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Single switch surface hopping for molecular quantum dynamics

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Abstract The aim of this text is to present a surface hopping approximation for molecular quantum dynamics obeying a Schrödinger equation with crossing eigenvalue surfaces. After motivating Schrödinger equations with matrix valued potentials, we describe the single switch algorithm and present some numerical results. Then we discuss the algorithm's mathematical justification and describe extensions to more general situations, where three eigenvalue surfaces intersect or the eigenvalues are of multiplicity two. We emphasize the generality of this surface hopping approximation for non-adiabatic transitions.

Keywords Molecular dynamics · Conical intersections · Surface hopping

1 Molecular quantum dynamics

1.1 The Schrödinger equation

The quantum-mechanical description of molecular dynamics is given by the time-dependent Schrödinger equation

$$\begin{cases} i\varepsilon\,\partial_t \Psi^\varepsilon = H^\varepsilon_{mol}\,\Psi^\varepsilon, \\ \Psi^\varepsilon_{t=0} = \Psi^\varepsilon_0 \in L^2(\mathbf{R}^{3N}, \mathbf{C}). \end{cases} \tag{1.1}$$

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The integer N is $N = k_e + k_n$, where k_n is the number of nuclei and k_e the number of electrons. If $q \in \mathbf{R}^d, d = 3k_n$, denotes the nucleonic coordinates, then the Hamiltonian H^ε_{mol} writes

$$H^\varepsilon_{mol} = -\frac{\varepsilon^2}{2}\Delta_q + H_e(q),$$

where $H_e(q)$ is the electronic Hamiltonian. It comprises the electrons' kinetics, the electronic interaction and the interaction between electrons and nuclei for fixed nucleonic position q. In atomic units, the electronic mass is one, while the average nucleonic mass M is large. Therefore the parameter ε is small:

$$\varepsilon = \sqrt{1/M} \ll 1.$$

Placing ε in front of the time derivative in (1.1) singles out the effective time scale, on which relevant nucleonic quantum motion is expected.

1.2 The energy surfaces

We consider $\sigma_*(q)$ a closed isolated subset of the spectrum $\sigma(H_e(q))$, we suppose that

$$\sigma_*(q) = \{\lambda^+(q),\ \lambda^-(q)\}, \qquad \lambda^-(q) \leq \lambda^+(q)$$

with $\lambda^+(q)$ and $\lambda^-(q)$ eigenvalues of multiplicity 1, and we suppose that there exists a smooth real-valued basis of the vector space $\Lambda(q)$ which is the sum of the eigenspaces associated with $\lambda^+(q)$ and $\lambda^-(q)$.

If the initial data $\Psi^\varepsilon_0(q) \in \Lambda(q)$, then Ψ^ε can be approximated by a Born-Oppenheimer solution Ψ^ε_{BO} modulo an error of order ε: $\exists C > 0, \forall t > 0$,

$$\|\Psi^\varepsilon(t) - \Psi^\varepsilon_{BO}(t)\|_{L^2} \ \leq\ C(1 + |t|)\,\varepsilon.$$

Since the basis of $\Lambda(q)$ is real-valued, the nucleonic components of Ψ^ε_{BO} satisfy the Schrödinger system

$$\begin{cases} i\varepsilon\partial_t\psi^\varepsilon = -\frac{\varepsilon^2}{2}\Delta_q\psi^\varepsilon + V(q)\psi^\varepsilon, \\ \psi^\varepsilon_{t=0} = \psi^\varepsilon_0 \in L^2(\mathbf{R}^d, \mathbf{C}^2), \end{cases} \tag{1.2}$$

where the potential $V(q)$ is a smooth function, whose values are 2×2 real symmetric matrices (see [19] or [18]); besides, the eigenvalues of $V(q)$ are $\lambda^+(q)$ and $\lambda^-(q)$.

We denote by g the gap function

$$g(q) = \lambda^+(q) - \lambda^-(q).$$

The function g is non-negative and smooth outside the set

$$S = \{q \in \mathbf{R}^d;\ g(q) = 0\},$$

on which the eigenvalues coincide.

1.3 The effective potential

We write

$$V(q) = \alpha(q)\,\mathrm{Id} + V_0(q),$$

where $\alpha(q) = \frac{1}{2}\left(\lambda^+(q) + \lambda^-(q)\right)$ is the half of the trace of the matrix $V(q)$, and $V_0(q)$ denotes the trace-free part of $V(q)$,

$$V_0(q) = \begin{pmatrix} \beta(q) & \gamma(q) \\ \gamma(q) & -\beta(q) \end{pmatrix}.$$

In this notation, $g(q) = 2\sqrt{\beta(q)^2 + \gamma(q)^2}$. The matrix $V(q)$ is the prototype potential for crossings of two eigenvalues of multiplicity 1.

Consider now the eigenprojectors $\Pi^{\pm}(q)$:

$$\Pi^{\pm}(q) = \frac{1}{2}\left(\mathrm{Id} \pm \frac{2}{g(q)} V(q)\right).$$

They are smooth away from the crossing S. We choose initial data for the wave function which are localized along the plus or the minus level. They are of the form

$$\psi_0^\varepsilon(q) = \Pi^+(q)\psi_0^\varepsilon(q) \quad \text{or} \quad \psi_0^\varepsilon(q) = \Pi^-(q)\psi_0^\varepsilon(q).$$

We analyze the solution to (1.2) for small values of ε.

1.4 The Wigner transform

The wave function by itself has no physical meaning, and the quantities of interest are quadratic functions of it such as

- the energy level populations:

$$t \mapsto \left(\Pi^{\pm}(q)\psi^\varepsilon(t,q), \psi^\varepsilon(t,q)\right)_{L^2(\mathbf{R}^d,\mathbf{C}^2)},$$

- the position expectation value with respect to the jth direction:

$$t \mapsto \left(q_j\psi^\varepsilon(t,q), \psi^\varepsilon(t,q)\right)_{L^2(\mathbf{R}^d,\mathbf{C}^2)},$$

- the momentum expectation value with respect to the j-th direction:

$$t \mapsto \left(-i\varepsilon\partial_j\psi^\varepsilon(t,q), \psi^\varepsilon(t,q)\right)_{L^2(\mathbf{R}^d,\mathbf{C}^2)}.$$

The analysis of these quadratic functionals leads to the study of quantities of the form

$$L^\varepsilon(a(q)) = \int_{\mathbf{R}^d} \big(a(q)\psi^\varepsilon(t,q), \psi^\varepsilon(t,q)\big)_{\mathbf{C}^2}\, dq$$

or

$$L^\varepsilon(b(p)) = (2\pi)^{-d} \int_{\mathbf{R}^d} \big(b(p)\widehat{\psi^\varepsilon}(t,p/\varepsilon), \widehat{\psi^\varepsilon}(t,p/\varepsilon)\big)_{\mathbf{C}^2}\, dp$$

with $a, b \in \mathcal{C}^\infty(\mathbf{R}^d, \mathbf{C}^{2,2})$. Therefore, we focus on the description of the time evolution of the Wigner transform of $\psi^\varepsilon(t)$,

$$W^\varepsilon\big(\psi^\varepsilon(t)\big)(q,p) = (2\pi)^{-d} \int_{\mathbf{R}^d} \psi^\varepsilon\Big(q - \frac{\varepsilon}{2}v, t\Big) \otimes \overline{\psi^\varepsilon}\Big(q + \frac{\varepsilon}{2}v, t\Big)\, \mathrm{e}^{i\,v\cdot p}\, dv, \quad (1.3)$$

which plays the role of a generalized density on phase space. Indeed, one can check that

$$L^\varepsilon(a(q)) = \int_{\mathbf{R}^{2d}} \mathrm{tr}\,\big(a(q)W^\varepsilon(\psi^\varepsilon(t))(q,p)\big)\, dq\, dp,$$
$$L^\varepsilon(b(p)) = \int_{\mathbf{R}^{2d}} \mathrm{tr}\,\big(b(p)W^\varepsilon(\psi^\varepsilon(t))(q,p)\big)\, dq\, dp.$$

We mention that other density functions on phase space could be considered in place of the Wigner function. However, the single switch approximation we are aiming at is tailored to the Wigner function, see also [14, §7.2].

We focus here on quadratic quantities related to one precise mode and study the diagonal part of the Wigner transform, $\Pi^\pm(q)W^\varepsilon(\psi^\varepsilon(t))(q,p)\Pi^\pm(q)$, before and after passing the crossing S. Since the eigenvalues are of multiplicity 1, these matrices are utterly characterized by their traces, and we study

$$w^\varepsilon_\pm(t,q,p) = \mathrm{tr}\,\big(\Pi^\pm(q)W^\varepsilon(\psi^\varepsilon(t))(q,p)\Pi^\pm(q)\big).$$

Our aim is to describe the evolution of $w^\varepsilon_\pm(t)$ in terms of $w^\varepsilon_+(0)$ or $w^\varepsilon_-(0)$ for small values of ε.

1.5 The classical trajectories

We consider the classical flow

$$\Phi^t_\pm : \mathbf{R}^{2d} \to \mathbf{R}^{2d}, \quad \Phi^t_\pm(q_0,p_0) = \big(q^\pm(t), p^\pm(t)\big)$$

associated with the Hamiltonian curves of $\frac{|p|^2}{2} + \lambda^{\pm}(q)$:

$$\begin{cases} \dot{q}^{\pm}(t) = p^{\pm}(t), \quad \dot{p}^{\pm}(t) = -\nabla\lambda^{\pm}\left(q^{\pm}(t)\right), \\ q^{\pm}(0) = q_0, \quad p^{\pm}(0) = p_0 \end{cases}$$

- As long as $g(q) = O(1)$, the classical flows $\Phi_{\pm}^t$ are enough for an approximate description of the dynamics:

$$\int_{\mathbf{R}^{2d}} \left(w_{\pm}^{\varepsilon}(t) - w_{\pm}^{\varepsilon}(0) \circ \Phi_{\pm}^{-t}\right)(q, p)\, a(q, p)\, dq\, dp = O(\varepsilon).$$

  This is an approximation in the spirit of the Egoroff Theorem.
- If $g(q)$ is much larger than $\sqrt{\varepsilon}$ in a sense that can be made precise, one can prove that this approximation description still holds in a weaker sense (see Proposition 2.3 in [7] for precise statements).
- If $g(q) = O(\sqrt{\varepsilon})$ this approximation is no longer valid, and there are non-adiabatic transitions between the levels. The energy propagated until the transition region on one level may pass (partially or utterly) to the other one.

We denote by $\mathcal{U}_\varepsilon$ the transition region

$$\mathcal{U}_\varepsilon = \{q \in \mathbf{R}^d;\ g(q) \leq R\sqrt{\varepsilon}\},$$

where $R > 0$ is a constant arbitrarily chosen. It is in this region that the Egoroff type approximation fails and where transitions between the levels occur.

Note that the classical trajectories are well defined as long as g is smooth, i.e. as long as $g(q) \neq 0$. However, if the assumption

$$(p \cdot \nabla\beta(q),\, p \cdot \nabla\gamma(q)) \neq 0 \tag{1.4}$$

is satisfied near a crossing point $q \in S$, then any classical trajectory reaching the point q with momentum p has a unique continuation through it (see [6]). We will see the importance of this condition in Sect. 5, when discussing the limitations of our approximation.

2 The single switch algorithm

2.1 Main description

We suppose that the initial data are localized along the plus level: $\psi_0^{\varepsilon}(q) = \Pi^{+}(q)\psi_0^{\varepsilon}(q)$. The situation where the initial data is on the other level is treated analogously. For high dimensions, a Monte-Carlo approach is more appropriate than a grid-based algorithm (see Sect. 5.1 for such a procedure). The single switch algorithm consists of four steps:

(1) One samples the initial Wigner functions $(q, p) \mapsto w_+^\varepsilon(0, q, p)$ to obtain a set of $N^+(0)$ phase space points

$$(q_j^+, p_j^+), \qquad 1 \le j \le N^+(0),$$

so that

$$\frac{1}{N^+(0)} \sum_{j=1}^{N^+(0)} a(q_j^+, p_j^+) \approx \int a(q, p) w_+^\varepsilon(0, q, p) dq\, dp.$$

We note that the numerical computation of the oscillatory Fourier integrals (1.3) determining the values of $w_+^\varepsilon(0)$ is challenging in high dimensions, see also [14].

(2) One proceeds to classical transport of the sampling points and obtains at each time t a family of points

$$(q_j^+(t), p_j^+(t)), \qquad 1 \le j \le N^+(0).$$

(3) Whenever these trajectories attain a local minimal eigenvalue gap inside the transition region $\mathcal{U}_\varepsilon$, one allows for hops to the other surface. Suppose the trajectory $t \mapsto (q^+(t), p^+(t))$ reaches its minimal gap at time t^*, that is, $t \mapsto g(q^+(t))$ attains a local mimimum for $t = t^*$. One evaluates the transition rate

$$T_\varepsilon(q^*, p^*) = \exp\left(-\frac{\pi}{4\varepsilon} \frac{g(q^*)^2}{|\det p^* \cdot \nabla V_0(q^*)|^{1/2}}\right)$$

in the point

$$(q^*, p^*) = (q^+(t^*), p^+(t^*)),$$

where

$$|\det p^* \cdot \nabla V_0(q^*)| = \left(p^* \cdot \nabla \beta(q^*)\right)^2 + \left(p^* \cdot \nabla \gamma(q^*)\right)^2.$$

Then one uses an accept-reject procedure and compares with a pseudo random number ξ uniformly distributed in the interval [0,1]. If $\xi < T_\varepsilon(q^*, p^*)$, then the trajectory is continued on the upper level. Otherwise, one hops to the lower level and initiates a trajectory in $(q^-(t^*), p^-(t^*)) = (q^*, p^* + \omega(q^*, p^*))$, where the drift may be chosen as

$$\omega(q^*, p^*) = g(q^*) \frac{p^*}{|p^*|^2}.$$

In this way one obtains a family of points

$$(q_j^\pm(t), p_j^\pm(t)), \qquad 1 \le j \le N^\pm(t).$$

In Sect. 2.2 below the drift and a simple criterium for determining local minimal gaps are discussed, while a heuristic derivation of the transition rate is provided in Sect. 4.1.

(4) At some final time t_f, we are left with two sets of phase space points, one related with the upper surface and the other with the lower one. If $N = N^+(t_f)$ points $(q_1, p_1), \ldots, (q_N, p_N)$ have arrived on the upper surface, for example, then expectation values can be approximated as

$$\int_{\mathbf{R}^{2d}} a(q,p) w_+^{\varepsilon}(t,q,p) dq\, dp \;\approx\; \frac{1}{N}\sum_{j=1}^{N} a(q_j, p_j).$$

2.2 Drift and jump criterium

We now motivate the choice of the drift and discuss a criterium for local minimal gaps. At a jump point (q^*, p^*) one shifts the initial momentum of the created trajectory in order to preserve the energy of the trajectories up to $O(\varepsilon)$. Indeed, the energy of a plus incoming trajectory is

$$\tau^+(q^*, p^*) = \frac{1}{2}|p^*|^2 + \alpha(q^*) + \frac{1}{2}g(q^*)$$

and the energy of a minus outgoing trajectory with momentum $p^*_{out} = p^* + \omega(q^*, p^*)$ is

$$\tau^-(q^*, p^*_{out}) = \frac{1}{2}|p^* + \omega(q^*, p^*)|^2 + \alpha(q^*) - \frac{1}{2}g(q^*).$$

The condition $\tau^-(q^*, p^*_{out}) = \tau^+(q^*, p^*) + O(\varepsilon)$ is equivalent to $\omega(q^*, p^*) \cdot p^* + \frac{1}{2}|\omega(q^*, p^*)|^2 = g(q^*) + O(\varepsilon)$. This can be ensured by choosing

$$\omega(q^*, p^*) = g(q^*)\frac{p^*}{|p^*|^2},$$

since $g(q^*)^2 = O(\varepsilon)$. Note that in the work of Hagedorn and Joye (see [11] and [12]) a similar drift is required.

For monitoring the size of the gap we work with the smooth quantity

$$g(q)^2 = 4\left(\beta(q)^2 + \gamma(q)^2\right).$$

We observe that along a plus trajectory, we have

$$\begin{aligned}\frac{d}{dt}\left[g(q^+(t))\right]^2 &= 2\, g(q^+(t))\frac{d}{dt}g(q^+(t)) \\ &= 2\, g(q^+(t))\, p^+(t)\cdot\nabla g(q^+(t)).\end{aligned}$$

Therefore at time t^*, the function $t \mapsto g(q^+(t))\, p^+(t) \cdot \nabla g(q^+(t))$ changes sign from negative to positive, and a jump point (q^*, p^*) satisfies the equation

$$g(q^*)p^* \cdot \nabla g(q^*) = 0. \tag{2.1}$$

3 Numerical realization

To illustrate the behavior of the single switch algorithm we consider a simple example of an avoided crossing in one space dimension, which meets the range of validity of our analysis. Further numerical results for avoided crossings have been obtained in [8], where the test cases discussed by J. Tully in [21] are revisited. Successful simulations with the single switch algorithm for conical crossings have been reported in [7,14,16], where model systems for the cis-trans isomerization of retinal in rhodopsin, the internal conversion of pyrazine, and Jahn-Teller Hamiltonians have been treated.

The eigenvalues of the potential considered here are defined by smooth functions and the coefficients except for the gap parameter δ are of order one with respect to the semiclassical parameter ε. The potential matrix is of the form

$$V(q) = \begin{pmatrix} \arctan(q) & \delta \\ \delta & -\arctan(q) \end{pmatrix}. \tag{3.1}$$

The surfaces have their minimal gap at $q = 0$, see Fig. 1a. The initial data are multiples of a Gaussian wave packet with phase space centers $(q_0, p_0) \in \mathbf{R}^2$ and of a real-valued eigenvector $e^{\pm}(q)$ of the matrix $V(q)$:

$$\psi_0(q) = (\pi\varepsilon)^{-1/4} \exp\left(-\frac{1}{2\varepsilon}(q-q_0)^2 + \frac{i}{\varepsilon}p_0(q-q_0)\right) \mathrm{e}^{\pm}(q).$$

The semiclassical parameter ε is chosen as $\varepsilon = 10^{-3}$, the gap parameter as $\delta = \sqrt{\varepsilon}$. The initial data are associated with the upper eigenvector $\mathrm{e}^+(q)$ and are centered in the point $(q_0, p_0) = (-1, 1)$. We simulate the dynamics for the time interval $[0, T] = [0, 2]$.

The reference values are obtained from a numerically converged grid based solver, a Strang splitting scheme with Fourier differencing. Since the initial wave function is a Gaussian wave packet, the sampling from $w_+^\varepsilon(0)$ is realized by drawing $N = 2,000$ sampling points from a two-dimensional normal distribution. The results gathered in Fig. 1b are the mean of ten independent runs of the single switch algorithm with the same number of initial trajectories. The classical transport is discretized by a symplectic fourth order Runge Kutta scheme.

After time $t = 0.6$ the wave function enters the crossing region and then the upper level population drops down to 0.86. While running downhill the eigenvalue surface, the momentum expectation value of the upper level monotonically increases up to 1.6. On the other side of the crossing, the upper surface has a positive slope, and the momentum expectation gradually decreases down to 0.8. The surface hopping algorithm computes the lower level population with an maximal error of 0.075 occurring

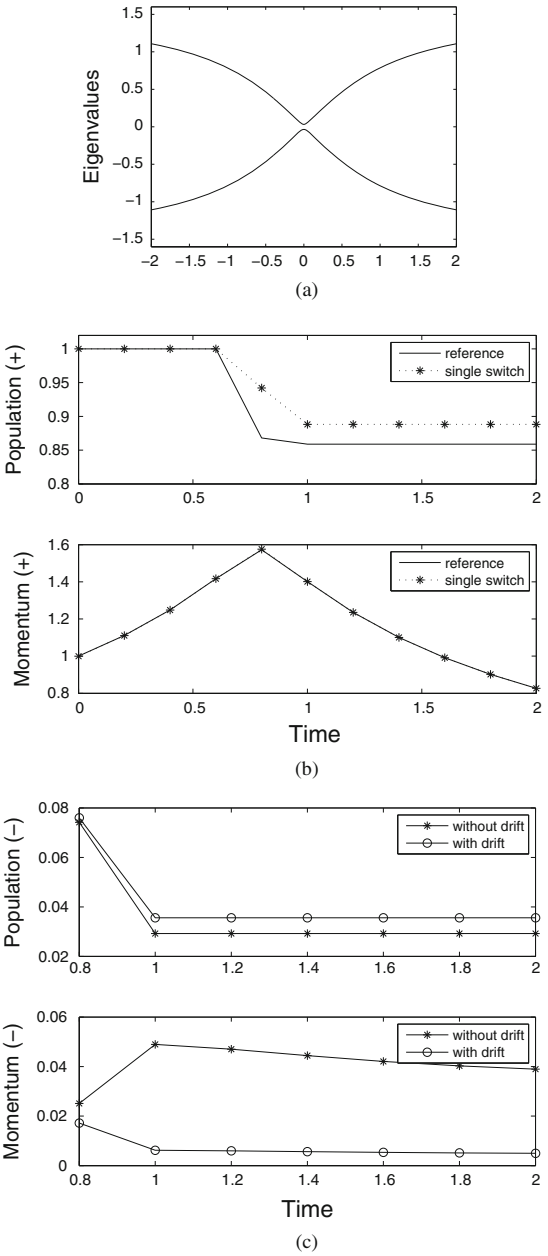

Fig. 1 When the solution passes by the avoided crossing, the level population changes. The single switch algorithm resolves the non-adiabatic dynamics with an error of few percent. **a** The eigenvalue surfaces of (3.1). **b** The dynamics of the population and the momentum expectation value for the *upper level*. **c** The accuracy of the single switch algorithm for the population and momentum expectation value of the *lower level*

when the wave function passes the crossing, see Fig. 1c. Afterwards the population error drops down to 0.03. The accuracy of the population is rather insensitive to the drift. However, the lower level momentum expectation loses accuracy by a factor of eight when supressing the drift.

4 Theoretical justifications

The single switch algorithm follows ideas introduced by the second author with S. Teufel in [17] which initiated the application of theoretical work on conical intersections by the first author and P. Gérard in [5]. The rigorous derivation of the algorithm has been performed in the context of codimension 2 crossings in [7] and of avoided crossing in [8]. Both papers use a normal form stated by Y. Colin de Verdière in [2] which reduces the initial Schrödinger equation in the transition zone to the well-known Landau-Zener model studied in the 30's (see [15] and [23]). Then the transition rate $T_\varepsilon(q^*, p^*)$ is a multidimensional version of the celebrated Landau-Zener formula, see also [4].

4.1 Heuristic justification of the transition rate

The mathematical justification of the transition rates relies on a normal form which reduces the mechanism of the transitions to the one of the Landau-Zener model. A heuristic reduction to the Landau-Zener system comes from linearization along a trajectory. Let us suppose that we have an avoided crossing with minimal gap of size δ at the point q^* such that

$$\gamma(q^*) = \delta\gamma^* + O(\delta^2), \quad \beta(q^*) = 0.$$

We suppose δ small, in particular $\delta \ll \sqrt{\varepsilon}$. For simplicity, we also assume $\alpha = 0$ and we consider a plus trajectory arriving at time $t^* = 0$ in (q^*, p^*). We perform a Taylor expansion close to $t = 0$ of the function $H(q^+(t), p^+(t))$, where

$$H(q, p) := \frac{|p|^2}{2} + V(q).$$

We obtain

$$H(q^+(t), p^+(t)) = \left(\frac{|p^*|^2}{2} + tf^*\right)\mathrm{Id} + \begin{pmatrix} t\beta^* & \delta\gamma^* \\ \delta\gamma^* & -t\beta^* \end{pmatrix} + O(\delta^2 + t^2),$$

where

$$f^* = -p^* \cdot \nabla\lambda^+(q^*), \quad \beta^* = p^* \cdot \nabla\beta(q^*).$$

By the non-degeneracy assumption (1.4), we have $p \cdot \nabla\beta(q) \neq 0$ close to (q^*, p^*), and therefore $\beta^* \neq 0$; we suppose $\beta^* > 0$ and we set

$$s = \frac{t}{\sqrt{\varepsilon}}\sqrt{\beta^*}, \qquad \eta = \frac{\delta}{\sqrt{\varepsilon}}\frac{\gamma^*}{\sqrt{\beta^*}},$$
$$\psi^\varepsilon(t, q) = \mathrm{e}^{-i(t|p^*|^2 + t^2 f^*)/(2\varepsilon)} u^\varepsilon(s, \eta).$$

Then the Schrödinger Eq. (1.2) reduces to the Landau-Zener system

$$i\partial_s u^\varepsilon - \begin{pmatrix} s & \eta \\ \eta & -s \end{pmatrix} u^\varepsilon = 0, \tag{4.1}$$

where, strictly speaking, the right-hand side is not 0 but $O(\sqrt{\varepsilon})$ locally. The evolution of u^ε is well-known:

$$u^\varepsilon(s,\eta) = \begin{pmatrix} \mathrm{e}^{is^2}|s|^{i\eta^2/2} & \alpha^\varepsilon_{1,\pm}(\eta) \\ \mathrm{e}^{-is^2/2}|s|^{-i\eta^2/2} & \alpha^\varepsilon_{2,\pm}(\eta) \end{pmatrix} + o(1) \quad \text{as} \quad s \to \pm\infty,$$

where $\alpha^\varepsilon_{1,\pm}$ characterizes the $\pm$-mode for $s > 0$ and $\alpha^\varepsilon_{2,\pm}$ the $\mp$-mode for $s < 0$. Besides,

$$\begin{pmatrix} \alpha^\varepsilon_{1,+} \\ \alpha^\varepsilon_{2,+} \end{pmatrix} = \begin{pmatrix} a(\eta) & -\overline{b(\eta)} \\ b(\eta) & a(\eta) \end{pmatrix} \begin{pmatrix} \alpha^\varepsilon_{1,-} \\ \alpha^\varepsilon_{2,-} \end{pmatrix} \quad \text{with} \quad a(\eta) = \mathrm{e}^{-\pi\eta^2/2}.$$

The transition coefficient for the Landau-Zener system is

$$T_{LZ}(\eta) = a(\eta)^2 = \mathrm{e}^{-\pi\eta^2}.$$

Via

$$\eta = \frac{\delta}{\sqrt{\varepsilon}} \frac{\gamma^*}{\sqrt{\beta^*}} = \frac{1}{2\sqrt{\varepsilon}} \frac{g(q^*)}{\sqrt{p^* \cdot \nabla_q \beta(q^*)}} + O(\delta^2)$$

we obtain

$$T_{LZ}(\eta) = \exp\left(-\frac{\pi}{4\varepsilon} \frac{g(q^*)^2}{|p^* \cdot \nabla\beta(q^*)|}\right)(1 + o(1)) = T_\varepsilon(q^*, p^*)(1 + o(1)).$$

4.2 Range of validity of the algorithm

We now focus on the specific assumptions for proving a rigorous mathematical derivation in the context of codimension 2 crossings (see [7]) or avoided crossings (see [8]). If those are not satisfied, the approximation is no longer valid, as shown by the examples in [8]. We choose $R > 0$ fixed and assume that the transition region

$$\mathcal{U}_\varepsilon = \{q \in \mathbf{R}^d,\ g(q) \le R\sqrt{\varepsilon}\}$$

is compact. Morover, we suppose:

- The test function $a \in \mathcal{C}_c^\infty\left(\mathbf{R}^{2d}\right)$ defining the expectation value of interest must have its support away from the transition region $\mathcal{U}_\varepsilon$, since the non-adiabatic transitions are only described effectively by the hopping mechanism.

- The initial data $(\psi_0^\varepsilon)_{\varepsilon>0}$ are associated with one specific mode, let's say plus, localized away from the transition region $\mathcal{U}_\varepsilon$ and away from the set, which contains the points issuing classical trajectories, which are degenerate in the sense, that

$$(p \cdot \nabla\beta(q),\, p \cdot \nabla\gamma(q)) = 0$$

  when reaching a local minimal gap in $\mathcal{U}_\varepsilon$. This assures the reduction to the Landau-Zener model (4.1).
- Within the time-interval $[0, t_f]$, each of the plus-trajectories arriving at the support of the observable at time t_f has performed at most one jump possibly generating minus-trajectories which have not jumped at all. These assumptions are needed, since possible interferences between $\Pi^+\psi^\varepsilon(t)$ and $\Pi^-\psi^\varepsilon(t)$ in the transition region are not resolved due to the neglect of the off-diagonal components of the Wigner transform in the approximation.

We emphasize, that our approximation does not apply to the degenerate situation where Hamiltonian trajectories arrive near the crossing with zero momentum, since then $(p_* \cdot \nabla\beta(q_*),\, p_* \cdot \nabla\gamma(q_*)) = 0$. So far, the are only few mathematical results on degenerate crossings, see e.g. [3] for resolvant estimates for degenerate codimension one crossings.

4.3 Adiabatic situations

We now consider two adiabatic situations with crossings: diagonal potentials and smoothly diagonalizable ones. We first suppose that $\gamma(q) = 0$ for all $q \in \mathbf{R}^d$. Then, the gap is given by $g(q) = |\beta(q)|$, the crossing set is $S = \{q \in \mathbf{R}^d;\ \beta(q) = 0\}$, and the genericity assumption (1.4) writes as $p \cdot \nabla\beta(q) \neq 0$. Moreover, the jump criterium (2.1) becomes

$$\beta(q^*)\, p^* \cdot \nabla\beta(q^*) = 0,$$

and there are only jumps at the points where $\beta(q^*) = 0$, which are in the crossing set. Therefore, the transition rate is $T_\varepsilon(q^*, p^*) = 1$: The energy propagates along the trajectories associated with the eigenvalues $\alpha(q) \pm |\beta(q)|$ with switches form the plus to minus (or conversely) at each crossing point: The resulting curves are the Hamiltonain trajectories associated with $\alpha(q) + \beta(q)$ and $\alpha(q) - \beta(q)$. Therefore, our algorithm respects the adiabatic theorem for diagonal potentials.

Let us now consider a potential V which has smooth eigenprojectors and smooth eigenvalues with a non-empty crossing set (this happens for example for codimension 1 crossings, see [13]). The matrix $V(q)$ now writes

$$V(q) = \alpha(q)\,\mathrm{Id} + \frac{1}{2} g(q)\left(\Pi^+(q) - \Pi^-(q)\right)$$

with smooth functions $g(q)$, $\Pi^+(q)$ and $\Pi^-(q)$. Therefore, one can find a smooth normed vector $\mathrm{e}(q)$ such that $\Pi^+(q) - \Pi^-(q) = \mathrm{Id} - 2\,\mathrm{e}(q) \otimes \mathrm{e}(q)$, and it is not

difficult to see that such a matrix writes

$$\Pi^+(q) - \Pi^-(q) = \begin{pmatrix} \cos\theta(q) & \sin\theta(q) \\ \sin\theta(q) & -\cos\theta(q) \end{pmatrix}$$

for a smooth function $\theta(q)$. Therefore,

$$\beta(q) = \frac{1}{2} g(q)\cos\theta(q) \quad \text{and} \quad \gamma(q) = \frac{1}{2} g(q)\sin\theta(q),$$

and the genericity condition (1.4) implies

$$p \cdot \nabla g(q) \neq 0$$

for $q \in \mathcal{U}_\varepsilon$. Hence, the jump criterimum (2.1) is satisfied only for points in the crossing set, where the transition rate is $T_\varepsilon(q^*, p^*) = 1$. Here again, the surface hopping description preserves the adiabatic theorem: The quantities $w_\pm^\varepsilon$ propagate along the smooth trajectories associated with $\alpha(q) \pm g(q)$.

5 Generalizations

It is also possible to generalize the algorithm to potentials with crossings of three eigenvalues such as Pseudo-Jahn Taller's potentials and to potentials where the eigenvalues are of multiplicity 2 (Hagedorn's potential). We now discuss these issues.

5.1 Twofold eigenvalues

In the monograph [10], Hagedorn derives potentials

$$V_{hag}(q) = \alpha(q)\mathrm{Id} + \begin{pmatrix} V_0(q) & \mathbf{0}_2 \\ \mathbf{0}_2 & V_0(q) \end{pmatrix},$$

which are 4 by 4 matrices with twofold eigenvalues $\lambda^+(q)$ and $\lambda^-(q)$: their crossing set is of codimension two, three or five. For these models, the solution to the Schrödinger equation

$$\begin{cases} i\varepsilon\partial_t\psi^\varepsilon = -\frac{\varepsilon^2}{2}\Delta_q\psi^\varepsilon + V_{hag}(q)\psi^\varepsilon, \\ \psi^\varepsilon_{t=0} = \psi^\varepsilon_0 \in L^2(\mathbf{R}^d, \mathbf{C}^4), \end{cases} \tag{5.1}$$

is a vector of $\mathbf{C}^4$. The fact that the eigenspaces are twofold implies that the diagonal parts of the Wigner transform $W^\varepsilon(\psi^\varepsilon(t))$ are no longer characterized by their traces and one has to work with the matrices $\Pi^\pm W^\varepsilon(\psi^\varepsilon(t))\Pi^\pm$ themselves. For considering matrix valued observables

$$a(q, p) = a^+(q, p)\Pi^+(q) + a^-(q, p)\Pi^-(q)$$

the single switch algorithm has to be modified as follows (see also [7]). For simplicity, we still consider initial data localized on the plus level:

(1) The initial sampling works with the four-by-four matrix $\Pi^+(W^\varepsilon(\psi_0^\varepsilon))\Pi^+$ and produces phase space points $(q_j^+, p_j^+) \in \mathbf{R}^{2d}$ with associated matrix-valued weights $W_j^+ \in \mathbf{C}^{4,4}$,

$$(q_j^+, p_j^+, W_j^+), \qquad 1 \le j \le N^+(0).$$

(2) Classical transport by $\dot{q}^+ = p^+$, $\dot{p}^+ = -\nabla_q \lambda^+(q^+)$,

$$(q_j^+(t), p_j^+(t)), \qquad 1 \le j \le N^+(0).$$

(3) Possibility of surface hopping when a trajectory attains a local minimal gap with transition probability $T_\varepsilon(q^*, p^*)$. If the trajectory remains on the same level, one conjugates the weight with a unitary matrix $\mathcal{R}(q^*, p^*)$. (A precise formula for this matrix is given in [7].) That is, a remaining trajectory carries the weight

$$\mathcal{R}(q^*, p^*)\, W_j^+\, \mathcal{R}(q^*, p^*).$$

(4) Computation of final expectation values via phase space summation.

The new phenomenon is the conjugation by the matrix $\mathcal{R}(q^*, p^*)$ which ensures that the transported matrix is correctly polarized after passing the crossing.

5.2 Pseudo Jahn-Teller Hamiltonian

Let us suppose that the potential in the Schrödinger equation is given by

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

The wave function is now a vector of $\mathbf{C}^3$ and we have three modes 0, $\sqrt{q_1^2 + q_2^2}$ and $-\sqrt{q_1^2 + q_2^2}$ which interact together. Surface hopping extends to this context, which is supported by the mathematical results of [9]. Beginning with initial data localised on the plus level, at the minimal gap (which is evaluated by the function $|q|$), one generates two trajectories: one for the minus level and one for the 0-level. The transitions probabilities of the underlying model problem have been calculated by Brundobler and Elser (see [1]). However, for the moment, the generalization to more general potentials

$$V_{PJT}(q) = \alpha(q)\mathrm{Id} + \begin{pmatrix} \beta(q) & 0 & \gamma(q) \\ 0 & -\beta(q) & \gamma(q) \\ \gamma(q) & \gamma(q) & 0 \end{pmatrix}$$

is not clear.

6 Conclusion

The single switch algorithm has a rigorous mathematical derivation which also provides asymptotic error estimates (see [7] and [8]); this analysis has been carried out in the context of codimension 2 crossings and avoided ones. However, the algorithm can be implemented *de facto* in more general situations and even gives leading order approximations in adiabatic situations.

The single switch algorithm is a surface hopping algorithm in the continuity of the first one introduced by Tully and Preston in the 70's (see [20,21]). Since surface hopping schemes are applicable in high dimensional configuration spaces, as soon as the sampling of the initial data is achieved, they are very popular for simulating non-adiabatic dynamics.

The specific feature of the single switch algorithm is its hopping criterium. Non-adiabatic transitions are only allowed at local minimal surface gaps for sufficiently small gaps. In that respect, the surface hopping algorithm of Voronin, Marques and Varandas (see [22]) is the algorithm in the chemical literature, which is closest to the single switch approach. Most of the well-established surface hopping schemes allow for non-adiabatic transitions at any time (see [16] for a comparison).

The main open problem are interlevel interferences near the crossing: How does one resolve the dynamics of two wave packets arriving in the transition region on two different levels and interacting with each other? One can construct specific initial data (see [4]) such that the algorithmic description presented here is no longer valid and produces wrong numerical results [8].

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