Approximation Properties and Limits of the Quantum-Classical Molecular Dynamics Model

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Abstract. In molecular dynamics applications there is a growing interest in including quantum effects for simulations of larger molecules. This paper is concerned with *mixed quantum-classical* models which are currently discussed: the so-called QCMD model with variants and the time-dependent Born-Oppenheimer approximation. All these models are known to approximate the full quantum dynamical evolution—under different assumptions, however. We review the meaning of these assumptions and the scope of the approximation. In particular, we characterize those typical problematic situations where a mixed model might largely deviate from the full quantum evolution. One such situation of specific interest, a non-adiabatic excitation at certain energy level crossings, can promisingly be dealt with by a modification of the QCMD model that we suggest.

1 Introduction

In molecular dynamics applications there is a growing interest in *mixed quantum-classical* models various kinds of which have been proposed in the current literature. We will concentrate on two of these models: the *adiabatic* or time-dependent Born-Oppenheimer (BO) model, [8,13], and the so-called QCMD model.[1] Both models describe 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. In the BO model this wavefunction is *adiabatically* coupled to the classical motion while the QCMD model consists of a *singularly perturbed* Schrödinger equation nonlinearly coupled to classical Newtonian equations, §2.2.

This paper is meant as a contribution to *systematize* the quantum-classical modeling of molecular dynamics. Hence, we are interested in an extended theoretical understanding of the models rather than to further contribute to the bunch of numerical experiments which have been performed on certain models by applying them to particular molecular systems. Thus, we will carefully review the assumptions under which our models are known to approximate the full quantum dynamical (QD) evolution of the system. This knowledge

[1] The number of articles applying this model is so large that we only mention four articles, [2][3][9][17], as the starting points to different lines of discussion.

allows for a characterization of the typical problematic situations where the mixed models might largely deviate from the QD evolution.

The present paper is organized as follows: In a first step, the derivation of QCMD and related models is reviewed in the framework of the semiclassical approach, §2. This approach, however, does not reveal the close connection between the QCMD and BO models. For establishing this connection, the BO model is shown to be the adiabatic limit of both, QD and QCMD, §3. Since the BO model is well-known to fail at *energy level crossings*, we have to discuss the influence of such crossings on QCMD-like models, too. This is done by the means of a relatively simple test system for a specific type of such a crossing where non-adiabatic excitations take place, §4. Here, all models so far discussed fail. Finally, we suggest a modification of the QCMD system to overcome this failure.

To simplify we restrict our study to the case of a system with just two "particles" of significantly different masses, m and M, having coordinates $x \in \mathbb{R}^m$ and $q \in \mathbb{R}^d$. Thus, the time-dependent Schrödinger equation becomes

$$i\hbar\,\partial_t\Psi \;=\; \Big(-\tfrac{\hbar^2}{2M}\mathcal{T}_q \;-\; \tfrac{\hbar^2}{2m}\mathcal{T}_x \;+\; V(x,q)\Big)\;\Psi.$$

Here, the kinetic operators are typically given by the corresponding Laplacians $\mathcal{T}_q = \Delta_q$ and $\mathcal{T}_x = \Delta_x$ or similar selfadjoint differential operators. The corresponding solution $\Psi = \Psi(x,q,t)$ describes what we call the full QD evolution of the system.

By assumption, the mass ratio $\epsilon^2 = m/M$ is a small parameter. Thus, rescaling the Schrödinger equation properly in time and potential transforms[2] it into the singularly perturbed equation

$$i\epsilon\,\partial_t\Psi \;=\; \Big(-\tfrac{\epsilon^2}{2}\mathcal{T}_q \;-\; \tfrac{1}{2}\mathcal{T}_x \;+\; V(x,q)\Big)\;\Psi. \tag{1}$$

In many applications, x and q will not necessarily be coordinates of "particles" but other degrees of freedom of the system under consideration. Typically however, a proper choice of the coordinate system allows the initial quantum state to be approximated by a product state (cf. [11], §IIb):

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

We will throughout assume this initial condition to be given.

2 Semiclassical Approach to QCMD

The semiclassical approach to QCMD, as introduced in [10], derives the QCMD equations within two steps. First, a *separation* step makes a tensor ansatz for the full wavefunction separating the coordinates x and q:

$$\Psi(x,q,t) \;\approx\; \Psi_\otimes \;=\; \phi(q,t)\,\cdot\,\psi(x,t). \tag{3}$$

[2] Time is scaled according to $\hbar t/\sqrt{mM} \to t$, implying a new potential $(m/\hbar^2)V$.

Second, a *semiclassical*, or *WKB*, ansatz approximates the "classical" wavefunction ϕ by

$$\phi(q,t) \approx \phi_{\mathrm{QC}} = a(q,t)\, \exp\left(\tfrac{i}{\epsilon} S(q,t)\right). \tag{4}$$

We will study the equations of motion that result from inserting all this in the full Schrödinger equation, Eq. (1). However, we would like to remind the reader that *not* the derivation of these equations of motion is the main topic here but the question of the quality of the underlying approximations.

2.1 Separation and TDSCF

Inserting the separation ansatz, i.e., $\Psi_\otimes$, results in two nonlinearly coupled single particle Schrödinger equations, the so-called *time dependent self-consistent field* (TDSCF) equations:[3]

$$i\epsilon\partial_t\phi = \left(-\tfrac{\epsilon^2}{2}\mathcal{T}_q + \langle\psi, V\psi\rangle\right)\phi, \qquad i\epsilon\partial_t\psi = \left(-\tfrac{1}{2}\mathcal{T}_x + \langle\phi, V\phi\rangle\right)\psi. \tag{5}$$

Here, $\langle\psi, V\psi\rangle = U_\phi$ denotes the ψ-averaged potential as seen by ϕ, still depending on the coordinate q. Likewise, $U_\psi = \langle\phi, V\phi\rangle$ includes integration with respect to q and depends on x. In the following, $\langle\cdot,\cdot\rangle$ will similarly denote integration with respect to x, q, or x and q, yielding expressions that depend on the other coordinate.

Approximation property We assume that the "classical" wavefunction ϕ is an approximate δ-function, i.e., for all times $t \in [0,T]$ the probability density $|\phi(t)|^2 = |\phi(q,t)|^2$ is concentrated near a location $q(t)$ with "width," i.e., position uncertainty, $\delta(t)$. Then, the quality of the TDSCF approximation can be characterized as follows:

Theorem 1 (Thm. 4.1. in [6]). *For all $t \in [0,T]$, let ϕ have compact support*[4] *of width $\delta(t) < \delta$. Then, the TDSCF wavefunction $\Psi_\otimes$ approximates the full QD solution Ψ of Eq. (1) up to an error of order δ, i.e.,*

$$\Psi_\otimes = \Psi + \mathcal{O}(\delta) \quad \textit{in} \quad [0,T].$$

Thus, TDSCF is the better an approximation of full QD the sharper located the probability density $|\phi|^2$ remains in the course of the evolution.

2.2 Semiclassical Ansatz and QCMD

Inserting Ψ_{QC} into Eq. (1), or equivalently the WKB-ansatz for ϕ into the TDSCF system Eq. (5), results in equations of motion for a and S (for details cf. [6,10]) and an one-particle Schrödinger equation,

$$i\epsilon\partial_t\psi_{\mathrm{ens}} = \left(-\tfrac{1}{2}\mathcal{T}_x + \int V(x,q)\, a^2(q,t)\, dq\right)\psi_{\mathrm{ens}}. \tag{6}$$

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[3] More precisely, Eq. (5) is only valid up to additional phase terms, cf. [6], §IVa, or [11], §IIIa, for details.

[4] In this case, let δ be the diameter of the support: $\delta(t) = \operatorname{diam}\operatorname{supp}|\phi(t)|^2$.

Notice that the solution ψ_{ens} is not identical to the TDSCF solution ψ but an approximation of it. The evolution of a and S in time may conveniently be described via the following classical Newtonian equations of motion: Given the initial values

$$a(q,0) \;=\; a_*(q) \qquad \text{and} \qquad S(q,0) \;=\; S_*(q), \tag{7}$$

we denote by $q(t) = q(t;q_0,\dot{q}_0)$ and $\dot{q}(t) = \dot{q}(t;q_0,\dot{q}_0)$ the solutions of the initial value problem

$$\ddot{q} \;=\; -\mathrm{grad}_q\,\langle\psi_{\text{ens}}, V\psi_{\text{ens}}\rangle(q), \qquad q(0) = q_0,\; \dot{q}(0) = \dot{q}_0 = \nabla S_*(q_0). \tag{8}$$

The *probability density* a^2 at a point $q = q(t) = q(t;q_0,\dot{q}_0)$ is obtained by transport of the initial probability, i.e.,

$$a^2(q(t;q_0,\dot{q}_0),t) \;=\; a_*^2(q_0,\dot{q}_0). \tag{9}$$

In addition, the *action* or *phase* S at $q = q(t)$ is given by integrating the corresponding Lagrangian along this trajectory, [1]:

$$S(q(t;q_0,\dot{q}_0),t) \;=\; S_*(q_0) + \int_0^t \left(\tfrac{1}{2}\dot{q}(s) \;-\; \langle\psi_{\text{ens}}, V\psi_{\text{ens}}\rangle(q(s))\right)\, ds. \tag{10}$$

Since Eq. (6) depends on the probability density $|\phi(q,t)|^2 = a^2(q,t)$ only, we may put the solution for S aside. Thus, we get a system that couples the classical equation Eq. (8) for computing a^2 to the one-particle Schrödinger equation, Eq. (6). A numerical simulation of the evolution as described by Eqs. (6), (8), and (9) has to compute a *bundle* of classical trajectories that sample the probability distribution a^2 and are nonlinearly coupled via Eq. (6).

We assume now, that the initial probability distribution $|\phi|^2\big|_{t=0} = a_*^2$ is an approximate δ-function at q_0. In this case, Eq. (9) makes it obvious, a^2 *remains* to be an approximate δ-function as long as the approximation is valid. Thus, the single trajectory $q(t) = q(t;q_0,\dot{q}_0)$ is an appropriate sampling of the probability density and $a^2(q,t) = \delta(q-q(t))$ simplifies the integral in Eq. (6) so that the final *QCMD equations* of motion read

$$\begin{aligned} i\epsilon\partial_t\psi_{\text{QC}} &= \left(-\tfrac{1}{2}\mathcal{T}_x \;+\; V(x,q(t))\right)\,\psi_{\text{QC}}, \\ \ddot{q} &= -\mathrm{grad}_q\langle\psi_{\text{QC}}, V\psi_{\text{QC}}\rangle(q). \end{aligned} \tag{11}$$

Caustics The above formulae can only be valid as long as Eq. (9) describes a unique map in position space. Indeed, the underlying Hamilton-Jacobi theory is only valid for the time interval [0,T] if at all instances $t \in [0,T]$ the map $(q_0,\dot{q}_0) \to q(t;q_0,\dot{q}_0)$ is one-to-one, [6,19,1], i.e., as long as trajectories with different initial data do *not* cross each other in position space (cf. Fig. 1). Consequently, the *detection* of any caustics in a numerical simulation is only possible if we propagate a trajectory bundle with different initial values. Thus, in pure QCMD, Eq. (11), caustics *cannot* be detected.

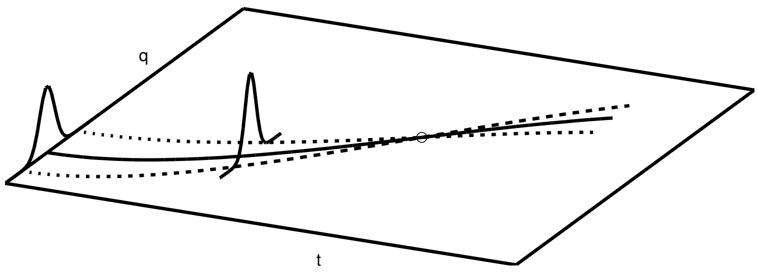

Fig. 1. Illustration of a caustic. Different trajectories sample the probability distribution. If they cross each other in position space, the transport or probability density is not longer unique and the approximation might break down.

Approximation property Excluding caustics we can exploit the results of semiclassical approximation theory [19]. This leads to the following statement:

Theorem 2 (Thm. 4.2. in [6]). *Let ϕ initially*[5] *have width $\delta(0) < \delta$ and let ϵ be small enough. Moreover, assume that caustics do not appear in time interval $[0,T]$. Then, the semiclassical wavefunctions ψ_{ens} and ψ_{QC} approximate the TDSCF wavefunction ψ up to an error of order $\delta^2+\epsilon$, i.e.,*

$$\psi_{\mathrm{ens}} = \psi + \mathcal{O}(\delta^2+\epsilon) \quad \textit{and} \quad \psi_{\mathrm{QC}} = \psi + \mathcal{O}(\delta^2+\epsilon) \qquad \textit{in } [0,T].$$

The QCMD solution q approximates expectation value of the classical position, $\langle q\rangle_{\mathrm{QD}} = \langle \Psi_{\mathrm{QD}}, q\Psi_{\mathrm{QD}}\rangle$, of the full QD solution Ψ_{QD} as:

$$q(t) = \langle q\rangle_{\mathrm{QD}} + \mathcal{O}(\delta^2+\epsilon) \qquad \textit{in } [0,T].$$

Referring to Thm. 1 we can conclude that—excluding caustics—QCMD (and QCMD bundles) approximates full QD up to an error of order $\mathcal{O}(\delta+\epsilon)$. These approximation result extends to cases in which certain types of caustics (focal points) are present by including phase shifts; cf. [19]. However, this cannot fully explain the bunch of numerical observations in which the presence of caustics does *not* influence the quality of the approximation at all. Thus, we might be interested in a justification of QCMD which avoids the problem of caustics. We will achieve this via studying the adiabatic limit of QCMD in §3.

2.3 Density Formulation of Semiclassical QCMD Bundles

A particularly convenient notation for trajectory bundle system can be introduced by using the classical Liouville equation which describes an ensemble of

[5] Because of Eq, (9), the condition from Thm. 1 concerning the small width can herein be restricted to the initial condition.

Hamiltonian trajectories by a phase space density $f = f(q, \dot{q}, t)$. In textbooks of classical mechanics, e.g. [12], it is shown that Liouville's equation

$$\partial_t f = \mathcal{L}[V]f, \qquad \mathcal{L}[V] = \left(\nabla_q V(q)^T \cdot \nabla_{\dot{q}} + \dot{q}^T \cdot \nabla_q\right), \tag{12}$$

describes the transport of an initial probability density $f(q, \dot{q}, 0) = f_*$ along the trajectories of the classical equation of motion $\ddot{q} = -\mathrm{grad}_q V$ in the sense that

$$f(q(t), \dot{q}(t), t) = f_*(q_0, \dot{q}_0). \tag{13}$$

Here, we denote by $(q(t), \dot{q}(t))$ the trajectory starting at $(q_0, \dot{q}_0)$. Thus, the transport of the semiclassical probability density a^2 according to Eq. (9) is just given by the Liouville equation with the potential $\langle \psi_{\mathrm{ens}}, V\psi_{\mathrm{ens}}\rangle$ and $a^2(q, t) = \int f(q, \dot{q}, t) d\dot{q}$:

$$\begin{aligned} i\epsilon\partial_t \psi_{\mathrm{ens}} &= \left(-\tfrac{1}{2}\mathcal{T}_x + \textstyle\int f(q, \dot{q}, t) V(x, q)\, dq\, d\dot{q}\right) \psi_{\mathrm{ens}}, \\ \partial_t f &= \mathcal{L}[\langle \psi_{\mathrm{ens}}, V\psi_{\mathrm{ens}}\rangle]\, f. \end{aligned} \tag{14}$$

We will refer to this model as to the *semiclassical QCMD bundle*. Eqs. (7) and (8) would suggest certain initial conditions for f_*. However, those would *not* include any momentum uncertainty, resulting in a wrong disintegration of the probability distribution in q as compared to the full QD. For including an initial momentum uncertainty, a Gaussian distribution in position space is used

$$f(q, \dot{q}, 0) = f_*(q, \dot{q}) = \tfrac{1}{\alpha} \exp\left(-\tfrac{1}{\delta^2}(q - q_*)^2\right) \exp(-\tfrac{2\delta^2}{\epsilon^2}(\dot{q} - \dot{q}_*)^2), \tag{15}$$

with a normalizing constant α and an initial momentum expectation $\dot{q}_*$.

3 Adiabatic Limit Approach to QCMD

If the parameter ϵ is very small, we are in the case of M being much larger than m. Thus, the limit $\epsilon \to 0$ is the limit of infinite mass M, i.e., the *adiabatic limit* of fast quantum motion of small particles around (infinitely) slowly changing positions of increasingly heavy "nuclei." We will study the *limit equations* governing the QCMD solutions for this adiabatic limit. Therefore, we rewrite the QCMD system, Eq. (11), by explicitly denoting the dependence of its solution $(q_\epsilon, \dot{q}_\epsilon, \psi_\epsilon)$ on the parameter ϵ:[6]

$$\begin{aligned} \ddot{q}_\epsilon &= -\mathrm{grad}_q \langle \psi_\epsilon, H(q_\epsilon)\psi_\epsilon\rangle, & q_\epsilon(0) &= q_*,\ \dot{q}_\epsilon(0) = \dot{q}_* \\ i\epsilon\partial_t\psi_\epsilon &= H(q_\epsilon)\,\psi_\epsilon, & \psi_\epsilon|_{t=0} &= \psi_*. \end{aligned} \tag{16}$$

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

$$H(q) = -\tfrac{1}{2}\mathcal{T}_x + V(x, q). \tag{17}$$

[6] We will often add an index ϵ in order to refer to a family of solutions.

We restrict ourselves to finite-dimensional Hilbert spaces,[7] making H a Hermitian matrix. We denote the eigenvalues of $H(q)$ by $E_k(q)$ and consider the spectral decomposition

$$H(q) \;=\; \textstyle\sum_k E_k(q)\, P_k(q), \tag{18}$$

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.[8] The surfaces $E_k = E_k(q)$ are called *energy levels*. Those positions q_c at which *energy level crossings* occur, i.e.,

$$E_k(q_c) \;=\; E_l(q_c) \qquad \text{for some } k \neq l,$$

will be the points of special interest in this section.

3.1 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 [4,20]: 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 population of the energy levels remain *invariant* during the evolution:

$$\lim_{\epsilon\to 0} \theta_k^\epsilon(t) = \lim_{\epsilon\to 0}\langle\psi_\epsilon, P_k(q_\epsilon)\psi_\epsilon\rangle \;=\; \theta_k^0 = \langle\psi_*, P_k(q_*)\psi_*\rangle. \tag{19}$$

The *constant* θ_k^0 is the initial population of level E_k and thus computable from the initial data, Eq. (16). All this turns out to be true if the following assumption on the eigenspaces and eigenenergies of $H(q)$ is fulfilled:

(A) The spectral decomposition Eq. (18) of H depends smoothly on q.

This assumption allows to prove that the limit solution $q_{\rm BO} \;=\; \lim_{\epsilon\to 0} q_\epsilon$ is given by:

$$\ddot{q}_{\rm BO} \;=\; -\mathrm{grad}_q \textstyle\sum_k \theta_k^0\, E_k(q_{\rm BO}), \qquad q_{\rm BO}(0) = q_*,\, \dot{q}_{\rm BO}(0) = \dot{q}_*. \tag{20}$$

We refer to this equation as to the *time-dependent Born-Oppenheimer* (BO) model of adiabatic motion. Notice that Assumption (A) does *not* exclude energy level crossings along the limit solution $q_{\rm BO}$. Using a density matrix formulation of QCMD and the technique of weak convergence one can prove the following theorem about the connection between the QCMD and the BO model:

[7] 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 Thm. 3 to the infinitely dimensional case, see [5].

[8] If the eigenspace to E_k is one-dimensional and Φ_k is a corresponding normalized eigenvector, then we have $P_k = \Phi_k^* \otimes \Phi_k$ and the population is $\theta_k = |\langle\Phi_k, \psi\rangle|^2$.

Theorem 3 (Thm. III.1 in [5], Thm. 2.1 in [7]). *Let $q_{\mathrm{BO}} = q_{\mathrm{BO}}(t)$ be the solution of the BO equation, Eq. (20), and assumption (A) be given. Any energy level crossing at $q_{\mathrm{BO}}(t_c)$ with $t_c \in [0,T]$ fulfills the transversality condition*

$$\tfrac{d}{dt}(E_k(q_{\mathrm{BO}}(t)) - E_l(q_{\mathrm{BO}}(t)))\big|_{t=t_c} \neq 0.$$

Then, the adiabatic invariance Eq. (19) holds and the limit of the sequence q_ϵ of QCMD solutions is q_{BO}.

3.2 Adiabatic Limit of QD

Thus, 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, [8], [13], and [18]. We will follow Hagedorn [13] whose results are based on the product state assumption Eq. (2) for the initial state with a special choice concerning the dependence of ϕ_* on ϵ:

$$\phi_*(q) \;=\; \tfrac{1}{A_\epsilon}\,\exp\left(-\tfrac{1}{4\epsilon}(q-q_*)^2\right)\exp\left(\tfrac{i}{\epsilon}\dot{q}_* q\right), \tag{21}$$

with the initial momentum expectation $\dot{q}_*$ and a normalization constant A_ϵ. This scaling guarantees that the wavefunction ϕ behaves uniformly classically.[9] Using this initial condition and the BO solution q_{BO} a wavefunction Ψ_{BO} is constructed which approximates the full QD solution Ψ_ϵ up to an error $\mathcal{O}(\sqrt{\epsilon})$, [13].[10] For simplicity, let us discuss the position expectation

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

instead of the wavefunctions. Here, the statement of Hagedorn is:

Theorem 4 (Thm. 2.1 in [13]). *Assume $q_{\mathrm{BO}} = q_{\mathrm{BO}}(t)$ to be the solution of the BO equation, Eq. (20), in a finite time interval $[0,T]$. Moreover, let there be no energy level crossings along q_{BO}. Then, for ϵ small enough, we have*

$$\langle q\rangle_\epsilon^{\mathrm{QD}} \;=\; q_{\mathrm{BO}} \,+\, \mathcal{O}(\sqrt{\epsilon}) \qquad \text{in } [0,T].$$

Altogether, the three different models discussed so far are interconnected as sketched in Fig. 2. Now, we can by-pass the problems connected to caustics: For ϵ being small enough QCMD is justified as an approximation of QD if we exclude energy level crossings and discontinuities of the spectral decomposition.

However, there remains one major question:

[9] Let be $V = 0$. Then, ϕ describes a free particle. With Eq. (21), the disintegration of the wavepaket makes its width increase like $\sqrt{\epsilon}\sqrt{1+t^2/4}$ in the limit $\epsilon \to 0$. Thus, the velocity of its disintegration is classical and independent from ϵ.

[10] Ψ_ϵ is the family of solutions of Eq. (1) with initial states due to Eq. (2) and Eq. (21). The initial quantum state ψ_* is assumed to be independent from ϵ with only finitely many energy levels E_k, $k = 1, \dots, n$ being initially excited.

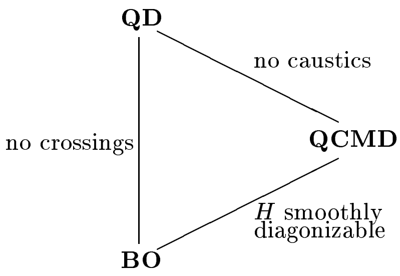

Fig. 2. The BO model is the adiabatic limit of full QD if energy level crossings do not appear. QCMD is connected to QD by the semiclassical approach if no caustics are present. Its adiabatic limit is again the BO solution, this time if the Hamiltonian H is smoothly diagonalizable. Thus, QCMD may be justified indirectly by the adiabatic limit excluding energy level crossings and other discontinuities of the spectral decomposition.

Can QCMD describe *non-adiabatic processes*; is there any situation in which BO fails but QCMD or its bundle variants are still useful?

By what we have seen before such a situation can only occur if there is an energy level crossing where Assumption (A) of Thm. 3 is hurt. In the next section, we will present a test example of this situation.

3.3 Energy Level Crossings with Non-Adiabatic Excitations

In his book [16], HAGEDORN classifies all energy level crossings that can occur generically with an electronic Hamiltonian according to the associated symmetries. Each symmetry yields a finite number of typical, generic energy level crossings. These generic situations are mathematically described by a *normal form* which reduces the general problem Eq. (1) to a simple low dimensional test problem. For time-reversible Hamiltonians there is just one normal form of an energy level crossing which moreover hurts the Assumption (A).

This normal form reduces the Schödinger equation, Eq. (1), to a specific form where $q \in \mathbb{R}^2$ remains a particle's position but x becomes a spin-like coordinate:

$$i\epsilon\dot{\Psi} = \left(-\tfrac{\epsilon^2}{2}\mathcal{T}_q + H(q)\right)\Psi. \tag{22}$$

Herein, $H = H(q)$ and $\mathcal{T}_q$ denote 2×2 Hermitian matrices, the entries of H being potential operators and $\mathcal{T}_q$ being diagonal

$$\mathcal{T}_q = \begin{pmatrix} \Delta_q & 0 \\ 0 & \Delta_q \end{pmatrix}. \tag{23}$$

Thus, $\Psi \in L^2(\mathbb{R}^2) \times L^2(\mathbb{R}^2)$ consists of two components $\Psi = (\Psi_1, \Psi_2)^T$, each of which a function in the usual Hilbert space. The Hamiltonian is specified by the particular matrix

$$H(q) = \begin{pmatrix} q^1 & q^2 \\ q^2 & -q^1 \end{pmatrix}. \tag{24}$$

The eigenvalues of H are $E_1(q) = -|q|$ and $E_2(q) = |q|$. Excluding the crossing at the origin $q = 0$ and using polar coordinates $q^1 = r\cos\varphi$ and $q^2 = r\sin\varphi$, yields the corresponding eigenvectors in the form

$$\Phi_1 = \begin{pmatrix} -\sin(\varphi/2) \\ \cos(\varphi/2) \end{pmatrix}, \qquad \Phi_2 = \begin{pmatrix} \cos(\varphi/2) \\ \sin(\varphi/2) \end{pmatrix}.$$

The occurrence of the argument $\varphi/2$ shows that these eigenvectors are defined up to a sign only. For a unique representation we have to cut the plane along a half-axis. By this, Φ_1 and Φ_2 become smooth vector fields uniquely defined on the cut plane. They cannot, however, be continued over the cut, but change their roles there instead. Thus, we have the situation of a crossing at which the eigenvector field is discontinuous and Assumption (A) of Thm. 3 is hurt.

In the pure BO model, this discontinuity will be ignored. Let the initial values be given by

$$q_* = (q_*^1, 0), \qquad \dot{q}_* = (\dot{q}_*^1, 0), \qquad \psi_* = (1, 0)^T, \tag{25}$$

with $q_*^1 > 0$ and $\dot{q}_*^1 < 0$ so that the initial motion is towards the crossing. In this case, the pure BO equations read $\ddot{q}^1 = -1$ and $\ddot{q}^2 = 0$, i.e., the solution is

$$q_{\mathrm{BO}}^1(t) = -\tfrac{1}{2}t^2 + \dot{q}_*^1\, t + q_*^1, \qquad q_{\mathrm{BO}}^2(t) = 0,$$

moving through the crossing at $t_c = \sqrt{(\dot{q}_*^1)^2 + 2q_*^1} + \dot{q}_*^1$.

As long as we have not passed the crossing, i.e., for $t < t_c$, Thm. 4 describes the limit $\epsilon \to 0$. Thus, the populations will be constant in $[0, t_c)$ in the limit $\epsilon \to 0$: $\theta_1 = 1, \theta_2 = 0$. The crossing itself induces a true excitation of the second energy level, [14,16]:[11]

$$\theta_2^\epsilon(t) = \theta_2^+ + o(1), \text{ for } t = t_c + \delta, \text{ with } \theta_2^+ = \left[1 + \frac{\pi}{\dot{q}_{\mathrm{BO}}^1(t_c)}\right]^{-1}. \tag{26}$$

Thus, passing the crossing induces a deeply *non-adiabatic* process. Directly behind the crossing Thm. 4 applies again, so that the information concerning the redistribution of population at the crossing is sufficient to denote the limit solution q_{Ha} for $\epsilon \to 0$: While the second component remains zero ($q_{\mathrm{Ha}}^2 \equiv 0$) we now have

$$q_{\mathrm{Ha}}^1(t) = \begin{cases} q_{\mathrm{BO}}^1(t) & : \ t < t_c \\ (2\theta_2^+ - 1)(t - t_c)^2 + \dot{q}_{\mathrm{BO}}^1(t_c)(t - t_c) & : \ t \geq t_c \end{cases}. \tag{27}$$

[11] For the connection of this result to the well-known Landau-Zener formula [23] see [15].

With initial conditions Eq. (25), the QCMD solution can be determined explicitly. Surprisingly, there is for all ϵ:

$$q_\epsilon \equiv q_{\mathrm{BO}}, \quad \psi_\epsilon^1(t) = \exp\left(-\frac{i}{\epsilon}\int_0^t q_\epsilon^1(\tau)\,d\tau\right), \quad \psi_\epsilon^2 \equiv 0. \tag{28}$$

Thus, neither BO nor QCMD can describe the non-adiabatic excitation at the crossing. However, as studied in [7], there is yet another feature of the QCMD model that could turn out to be useful here and might help to include the non-adiabatic process. After the crossing the adiabatic limit of QCMD is, in a sense, *not uniquely determined*:

Theorem 5 (§4 in [7]). *Let $q_{\mu,\epsilon}$ be the QCMD solution to the initial conditions*

$$q_* = (q_*^1, 0), \qquad \dot{q}_* = (\dot{q}_*^1, \mu), \qquad \psi_* = (1,0)^T$$

with $\mu > 0$. Then, the limit process $\epsilon, \mu \to 0$ is not unique, specifically

$$\lim_{\epsilon\to 0} q_{\mu=0,\epsilon} \equiv q_{\mathrm{BO}} \quad \text{and} \quad \lim_{\mu\downarrow 0}\lim_{\epsilon\to 0} q_{\mu,\epsilon}(t) = q_{\mathrm{BO}}(t) + (t^2, 0) = \tilde{q}_{\mathrm{BO}}(t).$$

Actually all points $\bar{q}$ between the two curves q_{BO}^1 and $\tilde{q}_{\mathrm{BO}}^1$ can be obtained as a limit solutions belonging to a particular pair of sequences $\epsilon, \mu \to 0$.

In a way, the limit set is thus the entire *funnel* between the two extreme cases q_{BO}^1 and $\tilde{q}_{\mathrm{BO}}^1$, Fig. 5. This effect is called *Takens-chaos*, [21,5,7]. As a consequence of this theorem each momentum uncertainty effects a kind of "disintegration" process at the crossing. Thus, one can reasonably expect to reproduce the true excitation process by using QCMD trajectory bundles for "sampling the funnel." To realize this idea, we have to study the full quantum solution and compare it to suitable QCMD trajectory bundles.

4 Energy Level Crossings and QCMD Bundles

To illustrate the effect of the crossing on a QD solution Ψ_ϵ, Fig. 3 shows the projection of the probability density $|\Psi_\epsilon|^2$ onto the q^1-plane for $\epsilon = 1/100$. We observe that the density disintegrates after passing the crossing. Its two main arms propagate along the curves q_{BO} and $\tilde{q}_{\mathrm{BO}}$ described above, i.e., the funnel of Thm. 5 reappears in the QD solution, however, this time, with an internal statistical structure. Fig. 4 shows the corresponding picture for a suitable QCMD trajectory bundle computation that clearly reflects the properties of the full QD solution. The following paragraphs explain how this QCMD bundle has been constructed.

4.1 Different Trajectory Bundles

Unfortunately, the semiclassical QCMD bundles, Eq. (14) in §2.3, are only of limited use here. To understand this, let us consider the q-expectation $[q]$

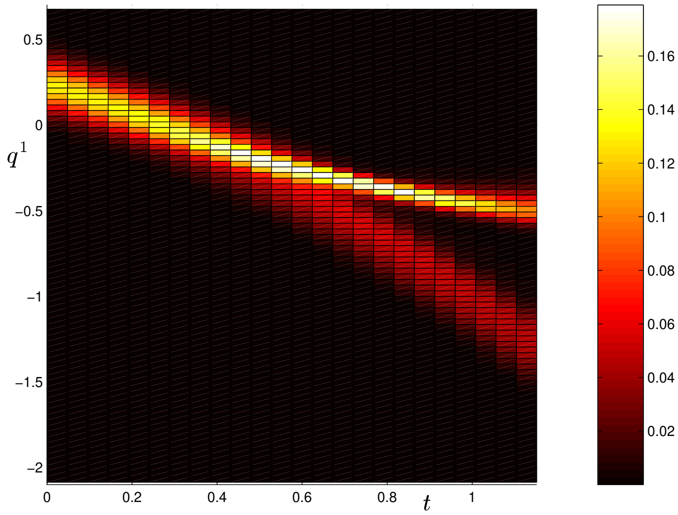

Fig. 3. Quantum solution Ψ_ϵ of the test system of §3.3 for $\epsilon = 1/100$. Ψ_ϵ computed numerically using Fourier pseudospectral methods in space and a symplectic discretization in time. Reduced q^1-density $\int |\Psi_\epsilon(q^1, q^2, t)|^2 dq^2$ versus t and q^1. Initial data due to (21) and (25) with $q_*^1 = 0.2$ and $\dot q_*^1 = -0.8$.

of its solution $(\psi_{\rm ens}, f)$. Recall that the expectation of a classical observable $A = A(q, \dot q)$ with respect to the phase-space density f is given by

$$[A](t) \;=\; \int \, A(q,\dot q)\, f(q,\dot q,t)\, d\dot q\, dq.$$

Integration of Eq. (14) directly yields

$$\tfrac{d^2}{dt^2}[q] \;=\; -[\langle \psi_{\rm ens}, {\rm grad}_q V(q) \psi_{\rm ens}\rangle].$$

Because the Hamiltonian $H = V$ depends *linearly* on q, the last expectation value is actually independent of f:

$$\begin{aligned}[\langle \psi_{\rm ens}, {\rm grad}_q V(q) \psi_{\rm ens}\rangle] &= \int \langle \psi_{\rm ens}, {\rm grad}_q V(q) \psi_{\rm ens}\rangle \, f(q,\dot q,t)\; dq d\dot q \\ &= \underbrace{\langle \psi_{\rm ens}, {\rm grad}_q V(q) \psi_{\rm ens}\rangle}_{\text{independent from } f} \cdot \underbrace{\int f(q,\dot q,t) dq d\dot q}_{=1}.\end{aligned}$$

Thus, $[q]$ and $\psi_{\rm ens}$ obey the following single trajectory QCMD system

$$i\epsilon \dot\psi_{\rm ens} = V([q])\psi_{\rm ens}, \qquad \tfrac{d^2}{dt^2}[q] = -\langle \psi_{\rm ens}, {\rm grad}_q V([q]) \psi_{\rm ens}\rangle.$$

Hence, we just have proven the following proposition:

Proposition 6. *Let $(\psi_{\rm ens}, f)$ be the solution of the bundle equation, Eq. (14), and $[q]$ be the corresponding q-expectation. If the potential V depends linearly on q, $[q]$ is identical with the solution q of the single trajectory QCMD model with initial values $q(0) = [q](0)$, $\dot q(0) = [\dot q](0)$, and $\psi(0) = \psi_{\rm ens}(0)$.*

Since QCMD reproduces the BO solution, we again have $[q] = q_{\rm BO}$ ignoring the non-adiabatic excitation process at the crossing. Consequently, we have to modify the very concept of QCMD bundles.

Remark: The statement of Prop. 6 is also valid for the q-expectation $\langle q\rangle = \langle \Psi_\otimes, q\Psi_\otimes\rangle$ of the TDSCF solution. Consequently, *TDSCF fails near the crossing*, a fact, which emphasizes that the reason for this failure is connected to the separation step.

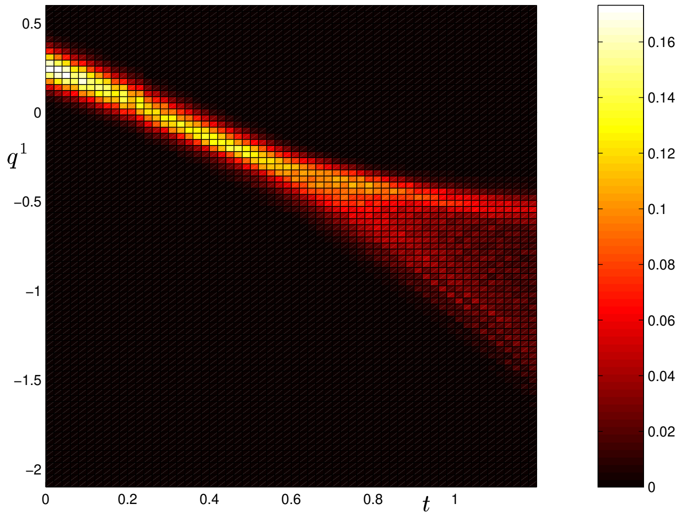

Fig. 4. q^1-density p, Eq. (30), of a simulation for $\epsilon = 1/100$ using the uncoupled QCMD bundle. Same situation as in Fig. 3.

Actually, Fig. 4 has been obtained using the following modification of the QCMD bundle: one propagates an *ensemble* of *independent*, single QCMD trajectories $(q_k, \dot q_k, \psi_k)$, $k = 1, \ldots, N$:

$$i\epsilon\partial_t\psi_k = \left(-\tfrac{1}{2}\mathcal{T}_x + V(x, q_k(t))\right)\psi_k, \qquad \ddot q_k = -\mathrm{grad}_q\langle\psi_k, V\psi_k\rangle(q_k). \quad (29)$$

Initially, all the ψ_k are identical: $\psi_k(t=0) = \psi_*$ and the classical states $(q_k, \dot q_k)$ sample the density $|\phi_*(t=0)|^2$ according Eq. (15),[12] i.e., there is a weight factor w_k for each trajectory k. Consequently, for each time t the probability distribution $p(q^1)$ in q^1 can be approximated on any sufficiently large interval $[q^1, q^1 + \Delta q^1]$ by adding the weights of all trajectories passing this interval at time t:

$$p(t)|_{[q^1,q^1+\Delta q^1]} = \sum_{q_k^1(t)\in[q^1,q^1+\Delta q^1]} w_k. \quad (30)$$

[12] For Hagedorn's initial condition Eq. (21), we have to choose $\beta = 2/\epsilon$ in Eq. (15).

A comparison of Fig. 4 and Fig. 3 shows that this *uncoupled QCMD bundle* reproduces the disintegration of the full QD solution. However, there are minor quantitative differences of the statistical distribution. Fig. 5 depicts the corresponding q^1-expectation values together with HAGEDORN's limit q^1-expectation q_{Ha} of QD for $\epsilon \to 0$. We observe that for $\epsilon = 1/100$ and $\epsilon = 1/500$ the q^1-expectation of the uncoupled QCMD bundle approximates the q^1-expectation of the corresponding QD solution which lie close to q_{Ha}.

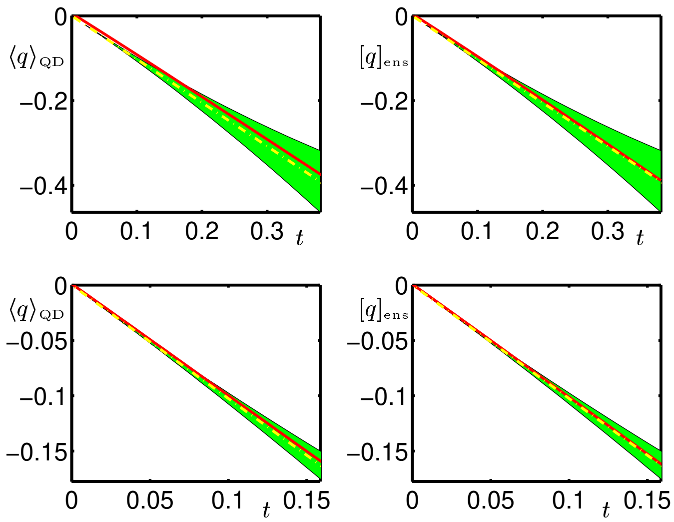

Fig. 5. Comparison of the q_1 expectation value of the uncoupled QCMD bundle ($[q]_{\mathrm{ens}}$) and full QD ($\langle q \rangle_{\mathrm{QD}}$) for the test system for $\epsilon = 1/100$ (pictures on top) and $\epsilon = 1/500$ (below). Initial data as in Fig. 3. The shaded domain indicates the funnel between the two curves q_{BO} and $\tilde{q}_{\mathrm{BO}}$ (cf. Thm. 5). The light dashed line shows Hagedorn's limit solution q_{Ha} and the dense lines $\langle q \rangle_{\mathrm{QD}}$ (left hand pictures) and $[q]_{\mathrm{ens}}$ (right hand pictures).

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