out of electronic coherence that occurs as trajectories diverge in phase space.

(8) The method should be a molecular dynamics ap-

proach. Thus, the method should reduce to conventional molecular dynamics when electronic transitions have vanishing probability. Furthermore, the atomic positions as a function of time should be accurately described by the ensemble of trajectories, even in regions of strong electronic coupling. The probability of a final or intermediate outcome should be obtained simply by summing the trajectories that achieve that outcome.

(9) Finally, the method must be accurate. This is the most difficult criterion to achieve. No classical mechanical theory of molecular motion can be accurate in all situations, so we are forced to limit our goals: the range of useful accuracy of the method should include as large a number as possible of interesting experimental situations, and should include situations involving large numbers of atoms, many electronic states and low (thermal) energies.

Additional desirable features could be added to the list, but these will suffice for now. It is unlikely that any single method will best satisfy all of the criteria. Rather, different applications will require different procedures. Nevertheless, it would be valuable to find a method that incorporates the features listed here for as broad a range of applications as possible. In the next section we propose a candidate for such a method. The algorithm we propose satisfies all of the criteria listed except, perhaps, the most important one (number 9). Furthermore, it appears to be the simplest method that does so.

III. THE METHOD

As before, let \mathbf{r} designate the electronic coordinates and \mathbf{R} the atomic positions. More generally, \mathbf{r} could be any "internal" quantized coordinates including, for example, a high frequency vibration if desired, and \mathbf{R} are the "external" classical coordinates. The total Hamiltonian describing both electronic and atomic motion can be written

$$H = T_R + H_0(\mathbf{r}, \mathbf{R}), \quad (3)$$

where $H_0(\mathbf{r}, \mathbf{R})$ is the electronic Hamiltonian for fixed atomic positions and T_R is the atomic motion kinetic energy operator. We now select any orthonormal set of electronic basis functions $\phi_j(\mathbf{r}; \mathbf{R})$ that depend parametrically on the atomic positions. These may be adiabatic (Born–Oppenheimer) wave functions, or any other convenient set of electronic wave functions. We define matrix elements of the electronic Hamiltonian with respect to the basis functions

$$V_{ij}(\mathbf{R}) = \langle \phi_i(\mathbf{r}; \mathbf{R}) | H_0(\mathbf{r}, \mathbf{R}) | \phi_j(\mathbf{r}; \mathbf{R}) \rangle, \quad (4)$$

where as before brackets denote integration over electronic coordinates only. We also define the "nonadiabatic coupling vector" $\mathbf{d}_{ij}(\mathbf{R})$

$$\mathbf{d}_{ij}(\mathbf{R}) = \langle \phi_i(\mathbf{r}; \mathbf{R}) | \nabla_{\mathbf{R}} \phi_j(\mathbf{r}; \mathbf{R}) \rangle, \quad (5)$$

where the gradient is defined with respect to the atomic coordinates \mathbf{R} .

We now assume that atomic motion can be described by some as yet unspecified trajectory

$$\mathbf{R} = \mathbf{R}(t), \quad (6)$$

where t is time. We assume that $\mathbf{R}(t)$ is a continuous func-

tion of time, but it need not have continuous derivatives, and it need not be the solution of any classical mechanical equations of motion. The electronic Hamiltonian $H_0(\mathbf{r};\mathbf{R})$ is now a time-dependent operator, depending on time through $\mathbf{R}(t)$. We define a wave function $\psi(\mathbf{r},\mathbf{R},t)$ that describes the electronic state at time t . We expand $\psi(\mathbf{r},\mathbf{R},t)$ in terms of the electronic basis functions

$$\psi(\mathbf{r},\mathbf{R},t) = \sum_j c_j(t) \phi_j(\mathbf{r};\mathbf{R}). \quad (7)$$

The $c_j(t)$ are the complex-valued expansion coefficients. Substituting Eq. (7) into the time dependent electronic Schrödinger equation, multiplying from the left by $\phi_k(\mathbf{r},\mathbf{R})$ and integrating over \mathbf{r} gives

$$i\hbar \dot{c}_k = \sum_j c_j (V_{kj} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{kj}). \quad (8)$$

To obtain Eq. (8) we have made use of the chain rule,

$$\left\langle \phi_k \left| \frac{\partial \phi_j}{\partial t} \right. \right\rangle = \dot{\mathbf{R}} \cdot \mathbf{d}_{kj}(\mathbf{R}). \quad (9)$$

Equation (8) is the standard classical path method result.² For any assumed trajectory $\mathbf{R}(t)$, this set of coupled differential equations can be integrated numerically to obtain the amplitudes c_j of each electronic state. Note that there are two terms which promote transitions between electronic states, the off-diagonal elements of the electronic Hamiltonian V_{kj} and the nonadiabatic coupling $\dot{\mathbf{R}} \cdot \mathbf{d}_{kj}$. The V_{kj} vanish if the electronic basis functions have been defined in the adiabatic representation.

It will be convenient to rewrite Eq. (8) in the equivalent density matrix notation.¹⁵ Define

$$a_{kj} = c_k c_j^* \quad (10)$$

Eq. (8) then becomes

$$i\hbar \dot{a}_{kj} = \sum_l \{ a_{lj} [V_{kl} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{kl}] - a_{kl} [V_{lj} - i\hbar \dot{\mathbf{R}} \cdot \mathbf{d}_{lj}] \}, \quad (11)$$

where we have used the following properties of a set of orthonormal basis functions ϕ_j

$$\begin{aligned} \mathbf{d}_{jj}^* &= -\mathbf{d}_{jj}, \\ \mathbf{d}_{jj} &= 0. \end{aligned} \quad (12)$$

The diagonal elements a_{jj} are the electronic state populations, and the off-diagonal elements a_{kj} define the coherence. From Eq. (11), the populations satisfy

$$\dot{a}_{kk} = \sum_{l \neq k} b_{kl}, \quad (13)$$

where

$$b_{kl} = 2\hbar^{-1} \text{Im}(a_{kl}^* V_{kl}) - 2 \text{Re}(a_{kl}^* \dot{\mathbf{R}} \cdot \mathbf{d}_{kl}). \quad (14)$$

If the initial electronic state is chosen to be a pure state, then Eq. (11) is entirely equivalent to Eq. (8). Equation (11) is more general, however, since it admits the possibility of an initial mixed state.

Our task is to develop a procedure for self-consistent selection of the trajectory $\mathbf{R}(t)$ that best satisfies the requirements listed in the previous section. We have already restricted the choice to real-valued trajectories for practical

reasons. We have also argued that, at least in weak coupling regions, a trajectory must move on a single potential energy surface, not some weighted average. The simplest way to achieve this is to require that each trajectory move on a single potential energy surface at all times, interrupted only by the possibility of sudden switches from one state to another that occur in infinitesimal time. This will be a basic feature of our proposed method. It is not a necessary one, however. It is feasible to design a theory in which trajectories evolve on an effective potential that changes smoothly from that of the initial state to that of the final state during a finite time interval. Such a method is currently under development by Webster and co-workers,⁴³ following earlier work of Pechukas.⁵ See also the method of Dunne *et al.*¹⁵ Our choice of sudden state switches was made only for simplicity.

The sudden switching of electronic states is a feature of the standard surface-hopping procedure.^{7,8} The surface-hopping method has been successfully applied to a variety of situations which involve very localized regions of electronic coupling. It is not too surprising that a sudden switch of electronic states is appropriate in such cases. The sudden switch is more suspect in the present method for which switches can occur over extended regions of coupling. However, it may not be as harsh an approximation as it appears. When attempting to compare classical and quantal dynamics, it is generally useful to consider the behavior of a swarm of trajectories rather than an individual trajectory. With the present method, each trajectory may make a sudden switch of states. But for a swarm of trajectories entering a broad region of coupling, some trajectories will switch early, others later, and the net result will be a gradual flow of flux from one state to the other. Thus, the sudden switch procedure may be quite acceptable even in situations where transitions are not localized. Furthermore, the resulting distribution of switching points provides a natural way to damp out quantum coherence effects, as discussed below.

A central feature of the method presented here is the algorithm that determines when an electronic state switch will occur. We propose an algorithm which minimizes the number of state switches, subject to maintaining the correct statistical distribution of state populations at all times. Justification for this "fewest switches" criterion is given below. The algorithm that satisfies this criterion can be easily derived. Consider, first, a two-state system with a large number N of trajectories. At time t we assume that the number of trajectories assigned to state 1 is $N_1' = a_{11}' N$, where a_{11}' is the probability obtained by integration of Eq. (11). Similarly, $N_2' = a_{22}' N$ at time t . At a short time $t + \Delta t$ later, the state probabilities have changed slightly to a_{11} and a_{22} . For definiteness, let us assume $a_{11} < a_{11}'$, $a_{22} > a_{22}'$. In order to maintain the correct state populations $N_1 = a_{11} N$ and $N_2 = a_{22} N$, the number of trajectories switching from state 1 to state 2 in this time interval must exceed the number switching from 2 to 1. The fewest number of trajectory switches that can accomplish this is obtained if no switches from state 2 to state 1 occur, and $(a_{11}' - a_{11}) N$ switches from state 1 to state 2 occur. Since there are initially $a_{11}' N$ trajectories in state 1, the probability that one of these will switch during this time interval is $(a_{11}' - a_{11})/a_{11}' \approx \dot{a}_{22} \Delta t / a_{11}'$ for small

Δt . Thus, for a two-state system, the algorithm is as follows: Consider a trajectory which is in state 1 at integration step i . The trajectory is now integrated one time interval Δt , on state 1, to step $i + 1$. Equation (8) or Eq. (11) is also integrated to obtain the state probabilities at step $i + 1$, a_{11} and a_{22} . A uniform random number ξ between 0 and 1 is generated. A state switch from 1 to 2 will be invoked if

$$\frac{\Delta t b_{21}}{a_{11}} > \xi, \quad (15a)$$

where b_{21} is defined in Eq. (14). Similarly, if the system is in state 2 a switch to state 1 will be invoked if

$$\frac{\Delta t b_{12}}{a_{22}} > \xi. \quad (15b)$$

Note that for the two-state case, b_{21} is equal to the time derivative of a_{22} , so the algorithm is consistent with the fewest switches criterion discussed above. No transitions occur in regions of vanishing coupling. Furthermore, if the integration time step Δt is reduced the switching probability per step will be reduced by the same factor, but there will be proportionately more steps so the net switching probability through a finite region or finite time is independent of step size, as required. At any given time step, the switching probability is very small, approaching zero as Δt approaches zero. Finally, this algorithm will achieve the correct statistical populations of states 1 and 2. Thus, for a large ensemble of trajectories, the fraction that are in state 1 and state 2 at any time t will approach $a_{11}(t)$ and $a_{22}(t)$, respectively. This is easy to demonstrate. The net fractional increase $F(t)$ of trajectories into state 1 in a time interval t to $t + \Delta t$ is

$$F(t) = -P_1(t)F_1(t) + P_2(t)F_2(t), \quad (16)$$

where $P_i(t) = a_{ii}(t)$ is the fraction of trajectories in state i at time t , and $F_i(t)$ is the fraction of trajectories on state i that switch to the other state during the time interval. From Eq. (15),

$$F_1(t) = -\Delta t \dot{P}_1(t) H[-\dot{P}_1(t)]/P_1(t), \quad (17a)$$

$$\begin{aligned} F_2(t) &= -\Delta t \dot{P}_2(t) H[-\dot{P}_2(t)]/P_2(t), \\ &= \Delta t \dot{P}_1(t) H[\dot{P}_1(t)]/P_2(t), \end{aligned} \quad (17b)$$

where $H(x)$ is the standard Heaviside (step) function. Substituting Eq. (17) into Eq. (16) gives

$$\begin{aligned} F(t) &= \Delta t \{ \dot{P}_1(t) H[-\dot{P}_1(t)] + \dot{P}_1(t) H[\dot{P}_1(t)] \} \\ &= \Delta t \dot{P}_1(t). \end{aligned} \quad (18)$$

Thus, for an infinitesimal Δt , the rate of change of $P_1(t)$ is $\dot{P}_1(t)$, as required. Extension of this algorithm to many electronic states is straightforward, so we are now ready to present the method of molecular dynamics with electronic transitions.

We assume that we have a practical way of generating all of the required interactions, the matrix elements of the electronic Hamiltonian $V_{ij}(\mathbf{R})$, and the nonadiabatic couplings $\mathbf{d}_{ij}(\mathbf{R})$, for all relevant atomic positions \mathbf{R} . Molecular dynamics with electronic transitions then proceeds as follows:

Step 1. Initial conditions for the first trajectory are assigned consistent with the experiment to be simulated. This

includes assignment of the initial positions and momenta of all of the atoms, and assignment of the initial electronic density matrix elements a_{kj} . Typically, only a single electronic state k will be populated initially, i.e., $a_{ij} = \delta_{ik}\delta_{jk}$. There is no reason, however, why the initial conditions could not correspond to a coherent or incoherent mixture of electronic states.

Step 2. The classical mechanical equations of motion for the atoms on the current potential energy surface V_{kk} are integrated for a small time interval Δt . Equations (8) for the electronic amplitudes or Eq. (11) for the density matrix elements are integrated along this trajectory. The time interval Δt may be a single numerical integration time step, or a few steps, so long as it is sufficiently short that the electronic probabilities change only slightly during any interval.

Step 3. The switching probabilities g_{kj} from the current electronic state k to all other states j are computed from the density matrix elements using Eq. (14) and the expression

$$g_{kj} = \frac{\Delta t b_{jk}}{a_{kk}}. \quad (19)$$

If g_{kj} from Eq. (19) is negative, it is set equal to zero. A uniform random number, ξ , $0 < \xi < 1$, is then selected to determine whether a switch to any state j will be invoked. For example, if $k = 1$, a switch to state 2 will occur if $\xi < g_{12}$. A switch to state 3 will occur if $g_{12} < \xi < g_{12} + g_{13}$, etc.

Step 4. If no switch occurs (the vast majority of outcomes), return to step 2. If a switch to a different electronic state k' has occurred, the trajectory will now begin to evolve on the potential energy surface $V_{k'k'}$. Furthermore, if at the current atomic positions \mathbf{R} , $V_{kk}(\mathbf{R}) \neq V_{k'k'}(\mathbf{R})$, then a velocity adjustment must be made in order to conserve total energy. We choose to make this adjustment to the component of velocity in the direction of the nonadiabatic coupling vector $\mathbf{d}_{kk'}(\mathbf{R})$ at the position of the transition \mathbf{R} . If $V_{k'k'}(\mathbf{R}) > V_{kk}(\mathbf{R})$ and the velocity reduction required is greater than the component of velocity to be adjusted ("virtual" transition), then the state switch is not invoked. Adjustment of the component of velocity along the nonadiabatic coupling vector has been employed in surface hopping models,^{8,23-28} and has been justified by semiclassical arguments.¹³ After the velocity adjustment has been made (if needed), return to step 2.

This procedure is repeated until the trajectory has been declared finished by whatever criterion is appropriate. The sequence is then repeated for as many independent trajectories as required to obtain statistically significant conclusions. Note that with the procedure proposed here, the electronic density matrix elements a_{ij} are integrated continuously, with no resetting, throughout the entire trajectory, irrespective of how many state switches have occurred. In this way electronic quantum coherence effects are retained in this otherwise classical mechanical theory. Consequences of this technique for treating coherence are discussed below.

The core of the proposed method is the fewest switches criterion. One argument for imposing this constraint is illustrated schematically in Fig. 2. Consider a two-state problem, and let us examine an alternative switching algorithm. As before, at the end of each integration step a uniform random

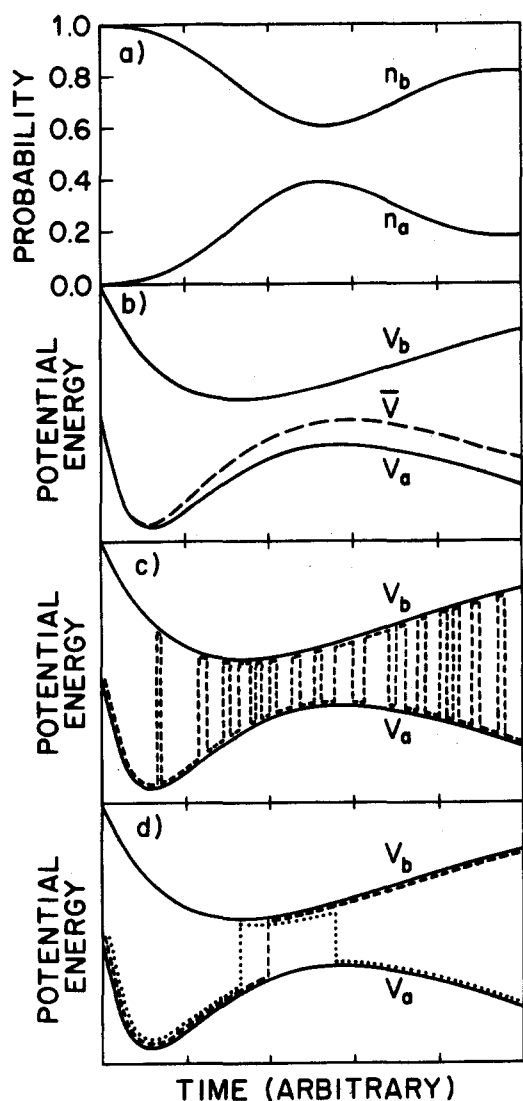


FIG. 2. Schematic illustration of possible surface switching methods. (a) Assumed evolution of state probabilities through a strong electronic coupling region as a function of time. (b) Solid curves are schematic potential energy surfaces. Dashed curve is a schematic effective potential as defined by a single trajectory approach. (c) Dashed curve is a schematic illustration of a rapidly switching trajectory, with probabilities of being on state 1 and state 2 at any time t given by $a_{11}(t)$ and $a_{22}(t)$, respectively. For switching time approaching zero, this trajectory becomes essentially equivalent to one that follows the effective potential in (b). (d) Dashed and dotted curves are two possible trajectories symbolic of the method proposed in this paper.

number ξ is generated. But now, if $\xi < a_{11}$ the trajectory will remain in state 1 or switch to state 1 if it was in state 2. If $\xi > a_{11}$, the trajectory will remain on or switch to state 2. This algorithm will, for an ensemble of trajectories, also produce the correct state populations at each time step. But the algorithm is unacceptable for other reasons, as illustrated in Fig. 2. Assume that the state populations evolve as a function of time as indicated in Fig. 2(a). Figure 2(b) illustrates schematically the effective potential \bar{V} , Eq. (2), that the system would evolve on with a best single trajectory procedure, e.g., the time-dependent Hartree method. Note that after it

leaves the region of electronic coupling, the system evolves on an unphysical weighted average interaction potential. The switching algorithm just discussed is illustrated in Fig. 2(c). At every integration step there is a relatively large probability of a state switch, as illustrated by the schematic trajectory. As the integration time interval becomes arbitrarily small, state switches occur at arbitrarily close intervals of time. The net effect is that the trajectory evolves on a weighted average of the two potentials. Thus this rapid switching algorithm essentially reproduces the unsatisfactory time-dependent Hartree result. Furthermore, state switches continue to occur even when the system is outside the region of strong electronic coupling, again unacceptable. The proposed fewest switches algorithm, illustrated in Fig. 2(d), overcomes these deficiencies.

IV. COMPARISON WITH ACCURATE QUANTUM RESULTS

In this section we apply the method proposed above to three model problems for which we have also obtained accurate numerical quantum mechanical solutions. Each of the models is a one-dimensional, two-state system with an atomic mass chosen to be 2000 a.u. (atomic units will be used throughout). For comparison, the mass of the hydrogen atom is 1836 a.u., so we may anticipate significant quantum effects associated with motion on a single potential energy surface that the classical theory has no hope of reproducing.

The quantum solutions were obtained by propagating wave packets by the fast Fourier transform technique. We employed exactly the procedure reported by Kosloff and Kosloff,⁴⁴ generalized to two electronic states. The wave packet $\psi(x, t)$ was initially chosen to be Gaussian,

$$\psi(x, 0) = \exp(ikx) \exp[-(x/\sigma)^2]. \quad (20)$$

The width parameter σ was typically chosen to be 20 times the inverse of the momentum k . Thus the initial wave packet had an energy spread of about $\pm 10\%$ of its initial energy, resulting in the possibility of some damping of quantum interference effects. For the examples studied, this was not a significant problem. Both diabatic and adiabatic representations were employed for the quantal calculations, giving the same results, as required.

The molecular dynamics simulations employed the adiabatic representation in all cases. Equation (8) for the electronic amplitudes and the classical mechanical equations of motion for the particle were integrated numerically using the Runge-Kutta-Gill method.⁴⁵ This method was chosen because it is a self-starting method, so no special treatment was required at each state switch. Results were shown to be independent of the integration time interval Δt so long as it was chosen sufficiently small. A sampling of 2000 trajectories was obtained for each run. The probabilities of each final outcome reported for the molecular dynamics methods were obtained by dividing the number of trajectories that achieved that outcome by the total, 2000, i.e., trajectories were simply counted with equal weightings.

A. Simple avoided crossing

The first model problem is defined by the following interactions in the diabatic representation:

$$\begin{aligned}
 V_{11}(x) &= A [1 - \exp(-Bx)], & x > 0, \\
 V_{11}(x) &= -A [1 - \exp(Bx)], & x < 0, \\
 V_{22}(x) &= -V_{11}(x), \\
 V_{12}(x) &= V_{21}(x) = C \exp(-Dx^2).
 \end{aligned}
 \tag{21}$$

The choices of parameters used for this calculation were $A = 0.01$, $B = 1.6$, $C = 0.005$, and $D = 1.0$, all in atomic units. The electronic states and potential energy curves in the adiabatic representation are obtained by diagonalizing the 2×2 matrix of elements V_{ij} . The resulting adiabatic potentials are shown in Fig. 3(a). Also shown in this figure is the nonadiabatic coupling strength d_{12} , defined by Eq. (5). The system was prepared in the lowest energy state in the asymptotic negative x region with a positive momentum, and the equations of motion were integrated until the particles or packet had completely left the interaction region. Comparison of the trajectory results with the quantum mechanical standard is shown in Fig. 4(a)–(c). Also shown for

comparison is the result of the Landau–Zener approximation² for the probability of transition P_{12} between adiabatic states

$$P_{12} \approx \exp \left[-2\pi V_{12}^2 / \left(\frac{dV_{11}}{dx} - \frac{dV_{22}}{dx} \right) \dot{x} \right] \tag{22}$$

with all parameters including the velocity \dot{x} evaluated at the crossing $x = 0$.

Agreement between trajectory and quantal results is essentially quantitative, except for the lowest energy quantal point calculated which shows some tunneling through the potential barrier of the lower adiabatic surface. Agreement at the higher energies is no surprise; even the Landau–Zener approximation is adequate here. Single path methods and standard surface-hopping methods will be of quantitative accuracy at high energy also.

The model is more challenging for kinetic energies below the asymptotic energy of the upper potential curve, in this case $E < 0.02$ a.u. or $k < 8.9$ a.u. [the position of the discontinuity in the trajectory results of Fig. 4(c)]. Below this energy there can be no final population in the upper electronic state (although single path methods will give considerable upper state population). However, in the range $7.7 < k < 8.9$, the particle has enough energy to be temporarily trapped in the well of the upper state. This trapping produces a possibility of momentum reversal, i.e., the particle may scatter back to negative x as shown by the peak in Fig. 4(b). The quantal and trajectory results are in excellent agreement for this process that cannot be described at all by single trajectory methods.

Finally, at momenta $k < 4.5$ the classical particle cannot surmount the potential barrier of the lower adiabatic state, and is reflected with 100% probability. Thus, there is step function behavior in the trajectory results for transmission [Fig. 4(a)] and reflection [Fig. 4(b)]. The quantal results round off this step function somewhat due to tunneling and barrier reflection. But the rounding is not too severe, particularly considering that the atomic mass selected is about equal to that of the hydrogen atom.

B. Dual avoided crossing

The second model problem is much more demanding for any classical mechanical based theory. It exhibits two avoided crossings which will produce quantum interference effects (Stueckelberg oscillations²) in the excitation probabilities. The interactions in the diabatic representation are

$$\begin{aligned}
 V_{11}(x) &= 0, \\
 V_{22}(x) &= -A \exp(-Bx^2) + E_0, \\
 V_{12}(x) &= V_{21}(x) = C \exp(-Dx^2),
 \end{aligned}
 \tag{23}$$

with the parameters chosen to be $A = 0.10$, $B = 0.28$, $E_0 = 0.05$, $C = 0.015$, and $D = 0.06$. The resulting adiabatic potential curves and nonadiabatic coupling are shown in Fig. 3(b).

The quantal and trajectory results are in good agreement at the high energies, both exhibiting strong Stueckelberg oscillations, Figs. 5(a)–5(c). The ability of the molecular dynamics method to reproduce this quantum effect is a

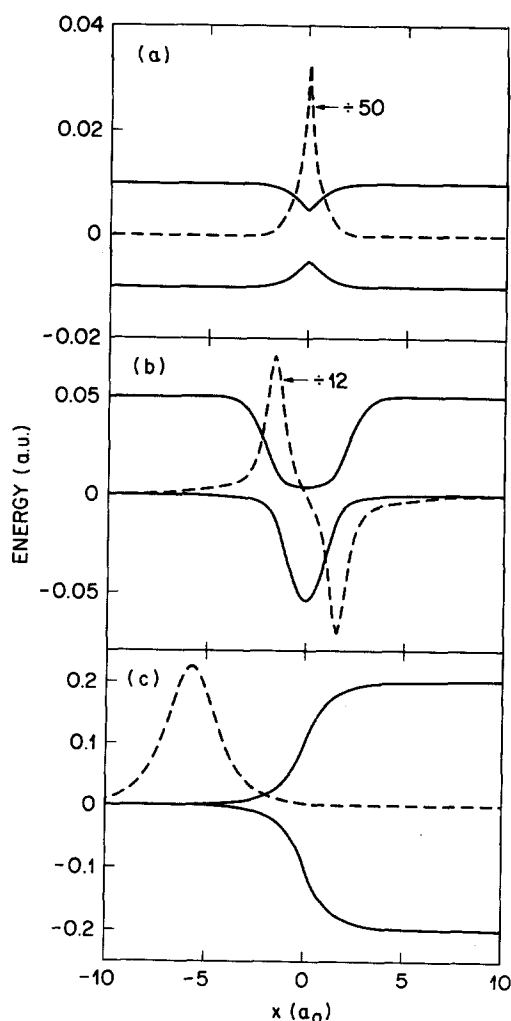


FIG. 3. Adiabatic potential energy curves (solid) and nonadiabatic coupling strength (dashed) as a function of position x . All quantities are in atomic units. (a) Simple avoided crossing model. (b) Dual crossing model. (c) Extended coupling with reflection model.

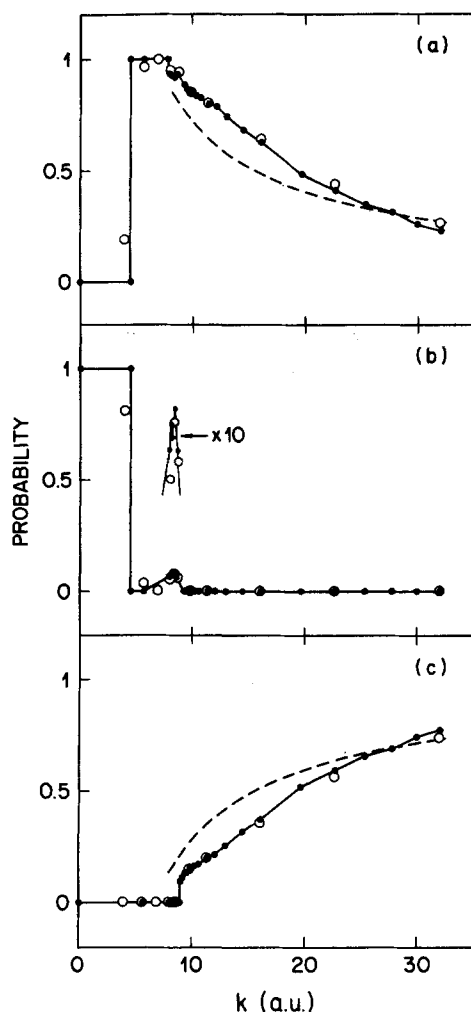


FIG. 4. Simple avoided crossing model. (a) Probability of transmission on the lower electronic state. (b) Probability of reflection on the lower state. (c) Probability of transmission on the upper state. Open circles are accurate quantum mechanical results. Dashed curves are the Landau-Zener approximation. Filled circles, connected by straight lines, are the results of the molecular dynamics with electronic transitions method. Each solid point was computed from 2000 trajectories. The statistical uncertainty of each solid point is ≤ 0.02 .

result of integrating Eq. (8) coherently throughout the entire trajectory. We emphasize that the molecular dynamics probabilities shown in Figs. 4–6 were obtained simply by counting the trajectories that ended up in each state. Thus, not only must the amplitudes computed by Eq. (8) correctly incorporate the quantum interferences, but the switching algorithm, Eq. (19), must achieve a statistical apportioning of the trajectories to each state that correctly reproduces the probabilities $|c_i^2|$ computed by Eq. (8).

At low energies the trajectory and quantal oscillations become out of phase, as shown in Figs. 5(a)–5(c). The discrepancy is particularly significant at energies below 0.05, ($\log_e E < 3$), for which the excited state is not asymptotically accessible. At these energies the excited state is still accessible in the region of its well. Flux trapped in the well may be

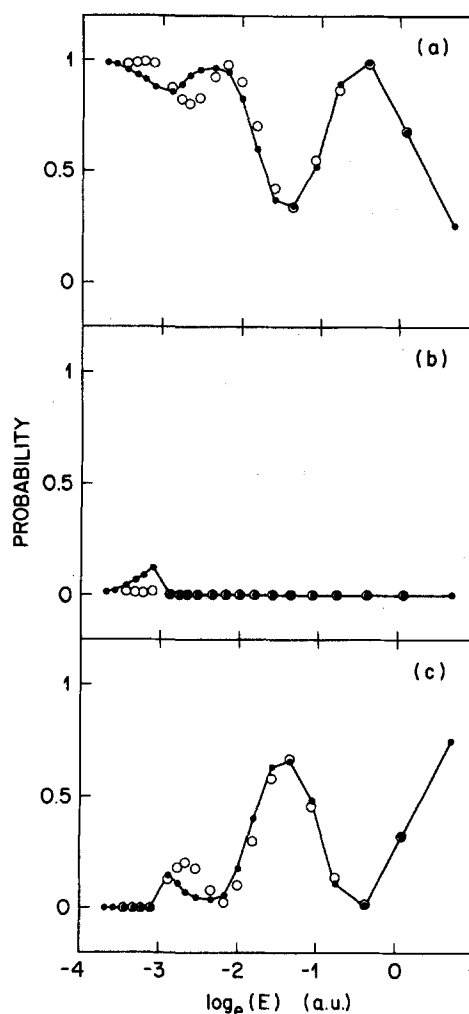


FIG. 5. Dual avoided crossing model. (a) Probability of transmission on the lower state. (b) Probability of reflection on the lower state. (c) Probability of transmission on the upper state. Symbols are the same as for Fig. 4.

reflected back in the negative x direction. The probability of reflection is thus controlled entirely by nonadiabatic transitions, and is very sensitive to quantum interference effects.

The final assessment of the performance of the trajectory method for this model problem is mixed. It is certainly encouraging that the method can reproduce the quantum interference effects so well at high energy, but the low energy discrepancy is disappointing. We can be hopeful that in many-atom systems at low energies the quantum interference effects will largely wash out, thereby removing the source of this type of discrepancy. This will have to be investigated in future studies.

C. Extended coupling with reflection

The third and final model we examine is probably the most difficult for a classical mechanical based theory to address. It involves an extended region of strong nonadiabatic coupling. In addition, the excited potential curve is repulsive for values of $x > 0$, so trajectories on the excited state will be

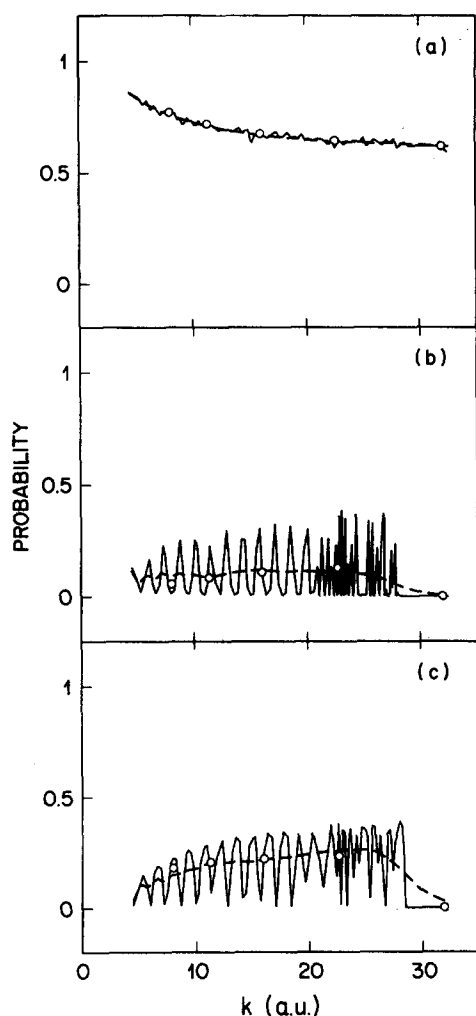


FIG. 6. Extended coupling with reflection model. (a) Probability of transmission on the lower state. (b) Probability of reflection on the lower state. (c) Probability of reflection on the upper state. Symbols are the same as for Fig. 4. Dashed curves were obtained by averaging the molecular dynamics results over a Gaussian distribution of initial momenta, with width equal to that of the wave packet employed in the quantal calculation.

reflected while those on the ground state will be transmitted. Single trajectory approaches are useless for this model, at least at low energies. Nevertheless, the model is representative of the majority of physically relevant low-energy, many-atom systems; trajectories on different potentials generally end up in very different regions of space.

The interactions in the diabatic representation are

$$\begin{aligned} V_{11} &= A, & V_{22} &= -A, \\ V_{12} &= B \exp(Cx), & x < 0, \\ V_{12} &= B [2 - \exp(-Cx)], & x > 0. \end{aligned} \quad (24)$$

The parameters were chosen to be $A = 6 \times 10^{-4}$, $B = 0.10$, and $C = 0.90$. The adiabatic potential curves and nonadiabatic coupling strength are shown in Fig. 3(c). For this model, both the trajectory and quantal calculations were performed exclusively in the adiabatic representation since the potential energy coupling V_{12} does not vanish as $x \rightarrow \infty$;

i.e., the diabatic states are coupled asymptotically.

Results are shown in Figs. 6(a)–6(c). Agreement between the quantal and trajectory values for the transmission probability is excellent at all energies [Fig. 6(a)]. Thus, the extended coupling region appears to pose no problem to the trajectory approach; electronic transitions need not be confined to localized regions.

There are two possible final reflected channels, states 1 and 2. The sums of the probabilities of the two reflected channels are in excellent agreement, since they equal one minus the transmitted probabilities. The partitioning between the two reflected channels is not in detailed agreement. The quantum mechanical results show a smooth dependence on energy, whereas the trajectory results show a high frequency oscillation. Thus, the trajectory method exhibits a quantum interference effect that is absent in the true quantal result. This interference effect arises via Eq. (8) from phase coherence between the first and second passages through the electronic coupling region, i.e., a Stueckelberg oscillation analogous to the previous model. The oscillations are absent in the quantal solution because only one of the two interfering wave packets is present at the second arrival in the coupling region. The excited state wave packet has reflected off the barrier and returned, but the ground state wave packet has continued to large positive x , never to return. Thus there should be no interference.

Fortunately, on average the trajectory result is accurate, and the oscillations are of sufficiently high frequency that in realistic multidimensional applications they would be expected to wash out. The dashed curves of Fig. 6 were obtained by averaging the trajectory results over the same spread of momenta embodied in the wave packet employed in the quantal calculation. Oscillations are almost completely removed, and classical and quantal calculations are thus in complete agreement. It is interesting, however, that the shortcoming of the classical mechanical based theory in this case is that it exhibits too much phase coherence, not too little.

V. DISCUSSION

We have presented a method for carrying out molecular dynamics simulations in systems in which electronic transitions occur. The method is practical, and can be applied to situations involving large numbers of atoms. It should also be applicable to other mixed quantum-classical situations such as vibrational relaxation. The method has features in common with the standard surface-hopping technique, but the proposed method does not require that state switches occur only in localized regions, it can accommodate any number of coupled electronic states, and it retains electronic phase coherence along the entire trajectory. The method automatically chooses when and where a state switch occurs, and the electronic state populations at any time are given simply by the fractional number of trajectories that are assigned to that state.

As with any mixed quantal-classical dynamics approach, the method cannot succeed in all situations. A major source of concern with the method is the treatment of electronic coherence. Equations (8) or, equivalently, Eqs. (11) governing the evolution of the electronic states are integrat-

ed coherently throughout the entire trajectory. This is essential to reproduce quantum interference effects such as those that arise in the second model problem of the previous section. But in many-atom systems, coherence effects should tend to wash out.⁴⁶ This occurs in the present model in a natural way. For an ensemble of trajectories with identical initial conditions, each individual trajectory will follow its own separate path. Each trajectory will switch to a different state at a slightly different time, and therefore evolve differently. This spreading of trajectories will increase with increasing time, particularly in situations exhibiting exponentially diverging trajectories. Since the electronic amplitudes are evaluated separately along each trajectory, the divergence of paths will lead to a loss of phase coherence when summing the results of all trajectories.

This treatment of coherence may not be optimal for all situations. In particular, in order for the proper loss of coherence to be manifested, a large ensemble of trajectories may be required. This may be prohibitively laborious in some condensed phase applications where conventionally only one or a very few trajectories are integrated. It might be advantageous in such cases to perform some "prior averaging" by introducing a coherence damping. A simple way to do this within the current method is to employ a modification of Eq. (11) in which a damping term has been added⁴⁷

$$i\hbar\dot{a}_{kj} = \sum_l \{a_{lj} [V_{kl} - i\hbar\mathbf{R}\cdot\mathbf{d}_{kl}] - a_{kl} [V_{lj} - i\hbar\mathbf{R}\cdot\mathbf{d}_{lj}] \} - i\hbar\gamma(1 - \delta_{kj})a_{kj}, \quad (25)$$

where the delta function δ_{kj} insures that the diagonal elements are not damped. Whether this or some alternative coherence damping procedure will be useful for particular applications must await further study. There are some obvious objections to employing Eq. (25), however. First, there is no clear method for choosing the magnitude of the arbitrary damping parameter γ . More importantly, it may well be essential to retain some coherence effects, even in condensed phase applications. For example, the undamped equations, Eq. (11), are invariant to a change in representation, e.g., adiabatic vs diabatic. But a diabatic state corresponds to a coherent mixture of adiabatic states. If an adiabatic basis were used in a region where diabatic states were more natural, or vice-versa, damping of coherence as in Eq. (25) would be improper. Thus, inclusion of an *ad hoc* coherence damping destroys the invariance to choice of representation and requires prior insight into the physics of the situation, thereby compromising the unbiased applicability of the method.

A second concern with the current method is the assumption that electronic state switches happen suddenly, in infinitesimal time. This appears to the author to be a reasonable assumption. As discussed, an ensemble of trajectories evolves smoothly from one state to another, with some trajectories making the sudden switch early and some late. But intuition is certainly not adequate justification. This assumption must be tested. An alternative method for molecular dynamics with electronic transitions under development by Webster *et al.*,⁴³ does not require transitions to occur suddenly. Rather, an effective Pechukas force⁵ carries the

trajectory smoothly from one potential energy surface to another. It will be instructive to compare results of the proposed method of Webster *et al.*, with those of the present method on identical problems.

In summary, based on the initial tests of the previous section, the method developed here is quite promising. It is very difficult to make a definitive test of such a method, of course. One dimensional models generally greatly exaggerate the defects of classical mechanical based theories. In particular, the models examined here exhibit strong quantal behavior (the particle mass was taken to be that of a hydrogen atom). Nevertheless, agreement is encouraging. It would be preferable to compare the method against an accurate quantal treatment of a realistic many-dimensional system, but tractable quantum mechanical methods for such systems do not yet exist. Comparison with experiment is unreliable because of the uncertainty of the assumed interaction potentials. The model problems examined here give only a preliminary indication of the validity of the approach. But two of the model problems were intentionally chosen to pose a difficult challenge to the method. If the success on these problems carries over to more complex systems, then the method proposed here could greatly increase the number of processes amenable to realistic simulation by molecular dynamics.

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