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Non–Adiabatic Effects in Quantum–Classical Molecular Dynamics

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Abstract

In molecular dynamics applications there is a growing interest in mixed quantum-classical models. The article is concerned with the so-called QCMD model. This model describes most atoms of the molecular system by the means of classical mechanics but an important, small portion of the system by the means of a wavefunction. We review the conditions under which the QCMD model is known to approximate the full quantum dynamical evolution of the system.

In most quantum-classical simulations the *Born-Oppenheimer model* (BO) is used. In this model, the wavefunction is adiabatically coupled to the classical motion which leads to serious approximation deficiencies with respect to non-adiabatic effects in the fully quantum dynamical description of the system. In contrast to the BO model, the QCMD model does include non-adiabatic processes, e.g., transitions between the energy levels of the quantum system. It is demonstrated that, in mildly non-adiabatic scenarios, so-called *surface hopping* extensions of QCMD simulations yield good approximations of the non-adiabatic effects in full quantum dynamics. The algorithmic strategy of such extensions of QCMD is explained and the crucial steps of its realization are discussed with special emphasis on the numerical problems caused by highly oscillatory phase effects.

Keywords: quantum-classical molecular dynamics, non-adiabatic processes, Schrödinger equation, highly oscillatory phase, adiabatic limit, quantum adiabatic theorem, Born-Oppenheimer model, energy level crossings, transition zone, QCMD-based surface hopping, QCMD trajectory bundle, long-stepsize integration schemes, averaging.

MSC classification: 81Q20, 81Q15, 81S25, 81V55, 92E10

1 Introduction

In molecular dynamics applications there is a growing interest in including specific quantum dynamical effects into the otherwise classical description of some large molecular system. Typical examples are proton transfer processes in the active site of an enzyme, electron diffusion in molten salts, or scattering effects on the electronic structure of the target molecule. Unfortunately, full quantum dynamical calculations for the entire molecule are beyond the scope of simulations, today and in the next decades. In the mixed quantum-classical approach to this problem, most atoms of the molecular system are described by the means of classical mechanics but important (and mostly small) portions of the system by the means of a wavefunction.

A typical example of these models, the so-called QCMD model, consists of a *singularly perturbed* Schrödinger equation nonlinearly coupled to classical Newtonian equations, see §2. We will carefully review the assumptions under which this model is known to approximate the full quantum dynamical (QD) evolution of the system. One important insight is that both, the QCMD model and the full QD evolution, in fact have the same *adiabatic limit system*, the well-known time-dependent Born-Oppenheimer (BO) model, see §2.1.

It is well-known that BO simulations are sufficient approximations of the full QD evolution in many important situations but lead to entirely wrong descriptions in as many other "non-adiabatic" cases. In contrast to the BO model, the QCMD model includes non-adiabatic processes, e.g., transitions between the energy levels of the quantum system or resonance effects near level crossings, §2.2. The literature on this topic contains a significant number of specific examples in which QCMD simulations yield better approximations of QD than the simple BO approximation. But the literature also contains important examples in which QCMD fails entirely because it is a single-trajectory model while the full QD solution develops *multi-configuration* character [11]. In the present article, these observations will be illustrated by means of a certain simple example, see §2.3.

Subsequently, a specific *surface hopping* extension of QCMD will be introduced and compared with similar approaches, §3. The insights gained in the example will then allow to understand the algorithmic strategy of such QCMD-based surface hopping algorithms: to exploit the advantages of the non-adiabatic effects in QCMD while preventing the algorithm from behaving like QCMD in situations where multiply-branched classical paths are required for an accurate description.

For an efficient realization of QCMD simulations numerical integrators are required which allow to use time steps much larger than the fastest quantum time scales. Such long-step integrators have to reproduce correctly the highly oscillatory phase effects in the quantum part of the system. The basic problems related to this requirement are discussed with special emphasis on the particular aspects in the context of QCMD-based surface hopping simulations, see §4.

2 QCMD Model

To keep the notation simple we restrict our study to the case of a system with just two degrees of freedom $x \in \mathbb{R}^{d_1}$ and $q \in \mathbb{R}^{d_2}$ with significantly different associated masses, m and M. We suppose that the mass ratio $\epsilon^2 = m/M$ is a small parameter. After an appropriate rescaling [21], the time-dependent Schrödinger equation of this systems becomes

$$i\epsilon\,\partial_t\Psi \;=\; \left(-\tfrac{\epsilon^2}{2}\Delta_q \;-\; \tfrac{1}{2}\Delta_x \;+\; V(x,q)\right)\,\Psi. \tag{1}$$

The corresponding solution $\Psi = \Psi(x,q,t)$ describes what we call the full QD evolution of the system. Typically, a proper choice of the coordinate system allows the initial quantum state to be approximated by a product state (cf. [7], §IIb):

$$\Psi(x,q,t=0) \;=\; \phi_*(q)\;\cdot\;\psi_*(x). \tag{2}$$

We will throughout assume this initial condition to be given.

The equations of motion of the *QCMD model* are given by

$$i\epsilon\partial_t\psi_{\mathrm{QC}} = H(q)\,\psi_{\mathrm{QC}} \quad\text{ and }\quad \ddot{q}_{\mathrm{QC}} = -\mathrm{grad}_q\langle\psi, V\psi\rangle(q_{\mathrm{QC}}), \tag{3}$$

where $H = H(q)$ is the q-parametrized Hamiltonian

$$H(q) \;=\; -\tfrac{1}{2}\Delta_x \;+\; V(x,q).$$

The QCMD solution can be understood as an approximation of the full QD evolution if the initial wavefunction ϕ_* is an approximate δ-function, e.g.,

$$\phi_*(q) \;=\; \tfrac{1}{A_\epsilon}\,\exp\left(-\tfrac{1}{4\epsilon}(q-q_*)^2\right)\exp\left(\tfrac{i}{\epsilon}\dot{q}_* q\right). \tag{4}$$

If this is the case and some other conditions are satisfied,[1] the QD solution $\Psi = \Psi(x,q,t)$ is approximately given by $\Psi(x,q,t) \approx \phi(q,t)\psi(x,t)$ with ϕ remaining an approximate δ-function moving along the classical part $q_{\mathrm{QC}} = q_{\mathrm{QC}}(t)$ of the QCMD solution and $\psi \approx \psi_{\mathrm{QC}}$ (for details compare [3]).

This approach, however, does not reveal the close connection between the QCMD and BO models. For establishing this connection, we will now summarize the approach of [4] showing that —under some non-resonance conditions— the BO model is the adiabatic limit of both, QD and QCMD.

[1]The main condition is the absence of caustics along the QCMD-solution, cf. [3].

2.1 Adiabatic Theory and BO Model

Subsequently, we will study the *limit equations* governing the QCMD solutions for the *adiabatic* limit $\epsilon \to 0$, in which the motions in the degree of freedom x are infinitely faster than the slow processes in the classical coordinate q. Therefore, we rewrite the QCMD system, Eqs. (3), by explicitly denoting the dependence of its solution $(q_\epsilon, \dot{q}_\epsilon, \psi_\epsilon)$ on the parameter ϵ:

$$\begin{aligned} i\epsilon\partial_t\psi_\epsilon &= H(q_\epsilon)\,\psi_\epsilon, & \psi_\epsilon|_{t=0} &= \psi_*, \\ \ddot{q}_\epsilon &= -\mathrm{grad}_q\langle\psi_\epsilon, H(q_\epsilon)\psi_\epsilon\rangle, & q_\epsilon(0) &= q_*,\ \dot{q}_\epsilon(0) = \dot{q}_*. \end{aligned} \tag{5}$$

We restrict ourselves to finite-dimensional Hilbert spaces,[2] making H a Hermitian matrix. We denote the eigenvalues of $H(q)$ by $E_k(q)$ and consider the spectral decomposition

$$H(q) \;=\; \textstyle\sum_k E_k(q)\,P_k(q), \tag{6}$$

where P_k is the orthogonal projection onto the eigenspace associated with E_k. With respect to a quantum state ψ, the number $\theta_k = \langle\psi, P_k\psi\rangle$ is the *population* of the *energy level* E_k.

2.1.1 Adiabatic Limit of QCMD

The limit equation governing $\lim_{\epsilon\to 0} q_\epsilon$ can be motivated by referring to the *quantum adiabatic theorem* which originates from work of Born and Fock [1, 14]: The classical position q influences the Hamiltonian very slowly compared to the time scale of oscillations of ψ_ϵ, in fact, "infinitely slowly" in the limit $\epsilon \to 0$. Thus, in analogy to the quantum adiabatic theorem, one would expect that the populations of the energy levels remain *invariant* during the evolution:

$$\lim_{\epsilon\to 0}\theta_k^\epsilon(t) = \lim_{\epsilon\to 0}\langle\psi_\epsilon, P_k(q_\epsilon)\psi_\epsilon\rangle \;=\; \theta_k^0 = \langle\psi_*, P_k(q_*)\psi_*\rangle.$$

The *constant* θ_k^0 is the initial population of level E_k and thus computable from the initial data, Eq. (5). All this turns out to be true: According to [4], the limit solution $q_{\mathrm{BO}} = \lim_{\epsilon\to 0} q_\epsilon$ is given by:

$$\ddot{q}_{\mathrm{BO}} \;=\; -\mathrm{grad}_q \textstyle\sum_k \theta_k^0\, E_k(q_{\mathrm{BO}}), \qquad q_{\mathrm{BO}}(0) = q_*,\ \dot{q}_{\mathrm{BO}}(0) = \dot{q}_*. \tag{7}$$

whenever the following assumption on the eigenspaces and eigenenergies of $H(q)$ is satisfied:

[2] The reader may think of a finite dimensional subspace of the original state space. This subspace may, e.g., be associated with a suitable discretization in space. For a generalization of the results presented in this subsection to the infinitely dimensional case, see [2].

(A) The spectral decomposition Eq. (6) of H depends smoothly on q and the transversality condition $\frac{d}{dt}(E_k(q_{\rm BO}) - E_l(q_{\rm BO})) \neq 0$ holds.

We refer to equation (7) as to the *time-dependent Born-Oppenheimer* (BO) model of adiabatic motion. Notice that Assumption (A) does *not* exclude *energy level crossings* (i.e., positions q_c at which $E_k(q_c) = E_l(q_c)$ for some $k \neq l$).

For simplicity we will assume in the following that, for every position q, all the eigenspaces of $H(q)$ are one-dimensional, i.e., for every energy level $E_k(q)$ there exists a normalized eigenvector $\Phi_k(q)$ such that

$$H(q)\Phi_k(q) \;=\; E_k(q)\Phi_k(q), \qquad \text{and} \qquad P_k(q) \;=\; \Phi_k(q) \otimes \Phi_k(q).$$

Then, the population of the energy level $E_k(q)$ with respect to the quantum state ψ is given by $\theta_k(q) = |\langle \Phi_k(q), \psi\rangle|^2$.

2.1.2 Adiabatic Limit of QD

The time-dependent BO model describes the adiabatic limit of QCMD. If QCMD is a valid approximation of full QD for sufficiently small ϵ, the BO model has to be the adiabatic limit of QD itself. Exactly this question has been addressed in different mathematical approaches, [5], [8], and [13]. We will follow Hagedorn [8] whose results are based on the product state assumption Eq. (2) for the initial state with ϕ_* assumed to be given by (4) and on the "no-crossings" assumption

(B) Along the BO solution $q_{\rm BO}$, crossings between initially occupied energy levels are excluded, i.e., for all pairs (E_k, E_l) of energy levels with $k \neq l$ and $\theta_k^0 + \theta_l^0 > 0$, we have $E_k(q_{\rm BO}(t)) \neq E_l(q_{\rm BO}(t))$ for all $t \in [0, T]$.

Using these conditions and the BO solution $q_{\rm BO}$, a wavefunction $\Psi_{\rm BO}$ is constructed which comes out to be the limit of the sequence of QD solution Ψ_ϵ for $\epsilon \to 0$, [8]. In particular, for the position expectation

$$\langle q \rangle_\epsilon^{\rm QD} \;=\; \langle \Psi_\epsilon, q\Psi_\epsilon\rangle(t),$$

the statement of Hagedorn is:

Theorem 1 (Thm. 2.1 in [8]) *Assume $q_{\rm BO} = q_{\rm BO}(t)$ to be the solution of the BO equation, Eq. (7), in a finite time interval $[0, T]$ and let assumption (B) be satisfied. Then, we have*

$$\lim_{\epsilon \to 0} \langle q \rangle_\epsilon^{\rm QD} \;=\; q_{\rm BO} \qquad \textit{in } [0, T].$$

That is, in the limit, the center of the QD wavepacket Ψ_ϵ moves along the BO-solution. Summarizing, QD and QCMD have the same adiabatic limit solution which is given by the BO model if the initial conditions are appropriate and if we exclude energy level crossings and discontinuities of the spectral decomposition. Consequently, QCMD is justified as an approximation of QD if only ϵ is small enough and these conditions are satisfied.

These are important results. However, the following question remains: Can QCMD describe anything beyond the correct adiabatic limit of QD? Can it describe *non-adiabatic effects*, i.e., deviations of the QD solution from its adiabatic limit for realistically small $\epsilon > 0$?

2.2 Non-Adiabaticity in QCMD

One can easily inspect the deviation of QCMD from its adiabatic limit if we reformulate its equation of motion in the coordinate system given by the eigenstate of the one-particle Hamiltonian H. In terms of the notation introduced above, we therefore make the following ansatz for the QCMD-wavepacket ψ_ϵ:

$$\psi_\epsilon(t) \;=\; \sum_k c_k^\epsilon(t)\,\Phi_k(q_\epsilon(t)).$$

Inserting this into the QCMD equations we find

$$\begin{aligned} i\epsilon\partial_t c_k^\epsilon &= E_k(q_\epsilon)c_k^\epsilon \;-\; i\epsilon\dot{q}_\epsilon \sum_l d_{kl}(q_\epsilon)\,c_l^\epsilon, \\ \ddot{q}_\epsilon &= -\nabla_q \sum_k |c_k^\epsilon|^2\,E_k(q_\epsilon) \;-\; \sum_{kl} (c_k^\epsilon)^* c_l^\epsilon\,\Delta E_{kl}(q_\epsilon)\,d_{kl}(q_\epsilon), \end{aligned} \tag{8}$$

where the coupling matrix elements d_{kl} and energy gaps ΔE_{kl} are given by

$$d_{kl}(q) \;=\; (d_{kl}^j), \quad d_{kl}^j \;=\; \langle \Phi_k(q), \partial_{q_j}\Phi_l(q)\rangle \quad \text{and} \quad \Delta E_{kl}(q) = E_k(q) - E_l(q).$$

Thus, the non-adiabatic coupling between the energy levels in QCMD is governed by the coupling matrix (d_{kl}). Whenever assumption (B) from above is valid one can show [2] that the deviation from the adiabatic solution induced by this non-adiabatic coupling is of order $\mathcal{O}(\epsilon)$!

2.2.1 First Order Corrections

Additionally, we are able to construct explicit expressions for the first order deviation terms: To this end, the coefficients c_k^ϵ must be represented in polar coordinates, i.e.,

$$c_k^\epsilon(t) \;=\; \sqrt{\theta_k^\epsilon(t)}\,\exp\left(-\frac{i}{\epsilon}\varphi_k^\epsilon(t)\right),$$

and one introduces the BO angle φ_k^{BO} as the solution of $\dot{\varphi}_k^{\mathrm{BO}} = E_k(q_{\mathrm{BO}})$ along the BO solution q_{BO} with $\varphi_k^{\mathrm{BO}}(0) = \varphi_k^\epsilon(0)$. In addition, we have to exclude all symmetric resonances of order four, i.e., to assume that in some neighborhood of $q_{\mathrm{BO}} = q_{\mathrm{BO}}(t)$:

$$E_k(q) + E_l(q) \neq E_j(q) + E_m(q) \quad \text{for} \quad k \neq j,\, k \neq m,\, l \neq j,\, l \neq m. \tag{9}$$

This condition allows to compute the non-adiabatic corrections to the adiabatic limit up to the leading orders in ϵ [2, 18]:

$$\begin{aligned} q_\epsilon &= q_{\mathrm{BO}} + \epsilon^2 \delta q^{2,\epsilon} + \mathcal{O}(\epsilon^3), & \dot q_\epsilon &= \dot q_{\mathrm{BO}} + \epsilon\, \delta \dot q_{1,\epsilon} + \mathcal{O}(\epsilon^2), \\ \theta_k^\epsilon &= \theta_k^0 + \epsilon\, \delta\theta_k^{1,\epsilon} + \epsilon^2 \delta\theta_k^{2,\epsilon} + \mathcal{O}(\epsilon^3), & \varphi_k^\epsilon &= \varphi_k^{\mathrm{BO}} + \mathcal{O}(\epsilon^2). \end{aligned}$$

Under the assumption of (9), we have the following two theorems:

Theorem 2 (Appendix C of [2]) *The first order corrections are given by*

$$\begin{aligned} \delta\theta_{1,\epsilon}^k &= 2\left(\Theta_{1,0}^k - \sum_{l\neq k,j} \frac{\dot q_{\mathrm{BO}}^j \sqrt{\theta_l^0\theta_k^0}}{\Delta E_{kl}(q_{\mathrm{BO}})} \sin\left(\epsilon^{-1}(\varphi_k^{\mathrm{BO}} - \varphi_l^{\mathrm{BO}})\right) d_{kl}^j(q_{\mathrm{BO}})\right) \\ \Theta_{1,0}^k &= \sum_{l\neq k,j} \frac{\dot q_\epsilon^j(0) \sqrt{\theta_l^0\theta_k^0}}{\Delta E_{kl}(q_\epsilon(0))} \sin\left(\epsilon^{-1}(\varphi_k^\epsilon(0) - \varphi_l^\epsilon(0))\right) d_{kl}^j(q_\epsilon(0)) \\ \delta\dot q_{1,\epsilon}^k &= \sum_{l,j} \sqrt{\theta_l^0\theta_k^0} \sin\left(\epsilon^{-1}(\varphi_k^{\mathrm{BO}} - \varphi_l^{\mathrm{BO}})\right) d_{kl}^j(q_{\mathrm{BO}}). \end{aligned}$$

This result implies $c_k^\epsilon(t) = \sqrt{\theta_k^0}\, \exp(-\frac{i}{\epsilon}\varphi_k^{\mathrm{BO}}(t)) + \mathcal{O}(\epsilon)$. Moreover, in the particular case, that initially the wavepacket occupies only one of the eigenstates, say Φ_μ, this theorem states that the first order corrections vanish identically. Then, the following is valid for the second order corrections:

Theorem 3 ([18]) *Whenever $\theta_l^0 = \delta_{\mu,l}$, the second order corrections for the populations in state l, $l \neq \mu$, are given by*

$$\begin{aligned} \delta\theta_{2,\epsilon}^l(t) = &\left(\frac{B_{\mathrm{BO}}^{l\mu}(t)}{\Delta E_{l\mu}^{\mathrm{BO}}(t)}\right)^2 + \left(\frac{B_{\mathrm{BO}}^{l\mu}(0)}{\Delta E_{l\mu}^{\mathrm{BO}}(0)}\right)^2 \\ &- 2\,\frac{B_{\mathrm{BO}}^{l\mu}(t)}{\Delta E_{l\mu}^{\mathrm{BO}}(t)}\frac{B_{\mathrm{BO}}^{l\mu}(0)}{\Delta E_{l\mu}^{\mathrm{BO}}(0)} \cos\left(\epsilon^{-1}\int_0^t \Delta E_{l\mu}^{\mathrm{BO}}(s)ds\right) + \mathcal{O}(\epsilon) \end{aligned} \tag{10}$$

with $B_{\mathrm{BO}}^{l\mu} := -\langle \Phi_l(q_{\mathrm{BO}}), \nabla_q \Phi_\mu(q_{\mathrm{BO}})\rangle \cdot \dot q_{\mathrm{BO}}$ and $\Delta E_{kl}^{\mathrm{BO}} = \Delta E_{kl}(q_{\mathrm{BO}})$.

2.3 An Avoided Crossing Example

In the subsequent, let us consider the particularly simple test case where the quantum subsystem can be described as a two state system and the classical subsystem is one-dimensional. Thus, $q \in \mathbb{R}^1$ and the full Schödinger equation has the form:

$$i\epsilon\,\dot{\Psi} \;=\; \left(-\tfrac{\epsilon^2}{2}\mathcal{T}_q \,+\, H(q)\right)\,\Psi, \tag{11}$$

with $H = H(q)$ and $\mathcal{T}_q$ denoting 2×2 hermitian matrices:

$$\mathcal{T}_q \;=\; \begin{pmatrix} \Delta_q & 0 \\ 0 & \Delta_q \end{pmatrix} \qquad \text{and} \qquad H(q) = \begin{pmatrix} V_1(q) & c \\ c & V_2(q) \end{pmatrix}.$$

The wavefunction $\Psi \in L^2(\mathbb{R}) \times L^2(\mathbb{R})$ consists of two components $\Psi = (\Psi_1, \Psi_2)^T$, each of which a function in q and t.

Herein, we choose the potentials to be $V_1(q) = q^2$ and $V_2(q) = 1/q$. The interpretation is the following: V_1 describes a harmonic bond, V_2 a repulsive potential, and c a weak coupling between these two (electronic) configurations. We choose $\epsilon = 0.01$ which is a suitable scaling for electrons. In the following we set $c = 0.1$. For the choices made, Fig. 1 shows the energy eigenvalues $E_1 = E_1(q)$ and $E_2 = E_2(q) < E_1(q)$ of $H(q)$ and the corresponding off-diagonal entry of the non-adiabatic coupling matrix d_{12}. Notice that there is some "transition zone" around $q = 1$ where the gap

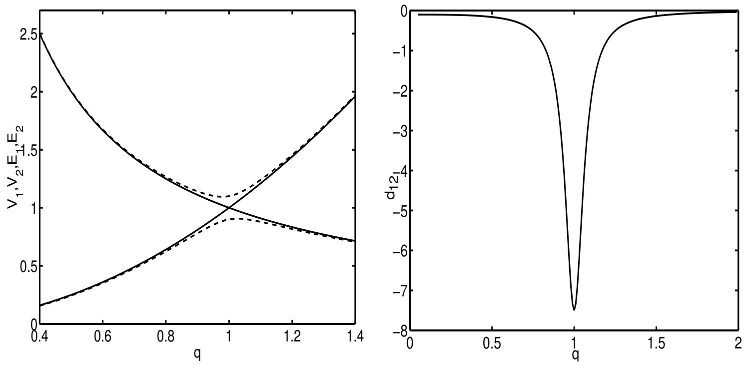

Figure 1: **(a)** Potentials V_1 and V_2 (*solid lines*) and energy levels E_1 and E_2 (*dashed lines*) versus q. **(b)** Non-Adiabatic coupling matrix element d_{12} versus q

between the two energy levels is minimal and the coupling matrix entry significantly large.

We are interested in the following initial condition: Let $\Phi_1 = \Phi_1(q)$ be the eigenvector to E_1, $q_0 = 0.4$ and $p_0 = 1$. Then the initial wavefunction is centered at q_0 with momentum expectation p_0 and the energy level E_1 is occupied only, i.e.,

$$\Psi(q,t=0) \;=\; \tfrac{1}{A}\exp\left(-\tfrac{1}{4\epsilon}(q-q_0)^2 \;-\; \tfrac{i}{\epsilon}p_0 q\right) \;\cdot\; \Phi_1(q_0).$$

Figure 2 illustrates the true quantum dynamical solution of (11) for the initial condition given. We observe that the centers of the two components Ψ_1 and Ψ_2 of the wavefunction diverge when crossing the transition zone. The motion of each of these two centers is governed by the Born-Oppenheimer solutions on the corresponding[3] energy levels E_1 and E_2 (cf. Fig. 3 (**b**)). We can conclude that the non-adiabatic effect of the transition zone induces some significant population of the initially unoccupied energy level whereas the motion outside of the transition zone is governed by classical dynamics on the energy levels and induces the observed divergence. Obviously, a *single* QCMD trajectory – even when representing the correct population dynamics – cannot reproduce this divergence. Thus, we follow the idea of splitting QCMD trajectories leading to a specific variant of so-called surface hopping.

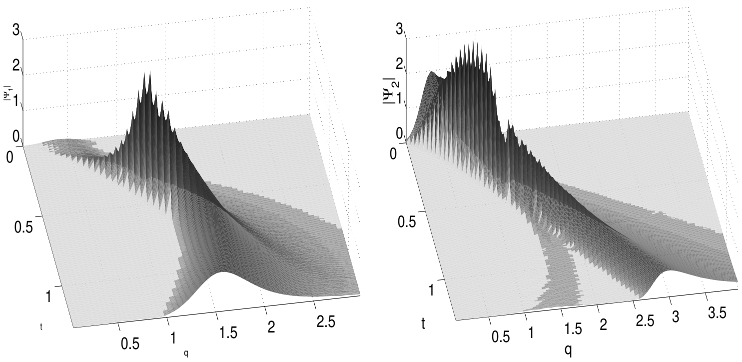

Figure 2: Avoided Crossing Example: Evolution of the full QD wavepacket in q and t for parameter $\epsilon = 0.01$. Absolute value of (**a**) Ψ_1 and (**b**) Ψ_2

3 QCMD-based Surface Hopping

Due to the previous section, a single QCMD trajectory may reproduce the QD evolution if ϵ is small enough, resonances (level crossings) are avoided, and the initial QD wavepacket $\Psi(\cdot,\cdot,t=0)$ is an approximate δ-function in the q-direction (cf. eqs. (2) and (4)). Since the full Schrödinger equation is linear, we may drop this last condition by decomposing the actual $\Psi(\cdot,\cdot,t=0)$ into finitely many approximate δ-functions at appropriately distributed locations q_0^j and momenta $\dot{q}_0^j$. Thus, we have to simulate the

[3]Away from the transition zone, the eigenvectors of H are approximately given by the two unit vectors.

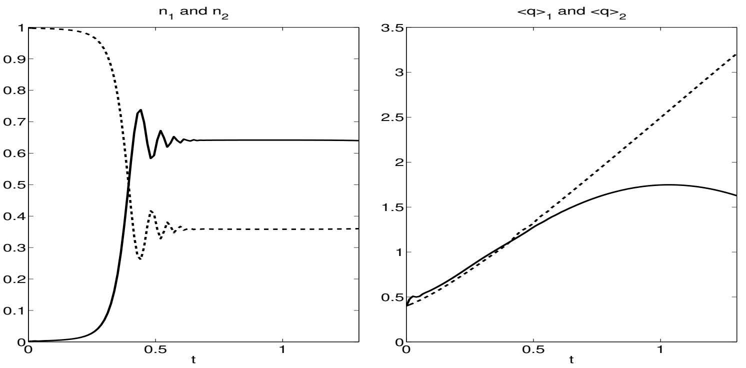

Figure 3: Full QD for $\epsilon = 0.01$: (**a**) Statistical weights $n_1 = \|\Psi_1\|_2^2$ and $n_2 = \|\Psi_2\|_2^2$ of the two components versus t. (**b**) Position expectation values $\langle q\rangle_k = \langle \Psi_k, q\Psi_k\rangle / n_k$ of the components

QCMD trajectory bundle starting at all the different $(q_0^j, \dot{q}_0^j)$ each with an initial x-wavefunction $\psi_0^j = \Psi(q_0^j, \cdot, t = 0)$. In a simulation of this kind, every QCMD-trajectory exhibits its own non-adiabaticity as discussed in §2.2, but any non-adiabatic effect mediated by coupling between different trajectories is excluded.

In [24], the "father" of the so-called *surface hopping* techniques [25, 22], C.J. Tully, shows that we can understand the non-adiabatic effects in full QD as a composition of two different contributions: the non-adiabatic effects along each QCMD trajectory given by the solution of (8) and the contribution of the coupling between the trajectories in the QCMD particle bundle constructed to represent the QD wavefunction.

In this section, a surface hopping algorithm is introduced which makes use of the QCMD solution in order to include non-adiabatic effects.

3.1 Surface Hopping Algorithm

Suppose that we start a trajectory at position q_0 with initial momentum $\dot{q}_0$ on the kth energy surface E_k, i.e., with initial QCMD-wavefunction $\psi_0 = \Phi_k(q_0)$. In the following we denote the QCMD trajectory, i.e., the solution of (5), by $(q(t), \dot{q}(t), \psi(t)) = \mathrm{QCMD}(t|\, q(0), \dot{q}(0), \psi(0))$, omitting the ϵ-dependence since ϵ now is assumed to have a fixed value. The key assumption of surface hopping techniques is as follows: We can use the non-adiabatic effects along the QCMD trajectory as an indicator for the deviation of the full QD evolution from its adiabatic limit. In other words: Whenever the non-adiabatic effects along the QCMD trajectory induce populations on some level $l \neq k$ which are significantly larger than zero, i.e., whenever $\theta_l \geq tol > 0$, one should additionally follow the path which corresponds to the dynamics on level E_l. But instead of starting a new trajectory on this level in every such case which would finally yield a combinatorial explosion, one stochastically decides whether or not to switch the energy level ("make a hop or not"). This algorithm should be constructed so that, at any instance in time for a large ensemble of particles, the fraction of trajectories assigned to any energy surface is approximately equal to the relative population of this energy level.

This idea leads to the following *QCMD-based surface hopping variant* of TULLY's surface hopping algorithm:

1. Start with a large ensemble of N independent QCMD-trajectories with states $(q_0^j, \dot{q}_0^j, \psi_0^j)$, $j = 1, \dots, N$, where every ψ_0^j belongs to a certain energy level k_j, that is, satisfies $\psi_0^j = \Phi_{k_j}(q_0^j)$. This trajectory bundle has to represent the initial QD wavepacket $\Psi(\cdot, \cdot, t = 0)$ in the ensemble sense.

2. For every single trajectory $j = 1, \dots, N$ repeat the following propagation:

   (a) Propagate the trajectory along the QCMD solution
   $$(q_{m+1}^j, \dot{q}_{m+1}^j, \psi_{m+1}^j) \;=\; \mathrm{QCMD}(\Delta t \,|\, q_m^j, \dot{q}_m^j, \psi_m^j)$$
   for some large time span Δt.

   (b) Compute the transition zone indicator Ξ for the trajectory on level k_j:
   $$\Xi \;=\; \sum_{l \neq k_j} \left| \frac{\langle \Phi_l(q_{m+1}^j), \nabla_q \Phi_{k_j}(q_{m+1}^j) \rangle \; \dot{q}_{m+1}^j}{\Delta E_{lk_j}(q_{m+1}^j)} \right|$$

   (c) If the indicator Ξ exceeds a preset threshold value Ξ_0, decide whether to make a hop or not (Step 2d). Otherwise continue with the propagation (Step 2a).

   (d) Compute the level populations $\theta_l = |c_l^j|^2$ with $c_l^j = \langle \Phi_l(q_{m+1}^j), \psi_{m+1}^j \rangle$. In the last step the trajectory j started on the energy level E_{k_j}; the energy level for the next step is selected via the hopping probabilities $P(k_j \to l) = |c_l^j|^2$, $k = 1, \dots, n$. If due to this random decision a hop onto the lth level is carried out, then set the wavefunction on energy level E_l and accordingly modify the momentum:
   $$\psi_{m+1}^j = \Phi_l(q_{m+1}^j), \quad \dot{q}_{m+1}^j = \mu(k_j \to l, q_{m+1}^j, \dot{q}_{m+1}^j), \text{ and } k_j = l$$
   Otherwise – if the random decision is to stay on level k_j – do nothing.

   (e) Continue the propagation with Step 2a.

The reader might have noticed that the transition zone indicator Ξ is deduced from the second order correction (10) of the populations. In contrast to indicators used in other approaches, it is not highly oscillatory.

The momentum adjustment is standardly realized in form of a correction in the direction of the non-adiabatic coupling vector [12]:

$$p_{\text{new}} = \mu(k_j \to l, q, p_{\text{old}}) \;=\; p_{\text{old}} + \tfrac{\alpha}{\|d_{k_j l}(q)\|_2}\, d_{k_j l}(q),$$

where the scalar coefficient α is chosen such that energy conservation is achieved, i.e., such that

$$\tfrac{1}{2}\left(|p_{\text{new}}|^2 \;-\; |p_{\text{old}}|^2\right) \;=\; \sum_\eta |c_\eta^j|^2 E_\eta(q) \;-\; E_l(q).$$

The above version of the scheme can be improved by removing the populations on the energy levels E_l, $l \neq k_j$, of trajectories initially on the k_jth level when leaving the transition zone, i.e., the region where the indicator Ξ exceeds the threshold Ξ_0. This ensures a Born-Oppenheimer-like motion outside of the transition zone.

Surface hopping algorithms vary mainly in the realization of the hopping procedure. In several aspects, the above proposed QCMD-based variant differs from typical realizations; the interested reader may compare the above algorithmic scheme with the detailed description of typical algorithmic steps in [12] or with the derivation of the standard realization [23].

3.2 Numerical Example

In this section, the performance of the proposed surface hopping algorithm is presented in application to the avoided crossing example from §2.3. For comparison, we solved the full Schrödinger equation (1) of the problem. Using $N = 2000$ trajectories with randomly distributed initial values sampling the initial wavefunction, we found an astonishingly good agreement between the purely quantum solution and the result of our surface hopping algorithm. The populations of the wavefunction components seem to be in accordance to the "exact" solution (cf., Figs. 4 and 5). But notice, just the absolute value of the components can be obtained by the surface hopping algorithm. The corresponding phase of $\Psi_1(q,t)$ and $\Psi_2(q,t)$ cannot be reconstructed.

Unfortunately, the results of our algorithm strongly depend on the parameters. Obviously, the number of sampling trajectories has a major influence on the accuracy of the computation. The algorithm reacts comparably sensitively on modifications of the transition zone threshold Ξ_0 and the size of the time interval Δt. The present authors think that only some careful mathematical analysis of the approximation properties may be able to cope with these difficulties – which are a common problem of surface hopping methods.

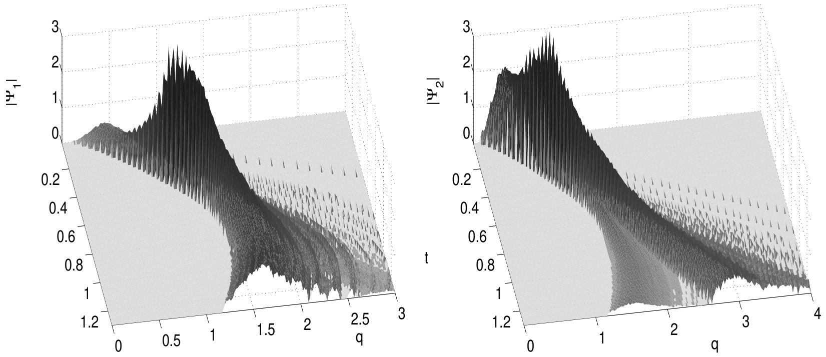

Figure 4: QCMD-based surface hopping algorithm: Reconstructed wavepacket evolution in q and t . Absolute value of **(a)** Ψ_1 and **(b)** Ψ_2 for $\epsilon = 0.01$

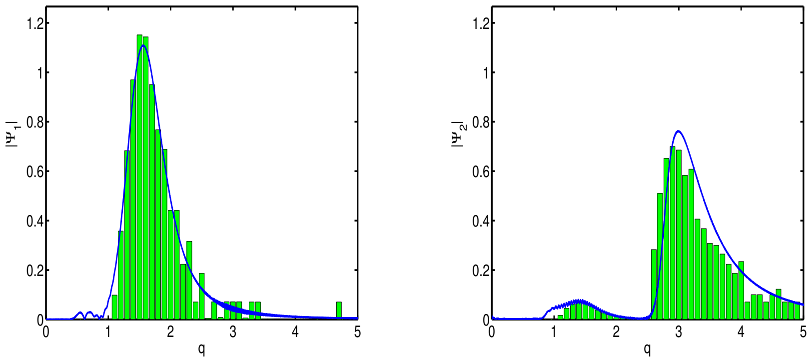

Figure 5: Comparison of quantum dynamically calculated solution (*lines*) and solution of QCMD-based surface hopping algorithm (*bars*) at time $t = 1.3$. Absolute value of **(a)** $\Psi_1(q, t = 1.3)$ and **(b)** $\Psi_2(q, t = 1.3)$ vs. q for $\epsilon = 0.01$

4 Numerical Integrators for QCMD

The numerical integration of the QCMD equations of motion includes the following crucial problem: the time scales of the quantum phase oscillations are of order $\mathcal{O}(\epsilon)$ and are nonlinearly coupled to the slow classical motion. Thus, any numerical reproduction of these highly oscillatory behavior is a challenging problem whenever ϵ is small. In fact, most of the presently used QCMD integrators require discretization steps of order $\mathcal{O}(\epsilon)$ in time. Several quite different types of such integrators have been developed (cf. [20, 16]); the results presented in Sec. 3 have been produced by means of the symplectic PICKABACK scheme [15].

However, for every QCMD simulation over an $\mathcal{O}(1)$ time span, such integrators require $\mathcal{O}(1/\epsilon)$ many time steps, which adds up to an undesirable numerical effort whenever light quantum particles as, e.g., electrons are concerned. Consequently, it is of outstanding interest to construct QCMD in-

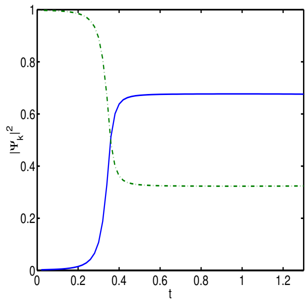

Figure 6: QCMD-based surface hopping algorithm for $\epsilon = 0.01$: Statistical weights $\|\Psi_1\|_2^2$ (*solid line*) and $\|\Psi_2\|_2^2$ (*dashed dotted*) of the two components of the reconstructed wavefunction versus t

tegrators that circumvent the pointwise resolution of the highly oscillatory quantum phases, but allow for $\mathcal{O}(1)$ time steps (adapted to the classical motion) while still propagating the quantum motion correctly. In order to summarize the present state of the discussion concerning such *long-stepsize integration schemes*, we have to distinguish between two different cases: (a) *essentially non-adiabatic* quantum processes for which the value of ϵ is significantly different from 0, and (b) *almost adiabatic* quantum processes where ϵ is close to 0 and the asymptotic scaling $\epsilon \to 0$ is of real interest. For the essentially non-adiabatic case, it is in fact possible to construct long-stepsize integration schemes by means of applying appropriate *exponential integrators* to the almost harmonic quantum phase oscillation, compare [17, 9, 10]. For almost adiabatic situations, however, it seems to be impossible to realize any *exact* reproduction of the quantal phases (in any pointwise sense). Thus, we have to ask whether it might at least be possible to reproduce correctly the "essential" dynamics of the QCMD system, i.e., the classical location and momentum as well as the quantum state population dynamics, while taking (arbitrary) errors in the quantal phases into account. For surface-hopping-like algorithmic schemes such "essential" QCMD simulations would be sufficient. But notice that any error in the phase might have a devastating effect on the other degrees of freedom because of the nonlinear coupling. However, a precise asymptotic analysis [19] reveals that under certain conditions so-called *averaging* integration schemes allow to correctly approximate the dynamics up to a given order in ϵ thus preventing an ϵ^{-1} error growth. Due to the highly oscillatory character of the analytic solution "correct" is now meant with respect to an averaging norm but not to a "pointwise" evaluation in time. Consequently, a mathematical justification of the QCMD-based surface hopping as an approximation of the full quantum evolution should reveal whether some pointwise reproduction of the quantal phase is necessary or not.

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