Single switch surface hopping for molecular dynamics

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Schedule of the talk

1. Introduction
2. The algorithm
3. Numerics
4. Extensions of the algorithm

1. INTRODUCTION

1.1. The Schrödinger equation

The dynamics of molecules is described in Born-Oppenheimer approximation by a Schrödinger equation

$$ih\partial_t\psi^h - \frac{h^2}{2}\Delta\psi^h + V(q)\psi^h = 0, \quad (q,t) \in \mathbf{R}^d \times \mathbf{R},$$
$$\psi^h(q,0) = \psi_0^h(q) \in L^2(\mathbf{R}^d, \mathbf{C}^N)$$

$V(q) \in \mathbf{C}^{N,N}$ is the potential: smooth, valued in the set of hermitian matrices and of subquadratic growth,

$$h = \sqrt{\frac{m_{electron}}{M_{nucleus}}} \ll 1,$$

$\psi^h(t,q)$ is the wave function.

1.2. Examples of Potentials

The Jahn-Teller Hamiltonian:

$$V_{JT}(q) = \phi_0(q)\mathrm{Id}_2 + \begin{pmatrix} \phi_1(q) & \phi_2(q) \\ \phi_2(q) & -\phi_1(q) \end{pmatrix}.$$

The pseudo Jahn-Teller Hamiltonian

$$V_{PJT}(q) = \phi_0(q)\mathrm{Id}_3 + \begin{pmatrix} \phi_1(q) & 0 & \phi_2(q)/\sqrt{2} \\ 0 & -\phi_1(q) & \phi_2(q)/\sqrt{2} \\ \phi_2(q)/\sqrt{2} & \phi_2(q)/\sqrt{2} & 0 \end{pmatrix}.$$

Hagedorn's potentials

$$V_{hag}(q) = \phi_0(q)\mathrm{Id}_4 + \begin{pmatrix} V_{JT}(q) & \mathbf{0}_2 \\ \mathbf{0}_2 & V_{JT}(q) \end{pmatrix}$$

The eigenvalues cross when $\phi_1(q) = \phi_2(q) = 0$.

1.3. Quadratic functions of the wave function

The position density: $q \mapsto \|\psi^h(t,q)\|^2_{C^N}$
describes the probability of finding the molecule at time t in the configuration q.

The energy level populations: $\|\Pi^\ell(q)\psi^h(t,q)\|_{L^2(\mathbf{R}^d,\mathbf{C}^N)}$
describes the population of the ℓ-th level if $\Pi^\ell(q)$ is a spectral projector of the matrix $V(q)$.

The momentum density: $p \mapsto (2\pi h)^{-d}\left\|\widehat{\psi^h}\left(t,\frac{p}{h}\right)\right\|_{C^N}$
describe the probability of finding the molecule at time t with the momentum p.

The momentum expectation in the j-th direction:
$\left(-ih\partial_j\psi^h(t,q),\psi^h(t,q)\right)_{L^2(\mathbf{R}^d,\mathbf{C}^N)}$.

1.4. The Wigner transform (1)

The key for calculating all these quadratic quantities! The Wigner transform is a generalized probability density in the phase space

$$W^h\Big(\psi^h(t)\Big)\,(q,p) = (2\pi)^{-d}\int \psi^h\Big(q-\tfrac{h}{2}v,t\Big)\otimes\overline{\psi}^h\Big(q+\tfrac{h}{2}v,t\Big)\;\mathrm{e}^{i\,v\cdot p}\,\mathrm{d}v.$$

Examples:

- The energy level populations:

$$\|\Pi^\ell(q)\psi^h(t,q)\|_{L^2(\mathbf{R}^d,\mathbf{C}^N)} = \mathrm{tr}\int W^h(\psi^h(t))(q,p)\,\Pi^\ell(q)\,dq\,dp.$$

- The momentum expectation in the j-th direction:

$$\Big(-ih\partial_j\psi^h(t,q),\psi^h(t,q)\Big)_{L^2(\mathbf{R}^d,\mathbf{C}^N)} = \mathrm{tr}\int p_j\,W^h(\psi^h(t))(q,p)\,dq\,dp.$$

1.4. The Wigner transform (2)

The aim: Describe

$$\Pi^{\ell}(q)\, W^{h}\Big(\psi^{h}(t)\Big)(q,p)\, \Pi^{\ell}(q)$$

or equivalently, describe

$$\int a(q,p)\Pi^{\ell}(q)\; W^{h}\Big(\psi^{h}(t)\Big)(q,p)\, dq\, dp$$

for scalar observables $a(q,p)$ which are smooth in q and p.

2. THE ALGORITHM

2.1. The single switch algorithm for Jahn-Teller Hamiltonians (1)

We choose $V(q) = V_{JT}(q)$ with two modes $E^{\pm}(q)$ and eigenprojectors $\Pi^{\pm}(q)$,

$$E^{\pm}(q) = \phi_0(q) \pm \sqrt{\phi_1(q)^2 + \phi_2(q)^2}.$$

The algorithm:

[A] Sampling of the initial Wigner function.

$\mapsto$[B] Classical transport of the sampling points.

$\mapsto$[C] Branching of the trajectories, whenever they attain a local minimal eigenvalue gap, and weighting according to a generalized Landau-Zener formula.

[D] Final computation of expectation values.

2.1. The single switch algorithm for Jahn-Teller Hamiltonians (2)

Which place in the large family of surface hopping semi-group?

- The 'father': J. Tully and R. Preston, J. Chem. Phys., **55** (1971).
- The 'brother': A. Voronin, J. Marques, and A. Varandas, J. Phys. Chem. **102** (1998).

Interest and new (?) features:

- It is based on a deterministic branching scheme.
- It has rigorous mathematical derivation.
- Its constitutive branching condition is made according to a multi-dimensional Landau-Zener formula.
- It generates fewer switches than most of the well-established surface hopping schemes, which in principle allow for non-adiabatic transitions at every time step of the discretization.

cf. C. Lasser and T. Swart, J. Chem. Phys. 129, (2008)

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- The algorithm allows for general initial data (not only gaussian).

Main drawback: The possibly incorrect approximation of inter-surface interferences if there are classical trajectories on different surfaces, which arrive with comparable momenta simultaneously near a conical intersection point.

2.2. The Sampling

One samples the initial Wigner functions

$$(q,p) \mapsto \mathrm{tr}\left(\Pi^{\pm}(q) W(\psi_0^h)(q,p)\right)$$

to obtain two sets of phase space points, one related with the upper and the other with the lower surface.

Difficulty: It requires the approximation of high-dimensional oscillatory Fourier integrals.

Reference on Monte Carlo techniques in that context : Monte Carlo sampling of Wigner functions and surface hopping quantum dynamics by S. Kube, C. Lasser, M. Weber (*Preprint*).

2.3. Transport

The sample points are transported along the classical trajectories of the corresponding Hamiltonian systems

$$\dot{q}_t^{\pm} = p_t^{\pm}, \qquad \dot{p}_t^{\pm} = -\nabla_q E^{\pm}(q_t^{\pm}).$$

Denote by $\Phi_t^{\pm}(q,p) = \left(q_t^{\pm}, p_t^{\pm}\right)$ the trajectories passing in (q,p) at time $t = 0$, then

Theorem [Lasser F. 07] : Let $R \in \mathbf{R}^+$,

$$\Pi^{\ell}(q)\, W^h\Big(\psi^h(t)\Big)\ (q,p)\, \Pi^{\ell}(q) = \Big(\Pi^{\ell}(q)\, W^h\Big(\psi^h(s)\Big)(q,p)\, \Pi^{\ell}(q)\Big) \circ \Phi^{\pm}_{-t+s}(q,p) + O(\sqrt{h}) + O(1/R^2) + O(1/R^5\sqrt{h})$$

in $\{\sqrt{\phi_1(q)^2 + \phi_2(q)^2} > R\sqrt{h}\}$.

2.4. Transitions (1)

• When do the jumps occur?

One monitors, when a trajectory $(q_t^{\pm}, p_t^{\pm})$ attains a local minimum along the surface gap, that is when the function

$$t \mapsto \sqrt{\phi_1(q_t^{\pm})^2 + \phi_2(q_t^{\pm})^2}$$

attains a local minimum, i.e. when .

$$\langle \mathrm{d}\phi(q)p \mid \phi(q) \rangle_{\mathbf{R}^2} = 0,$$

where $\mathrm{d}\phi(q)$ denotes the $2 \times d$ gradient matrix of $\phi(q) = (\phi_1(q), \phi_2(q))$.

• The jumps

At points (q, p) with local minimal gap, all trajectories split.

2.4. Transitions (2)

• The transition rate.

The new branch starts on the other surface in the same point (q, p) and has the old weight times a Landau-Zener factor

$$T(q,p) = \exp\left(-\frac{\pi}{h}\,\frac{|\phi(q)|^2}{|\mathrm{d}\phi(q)p|}\right).$$

The branch remaining on the same surface is reweighted by the factor $1 - T(q, p)$.

• More restrictive criterion of transitions

The Landau-Zener rate only causes a significant contribution, when the gap $|\phi(q)|$ is of order $h^{1/2}$. Hence, one can tighten the branching condition by additionally requiring, that the gap is of order $h^{1/2}$, which in turn reduces the number of trajectories.

2.4. Transitions (3)

Denote by $(\mathcal{L}_h^t)(W^h(\psi_0^h))$ the output of the algorithm at time t and suppose

(A1) $(\psi_0^h)_{h>0}$ is associated with $\mathrm{Ran}\Pi^+$, localized away from the crossing and away from the set which contains the points issuing classical trajectories, which arrive at the crossing without a unique continuation through it.

(A2) The test function $a \in \mathcal{C}_c^\infty\left(\mathbf{R}^{2d}, \mathbf{C}^{N\times N}\right)$ has its support at a distance larger than $R\sqrt{h}$ from the crossing.

(A3) Within the time-interval $[0, t_f]$, each of the plus-trajectories arriving at the support of a^+ at time t_f has performed at most one jump generating minus-trajectories arriving at the support of a^-, which have not jumped at all.

2.4. Transitions (4)

Denote by $(\mathcal{L}_h^t)_{t\geq 0}(W^h(\psi_0^h)$ the output of the algorithm at time t

Theorem (Lasser F. [07]):
If one has (A1), (A2) and (A3) and if $\chi \in \mathcal{C}_c^\infty([0,t_f],\mathbf{R})$, then, there exist positive constants $C, h_0 \in \mathbf{R}_+^*$ such that for all $0 < h < h_0$

$$\left|\mathrm{tr}\int_{\mathbf{R}^{2d+1}} \chi(t)\left(W^h\Big(\psi^h(t)\Big) - (\mathcal{L}_h^t)(W^h(\psi_0^h))\right)(q,p)\,a(q,p)\,\mathrm{d}q\,\mathrm{d}p\,\mathrm{d}t\right| \leq C\,h^{1/8}.$$

2.5. Final computations

At some final time t_f one obtains two sets of phase space points, one associated with the lower surface, the other with the upper surface. Each point carries its specific weight, depending upon how many transitions the trajectory has experienced and where in phase space they have occurred. If N points $(q_1, p_1), \ldots, (q_N, p_N)$ with associated weights $w_1, \ldots, w_N$ have arrived on the upper surface, for example, then any expectation value can be approximated as

$$\left\langle A\psi^+(t) \mid \psi^+(t) \right\rangle_{L^2} \approx \sum_{j=1}^{N} a(q_j, p_j) w_j \, \delta_j,$$

where $\delta_j \geq 0$ denotes a suitable quadrature weight. In the case of a grid based initial sampling, the quadrature weight is the volume element of the corresponding initial point.

3. THE NUMERICS (1)

We choose

$$
\begin{aligned}
V(q) &= \gamma|q|^2 + \begin{pmatrix} q_1 & q_2 \\ q_2 & -q_1 \end{pmatrix}, \quad \gamma = 3. \\
\psi_0^h(q) &= \frac{1}{\sqrt{\pi h}} \exp\Big(-\frac{1}{2h}|q-q_0|^2 + \frac{i}{h}\langle p_0, q-q_0\rangle_{\mathbf{R}^2}\Big)\, \chi^+(q) \\
\chi^+(q) &= (\cos\theta_q, \sin\theta_q) \ \text{ where } \ \frac{q}{|q|} = (\cos(2\theta_q), \sin(2\theta q)). \\
q_0 &= (5h^{1/2}, 0.5h^{1/2}). \\
h &= 0.001, 0.005, 0.01, 0.05, 0.1. \\
p_0 &= (-1, 0). \\
t_{\mathrm{f}} &= \begin{cases} \pi\,(2\gamma)^{-1/2} & \text{for } h = 0.001, \\ \frac{5}{3}\pi\,(2\gamma)^{-1/2} & \text{otherwise} \end{cases}
\end{aligned}
$$

(see Garcia-Fernández, Bersuker, A. Aramburu, and Moreno, Phys. Rev. B, **71**, 184117 (2005).)

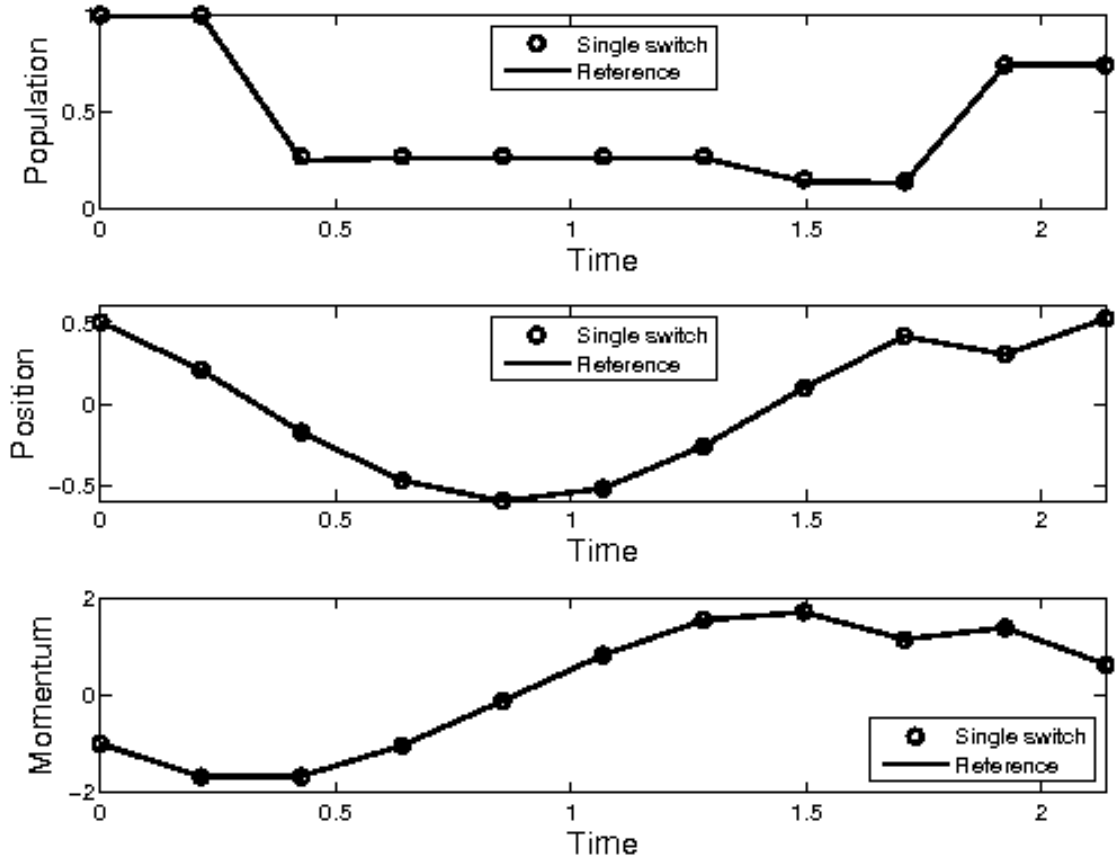
3. THE NUMERICS (2)

We calculate the population, the position and the momentum expectation along the first coordinate as a function of time, all of them associated with the upper surface.

$$
\begin{aligned}
t &\mapsto \langle \Pi^+ \psi^h(t) \mid \Pi^+ \psi^h(t) \rangle_{L^2}, \\
t &\mapsto \langle q_1 \Pi^+ \psi^h(t) \mid \Pi^+ \psi^h(t) \rangle_{L^2}, \\
t &\mapsto \langle -ih\partial_1 \Pi^+ \psi^h(t) \mid \Pi^+ \psi^h(t) \rangle_{L^2}.
\end{aligned}
$$

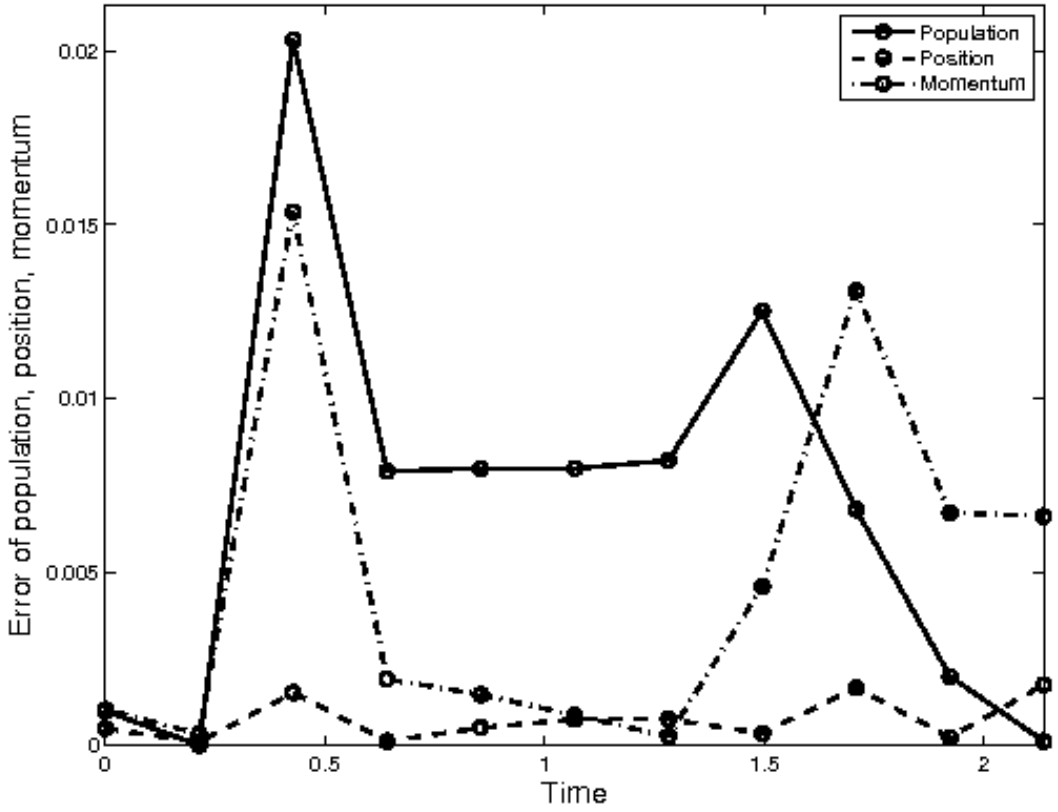
Then with the lower surface and we compare the results with those obtained for a reference solution computed with a rapidly converging splitting scheme.

FIGURE 1: Population, position and momentum expectation along the first coordinate as a function of time for the upper energy surface.



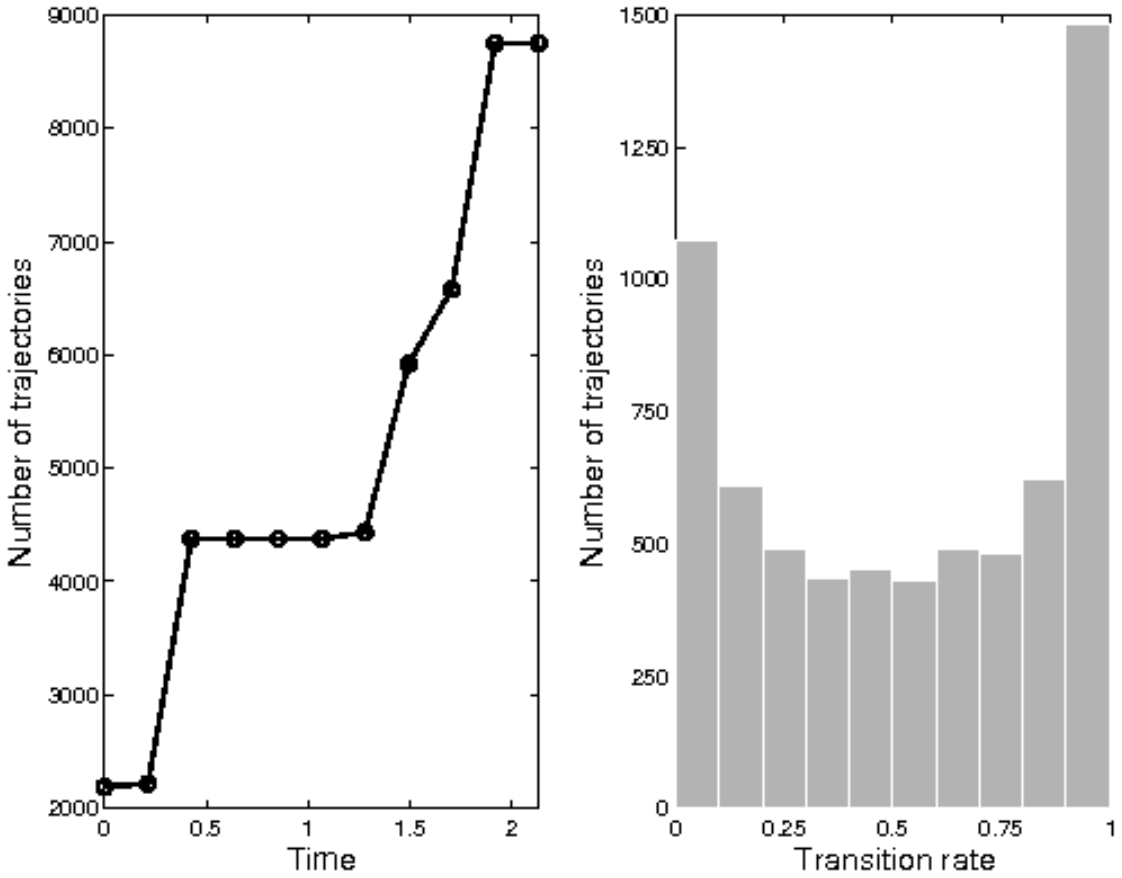
The results of the single switch algorithm follow the values of the reference solution. The plots correspond to the errors shown in next figure.

FIGURE 2: Absolute error of population, position and momentum expectation along the first coordinate as a function of time, all of them associated with the upper surface.



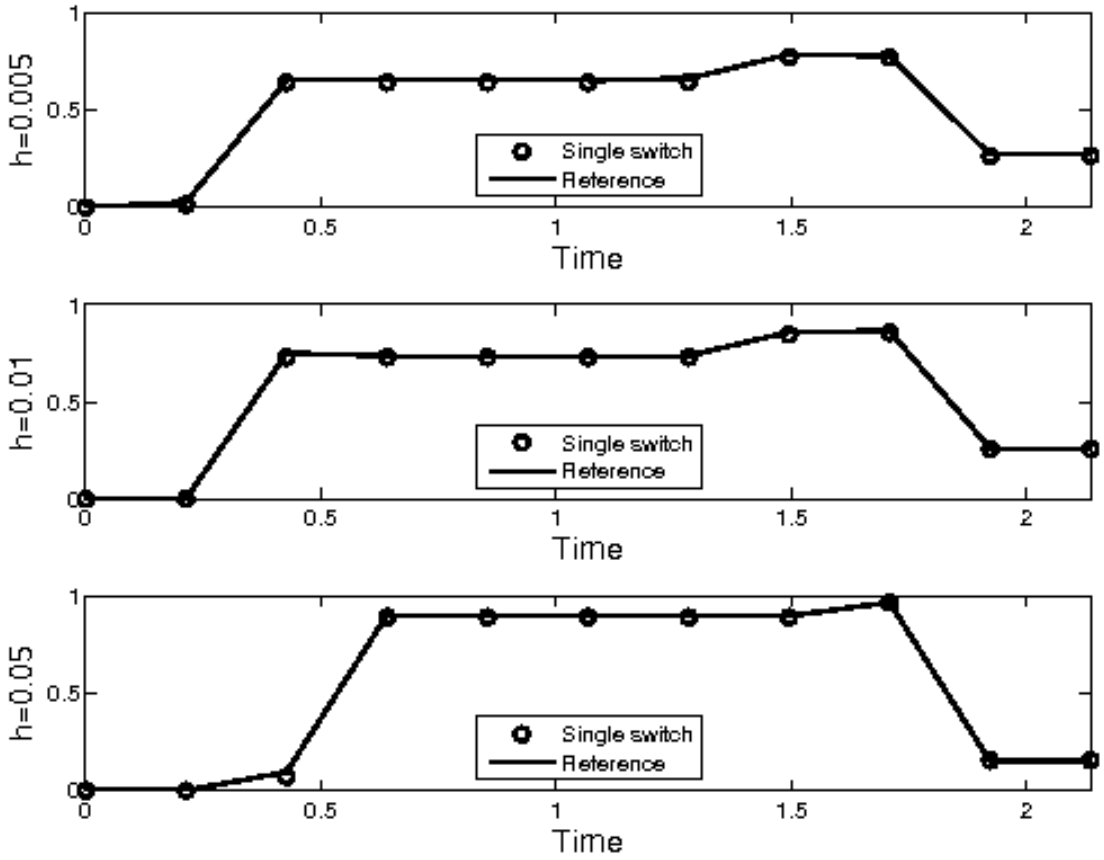
The reference solution is computed by a numerically converged splitting scheme. All errors stay below three precent.

FIGURE 3: Number of trajectories used by the single switch algorithm as a function of time.



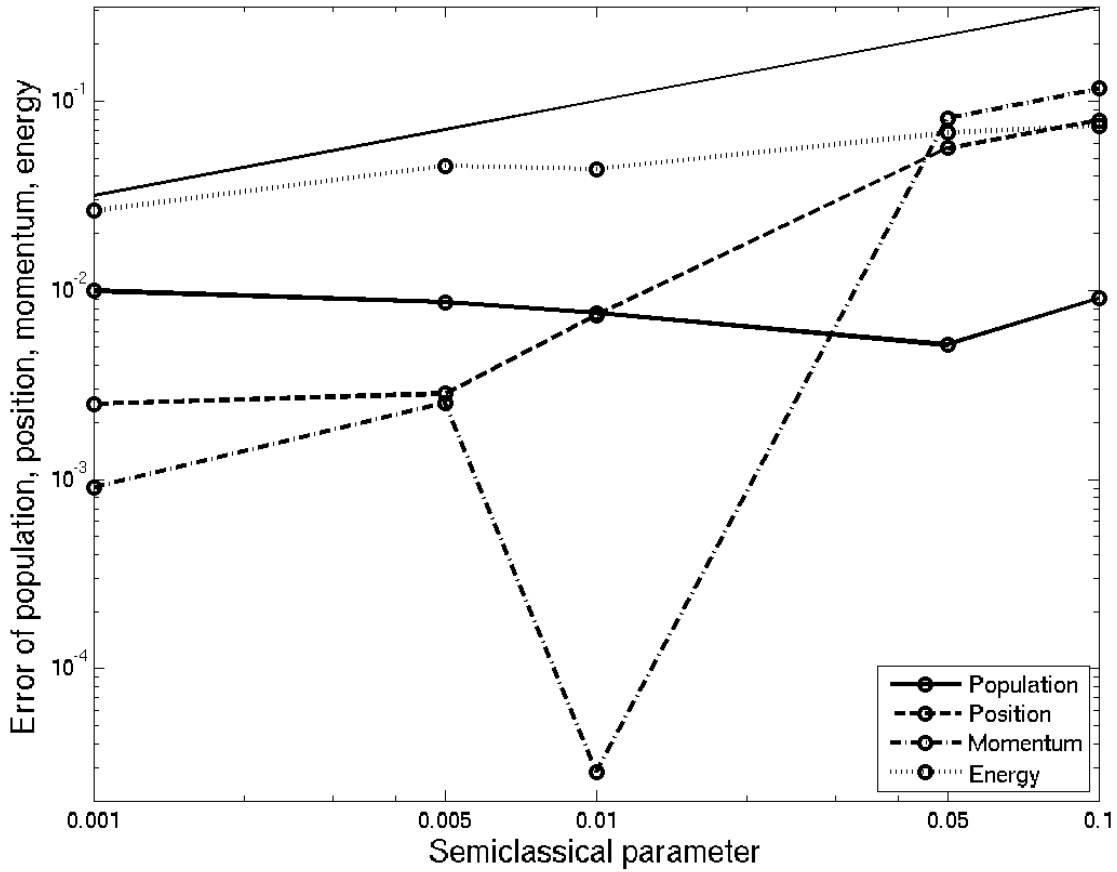
The histogram of the non-adiabatic transition rates shows maxima for small and large values of the rate. The arithmetic mean is 0.53.

FIGURE 4: Dependance on h.



Population of the lower surface as a function of time for $h = 0.005, 0.01$, and 0.05. The population changes three times, the first and the last time by more than fifty percent, inbetween by roughly ten percent.

FIGURE 5: Mean error of population, position and momentum expectation along the first coordinate as a function of the semiclassical parameter, all of them related with the lower surface.



The dotted line is the function $h \mapsto \sqrt{h}$.

4. EXTENSIONS OF THE ALGORITHM

4.1 Twofold eigenvalues.

Collaboration with C. Lasser

4.2 Pseudo Jahn-Teller hamiltonian (in progress).

Collaboration with V. Rousse

4.3 Avoided crossings (in progress).

Collaboration with C. Lasser

4.1. Twofold eigenvalues (1)

$$V(q) = V_{hag}(q) = \phi_0(q)\mathrm{Id}_4 + \mathcal{B}(\phi_1(q), \phi_2(q), \phi_3(q))$$

where

$$\mathcal{B}(v_1, v_2, v_3) = \begin{pmatrix} \begin{pmatrix} v_1 & v_2 + iv_3 \\ v_2 - iv_3 & -v_1 \end{pmatrix} & \mathbf{0} \\ \mathbf{0} & \begin{pmatrix} v_1 & v_2 - iv_3 \\ v_2 + iv_3 & -v_1 \end{pmatrix} \end{pmatrix}.$$

The modified observables:

$$b(q,p) = \Pi^{\pm}(q) b(q,p) \Pi^{\pm}(q).$$

Such $b(q,p)$ still commute with the potential matrix $V(q)$. If $\chi(q)$ is an eigenvector of $V(q)$, then the observable

$$b(q) = \chi(q) \otimes \chi(q)$$

describes orientation in one specific direction of one of the eigenspaces.

4.1. Twofold eigenvalues (2)

The algorithm:

A. Initial sampling for the two four-by-four matrices $\Pi^{\pm}(W\psi_0)\Pi^{\pm}$.

B. Classical transport by $\dot{q} = p$, $\dot{p} = -\nabla_q E^{\pm}(q)$.

C. Branching when a trajectory attains a local minimal gap, and same Landau-Zener rate AND conjugation of the matrix carried by the branch remaining on the same surface by

$$\mathcal{R}(q,p) = \mathcal{B}\left(\frac{\mathrm{d}\phi(q)p \wedge \phi(q)}{|\mathrm{d}\phi(q)p \wedge \phi(q)|}\right),$$

where $x \wedge y = (x_2y_3 - x_3y_2, x_3y_1 - y_3x_1, x_1y_2 - x_2y_1)$.
That is, the old and the new branch respectively carry the weights

$$(1 - T(q,p))\,\mathcal{R}(q,p)\,W\,\mathcal{R}(q,p) \quad \text{and} \quad T(q,p)W.$$

D. Computation of final expectation values.

4.1. Twofold eigenvalues (3)

New phenomenon: The orientation turns when passing at the crossing.

Question:

1- Is-it interesting from chemical point of view?

2- Has it been already observed?

4.2. Pseudo Jahn-Teller Hamiltonian

$$V(q) = V_{PJT}(q) = \begin{pmatrix} q_1 & 0 & q_2/\sqrt{2} \\ 0 & -q_1 & q_2/\sqrt{2} \\ q_2/\sqrt{2} & q_2/\sqrt{2} & 0 \end{pmatrix}.$$

New aspect: 3 modes 0, $\sqrt{q_1^2 + q_2^2}$ and $-\sqrt{q_1^2 + q_2^2}$.

Modification of the algorithm: The three modes interact, each one with the two other ones. The transitions probabilities have been calculated by S. Brundobler and V. Elser, S-matrix for generalized Landau-Zener problem, *J. Phys. A*, **26**, pp. 1211–1227 (1993).

Questions: Generalization to "$V_{PJT}(\phi_1(q), \phi_2(q)) + \phi_0(q)\mathrm{Id}_3$".

4.3. Avoided crossings

$V(q) = V(q, \delta)$ with $E^+(q, \delta) = E^-(q, \delta)$ as δ goes to 0.

Questions:

- Which is the correct jump criterion?
- How to choose the new trajectories?

cf. G. Hagedorn, A. Joye, Molecular propagation through small avoided crossings of electron energy levels, Rev. in Math. Physics, **11** (1999).

CONCLUSION

Other open questions:

- Dealing with the interferences (very interesting from mathematical point of view, from chemical point of view?). It requires to be able to propagate more information on the wave function, not only the diagonal part of the Wigner transform.
- Being able to say something for a potential which is the sum of a Jahn-Teller potential and a pseudo Jahn-Teller one.
- What about potentials which are non linear functions of the wave function?

$$V(q) = V_0(q) + h^{\alpha} \mid \psi^h(t,q) \mid^{2\beta} \mathrm{Id}, \quad \alpha, \beta > 0.$$

Is-it pertinent for chemistry?

References:

[1] C. Fermanian Kammerer, C. Lasser : Single switch surface hopping for molecular dynamics with transitions. Journal of Chemical Physics, **128**, 144102 (2008).

[2] C. Fermanian Kammerer, C. Lasser : Propagation through generic level crossings: a surface hopping semigroup. SIAM J. of Math. Anal. , **140**, 1, p. 103-133 (2008).