Implementation of surface hopping molecular dynamics using semiempirical methods

E. Fabiano T. W. Keal W. Thiel

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

Abstract

A molecular dynamics driver and surface hopping algorithm for nonadiabatic dynamics has been implemented in a development version of the MNDO semiempirical electronic structure package. The required energies, gradients and nonadiabatic couplings are efficiently evaluated on the fly using semiempirical configuration interaction methods. The choice of algorithms for the time evolution of the nuclear motion and quantum amplitudes is discussed, and different schemes for the computation of nonadiabatic couplings are analysed. The importance of molecular orbital tracking and electronic state following is underlined in the context of configuration interaction calculations. The method is applied to three case studies (ethylene, methaniminium ion, and methanimine) using the orthogonalization corrected OM2 Hamiltonian. In all three cases decay times and dynamics paths similar to high-level ab initio results are obtained.

Key words: surface hopping, molecular dynamics, potential-energy surfaces, conical intersections, nonadiabatic coupling terms, semiempirical methods

1 Introduction

Molecular dynamics (MD) [1–3] is widely used for the study of equilibrium and non-equilibrium properties in physics [4,5], chemistry [6–8] and biochemistry [7,9–12]. MD simulations usually rely on the Born-Oppenheimer approximation [13], which decouples electronic and nuclear motions. The electrons evolve on a single potential energy surface (PES) associated with a single electronic state which is obtained from the solution of the time-independent Schrödinger equation for a series of fixed nuclear geometries. Nuclear motion is usually described by classical equations.

The Born-Oppenheimer approximation is excellent when energy separations are large and the system is well described by a single quantum state. However,
when the energy separation of different PESs becomes comparable with the magnitude of the nonadiabatic coupling (typically in the proximity of conical intersections), the Born-Oppenheimer approximation breaks down and nonadiabatic effects must be explicitly taken into account. The incorporation of nonadiabatic effects in MD is essential for describing a wide range of phenomena including photochemistry, radiationless relaxation and charge transfer reactions.

A great number of methods have been developed for the treatment of nonadiabatic effects in MD [14–44]. Among these one of the most popular is the surface hopping method of Tully [15,16,20,31,45], where the nuclei evolve on a single PES and nonadiabatic effects are included by allowing hopping from one PES to another according to the weight of the respective electronic state. This approach gives an efficient description of nonadiabatic effects, is asymptotically correct in regions of large energy separation, includes classical-quantum correlation and with a proper choice of the switching criterion guarantees microscopic reversibility [20]. On the other hand the results are not independent of the representation used for the electronic states (adiabatic or diabatic), ambiguities may arise over the choice of possible switching criteria and the total energy is not automatically conserved (an external constraint is needed to fix the total energy in the event of hopping). Nevertheless, surface hopping generally performs very well for molecular applications [46–49] and has therefore been widely used for the study of nonadiabatic dynamics.

In this paper, we present our implementation of the surface hopping approach in a development version of the semiempirical MNDO package [50] and a detailed analysis of technical aspects of the method. We apply the surface hopping method to three case studies using the orthogonalization corrected OM2 Hamiltonian [51,52] for the description of the PESs and show that this approach yields results comparable to ab initio methods for nonadiabatic dynamics. Section 2 describes the theory of the surface hopping method, including the fewest switches algorithm for determining when hops occur and the velocity adjustments required to maintain energy conservation. In Section 3 we discuss the implementation of the algorithm and the molecular dynamics driver used for calculating surface hopping trajectories. The implementation is applied to ethylene, the methaniminium ion and methanimine in Section 4 and conclusions are presented in Section 5.

2 Theory

The surface hopping method employs an independent trajectory approximation. A swarm of trajectories is considered, each one evolving on a single potential energy surface. At each MD timestep there is a probability that a
trajectory propagating on one potential energy surface will hop to another surface. This probability is controlled by a stochastic switching algorithm, which must be designed in such a way to guarantee that at any time the fraction of all trajectories in a certain electronic state is, at least approximately, equal to the quantum population of the state.

In the surface hopping method nuclei are assumed to move along a classical trajectory $\mathbf{R}(t)$. The Hamiltonian describing the electron motion is

$$H(\mathbf{r}, \mathbf{R}) = -\frac{\hbar^2}{2} \sum_\alpha \frac{1}{m_\alpha} \nabla_{\mathbf{r}_\alpha}^2 + V_{rR}(\mathbf{r}, \mathbf{R})$$  \hspace{1cm} (1)$$

where $\alpha$ labels electronic degrees of freedom and $V_{rR}$ includes nuclear-electron and electron-electron potentials. Hamiltonian (1) is time dependent through $\mathbf{R}(t)$. The electronic system is described by the wavefunction $\Phi(\mathbf{r}, \mathbf{R}, t)$, which is the solution of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Phi(\mathbf{r}, \mathbf{R}, t)}{\partial t} = H(\mathbf{r}, \mathbf{R}) \Phi(\mathbf{r}, \mathbf{R}, t).$$  \hspace{1cm} (2)$$

The electronic wavefunction can be expanded in a basis of known orthogonal wavefunctions $\phi_i(\mathbf{r}, \mathbf{R})$

$$\Phi(\mathbf{r}, \mathbf{R}, t) = \sum_i c_i(t) \phi_i(\mathbf{r}, \mathbf{R})$$  \hspace{1cm} (3)$$

where $c_i(t)$ are complex-valued expansion coefficients. A common choice for the expansion is the adiabatic representation, i.e. the basis functions are solutions of the time-independent electronic Schrödinger equation

$$\left[ -\frac{\hbar^2}{2} \sum_\alpha \frac{1}{m_\alpha} \nabla_{\mathbf{r}_\alpha}^2 + V_{rR}(\mathbf{r}, \mathbf{R}) \right] \phi_i(\mathbf{r}, \mathbf{R}) = \epsilon_i \phi_i(\mathbf{r}, \mathbf{R}) \hspace{1cm} (4)$$

Substitution of Eq. (3) into the Schrödinger equation (2), multiplication on the left by $\phi_j^*(\mathbf{r}, \mathbf{R})$ and integration over $\mathbf{r}$ yields

$$i\hbar \frac{dc_j(t)}{dt} = \sum_i c_i(t) \left[ H_{ji} - i\hbar \hat{\mathbf{R}} \cdot \mathbf{d}_{ji} \right]$$  \hspace{1cm} (5)$$

where $H_{ji}$ and $\mathbf{d}_{ji}$ are

$$H_{ji}(\mathbf{R}) \equiv \int \phi_j^*(\mathbf{r}, \mathbf{R}) \left[ -\frac{\hbar^2}{2} \sum_\alpha \frac{1}{m_\alpha} \nabla_{\mathbf{r}_\alpha}^2 + V_{rR}(\mathbf{r}, \mathbf{R}) \right] \phi_i(\mathbf{r}, \mathbf{R}) d\mathbf{r},$$  \hspace{1cm} (6)$$
\[ \tilde{d}_{ji}(\tilde{R}) \equiv \int \phi^*_j(\vec{r}, \tilde{R}) \left[ \nabla_{\tilde{R}} \phi_i(\vec{r}, \tilde{R}) \right] d\vec{r}. \]  

(7)

and the chain rule

\[ \int \phi^*_j(\vec{r}, \tilde{R}) \frac{\partial \phi_i(\vec{r}, \tilde{R})}{\partial t} d\vec{r} = \dot{\tilde{R}} \cdot \tilde{d}_{ji} \]  

(8)

has been used.

In the adiabatic representation the Hamiltonian matrix of Eq. (6) is diagonal, and Eq. (5) simplifies to

\[ i\hbar \frac{dc_j(t)}{dt} = c_j(t) \epsilon_j - i\hbar \sum_i c_i(t) \dot{\tilde{R}} \cdot \tilde{d}_{ji} \]  

(9)

The amplitude of each quantum mechanical state at a given time is found by integrating Eq. (9) along the trajectory \( \tilde{R}(t) \). This information is used to determine whether a switch to a different classical trajectory should occur or not.

### 2.1 Fewest Switches Algorithm

The criterion for switching between states must result in a distribution of state populations over all trajectories that reflects the populations given by integrating Eq. (9). It is also important to achieve this result with a small number of hops, because a criterion which results in a large number of hops will give trajectories that effectively evolve on an average of the potential energy surfaces rather than on a single adiabatic surface[15]. Different choices are possible for the switching algorithm [44,53,54], but in practice the fewest switch algorithm (FSA) [15] is usually employed.

The FSA is derived by imposing that the number of switches required to reproduce the statistical distribution of state occupations is minimised. Switches between states are governed by a stochastic criterion and are usually assumed for simplicity to occur in an infinitesimal time period, although this is not a necessary condition. This causes state transitions to be discontinuous in any single trajectory, but over a swarm of trajectories this behaviour will be smoothed out as the transitions will occur at different times. The stochastic nature of the FSA implies that only average results over a swarm of trajectories can be compared with observable quantities.

For a swarm of \( N \) trajectories, the number of trajectories in state \( i \) at time \( t \)
is
\[ N_i(t) = \rho_{ii}(t)N \]  \hspace{1cm} (10)

where the density matrix is defined as
\[ \rho_{ii}(t) \equiv c_i^*(t)c_i(t) . \]  \hspace{1cm} (11)

At time \( t + dt \) the occupation of state \( i \) will change to
\[ N_i(t + dt) = \rho_{ii}(t + dt)N . \]  \hspace{1cm} (12)

Supposing that \( N_i(t) > N_i(t+dt) \), the minimum number of transitions needed for this change in occupation will be \( N_i(t) - N_i(t + dt) \) hops from state \( i \) to any other state and zero hops from any other state to state \( i \). The probability \( P_i(t)dt \) of a hop out of the state \( i \) in the infinitesimal time interval \( dt \) is therefore
\[ P_i(t)dt = \frac{N_i(t) - N_i(t + dt)}{N_i(t)} = \frac{\rho_{ii}(t) - \rho_{ii}(t + dt)}{\rho_{ii}(t)} \approx \frac{\dot{\rho}_{ii}dt}{\rho_{ii}} . \]  \hspace{1cm} (13)

The derivative of the density matrix can be written as
\[ \dot{\rho}_{ii} = c_i^*\dot{c}_i = \dot{c}_i^*c_i + c_i^*\dot{c}_i = (\dot{c}_i^*c_i)^* + c_i^*\dot{c}_i = 2\text{Re}(c_i^*\dot{c}_i) \]  \hspace{1cm} (14)

Substitution of Eq. (9) for \( \dot{c}_i \) gives
\[ P_i(t)dt = -2\frac{\hbar^{-1}\text{Im}(c_i^*c_i\epsilon_i)}{c_i^*c_i} - \sum_j \text{Re}(c_i^*c_j\dot{R}\cdot\vec{d}_{ij}) dt \]  \hspace{1cm} (15)

and since \( c_i^*c_i\epsilon_i \) is always real,
\[ P_i(t)dt = 2\frac{\sum_j \text{Re}(c_i^*c_j\dot{R}\cdot\vec{d}_{ij})}{c_i^*c_i} dt \]  \hspace{1cm} (16)

In most MD simulations the time interval is not infinitesimal, but set as large as possible to minimise computational expense. For a finite time interval the hopping probability is found by integrating the infinitesimal probability of Eq. (16) over the interval. The denominator of this integral can be considered constant since hopping cannot occur during the time interval and thus the
occupation of the state cannot change. Therefore the probability of a hop out of state \(i\) during a finite time interval \(\Delta t\) is given by

\[
P_i = 2 \sum_j \int_{t}^{t+\Delta t} \frac{\text{Re}(c_i^* c_j \tilde{R} \cdot \tilde{d}_{ij}) dt}{c_i^* c_i}
\]  

(17)

Since the probability for a switch from state \(i\) to any other state is the sum of all transition probabilities \(P_{ij}\) from state \(i\) to any state \(j\), the probability for a transition from \(i\) to \(j\) is

\[
P_{ij} = 2 \int_{t}^{t+\Delta t} \frac{\text{Re}(c_i^* c_j \tilde{R} \cdot \tilde{d}_{ij}) dt}{c_i^* c_i}
\]  

(18)

Since we assume that \(N_i(t) > N_i(t + dt)\) it is necessary to discard negative (unphysical) values for the probability. Therefore the transition probability \(g_{ij}\) can be defined as

\[
g_{ij} = \max (P_{ij}, 0).
\]  

(19)

In order to determine to which state (if any) a switch occurs, a uniform random number \(0 < \xi < 1\) is selected at each time step and a hop from state \(i\) to state \(k\) is performed if

\[
\sum_j g_{ij} < \xi < \sum_j g_{ij}.
\]  

(20)

2.2 Velocity adjustment

For a closed system the total energy must be conserved and a velocity adjustment should thus be made every time a switch occurs. The velocity adjustment is usually performed in the direction of the nonadiabatic coupling vector \(\tilde{d}\), since this choice is suggested by semiclassical analogies [16,55,56], but other choices can also be made [26,53,57–59]. If the velocity component along the nonadiabatic coupling vector is too small to compensate for the energy change due to hopping, the jump is rejected and the velocity along the nonadiabatic coupling vector is reversed (as in elastic scattering).

When the system jumps from a state \(i\) to a state \(j\), the electronic energy changes from \(\epsilon_i\) to \(\epsilon_j\). The kinetic energy of the system is adjusted to compen-
sate by rescaling the velocity of each nucleus $\beta$ by
\[
\dot{\vec{R}}_\beta^{(j)} = \dot{\vec{R}}_\beta^{(i)} - \gamma_{ij} \frac{\vec{d}_{ij}^\beta}{M_\beta}
\]  
(21)

where $\gamma_{ij}$ is a scaling factor to be determined, and
\[
\vec{d}_{ij}^\beta(\vec{R}) \equiv \int \phi_j^*(\vec{r},\vec{R}) \left[ \nabla_{\vec{R}_\beta} \phi_i(\vec{r},\vec{R}) \right] d\vec{r}.
\]  
(22)

The overall kinetic energy change is thus
\[
\frac{1}{2} \sum_\beta M_\beta \left( \dot{\vec{R}}_\beta^{(j)} \right)^2 - \frac{1}{2} \sum_\beta M_\beta \left( \dot{\vec{R}}_\beta^{(i)} \right)^2 = \frac{1}{2} \sum_\beta M_\beta \left[ \gamma_{ij}^2 \left( \frac{\vec{d}_{ij}^\beta}{M_\beta} \right)^2 - 2 \gamma_{ij} \frac{\dot{\vec{R}}_\beta \cdot \vec{d}_{ij}^\beta}{M_\beta} \right]
\]  
(23)

with
\[
a_{ij} \equiv \frac{1}{2} \sum_\beta \frac{\vec{d}_{ij}^\beta}{M_\beta}
\]  
(24)
\[
b_{ij} \equiv \sum_\beta \frac{\dot{\vec{R}}_\beta \cdot \vec{d}_{ij}^\beta}{M_\beta}.
\]  
(25)

Imposing conservation of total energy gives
\[
\gamma_{ij}^2 a_{ij} - \gamma_{ij} b_{ij} - (\epsilon_i - \epsilon_j) = 0.
\]  
(26)

If $b_{ij}^2 + 4a_{ij}(\epsilon_i - \epsilon_j) < 0$ there are no real solutions to Eq. (26) and a switch cannot occur. In this case the nuclear velocities are simply reversed, setting $\gamma_{ij} = b_{ij}/a_{ij}$. If $b_{ij}^2 + 4a_{ij}(\epsilon_i - \epsilon_j) \geq 0$, the scaling factor is
\[
\gamma_{ij} = \frac{b_{ij} + \sqrt{b_{ij}^2 + 4a_{ij}(\epsilon_i - \epsilon_j)}}{2a_{ij}} \quad \text{if } b_{ij} < 0
\]  
(27)
\[
\gamma_{ij} = \frac{b_{ij} - \sqrt{b_{ij}^2 + 4a_{ij}(\epsilon_i - \epsilon_j)}}{2a_{ij}} \quad \text{if } b_{ij} \geq 0.
\]  
(28)

In practice the fewest switches algorithm is not always able to guarantee self-consistency between the quantum populations and the fraction of trajectories
in a certain state [44,53,57,60–62]. This is because the FSA is derived without
considering rejected hoppings and also because it is assumed in Eq. (10) that
the quantum populations of different trajectories are the same at all times,
which is true in particular cases (i.e. for one-dimensional systems with a single
nonadiabatic coupling region or for systems with quasi-degenerate PESs) but
not in general. Nevertheless, the FSA remains one of the most widely used
switching criteria in surface hopping applications.

3 Implementation

The MNDO implementation of surface hopping employs the adiabatic rep-
resentation. Energies, gradients and nonadiabatic couplings are evaluated on
the fly using any of the available semiempirical Hamiltonians and GUGA
configuration interaction [63]. The CI expansion can be taken from multiple
reference configurations to improve the simultaneous description of several
(quasi)degenerate electronic states. The use of semiempirical methods for the
direct computation of PESs and nonadiabatic couplings offers a good compro-
mise between accuracy and computational efficiency. Semiempirical methods
are fast enough to allow the computation of the many thousands of ener-
gies, gradients and nonadiabatic couplings needed in a typical surface hopping
study. The OM2 method [51,52] is applied presently because it has been shown
to give a qualitatively correct description of the PESs around a series of coni-
cal intersections [64]. Earlier semiempirical methods such as AM1 may have to
be reparametrised to give surfaces of sufficient quality to be used for dynam-
ics [65]. In SCF calculations problems may arise from the (quasi)degeneracy
of two or more molecular orbitals in some geometrical configurations of the
molecule under investigation (e.g. bond breaking, torsion around a double
bond). These situations may be handled within the MNDO package by using
the open-shell SCF approach [66], including the ground state as a CI reference
configuration. Alternative semiempirical approaches reported in the literature
to treat MO degeneracy are the valence bond [22,67,68] and floating occupation
number [69,70] methods.

The general algorithm implemented for surface hopping proceeds as follows:

(1) Initialize velocities, gradients and quantum amplitudes.
(2) Propagate coordinates and velocities.
(3) Perform CI calculation and compute gradients and nonadiabatic coupling
vectors $\vec{d}_{ij}$ for all relevant CI states.
(4) Only in first step: store energies, nonadiabatic couplings, CI expansion
coefficients and go back to point 2. These quantities will be used in the
next MD step for state tracking and the interpolation procedure employed
in the solution of Eq. (9).
(5) Integrate Eq. (9) and evaluate Eq. (18) to compute probability defined by Eq. (19).

(6) Generate a random number and determine whether a switch to another potential energy surface occurs. If so, adjust velocities according to Eq. (21).

(7) Store all relevant quantities and go back to point 2.

At the beginning of the simulation initial conditions are set. Starting coordinates, velocities and the initial quantum state are defined and the corresponding gradient is computed to provide the initial forces on the nuclei. The time evolution of the nuclear degrees of freedom is implemented by the velocity Verlet algorithm [71]. This algorithm is particularly suited for surface hopping simulations because both the coordinates and velocities are computed at the same timestep, which is necessary for the surface hopping algorithm.

At point 3 of the algorithm all relevant adiabatic electronic states are computed and labelled in order of their energies. However, the ordering of states may change when the system crosses a conical intersection and this will result in an “unphysical” hopping. To avoid this problem it is necessary to track the character of the states from step to step so that the old states can be mapped to the new states and all the relevant quantities can be correctly assigned. This problem normally does not occur in conventional Born-Oppenheimer MD since simulations are usually performed in regions of large separation of the PESs where the Born-Oppenheimer approximation works well. In the surface hopping approach, on the other hand, conical intersection regions play a fundamental role since they are usually the regions with the highest nonadiabatic coupling and tracking of states is very important to perform the MD evolution correctly. In our implementation the states are explicitly tracked whenever the energy differences are smaller than a given threshold (default: 3 kcal/mol) by comparison of CI components. The product \( \langle \phi^{CI}(t) | \phi^{CI}(t + \Delta t) \rangle \) is computed and the states assigned according to a maximum “overlap” principle. An index mapping the old states to the new ones is generated and all the quantities depending on state ordering (i.e. energies, gradients and nonadiabatic couplings) are reordered accordingly. The hopping probability is then computed with the updated quantities. In this way the system evolves through the crossing following the original PES with the possibility of hopping to a different state retained. The maximum “overlap” procedure is also used to track MOs from one MD step to the next. The need for MO tracking is related to the use of a relatively small active space for CI expansion in semiempirical models. The tracking of states and MOs can be performed efficiently only if the change in the CI expansion and MO coefficients is small from one MD step to the next. To fulfill this requirement rather short time steps are usually needed. For example, in our calculations on ethylene we found that the number of trajectories for which there are tracking problems increases from less than 1% to more than 10% when the time step is increased from \( t=0.05 \) fs to 0.5 fs.
A small time step and a small variation of CI expansion coefficients are also required if nonadiabatic coupling terms are computed numerically (see below).

The nonadiabatic coupling vectors defined in Eq. (7) are computed following the theory of Refs. [72,73]. In the MNDO implementation [64], the quantity calculated is the gradient of the interstate coupling

\[ \vec{h}_{ij}(\vec{R}) = C_i^\dagger \frac{\partial H}{\partial \vec{R}} C_j^\dagger \]  

(29)

where \( C_i \) are the CI coefficients of state \( i \) and \( H \) is the CI electronic Hamiltonian matrix. The nonadiabatic coupling vector is related to the interstate coupling vector by

\[ \vec{d}_{ij}(\vec{R}) = \vec{h}_{ij}(\vec{R}) - \epsilon_i - \epsilon_j + \sum_{\mu,\nu} (\Gamma_{ij})_{\mu\nu} \langle \psi_{\mu} | \frac{\partial \psi_{\nu}}{\partial \vec{R}} \rangle \]  

(30)

where \( \Gamma_{ij} \) is the one-electron transition density matrix and \( \psi \) denotes molecular orbitals. The second term is neglected in the MNDO implementation, as the first term is known to dominate the expression in the region of a conical intersection [74,75].

The nonadiabatic coupling \( \dot{\vec{R}} \cdot \vec{d}_{ji} \) is obtained by simple dot-multiplication of the coupling vector by the velocity components. Alternatively, it is possible to compute a fully numerical nonadiabatic coupling using the simple approximation [45]

\[ \left[ \dot{\vec{R}} \cdot \vec{d}_{ij} \right] (t + \Delta t/2) \approx \frac{1}{2\Delta t} \left[ \langle \phi_i(t) | \phi_j(t + \Delta t) \rangle - \langle \phi_i(t + \Delta t) | \phi_j(t) \rangle \right]. \]  

(31)

In this case the nonadiabatic coupling vectors only need to be computed when hopping occurs. This results in a significant speed-up of calculations (total computational time is reduced by 30-35%), since the numerical procedure is much faster than the analytical one and only a few hopping events occur during each simulation. A comparison between analytical and numerical nonadiabatic couplings shows that the latter yield in general values very close to the analytical ones. However, localized oscillations may appear in numerically computed nonadiabatic couplings due to the difficult balancing between the need for a small time step to satisfy the approximations made in the derivation of Eq. (31) (in particular in regions of fast change of wavefunction CI components), and the limitations posed by finite numerical precision and division by \( \Delta t \). This situation is represented in Fig. 1, where the relative error of numerical nonadiabatic coupling with respect to analytical coupling for a selected portion of a trajectory of the methaniminium ion is shown. The errors are almost
always negligible with the exception of some small regions where moderate (\(\sim 6\%\)) or larger errors (20-30\%) occur. In any case, we found that final averaged results do not depend on whether the analytical or the numerical procedure was employed for the computation of the nonadiabatic couplings.

Like the gradients, the coupling terms can only be assigned correctly if the states are tracked. In addition the sign of the nonadiabatic couplings can change arbitrarily as they depend on the arbitrary phase of the GUGA-CI electronic wavefunction. In principle these sign changes do not cause problems since they only result in a change of sign of the real part of the quantum amplitudes \(\{c_i\}\) and therefore have no effect on observable quantities such as quantum populations. However, in practice the numerical solution to Eq. (9) (see below) requires a linear interpolation procedure involving nonadiabatic couplings computed at different timesteps. In this case a change of sign results in completely wrong interpolated values. Therefore it is necessary at every MD step to fix the phase of the CI wavefunctions to be consistent with the previous step.

At point 5 of the algorithm (see above) the quantum amplitudes are propagated by numerical solution of Eq. (9). In the MNDO implementation several methods can be used: second and fourth order Runge-Kutta methods (RK2, RK4), second and fourth order Adams-Bashforth-Moulton predictor-corrector schemes (ABM2, ABM4) and the exponential unitary propagator (UP)

\[ e^{-i\mathbf{H}_e(t+\Delta t/2)\Delta t} \]

with

\[ (\mathbf{H}_e)_{ij} = \frac{\epsilon_i \delta_{ij}}{\hbar} - i \dot{\mathbf{R}} \cdot \mathbf{d}_{ji}. \]

To improve the accuracy of the integration, all these methods require a much smaller integration step than that used for the nuclear dynamics. The UP method also requires the value of \(\mathbf{H}_e\) at half timesteps. To avoid excessive computational cost, linear interpolation is used to obtain adiabatic energies and nonadiabatic couplings at intermediate times between MD points. For the RK and ABM methods, which are not unitary, the electronic population is also renormalised at every MD step to avoid a slow drift of the total electronic population. Typically the renormalization factor differs from unity by \(10^{-4} - 10^{-5}\).

An example of the relative performance of the integration methods is shown in Tab. 1 for the case of ethylene. The global error after 150 fs in the computation of electronic population is reported for all the methods, for various numbers of integration steps and two different values of the MD time step.
The errors are given relative to the UP method using 1000 integration steps. The approximate computation time on one Intel Pentium 4 - EM64T 3.40 GHz processor is also reported to give an idea of the computational cost. The results show that, except when a very small number of integration steps is used, all methods give good results and fourth order methods can compete with the UP approach. In particular the RK4 method seems to offer the best compromise between accuracy and computational efficiency. The good performance of simple algorithms suggests that the integrated quantities are slowly varying for the time scale used. This observation is confirmed by the larger number of integration steps needed if a longer MD time step is chosen. We note finally that the use of simple and fast integration schemes and/or the use of a small number of integration steps is not very important because with any integration scheme the overall computational cost of the surface hopping simulation is dominated by the computation of energies, gradients and nonadiabatic couplings at each MD step (12-15 ms for ethylene at the AM1 level). In addition the difference increases very rapidly for larger systems and more accurate wavefunction models since computation time of energy, gradients and nonadiabatic coupling depends on the number of atoms in the system and on the scaling of the method used, whereas the integration of Eq. (9) and probabilities depends only on the number of states considered.

Integration of the numerator of Eq. (18) can be easily performed together with integration of Eq. (9) using the same reduced time step and a simple uniform grid. Computation of hopping probabilities from Eq. (19) is then straightforward. Errors in computation of hopping probabilities are found to be always much smaller than errors in computation of populations.

The choice of the routine used for generating random numbers in point 6 of the algorithm deserves attention [76]. Use of the intrinsic Fortran subroutine for the generation of random numbers is straightforward and generally gives good quality random series, but the quality of the results is entirely compiler-dependent. As an alternative we have implemented two further random number generators based on different conceptual approaches. The first is a Park-Miller random number generator with Bays-Durham shuffle (PM-BD) [77]. For relatively short periods like the one needed in surface hopping applications (< 10^6) this is known to be a very good random number generator and the shuffle procedure guarantees that there are no serial correlations. The second generator is based on a subtractive algorithm due to Knuth [77]. The Knuth algorithm may be a good alternative for machines that perform poorly for integer arithmetic since it can work entirely in floating point arithmetic.

When the hopping criterion is satisfied in point 6, velocity components along the nonadiabatic coupling vector of the two states involved are adjusted in order to conserve the total energy as described in section 2.1. If the velocity in the direction of the nonadiabatic coupling vector is not sufficient to al-
low energy conservation then hopping is not performed and the velocities are reversed in that direction.

After presenting the implemented procedures, we now give some recommendations for surface hopping simulations. Since the nonadiabatic coupling, as well as the CI expansion coefficients, can vary abruptly around conical intersections, the MD time step must be small (typically 0.1 fs, or even less for small molecules). The analytic evaluation of the nonadiabatic couplings is preferred over the numerical computation (Eq. (31)) because of its intrinsically higher accuracy. The use of the fully numerical procedure for the computation of the nonadiabatic couplings yields good results in general and saves a substantial amount of computational time. For these reasons it is a good choice for large simulations. Since the overall computational effort is dominated by the cost of the CI calculation (point 3 of the algorithm) it is advisable to use accurate high-level schemes for the numerical integration of the electronic Schrödinger equation (point 5 of the algorithm), i.e. at least a fourth-order scheme (ABM4, RK4 or UP, default: UP) with a small integration step (typically 100 times smaller than the MD step). The choice of the random number generator (point 6 of the algorithm) is normally less critical, but a portable routine such as the PM-BD or Knuth algorithm may be preferred to guarantee reproducibility of the results (default: PM-BD).

4 Applications

In order to test our surface hopping implementation we applied it to three case studies: the geometrical and electronic relaxation of ethylene and the methaniminium ion (CH$_2$NH$_2^+$) and the cis-trans photoisomerization of methanimine (CH$_2$NH). The initial configurations for the calculations were prepared as follows: a Born-Oppenheimer MD run on the ground state PES was performed and a series of snapshots taken. Configurations yielding a vertical excitation energy to the optically active state in the energy window $E_0^v \pm 0.15$ eV were selected, where $E_0^v$ is the vertical excitation energy in the ground state geometry optimized at the same level of computation. This procedure is intended to approximately sample configurations contributing to the center of the absorption band for a vertical photoexcitation from the ground state.

Energies, gradients and nonadiabatic couplings were determined using the OM2 [51,52] semiempirical Hamiltonian with GUGA configuration interaction [63]. The active space used was the smallest one yielding a reliable description of the states studied (two electrons and two orbitals for ethylene and methanimine and four electrons and three orbitals for the methaniminium ion). Nonadiabatic couplings were computed using the analytical procedure and quantum amplitudes were propagated using the UP method with 100 in-
tegration steps. The random numbers required by the FSA were generated using the PM-BD algorithm. All calculations were performed on one Intel Pentium 4 - EM64T 3.40 GHz processor.

4.1 Ethylene

The electronic relaxation of ethylene after a vertical excitation into the \( S_1 \) state was simulated. In Fig. 2 the population of \( S_0 (\pi^2) \), \( S_1 (\pi \pi^* \gamma) \) and \( S_2 (\pi^* \gamma^2) \) states averaged over 100 trajectories is reported. Each trajectory was propagated for 200 fs with a time step of 0.05 fs. Approximately 240 s of CPU time was required for each trajectory.

The molecule is initially in the \( S_1 \) state with an almost planar geometry. A torsional motion around the C-C bond starts immediately and the molecule is rapidly brought towards a twisted-orthogonal configuration. In this configuration the \( S_1 \) and \( S_2 \) states are almost degenerate and hopping between \( S_1 \) and \( S_2 \) is possible although not highly probable. Occupation of the \( S_2 \) state is in any case typically very short and the system rapidly decays back to the \( S_1 \) state.

The dynamics on the \( S_1 \) surface continues via pyramidalization of one of the two \( \text{CH}_2 \) groups. Two typical trajectories are reported in Fig. 3. Pyramidalization in the orthogonal configuration (lower panel, second snapshot) brings the \( S_0 \) and the \( S_1 \) energies very close and the system is in a region of high nonadiabatic coupling and high hopping probability. This mechanism is the main source of the increase of the number of trajectories in the \( S_0 \) state after 15 fs. At later times a hydrogen migration mechanism can also contribute to the hopping between \( S_1 \) and \( S_0 \) (upper panel, third snapshot).

The number of trajectories in the \( S_0 \) state continuously increases and after 200 fs more than 90% of trajectories are in the \( S_0 \) state. Correspondingly the number of trajectories in the \( S_1 \) state decreases while the number of trajectories in the \( S_2 \) state is negligible except in the first 50 fs. The decay behavior of the average population of \( S_1 \) state is well described by a single exponential function \( n_{S_1} = \exp(-t/\tau_{S_1}) \). The computed decay time is \( \tau_{S_1} = 70.8 \text{ fs} \).

Occasionally crossings between PESs are observed. In Fig. 4 two examples are shown. The three states are here denoted as N, V, and Z, corresponding to the occupations (HOMO,HOMO), (HOMO,LUMO) and (LUMO,LUMO) respectively. In the upper panel the system reaches the ethylidene conical intersection between states N and V. At the conical intersection hopping between the two states occurs. In the lower panel a conical intersection between states V and Z is reached. This is characterized by a large separation (1.88 Å) between the two \( \text{CH}_2 \) groups in an orthogonal configuration. About 7 fs after the crossing
a hop from state N to state V occurs and next from state V to state Z. Usually ethylene remains for a short time in state Z and then decays to state V. Here however state V is higher in energy than state Z and the hopping is rejected because of energy conservation. As a result the molecule ends its trajectory in state Z, which is a very rare event (no crossing between the V and Z PESs).

Calculations have also been performed at the AM1 [78] level for a closer comparison with the results of Ref. [65], although in the latter work a reparametrization of the AM1 method was performed and therefore a full comparison is not possible. The results are qualitatively similar to the results obtained with the OM2 method and compare well with the results reported in Ref. [65] ($\tau_{S_1} = 105 - 139$ fs). The deexcitation dynamics is slower at the AM1 level than at the OM2 level with a decay time $\tau_{S_1} = 127.1$ fs. In addition there is a higher occupation of the $S_2$ state for the entire time period studied with an average occupation of about 10% and a maximum occupation of about 20% at $t=50$ fs.

The $S_1$ decay time ($\tau_{S_1}$) needs to be converged with respect to the number of trajectories ($N_T$) used to compute the average. Presently this appears to be the case already for $N_T = 100$: in our OM2 study we find decay times of 64.5, 64.9, 69.8, 70.8, 71.0, 70.4 and 70.9 fs for $N_T = 25, 50, 75, 100, 150, 200$ and 300 respectively. The lower decay times with fewer trajectories can be rationalized by rare events that increase the lifetime of the $S_1$ state (e.g. transitions $S_1 \rightarrow S_2$ after which the molecule must normally return to $S_1$ before decaying to $S_0$). Such rare events are more likely to be absent when only a small number of trajectories are sampled, which effectively decreases the mean lifetime computed for $S_1$. When a larger number of trajectories is considered rare events are sufficiently represented and the decay time value slightly increases.

4.2 Methaniminium ion

The electronic relaxation of $\text{CH}_2\text{NH}_2^+$ after vertical excitation into the $S_2$ state is reported in Fig. 5. Trajectories have been propagated for 150 fs with a time step of 0.05 fs. The computation time for each trajectory was approximately 200 s.

A typical trajectory is reported in Fig. 6. At the beginning of the simulation the molecule is in the $S_2$ state. The C-N bond starts to elongate immediately and at around $t=5$ fs the molecule reaches the region of a planar conical intersection between $S_2$ and $S_1$ and hops to the $S_1$ state. The average number of trajectories in the $S_2$ state starts to rapidly decrease whereas the number of trajectories in the $S_1$ state increases. The decay time of $S_2$ is $\tau_{S_2} = 15.0$ fs.
A similar result is found at the SA-3-CASSCF(6,4) level \[79\] (τ_{S_2} = 9.6 fs) and MR-CISD/SA-3-CASSCF(4,3) level \[80\] (τ_{S_2} = 12 fs). After the hopping most trajectories undertake a torsional motion around the C-N axis and at around t=35 fs the molecule reaches the region of a twisted conical intersection between S_1 and S_0 (the same mechanism as proposed previously \[81,82\]). In this region there is a high probability of hopping from S_1 to S_0, therefore the average number of trajectories decreases in the S_1 state and increases in the S_0 state. The lifetime of the S_1 state can be obtained by fitting the average occupation of the S_1 state with the formula

\[ n_{S_1} = \frac{\tau_{S_1}}{\tau_{S_2} - \tau_{S_1}} \left( e^{-t/\tau_{S_2}} - e^{-t/\tau_{S_1}} \right) \]  \tag{34} \]

with \(\tau_{S_2}=15.0\) fs, fixed at the value previously calculated. The resulting decay time of the S_1 state is \(\tau_{S_1} = 82.7\) fs. After hopping to the S_0 surface the molecule evolves towards a planar conformation, with possible pyramidalization of one or both groups.

Another possibility after hopping to the S_1 surface is further stretching of the C-N bond accompanied by bi-pyramidalization. SA-3-CASSCF(6,4) calculations indicate that this process is the most important for the S_1 \(\rightarrow\) S_0 hopping \[79\], and MR-CISD/SA-3-CASSCF(4,3) calculations assign to this channel half of the S_1 \(\rightarrow\) S_0 transitions \[80\]. In our calculations only 30% of trajectories follow this path, probably because of small differences between the OM2 and the CAS PESs, in particular a more attractive OM2 potential at large C-N separations and a smaller OM2 torsional barrier. In addition the probability of hopping in this configuration is not very high at the OM2 level since the electronic population of the ground state grows only slowly along the stretching–bi-pyramidalization reaction coordinate, so hopping is disfavored. If hopping does not occur then the system usually evolves towards the twisted conical intersection configuration and hops to the S_0 state in this configuration. As a result the probability of S_1 \(\rightarrow\) S_0 hopping events in the twisted conical intersection configuration is increased. This difference in the description of the S_1 \(\rightarrow\) S_0 hopping dynamics is also likely to be the main cause for the longer decay time of the S_1 state at the OM2 level compared to the CAS results.

The decay time of the S_1 state is also increased by trajectories where a crossing occurs from S_0 to S_1 (Fig. 7, upper panel, after \(\approx 50\) fs) or from S_2 to S_1 (Fig. 7, lower panel, after \(\approx 5\) fs). In both cases the average number of trajectories in the S_0 state is subsequently reduced.
4.3 Methanimine

We have studied the cis→trans photoisomerization of methanimine (CH₂NH). Two typical trajectories for reactive (cis→trans) and non-reactive (cis→cis) events respectively are reported in Fig. 8. The trajectories were propagated for 200 fs with a time step of 0.05 fs, with each trajectory requiring approximately 100 s of CPU time.

The molecule is initially in a quasi-planar conformation in the first excited state (S₁). A fast torsional motion around the C-N double bond starts immediately and the molecule moves to a perpendicular configuration. The torsional angle oscillates several times around 90 degrees. The average torsional angle is shown for both reactive and unreactive trajectories in Fig. 9. In the same figure the average number of trajectories in the S₀ and S₁ state is shown. In the perpendicular configuration the energy separation between S₁ and S₀ is reduced. The energy separation can also be further reduced by a small pyramidalization of the CH₂ group. In this situation the hopping from the excited state to the ground state is highly probable. This situation is reflected by a continuous decrease of the number of trajectories in the S₁ state from t=25 fs to t=170 fs. After this time all the trajectories are in the S₀ state.

After hopping the molecule planarizes, either in the original configuration (cis) with a probability of 46%, or in the opposite configuration (trans) with a probability of 54%. The same system has been studied with nonadiabatic Car-Parrinello molecular dynamics calculations, which also found a majority of trajectories to be reactive [83].

5 Conclusions

We have presented an implementation of a surface hopping algorithm using semiempirical CI-MO wavefunctions for the direct evaluation of adiabatic energy surfaces and nonadiabatic couplings. Our implementation is integrated in a development version of the MNDO package [50] and offers a practical tool for the simulation of excited state dynamics and the study of de-excitation processes and photoreactions.

Several technical aspects of the implementation have been discussed. In particular we have stressed the importance of state tracking, which ensures the correct description of dynamics around PES crossings. We also discussed in detail several aspects of the fewest switches algorithm and performed studies of the efficiency of different numerical methods for the solution of the time-dependent electronic Schrödinger equation and of the fully numerical
procedure for the computation of nonadiabatic couplings.

The present implementation has been applied to the simulation of the nonadiabatic dynamics of three model systems (ethylene, methaniminium ion and methanimine) using the OM2 method [51,52] combined with GUGA configuration interaction [63]. Our results agree well with previous ab initio surface hopping studies, showing that this methodology can be successfully applied to the study of the electronic deexcitation and photoisomerization of molecular systems and that the OM2 method offers a good description of potential energy surfaces and of nonadiabatic couplings at a low computational cost. Therefore we conclude that the OM2 method is a promising approach for future surface hopping investigations on larger systems.

6 Acknowledgments

We thank Paul Strodel (then University of Paderborn) for initial coding of the Tully surface hopping algorithm. We are grateful for helpful discussions with Marcus Elstner (University of Braunschweig), Axel Koslowski (MPI Mülheim) and Marius Wanko (University of Bremen). This work is supported by the Deutsche Forschungsgemeinschaft (SFB 663).

References


Table 1
Global error in electronic population of ethylene after 150 fs for different integration methods, number of integration steps and MD time steps (\(\Delta t\)). The reference value comes from UP with 1000 steps. The approximate computational time (in milliseconds) needed for an integration cycle on one Intel Pentium 4-EM64T 3.40 GHz processor is also given.

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Fig. 1  Relative error of fully numerical nonadiabatic couplings with respect to analytical couplings over the course of a typical trajectory of the methaniminium ion.

Fig. 2  Average occupation of S₀, S₁ and S₂ states of ethylene as function of time, averaged over 100 trajectories. The trajectories were calculated using an OM2 Hamiltonian.

Fig. 3  Potential energy surfaces for typical trajectories of ethylene. The potential energy surface on which the system is propagated is indicated in bold.

Fig. 4  Examples of potential energy surface crossings in ethylene trajectories. The C-C bond is not indicated in the bottom panel to emphasize the large separation (1.88 Å) between the two CH₂ groups.

Fig. 5  Average occupation of S₀, S₁ and S₂ states of CH₂NH₂⁺ as function of time, averaged over 100 trajectories. The trajectories were calculated using an OM2 Hamiltonian.

Fig. 6  Potential energy surfaces for a typical trajectory of CH₂NH₂⁺. The potential energy surface on which MD propagation at each time step is performed is indicated in bold.

Fig. 7  Examples of potential energy crossings in trajectories of the methaniminium ion.

Fig. 8  Potential energy surfaces for typical reactive cis→trans (upper panel) and unreactive cis→cis (lower panel) trajectories of CH₂NH.

Fig. 9  Average torsional angle (upper panel) and average number of trajectories in S₀ and S₁ states (lower panel) for CH₂NH.
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