Critical appraisal of the fewest switches algorithm for surface hopping

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(Received 16 January 2007; accepted 15 February 2007; published online 5 April 2007)

In this paper the authors address the problem of internal consistency in trajectory surface hopping methods, i.e., the requirement that the fraction of trajectories running on each electronic state equals the probabilities computed by the electronic time-dependent Schrödinger equation, after averaging over all trajectories. They derive a formula for the hopping probability in Tully’s “fewest switches” spirit that would yield a rigorously consistent treatment. They show the relationship of Tully’s widely used surface hopping algorithm with the “exact” prescription that cannot be applied when running each trajectory independently. They also bring out the connection of the consistency problem with the coherent propagation of the electronic wave function and the artifacts caused by coherent Rabi-type oscillations of the state probabilities in weak coupling regimes. A real molecule (azobenzene) and two ad hoc models serve as examples to illustrate the above theoretical arguments. Following a proposal by Truhlar’s group [Zhu et al., J. Chem. Phys. 121, 7658 (2004) Zhu et al., J. Chem. Theory Comput. 1, 527 (2005)], they apply a decoherence correction to the state probabilities, in conjunction with Tully’s algorithm, and they obtain satisfactory results in terms of internal consistency and of agreement with the outcomes of quantum wave packet calculations. © 2007 American Institute of Physics, [DOI: 10.1063/1.2715585]

I. INTRODUCTION

Trajectory surface hopping (TSH) is one of the very first general methods1–14 designed to deal with the dynamics of non-Born-Oppenheimer processes in polyatomic molecules. In this method the system is divided into a classical (nuclei) and a quantum part (electrons). Many trajectories are usually run with the same or different initial conditions. Each trajectory, representing the time evolution of the classical degrees of freedom, evolves independently on a single electronic potential energy surface (PES) (the “current” state) with the possibility of occasional sudden hops among surfaces.

This kind of quantum/classical partition is computationally very convenient but suffers several drawbacks due to the complete neglect of the quantum features of the nuclear motion. Moreover, there is no generally accepted definition for a mixed quantum/classical system (as observed by Caro and Salcedo,15 this is because no such systems exist in nature) and then, a very large number of quantum/classical schemes have been developed, ranging from methods based on independent trajectories16–19 to more complicated approaches in which at least some aspects of the quantum nature of the nuclear motion are retained: full multiple spawning,20 quantum/classical Liouville dynamics,21–24–26 Bohmian trajectories,27 path integrals,28 and many others.29–34

However, the TSH method in its most popular implementation, i.e., Tully’s “fewest switches” approach7 (TFS), is still a good compromise between computational efficiency, conceptual simplicity, and accuracy of results,17 especially for medium-sized and large molecular systems.35 In this algorithm the electronic density matrix is propagated coherently along the trajectory and the transition probability is evaluated taking into account the variation in time of the diagonal density matrix elements. In this way the transitions only occur when needed, i.e., when the coupling among the electronic states is not negligible. Moreover, there is another simple but powerful idea behind the TFS approach: the number of state switches is minimized by imposing that, at each integration time step, the total flux of probability between any two states is obtained by one-way transitions.

A surface hopping algorithm should meet an internal consistency requirement: namely, at any time, the fraction of trajectories running on a given electronic state should be equal to the quantum probability (i.e., the diagonal density matrix element) of that state, averaged on the full bunch of trajectories. Even if the TFS algorithm was originally designed to be internally consistent, it has been recognized that in general this is not the case.10,14,36

The reason most often cited for the lack of internal consistency in surface hopping is the existence of “frustrated” hops. When a transition between two electronic states occurs, the nuclear kinetic energy is varied so that the total energy is conserved. Even if its theoretical necessity is questionable,25 the conservation of the energy during each trajectory greatly simplifies the analysis of results, besides trivially ensuring the energy conservation for the whole wave packet, which is the real physical requirement. If there is not enough nuclear kinetic energy to compensate for the sudden increase of the electronic potential energy, an upward transition is classically forbidden (or frustrated). A number of algorithms have been put forward to deal with frustrated hops in the framework of the TFS method,10,37,38 but the most common choice is to give up the transition and continue the trajectory without changes. Recently it has been recognized that frustrated hops are a necessary (albeit not sufficient) feature of the TFS algorithm to yield a long time quantum Boltzmann distribu-
tion of the trajectories on the electronic states for a quantum multilevel system coupled to a classical thermal bath.

In this paper, we will not focus on the problem of classically forbidden transition, but rather on a more fundamental source of inconsistency of the TFS algorithm, that is present even in the complete absence of frustrated hops. While this has already been recognized, a clear and formal identification of the underlying hypotheses of the TFS algorithm (and therefore its range of applicability) is lacking. Our first aim is to fill this gap. In particular, we shall write the expression of the “exact fewest switches” transition probability, based on the internal consistency criterium, and we shall show its relationship to Tully’s prescription. However, we shall see that such probability cannot be evaluated if each trajectory is run independently and that the consistency problem is related to the coherent propagation of the electronic wave function. The issue of quantum decoherence in mixed quantum-classical system has been addressed by a number of researchers (see, for instance, Refs. 14, 16, 17, 31, and 40 and references therein). We shall show that the lack of decoherence leads to a specific and evident failure of the TFS algorithm in a region of weak nonadiabatic coupling, both in a real system and in a simplified model. The decoherence scheme introduced by Truhlar and co-workers in the framework of a mean field approach can be applied within the TSH method to eliminate this problem.

II. THE SURFACE HOPPING SCHEME

The nuclear motion is represented by classical trajectories computed by integrating the Newton equations

\[
\dot{P}(t) = -\frac{\partial V(Q)}{\partial Q},
\]

\[
\dot{Q}_a(t) = \frac{P_a}{M_a},
\]

where \(Q\) and \(P\) are the sets of Cartesian nuclear coordinates and momenta, respectively. The molecule is considered to be in a given electronic state (the current state) at any time. Until we are in the adiabatic state \(|\psi_k\rangle\), the nuclear trajectory is driven by its PES: \(V(Q) = E_k(Q)\).

Let \(q\) be the collection of electronic coordinates. The electronic Hamiltonian \(\hat{H}_k(q; Q)\) as well as its eigenstates \(\psi_k(q; Q)\) and eigenvalues \(E_k(Q)\) are implicitly time dependent. If \(\Psi^{(j)}(t)\) is the nuclear trajectory, the time-dependent electronic state is written as

\[
|\Psi^{(j)}(t)\rangle = \sum_k C^{(j)}_k(t)|\psi_k^{(j)}\rangle,
\]

where the superscript \((j)\) is used to emphasize the trajectory dependence. The electronic wave function obeys the time-dependent Schrödinger equation (TDSE)

\[
i\hbar \frac{\partial |\Psi^{(j)}(t)\rangle}{\partial t} = \hat{H}_{el}^{(j)}|\Psi^{(j)}(t)\rangle.
\]

Using the expansion of the electronic wave function in the adiabatic basis we get the equations of motion for the probability amplitudes:

\[
\dot{C}^{(j)}_k = -iC^{(j)}_k\omega^{(j)}_k - \sum L C^{(j)}_L \langle \mathbf{Q}^{(j)} | \mathbf{G}^{(j)}_{KL} \rangle, \tag{4}
\]

where \(\omega^{(j)}_k = E_k/\hbar\) and \(\mathbf{G}^{(j)}_{KL}\) is the nonadiabatic coupling vector:

\[
\mathbf{G}^{(j)}_{KL} = \left( \psi_K | \frac{\partial}{\partial Q} | \psi_L \right). \tag{5}
\]

Equation (4) can be recast in the equivalent, adiabatic density matrix form:

\[
\dot{\rho}^{(j)}_{KL} = -i\rho^{(j)}_{KL}\omega^{(j)}_K + \sum_j \left( \rho^{(j)}_{KL}\mathbf{G}^{(j)}_{KL} \cdot \dot{\mathbf{Q}}^{(j)} \right), \tag{6}
\]

where \(\omega^{(j)}_K = \omega^{(j)}_K - \omega_L\) and \(\rho^{(j)}_{KL} = C_k^{(j)}C^*_L^{(j)}\). For later reference, the derivatives of the diagonal elements of the density matrix (state probabilities) can be arranged to

\[
\dot{\rho}^{(j)}_{KK} = -\sum_{L \neq K} B^{(j)}_{KL} \quad \text{where} \quad B^{(j)}_{KL} = 2 \text{Re}(\dot{\rho}^{(j)}_{KL}\mathbf{G}^{(j)}_{KL} \cdot \dot{\mathbf{Q}}^{(j)}). \tag{7}
\]

While the potential \(V(Q)\) in Eq. (1) is given by the adiabatic PES in the TSH scheme (see, e.g., Ref. 33, page 227), the integration of Eq. (6) can be profitably done in a diabatic basis.

In the next section we shall define a positive transition probability \(T^{(j)}_{K \to L}\) from the current state \(K\) to another state \(L\), at each integration time step \(\Delta t\) of the \(j\)th trajectory, on the basis of the \(B^{(j)}_{KL}\) and \(\rho^{(j)}_{KL}\) quantities. Given the \(T^{(j)}_{K \to L}\) probabilities, a (pseudo)random number \(R^{(j)}\) uniformly distributed in the interval \([0, 1]\) is generated and the transition from state \(K\) to state \(M\) is performed if

\[
\sum_{L=1}^{M} T^{(j)}_{K \to L} < R^{(j)} \leq \sum_{L=1}^{M} T^{(j)}_{K \to L}. \tag{8}
\]

Let \(N_K(t)\) be the number of trajectories which are in state \(K\) at time \(t\) and \(\Pi_K(t) = N_K(t)/N_T\) the corresponding fraction of the total number of trajectories \(N_T\). We shall denote by a superimposed bar the average of any quantity over all trajectories. So, \(\bar{p}_K\) is the averaged population of state \(K\):

\[
\bar{p}_K = \frac{1}{N_T} \sum_{K=1}^{N_T} \rho^{(j)}_{KK}, \tag{9}
\]

then the TSH algorithm is internally consistent if

\[
\Pi_K(t) = \bar{p}_K(t), \quad \forall K, t. \tag{10}
\]

In most applications the \(\Pi_K(t)\) functions are taken to represent the electronic population dynamics and the \(\bar{p}_K(t)\) are simply disregarded. In fact, this is consistent with the usual prescription for the evaluation of any observable, which is to average the electronic expectation values over all trajectories with equal weights.
After a jump from surface \( E_K \) to \( E_L \) the nuclear kinetic energy has to be changed from \( T \) to \( T' = T + E_K - E_L \). This is usually accomplished by adjusting the nuclear momenta along the nonadiabatic coupling vector \( G_{KL} \). If \( E_L - E_K > 0 \) it may happen that there is not enough nuclear kinetic energy to compensate for the sudden variation of potential electronic energy, which is the origin of the “frustrated hops.”

### III. INTERNAL CONSISTENCY AND DECOHERENCE IN SURFACE HOPPING

A TSH simulation is usually performed by running many trajectories, starting with different nuclear coordinates and momenta, and sometimes even with different electronic wave functions. The initial coordinates and momenta are usually sampled from a normal coordinate Wigner distribution or a classical Boltzmann distribution with any form of the potential function. Note that, given the stochastic nature of the TSH method, in general, converged results can be obtained only if many trajectories are launched from each starting point (or small volume) in the phase space. Therefore, in this section we shall focus on a subset of trajectories, all sharing the same initial conditions. If the internal consistency requirement is satisfied for such a subset, it will also be for any distribution of initial conditions, and vice versa.

We want to define an internally consistent transition probability, i.e., one that fulfills the requirements of Eq. (10). First, note that this goal would be trivially achieved by frequent hops, each one landing in state \( K \) with probability \( p_K = \rho_K(t) \). However, such an approach is, clearly, totally unphysical: we want to keep the fewest switches approach and define a transition probability which minimizes the number of hops (and therefore is connected to the \( p_K \) rather than to the \( \rho_K \)). Second, note that we have to work in terms of averaged quantities, as in Eq. (10). We want therefore to define an averaged transition probability \( \bar{T}_{K\rightarrow L} > 0 \) such that, in the small time interval \( \Delta t \),

\[
\Delta \Pi_K(t) = \bar{T}_{K\rightarrow L}(t) \Delta t, \quad \forall K,t,
\]

where \( \Delta \Pi_K(t) = \Pi_K(t + \Delta t) - \Pi_K(t) \). By definition of averaged transition probability we have

\[
\Delta \Pi_K = - \sum_L \Pi_K \bar{T}_{K\rightarrow L} + \sum_L \Pi_L \bar{T}_{L\rightarrow K}.
\]

Assuming fully coherent propagation of the electronic density matrix [by integration of Eq. (6)], the time derivative of the averaged state probabilities is given by Eq. (7):

\[
\dot{\bar{p}}_K = - \sum_{L \neq K} \bar{B}_{KL} \Delta t.
\]

Substituting expressions (12) and (13) in Eq. (11) we finally get

\[
\bar{T}_{K\rightarrow L} = \max \left\{ 0, \frac{\bar{B}_{KL}}{\Pi_K} \Delta t \right\}.
\]

We will refer to the above expression as to the exact fewest switches (EFS) transition probability. If the EFS transition probability could be computed and used for all trajectories, \( \Pi_K \) would coincide with \( \bar{p}_K \) at any time.

Note that Eq. (14) contains averaged quantities. Therefore, if the trajectories are run independently, the EFS transition probability cannot be evaluated; in this case there is no way to obtain an internally consistent algorithm of general validity. Running many trajectories in parallel, one could compute the \( B_{KL} \) and \( \Pi_K \) quantities that define \( \bar{T}_{K\rightarrow L} \), but this solution, besides being unpractical, is physically flawed. In fact, in this way the swarms of trajectories running into completely uncoupled channels (for instance, different reaction products) would influence each other. Note that this problem arises because the electronic density matrix is propagated according to Eq. (6) in a fully coherent way. As we shall see more in detail below, quantum decoherence effects can be added to the TSH scheme\(^{31}\) by some ad hoc procedure, such as resetting the electronic density matrix after a hop\(^{40}\) or after leaving a region of strong coupling,\(^{14}\) or by a smooth “decay of coherence.”\(^{16,17}\) In these cases, an (approximate) internal consistency can be achieved even without applying the EFS transition probability.

In Tully’s fewest switches algorithm a transition probability is defined for each trajectory:

\[
T_{K\rightarrow L}^{(<)} = \max \left\{ 0, \frac{B_{KL}}{P_K} \Delta t \right\}.
\]

Therefore, the averaged transition probability is

\[
\bar{T}_{K\rightarrow L} = \frac{\Delta t}{N} \sum_{j \neq K} \frac{B_{KL}^{(j)}}{P_K^{(j)}} \max \{0, B_{KL}^{(j)}\},
\]

where \( j \in K \) means that we only consider the trajectories running on the surface \( E_K \) at the time \( t \). Comparing Eqs. (14) and (16) it is immediately clear that, in the general case, \( \bar{T}_{K\rightarrow L} \) does not coincide with the exact fewest switches transition probability: the TFS algorithm is not internally consistent, even in the complete absence of frustrated hops. The implicit hypothesis, by which Tully’s algorithm would be internally consistent, is that all the trajectories (to be specific, all the trajectories sharing the same initial conditions, see the beginning of this section) give place to the same \( p_K^{(j)}(t) \), so that \( \bar{T}_{K\rightarrow L} = p_K(t) \). In this case it can be easily seen that \( \bar{T}_{K\rightarrow L} \) equals the EFS transition probability. However, hopping to another PES does affect the trajectory and therefore \( p_K^{(j)}(t) \), so the above assumption is not valid.

It has already pointed out\(^{14}\) that Tully’s algorithm is expected to work very well in one-dimensional systems, with a single passage through the coupling region. In fact, in this case the quantum state probabilities \( p_K^{(j)} \) can hardly be very different for two distinct trajectories. However, this is not true for a multidimensional system;\(^{14}\) in this case, after a passage through a coupling region \( p_K^{(j)} \) will strongly depend on the time and number of hops. To be specific, consider that in many photochemical reactions, and most frequently in photodissociations, the decay from excited to ground state takes place in the proximity of a minimum of the upper PES. This may or may not coincide with the cusp of a “peaked” conical intersection\(^{43}\) but is placed anyway in a near-
degeneracy region for the two PESs. In such situations, when a trajectory hops from the excited to the ground PES, it quits rather soon the near-degeneracy or coupling region where nonadiabatic events are probable; then, the probability of “backward” (ground→excited) hopping drops quickly towards zero. Instead, until the trajectory runs on the upper PES, it is attracted towards the minimum and it remains in the near-degeneracy region or it oscillates in and out of it. So, whether a hop takes place or not has a strong and qualitatively predictable influence on the $p_{\text{K}}^{(j)}$ functions. This problem will be illustrated in the next section with the help of an analytically solvable model.

A quantum wave packet, by going through a strong coupling region, is also split in two components, traveling on either electronic state. The two wave packets are initially coupled by the nonadiabatic terms of the Hamiltonian and keep exchanging population, but they end up evolving independently, as they travel into distant regions of the space of the nuclear coordinates and momenta. The truly quantum mechanical time evolution therefore entails a progressive decoherence, which is practically irreversible in many-dimensional systems. On the contrary, the semiclassical TDSE, Eq. (3), implies a fully coherent propagation of the electronic wave function due to the underlying assumption that the molecular geometry is described by a single point in the nuclear phase space (the same for all electronic states). Of the various procedures that can be used to introduce the decoherence in semiclassical schemes, we have adopted a simplified version of one put forward by Truhlar and co-workers.$^{16,17}$ in the framework of mean field methods. At each integration time step the coefficients $C_{\text{K}}$ are evaluated by solving Eq. (4) and are used to obtain the TFS transition probabilities, by which the current running state (labeled $M$) is determined by the TFS algorithm. Then we set

\[
C_{\text{K}}' = C_{\text{K}} e^{-\Delta t / \tau_{\text{KM}}}, \quad \forall \ K \neq M,
\]

\[
C_{\text{M}}' = C_{\text{M}} \left(1 - \sum_{K \neq M} |C_{\text{K}}'|^2 |C_{\text{M}}|^2 \right)^{1/2},
\]

\[
\tau_{\text{KM}} = \frac{\hbar}{|E_{\text{K}} - E_{\text{M}}|} \left(1 + \frac{C_{\text{K}}}{E_{\text{K}}}ight),
\]

where $E_{\text{kin}}$ is the nuclear kinetic energy and $C$ is a constant we put, following Zhu et al.$^{16}$ equal to 0.1 hartree; note that this scheme corresponds to the non linear decay of mixing (NLDM) prescription of Truhlar and co-workers.$^{17,46}$ The $C_{\text{K}}'$ are then used to continue the time evolution of the electronic wave function. The correction (17) of the expansion coefficients tends to equate the $\bar{p}_{\text{K}}$ populations to the $\Pi_{\text{K}}$ distributions of the trajectories in the quantum states and progressively cancels the coherence effects. However, the decoherence correction is negligible when the state probabilities undergo fast changes and the energy gap between two electronic states is small, i.e., in those cases where the TFS algorithm does not need to be amended. In Sec. V we shall examine a real example of excited state decay, where the lack of decoherence of the quantum/classical propagation causes a well identified artifact. We shall also set up a model, for which numerically exact quantum results can be computed, to analyze quantitatively this problem. In both cases the decoherence correction shows its usefulness.

IV. AN ABSTRACT MODEL FOR IRREVERSIBLE DECAY

We describe now a simple model for irreversible decay from an upper to a lower electronic state without explicit reference to the shape of the PES and coupling functions; in this sense we call it an “abstract” model. The decay of electronic excitation in polyatomics is, in fact, substantially irreversible, even when it is ultrafast, for the reasons discussed above: It is therefore important to see how the TFS algorithm performs in this case.

We consider then two states, with the molecule initially ($t=0$) in state 2. Our simplifying assumption is that the $p_{\text{K}}^{(j)}(t)$ functions are monotonically nonincreasing; in this way, $1 \rightarrow 2$ jumps are not allowed in the fewest switches scheme. As discussed above, this is quite reasonable in many circumstances. Since all trajectories share the same initial conditions (see above) until they are in state 2 the state probabilities are trajectory independent:

\[
p_{\text{K}}^{(j)}(t) = p_{\text{K}}^{(j)}(t), \quad \forall \ j \neq 2.
\]

After the jump on state 1 we have

\[
p_{\text{K}}^{(j=1)}(t) = q^{(j)}(t - t_j) p_{\text{K}}^{(2)}(t_j),
\]

where $t_j$ is the time at which the $j$th trajectory hops and, according to the above assumption, $q^{(j)}(x)$ are monotonically nonincreasing functions with $q^{(j)}(0)=1$ and $q^{(j)}(x) \in [0,1]$.

Using Eq. (16) we are able to write the averaged TFS transition probability in the present case:

\[
\bar{\Pi}_{2 \rightarrow 1}^{\text{Tully}} = \frac{\bar{p}_{\text{K}}}{p_{\text{K}}} \Delta t.
\]

At this point $\Pi_{2 \rightarrow 1}^{\text{Tully}}$ can be evaluated from Eq. (12) which reads, for small $\Delta t$,

\[
\Pi_{2 \rightarrow 1}^{\text{Tully}} = \frac{\bar{p}_{\text{K}}}{p_{\text{K}}} \Delta t,
\]

and therefore we simply get $\Pi_{2 \rightarrow 1}^{\text{Tully}}(t) = p_{\text{K}}^{(2)}(t)$, irrespective of the behavior of the probabilities in state 1 [i.e., of the $q^{(j)}(t)$ functions]. Of course this is not correct and, in particular, if $q^{(j)}(t)$ decays slower (faster) than $p_{\text{K}}^{(j)}(t)$ we expect the $\Pi_{2 \rightarrow 1}^{\text{Tully}}(t)$ function to overestimate (underestimate) the actual transition rate.

The decoherence correction is not directly applicable to this model, because we have not specified the energy difference between ground and excited states, nor the kinetic energy. However, we can examine the limiting case in which $\tau_{\text{KM}}$ is extremely short, so that the effectiveness of the correction is maximum. In this way, $p_{\text{K}}^{(j)}$ is always reset to $\delta_{M,2}$ at the end of a time step, for a trajectory running on state $M$. As a consequence, we always fulfill the consistency requirement ($\bar{p}_{\text{K}} = \Pi_{\text{K}}$), but, of course, with altered $p_{\text{K}}^{(j)}(t)$ functions. Therefore, the resulting populations are not necessarily equal.
to the EFS ones. Since $p_2^{(j)}$ is reset to 1, as long as the trajectory is in the excited state, its derivative is replaced by a constant, equal to $(p_2)_{\tau=0}$. With these assumptions, we have

$$ T_2^{\text{DC}} = - (p_2)_{\tau=0} \Delta t $$

and

$$ \Pi_2^{\text{DC}} = - (p_2)_{\tau=0} \Pi_2^{\text{DC}}. $$

Then, the decay is always exponential:

$$ \Pi_2^{\text{DC}}(t) = e^{-\frac{\tau}{\Pi_2^{\text{DC}}}}, $$

with $\tau^{\text{DC}} = (p_2)_{\tau=0}^{-1}$.

We examine now a couple of more specific examples. In both examples the $q^{(j)}(t)$ functions are assumed to be trajectory independent: $q^{(j)}(t') = q(t')$.

A. Case A

Suppose $q(t) = 1$, i.e., the probabilities stop changing after the $2 \rightarrow 1$ surface hop. The averaged TFS state probability $\bar{p}_2^{\text{Tully}}$ is given by

$$ \bar{p}_2^{\text{Tully}}(t) = p_2(t) \Pi_2^{\text{Tully}}(t) + \int_0^t q(t-t') p_2(t') \Pi_1^{\text{Tully}}(t') dt'. $$

Since $\Pi_1^{\text{Tully}}(t) = p_2(t)$ and $q(t) = 1$ we immediately get

$$ \bar{p}_2^{\text{Tully}}(t) = \frac{1}{2} [p_2(t) + 1], $$

and therefore $\Pi_2^{\text{Tully}}(t) < \bar{p}_2^{\text{Tully}}(t)$. The EFS averaged transition probability is given by

$$ \bar{p}_2^{\text{Tully}}(t) = \begin{cases} 
\frac{\exp(-2t/\tau)}{2\tau - \tau} \left( \frac{\tau'}{\tau} - \frac{\tau'}{\tau} \exp\left(\frac{2\tau' - \tau}{\tau\tau'} t\right) \right), & 2\tau' \neq \tau \\
\frac{\exp(-2t/\tau)}{\tau} (t+1), & 2\tau' = \tau.
\end{cases} $$

The corresponding EFS quantities are obtained using again Eq. (25) and imposing $\bar{p}_2(t) = \Pi_2(t)$. Note that the EFS averaged transition probability can only be found a posteriori once $\bar{p}_2(t)$ is known:

$$ T_2^{\text{EFS}} = - (\bar{p}_2)_{\tau=0} \Delta t, $$

and therefore the TFS transition probability, Eq. (20), is overestimated. Using the EFS transition probability and proceeding as above we get the EFS (i.e., the correct) $\Pi_2(t)$ and $\bar{p}_2(t)$ functions:

$$ \Pi_2^{\text{EFS}}(t) = \bar{p}_2^{\text{EFS}}(t) = \exp(p_2(t) - 1). $$

The decay rate is then overestimated by $\Pi_2^{\text{Tully}}(t)$ and underestimated by $\bar{p}_2^{\text{Tally}}(t)$.

The simplest formulas, within this variant of the model, are obtained by assuming a linear dependence of $p_2$ on time, i.e., $p_2(t) = 1 - t/\tau$ for $t \leq \tau$, and $p_2 = 0$ afterwards. In this case, the decoherence correction produces an exponential decay, $\Pi_2^{\text{DC}}(t) = e^{-\tau t}$, while the EFS result is exponential only for $t \leq \tau$ and constant for $t > \tau$ (see Fig. 1).

B. Case B

We consider now a slightly more complex model, whereby the probability of state 2 decays exponentially, but with different rates according to the state where the trajectory runs. Therefore we have $p_2(t) = e^{-\frac{2}{\tau'}} t$ and $q(t) = e^{-\frac{2}{\tau} t}$. The TFS relevant quantities are found using Eqs. (20), (21), and (25):

$$ T_2^{\text{Tully}}(t) = \frac{1}{\tau} \Delta t, $$

$$ \Pi_2^{\text{Tully}}(t) = e^{-\frac{2}{\tau} t}, $$

The corresponding EFS quantities are obtained using again Eq. (25) and imposing $\bar{p}_2(t) = \Pi_2(t)$.

state (i.e., the $\tau'$ decay), and the function we obtain is the same as $\Pi_2^{\text{Tally}}$:

$$ \Pi_2^{\text{DC}}(t) = \bar{p}_2^{\text{DC}}(t) = e^{-\frac{2}{\tau'} t}. $$

For a polyatomic molecule making a single passage through an interaction region one would probably find $\tau' > \tau$. The reason is that, after the $2 \rightarrow 1$ transition, the system is expected to quit rapidly the coupling region, as already noted above. We discuss then the case $\tau' > \tau$, which is illustrated in Fig. 2. As expected, $\Pi_2^{\text{Tally}}$ decays faster than the averaged state population $\bar{p}_2^{\text{Tally}}$, while the EFS behavior is found in between, just as in case A (Fig. 1). At short times ($t \ll \tau$) all treatments yield the same decay rate, but this agreement deteriorates at later times. Although it should be stressed that the decoherence procedure we apply is just an ad hoc cor-
preferred to them, as already advocated by Tully and several investigations by our group.35,44,45 The PESs and toisomerization of azobenzene, which has been the subject of are considerably different from zero.

\[ p \bar{K}_{Tully} \] necessarily an improvement over the commonly employed space–configurations interaction

independent, given the closeness of the PESs. On the other case of a Boltzmann distribution of starting geometries and

The problem is well illustrated by considering the photoisomerization of azobenzene, which has been the subject of several investigations by our group.35,44,45 The PESs and couplings for the azobenzene molecule were obtained on the fly during the dynamics calculations, using a semiempirical reparametrized AM1 Hamiltonian and complete active space–configurations interaction (CAS-CI) wave functions (four electrons in six orbitals) supplemented by all single excitations from the last five occupied to the first five virtual orbitals. The molecular orbitals were obtained by the SCF method with floating occupation numbers.41 The \( \text{cis} \rightarrow \text{trans} \) and \( \text{trans} \rightarrow \text{cis} \) photoisomerization of azobenzene after \( n \rightarrow \pi^* (S_0 \rightarrow S_1) \) excitation was also investigated with the full multiple spawning (FMS) method, using an ensemble of 20 different initial wave packets (10 for the CAB isomer).35 Looking at the fraction of trajectories in \( S_1, \Pi_2(t) \), the TSH-TFS results compared rather well with the FMS ones. According to both methods the photoisomerization is mainly due to the torsion of the N–N double bond. The decay of the \( n \rightarrow \pi^* (S_1) \) state occurs when the \( S_1 \sim S_0 \) crossing seam is approached, mainly by the same torsional motion, with the help of the symmetric opening of the NNC bond angles and of other geometrical deformations. Starting from \( \text{cis-} \)azobenzene (CAB) the dynamics is very fast (the \( S_1 \) state is depopulated almost completely in 100 fs) and the two approaches gave very similar results. For \( \text{trans-} \)azobenzene (TAB) we also had a good agreement for times below \( \sim 0.8 \) ps, but we found a long time component in the excited state decay by the FMS method, at variance with the TSH-TFS results. Figure 3 shows the FMS populations, averaged over 20 runs, and new TSH-TFS results, obtained by launching 100 trajectories for each FMS run, with the same initial conditions, but different starting random number seeds (in total, 2000 trajectories). The average probability \( \bar{p}_2(t) \) diverges very soon from the corresponding fraction \( \Pi_2(t) \) and becomes almost constant after 600 fs, while \( \Pi_2(t) \) keeps decreasing. We have already met such kind of discrepancy between the \( \bar{p}_K \) and \( \Pi_K \) functions by analyzing the abstract model of the previous section; there it was shown that the essential feature, leading to the lack of internal consistency, is the fast stabilization of the state probabilities after hopping from \( S_1 \) to \( S_0 \). We recall that in the abstract model no frustrated hops would occur. In the real case of azobenzene, we

**V. Surface Hopping Far from Strong Interaction Regions**

**A. A real test case: Azobenzene**

In this section we want to give a concrete example for a specific failure of the TSH-TFS scheme. We shall treat the case of a Boltzmann distribution of starting geometries and momenta, but we shall also focus on a set of trajectories, sharing the same initial conditions, that exhibit a critical behavior vis-à-vis of the quantum decoherence problem. We note that in a strong interaction region, the TFS algorithm is nearly exact (i.e., internally consistent) because in this case the quantum state probabilities \( \bar{p}_K^{(0)} \) are almost trajectory independent, given the closeness of the PESs. On the other hand, a specific problem arises in the case of weak coupling between two states, particularly when both state probabilities are considerably different from zero.

The problem is well illustrated by considering the photoisomerization of azobenzene, which has been the subject of several investigations by our group.35,44,45 The PESs and couplings for the azobenzene molecule were obtained on the fly during the dynamics calculations, using a semiempirical reparametrized AM1 Hamiltonian and complete active space–configurations interaction (CAS-CI) wave functions (four electrons in six orbitals) supplemented by all single excitations from the last five occupied to the first five virtual orbitals. The molecular orbitals were obtained by the SCF method with floating occupation numbers.41 The \( \text{cis} \rightarrow \text{trans} \) and \( \text{trans} \rightarrow \text{cis} \) photoisomerization of azobenzene after \( n \rightarrow \pi^* (S_0 \rightarrow S_1) \) excitation was also investigated with the full multiple spawning (FMS) method, using an ensemble of 20 different initial wave packets (10 for the CAB isomer).35 Looking at the fraction of trajectories in \( S_1, \Pi_2(t) \), the TSH-TFS results compared rather well with the FMS ones. According to both methods the photoisomerization is mainly due to the torsion of the N–N double bond. The decay of the \( n \rightarrow \pi^* (S_1) \) state occurs when the \( S_1 \sim S_0 \) crossing seam is approached, mainly by the same torsional motion, with the help of the symmetric opening of the NNC bond angles and of other geometrical deformations. Starting from \( \text{cis-} \)azobenzene (CAB) the dynamics is very fast (the \( S_1 \) state is depopulated almost completely in 100 fs) and the two approaches gave very similar results. For \( \text{trans-} \)azobenzene (TAB) we also had a good agreement for times below \( \sim 0.8 \) ps, but we found a long time component in the excited state decay by the FMS method, at variance with the TSH-TFS results. Figure 3 shows the FMS populations, averaged over 20 runs, and new TSH-TFS results, obtained by launching 100 trajectories for each FMS run, with the same initial conditions, but different starting random number seeds (in total, 2000 trajectories). The average probability \( \bar{p}_2(t) \) diverges very soon from the corresponding fraction \( \Pi_2(t) \) and becomes almost constant after 600 fs, while \( \Pi_2(t) \) keeps decreasing. We have already met such kind of discrepancy between the \( \bar{p}_K \) and \( \Pi_K \) functions by analyzing the abstract model of the previous section; there it was shown that the essential feature, leading to the lack of internal consistency, is the fast stabilization of the state probabilities after hopping from \( S_1 \) to \( S_0 \). We recall that in the abstract model no frustrated hops would occur. In the real case of azobenzene, we
find that 18.5% of the trajectories, after their last \( S_1 \rightarrow S_0 \) transition, make an attempt to hop to \( S_1 \) and fail. Since the frequency of \( S_1 \rightarrow S_0 \) hops is very high, most of the successful upward hops are followed very soon by a return to \( S_0 \); therefore, would the frustrated hops be carried out, they might moderately affect the \( \bar{p}_K \) functions, much less the \( \bar{K}_t / H_{20849} \) ones. We shall briefly return on this point at the end of this subsection.

We examine now the origin of the long lasting queue in the excited state population that is only found by the FMS simulations. Several experiments have brought out a biexponential decay of the \( n \rightarrow \pi^* \) state of TAB, and the importance of the long time component (\( \tau > 1 \) ps) is clearly related to the solvent viscosity (see Ref. 47 for a survey of this topic). However, the FMS results suggest that the solvent effect just amplifies the importance of a behavior that also the isolated molecule can exhibit; with certain initial conditions, the torsion of the \( N=\equiv N \) bond can be delayed by more than 1 ps, and the excited state decay is consequently much slower. In fact, out of the 20 FMS runs with different initial conditions, only one gave place to a long lasting excited state wave packet. This is obviously not enough to yield a valid statistical evaluation of the importance of this phenomenon, but it is an interesting qualitative clue to be further investigated.

Hereafter we shall focus on the particular set of initial conditions that yielded a long \( S_1 \) lifetime according to FMS. Figure 4 shows that in this case there is almost no decay until 1.5 ps, and the conversion to \( S_0 \) is practically complete before 1.7 ps. With the same initial conditions, we ran 100 trajectories (with different random seeds), propagated according to the TSH-TFS scheme with a time step of 0.2 fs. Each trajectory starts on the \( S_1 \) state and it is stopped when it has reverted to the ground state and is close to the \( S_0 \) equilibrium geometry of TAB or CAB. Both the FMS and the TSH-TFS results show a small and sudden decrease of the excited state population at \( t = 335 \) fs, because the wave packet approaches the crossing seam, without going through it. From that time on, while the FMS populations remain constant up to almost 1.5 ps, the fraction \( \Pi_2 \) of trajectories on the excited state shows a clear exponential decay and can be fitted with a decay law of the kind \( A \exp(-t/\tau) \), with \( \tau = 510 \) fs. Note also that, contrary to what is usually observed, in this case the averaged population \( \bar{p}_2 \) is more similar than \( \Pi_2 \) to the more accurate FMS results.

The origin of the exponential decay of \( \Pi_2 \) can be ex-
plained as follows. Most of the $S_1 \rightarrow S_0$ jumps occur at quite large energy differences ($E_{S_1} - E_{S_0} > 0.5$ eV) and transoid geometries. These hops originate from the tiny Rabi-type oscillations experienced by $p_2^2$ due to the weak $S_0 - S_1$ coupling at transoid geometries. The behavior of a “typical” trajectory is shown in Fig. 5. Around 335 fs the energy difference $E_{S_1} - E_{S_0}$ drops to its minimum (about 0.35 eV) and at the same time the dynamical coupling $\langle \psi_1|\dot{\psi}_2\rangle = G_{12} \dot{Q}$ shows a peak. This is enough to produce a sudden decrease of the $S_1$ state population, $p_2$ (for simplicity we drop the trajectory index from now on). For the rest of the time, the trajectory stays away from crossing regions ($E_{S_1} - E_{S_0} > 0.6$ eV) but $p_2$ shows oscillations in correspondence of minima of the energy difference and peaks of the dynamical coupling. These are Rabi-type oscillations of a two level system that are due to the complete lack of decoherence at the single trajectory level. In fact, far from the crossing regions the adiabatic energies and couplings can be roughly approximated as constants in a time interval $\delta t$ sufficiently long as to contain one oscillation of $p_2$. With this approximation Eq. (4) can be written, in a time interval $[t_0, t_0 + \delta t]$ and for the two state case here considered, as

$$\dot{A}_1 = A_2 F e^{-i\omega t},$$

$$\dot{A}_2 = -A_1 F e^{i\omega t},$$

where $A_2 = e^{i\omega t}, \omega = \omega_{21}$, and $F = G_{21} \ddot{Q}$ is the dynamical coupling. The solution of the above set of coupled equations in the time interval $\delta t$, where $\omega$ and $F$ are taken as constants, leads to the Rabi formula:

$$p_2(t) = p_2(t_0) + \left[1 - 2p_2(t_0)\right] F^2 \Omega^2 - \frac{o F}{\Omega^2} \Im(A_1^*(t_0)A_2(t_0)) \right] \sin^2(\Omega t)$$

where $\Omega = \sqrt{\omega^2/4 + F^2}$ is the Rabi frequency and $\Im (2)$ means real (imaginary) part of a complex quantity. For instance, the oscillation of $p_2$ around 440 fs has a period of about 4 fs, which is in line with the Rabi period $T_R = \pi/\Omega$ ($T_R = 5 - 3$ fs for $t = 435 - 445$ fs).

For $t > 335$ fs, when both electronic states are appreciably populated, the oscillations are more pronounced (as expected on the basis of the above formula) and they give rise to the $S_1 \rightarrow S_0$ transition at $t = 519$ fs. Once on $S_0$ the energy difference suddenly increases (by about 0.5 eV) resulting in a damping of the oscillations, rapidly reducing the TFS upward transition probability. Note also that, since the $S_1 \rightarrow S_0$ hops happen at a transoid geometry, the trajectory is rapidly attracted to the ground state $trans$ minimum and stopped.

The Rabi oscillations are also shown by the averaged quantity $\bar{p}_2$ in Fig. 4, because all the trajectories share the same set of initial conditions. Distinct trajectories hop at different times and, once in the $S_0$ PES, give rise to oscillations with different phases and frequencies that are washed out in the average. Note also that after a trajectory has been stopped, its contribution to the average $\bar{p}_2$ is assumed to be constant in time. Usually, TSH calculations are performed by running a swarm of trajectories with different initial conditions. The Rabi oscillations of the state probabilities are then averaged out, but they produce hops nevertheless.

The decoherence correction, described at the end of Sec. III, damps out the probability oscillations when a trajectory runs for a sufficiently long time $(\gg \tau_{KM})$ on the same PES. In our case, $\tau_{KM}$ depends mainly on the $S_1 - S_0$ energy gap [see Eq. (17)]; it is very large near the crossing seam and it can easily drop below 10 fs, especially when the trajectory runs on the ground state. The results are shown in Fig. 4; as expected, using the decoherence algorithm we get $\Pi_2 = \bar{p}_2$ and the exponential decay of $\Pi_2$ disappears, obtaining a pattern much more similar to the FMS results. Note that, contrary to what is commonly observed or claimed, the decoherence issue is important both for the fractions of trajectories $\Pi_K$ and for averaged state probabilities $\bar{p}_K$. For the trajectories with different initial conditions, such that the crossing seam is reached earlier and a fast decay takes place between 200 and 600 fs, the only significant effect of the decoherence correction is to equate $\bar{p}_K$ to $\Pi_K$. In this way we obtain a very good agreement between the results of 2000 trajectories and of the 20 FMS calculations, sharing the same initial conditions (see Fig. 6). Almost no frustrated hops occur in this case (only three times in the whole batch of trajectories); in fact, when a trajectory runs on the ground state, the probability $p_1(t)$ tends to increase because of the decoherence correction, unless a strong coupling region is again crossed, so no hops are attempted. This finding is in agreement with the conclusion of Fang and Hammes-Schiffer that the solution of the decoherence problem should have priority over any ad hoc treatment of the frustrated hops.

B. Comparison with exact quantum wave packet results for a simplified model

To gain further insight on the effect of Rabi oscillations we resort to a one-dimensional model system, appropriate for
a diatomic molecule \(AB\) with internuclear distance \(Q\). We define the electronic Hamiltonian matrix in the diabatic basis in this way,

\[
H_{11}(Q) = \alpha_1 e^{-\alpha_1 Q} + \Delta E,
\]

\[
H_{22}(Q) = \alpha_2 e^{-\alpha_2 Q},
\]

\[
H_{12}(Q) = b e^{-\beta(Q - R_c)^2} + \gamma \sin^2(Q),
\]

where \(R_c\) is such that \(H_{11}(R_c) = H_{22}(R_c)\). The time evolution is performed in the adiabatic basis. The electronic diabatic energies \(E_1(Q), E_2(Q)\) and couplings \(G_{12}(Q)\) are represented in Fig. 7 for the following values of the parameters (in a.u.):

\[
\alpha_2 = 0.5, \quad \alpha_1 = 0.2, \quad \alpha_2 = 0.5, \quad R_c = 5.0,
\]

\[
b = 0.0013, \quad \beta = 0.2, \quad \gamma = 0.0002, \quad \Delta E = 0.03,
\]

\[
\mu = 5000,
\]

where \(\mu\) is the reduced mass of the diatomic. As one can see from Fig. 7, the model consists of a crossing region “L” followed by a zone of weak but non-negligible coupling “W.” The oscillations with amplitude \(\gamma\) in the \(H_{12}(Q)\) matrix element are introduced in order to retain a small coupling between the adiabatic states even for large \(Q\). In a polyatomic molecule, similar oscillations would be present because of the vibrational motion along other coordinates.

In a full quantum approach, the total wave function \(|\Psi(t)\rangle\) can be written as

\[
|\Psi(t)\rangle = |\psi_1\rangle \chi_1(t) + |\psi_2\rangle \chi_2(t),
\]

where \(\chi_1\) is the wave packet belonging to state \(|\psi_1\rangle\). We start with a Gaussian wave packet on state 1:

\[
\chi_1(Q, t=0) = \left(\pi \Delta Q^2\right)^{-\Delta E/2} e^{-(Q - R_0)^2/2\Delta Q^2},
\]

\[
\chi_2(Q, t=0) = 0,
\]

where the center of the initial wave packet is \(R_0 = 3\) bohr and its width is \(\Delta Q = 0.1414\) 42 bohr. To mimic the quantum wave packet with the TSH method we ran a swarm of 5000 trajectories. The initial coordinates and momenta were sampled independently according to the quantum distribution corresponding to the wave packet (39). We remark that in this case the trajectories will not share the same set of initial conditions. The full quantum results are shown in Fig. 8, where we plot the population of state 1 \(p_1^{\text{quant}}(t) = \int |\chi_1(Q, t)|^2 dQ\). The passage through the avoided crossing causes \(p_1^{\text{quant}}\) to drop from 1 to 0.359; for \(t > 140\) fs the passage is completed and \(p_1^{\text{quant}}\) do not change anymore (only very tiny oscillations can be observed, with a maximum amplitude of \(4 \times 10^{-5}\)).

Also shown in Fig. 8 are the TSH-TFS results. One can see once more that in the region of strong coupling the TFS algorithm works very well. For \(t > 140\) fs \(\tilde{p}_1(t)\) is still in good agreement with the full quantum results, while \(\Pi_1(t)\) exhibits an exponential decay, corresponding to a first order kinetics

\[
\Pi_1(t) = \frac{k_1}{k_2} \Pi_2(t),
\]

\[
\Pi_1(t) = (\Pi_1(t_0) - k_2 \tau) e^{-t/(k_1 + k_2)} + k_2 \tau \quad (t > t_0),
\]

where \(k_1\) and \(k_2\) are the two rate constants, \(\tau = 1/(k_1 + k_2)\) and \(t_0 = 140\) fs. The rate constant \(k_1\) is, in turn, given by...
TABLE I. One-dimensional model system, region of weak coupling. $\gamma$ is the strength of the coupling, in a.u. [see Eq. (37)], $k_1$ and $k_2$ are the rate constants (in fs$^{-1}$) obtained by Eq. (42). Also shown are the averaged amplitudes of the oscillations of $p_j(t)$ for the trajectories running on states 1 and 2. The corresponding averaged oscillation periods are, respectively, 7.2 and 6.2 fs, irrespective of the coupling strength.

<table>
<thead>
<tr>
<th>$\gamma$</th>
<th>$\bar{p}_1$</th>
<th>$k_1 \times 10^4$</th>
<th>$k_2 \times 10^4$</th>
<th>Oscillation amplitudes ($\times 10^1$) On state 1</th>
<th>On state 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>0.32</td>
<td>3.68±0.6</td>
<td>1.04±0.1</td>
<td>0.6±0.1</td>
<td>0.3±0.1</td>
</tr>
<tr>
<td>0.0002</td>
<td>0.35</td>
<td>6.82±1.2</td>
<td>2.24±0.2</td>
<td>1.3±0.2</td>
<td>0.7±0.2</td>
</tr>
<tr>
<td>0.0004</td>
<td>0.42</td>
<td>11.78±2.1</td>
<td>5.16±0.4</td>
<td>2.7±0.4</td>
<td>1.4±0.4</td>
</tr>
</tbody>
</table>

\[ k_1 = \frac{1}{N_T} \sum_{j=1}^{N_T} \frac{1}{Z_1(t_0)} \int_{t_0}^{t_{\text{max}}} \max \left\{ 0, -\frac{\dot{p}_1^{(j)}}{p_1^{(j)}} \right\} dt, \] (42)

where $t_{\text{max}} \geq t_0$ and $Z_1(t)$ is the time spent by the trajectory $j$ on state 1, in the interval $(t_0, t_{\text{max}})$. An analogous expression can be written for $k_2$, simply swapping indices 1 and 2.

Note that each trajectory has a total energy larger than $E_2(R_e)$ and therefore no frustrated hops can arise in region W. Moreover, an internally consistent TSH scheme would give nearly exact results in the present case, since the $\bar{p}_K$ probabilities are practically equal to their quantum counterparts. The individual $p_K^{(j)}$ show Rabi oscillations, just as in the case of azobenzene, but here the oscillations cancel in the average because the trajectories start with different initial conditions: $\bar{p}_2(t)$ shows a noise with an amplitude of less than $10^{-4}$. The exponential decay of $\Pi_1$ begins when the trajectories reach the weak coupling region W and is due to the oscillations of the $p_K^{(j)}$ probabilities. In fact, the amplitude of the oscillations depends on the current state, and it is larger when the trajectory runs on state 1, because here the nuclear velocity and therefore the dynamical coupling are larger. As a consequence, $T_{\text{TSH}}^{1\rightarrow2} > T_{\text{TSH}}^{1\rightarrow1}$ and $\Pi_1$ decreases in time. In Table I, we show for three different values of the (weak) coupling constant $\gamma$ [see Eq. (37)], the averaged values of the amplitudes of the oscillations of $p_1$ in region W, together with the rate constants $k_1$ and $k_2$, obtained using Eq. (42). Overall, the data follow the expected trend: increasing the coupling strength $\gamma$ leads to an increase of both the oscillation amplitudes and the rate constants, while the averaged oscillation periods are insensitive to $\gamma$. Note that the product $k_1\bar{p}_1$ (respectively, $k_2\bar{p}_2$) is roughly in a linear relationship with the oscillation amplitude in state 1 (respectively, state 2).

In Fig. 8 we also show the TSH results obtained by the decoherence scheme described in Sec. III. The $\Pi_1(t)$ and $\bar{p}_1(t)$ functions are so close to each other that they are indistinguishable in the figure, so only $\Pi_1(t)$ is shown. As expected, the introduction of decoherence completely eliminates the exponential decay of $\Pi_1$ in the low coupling region by damping the $p_K^{(j)}$ oscillations. We note that a decoherence correction, if applied only after a surface hopping, as in other schemes, would not solve the problem caused by the $p_K^{(j)}$ oscillations; in fact, both in the model discussed in this section and in the case of azobenzene by only removing the oscillations in the final state one would obtain an even faster decay of the initial state. The decoherence correction does not affect significantly the dynamics in the strong coupling region; as a consequence, the overall agreement of both the $\Pi_1(t)$ and $\bar{p}_1(t)$ functions with the quantum results is very satisfactory.

VI. CONCLUSIONS

In this paper we address the issues of the internal consistency and of the introduction of quantum decoherence in surface hopping calculations, with specific reference to Tully’s fewest switches (TFS) algorithm. Disregarding the problem of frustrated hops, which has already been addressed by several authors, we have derived an exact (i.e., internally consistent) transition probability, which minimizes the number of state switches and distributes the trajectories on the electronic states according to the averaged state probabilities. Based on this result, two remarks can be done: (a) the exact transition probability cannot be obtained if the trajectories are run independently, with a fully coherent propagation of the electronic wave function and (b) the TFS transition probability is equal to the exact one only if all the trajectories sharing the same initial conditions give place to the same state probabilities, in spite of their different hopping times. This requirement is quite demanding but is usually fulfilled rather well in regions of strong coupling, so that the TFS algorithm is quite adequate in such cases, as generally recognized. The divergence of trajectories running on different PES, makes the above hypothesis no longer valid if the wave packet (i.e., the swarm of trajectories) splits in two after crossing a strong coupling region. In this sense, the problem of internal consistency of the TFS algorithm is intimately connected with the issue of decoherence in the propagation of the electronic wave function. Not surprisingly, therefore, the inconsistency can be (at least partly) solved by resorting to some decoherence scheme.

We have analyzed several examples of nonadiabatic dynamics both on real systems (azobenzene, with different initial conditions) and on models. In some cases the fraction of trajectories actually running on each electronic PES, computed by the TFS algorithm, turns out to be a better approximation of the most accurate results, with respect to the average probabilities obtained by a fully coherent propagation of the electronic wave function. This seems to be the most commonly encountered situation. However, we also find examples where the opposite is true, and the fractions of trajectories are affected by a serious artifact. We have applied a “decoherence correction,” very similar to the one proposed...
by Truhlar and co-workers,\textsuperscript{16,17} to the state probabilities computed by the electronic time-dependent Schrödinger equation. This approach improves the agreement with the results of quantum calculations (where available) in the examples we have investigated and appears to be more effective than direct attempts to solve the consistency problem by modifying the fewest switches algorithm or to eliminate the frustrated hops.

ACKNOWLEDGMENTS

This work was supported by grants of the Italian MIUR and of the University of Pisa.

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