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Abstract

This paper presents a mathematical derivation of a model for quantum-classical molecular dynamics (QCMD) as a *partial* classical limit of the full Schrödinger equation. This limit is achieved in two steps: separation of the full wavefunction and short wave asymptotics for its "classical" part. Both steps can be rigorously justified under certain smallness assumptions. Moreover, the results imply that neither the time-dependent self-consistent field method nor mixed quantum-semi-classical models lead to better approximations than QCMD since they depend on the separation step, too. On the other hand, the theory leads to a characterization of the critical situations in which the models are in danger of largely deviating from the solution of the full Schrödinger equation. These critical situations are exemplified in an illustrative numerical simulation: the collinear collision of an Argon atom with a harmonic quantum oscillator.

Keywords: quantum-classical molecular dynamics, mixed quantum-classical models, separation, short wave asymptotics, WKB method, semi-classical approximation, time-dependent self-consistent field approximation, biomolecules.

AMS classification: 81Q15, 81Q20, 81V55, 92C40

1 Introduction

Biomolecular systems are characterized by a large number of degrees of freedom. It meets universal acceptance that a prediction of biomolecular processes from first principles should ideally be based on a fully quantum dynamical description of all of these degrees of freedom. Unfortunately, for large systems the simulation of such a quantum model is impossible even on the biggest and fastest computers, now and probably for the next decades. Therefore, typical simulations of biomolecular systems are based on classical molecular dynamics (MD) assuming that the system of interest obeys a classical Hamiltonian equation of motion. In this case quantum theory is only used in order to construct the atom-to-atom interaction potentials in the context of Born-Oppenheimer approximation.

In many situations classical MD allows a sufficiently accurate description of complex realistic molecular systems. But it simply cannot be valid if the nature of the process under consideration is "deeply quantum mechanically", e.g., optical excitation processes, or transfer of key-protons in the active sites of an enzyme. In those cases a quantum dynamical description is unavoidable. However, since a full quantum description of, e.g., a complete enzyme is still not feasible, one is interested in a *mixed quantum-classical* approach to MD which allows to describe most atoms by the means of classical mechanics but an important, small portion of the underlying system by the means of quantum mechanics.

In the literature various models are proposed: Most of them fit into the scheme shown and explained in Figure 1. In mixed approaches the full quantum system is first separated via the tensor product ansatz into several parts with a coupled quantum description. Then, the evolution of *each* part can be modeled on different levels: quantally, semi-classically, or (purely) classically. All the proposed models can clearly be classified via the different description levels they are mixing: some remain on the quantum level for all parts and are well-known as *time-dependent self-consistent field* (TDSCF)-methods (cf. [15][12] in our context; a lot of references in nuclear physics use the notion of *time-dependent Hartree approximation* or *time-dependent mean-field approximation*); other methods combine semi-classical models for most of the parts with a quantum description for the particularly interesting part, usually called *quantum-semi-classical* (QSCMD)-models (see [11] and the references cited therein). However, we are particularly interested in *quantum-classical molecular dynamics* (QCMD)-models, which use Hamiltonian equations for space and momentum of the "classical" atoms (for biomolecular systems see [5][6][2]; more references may be found in studies for van der Waals molecules, e.g., [13][19]).

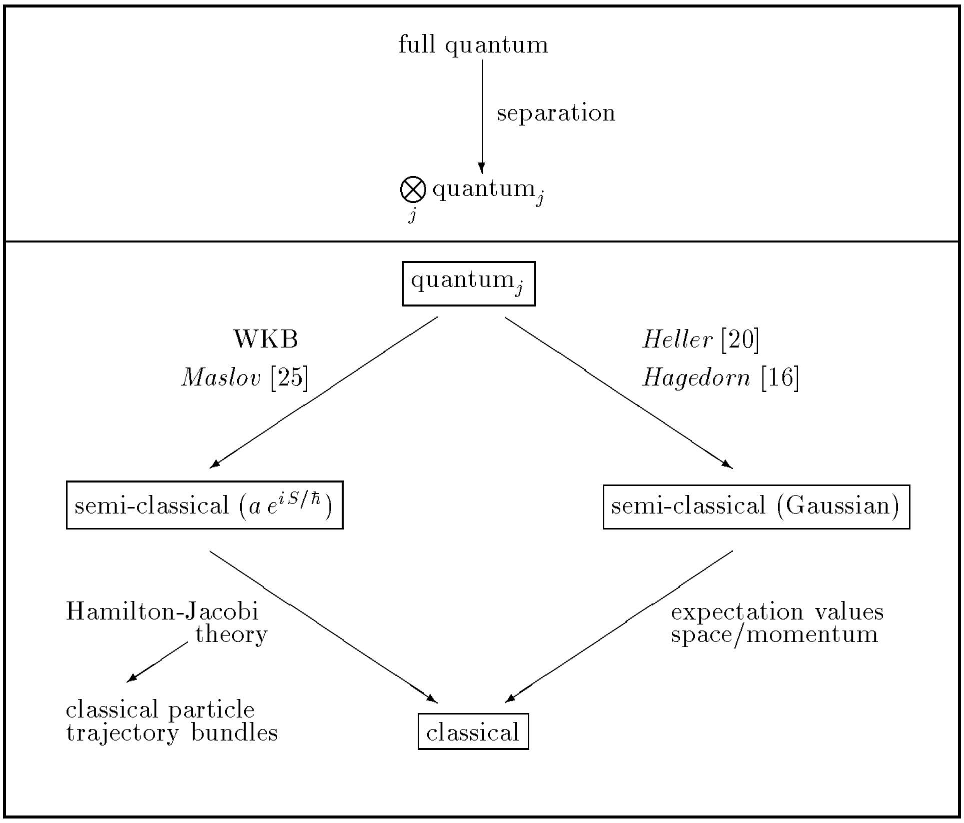

Figure 1: Different approaches to quantum-(semi-)classical models. In mixed approaches the full quantum system is first separated via the tensor product ansatz into parts j with coupled quantum description. Then, the evolution of each part j can be modeled on different levels: quantally, semi-classically, or (purely) classically. For the entire system or for each single part, the derivation of the different models from the original quantum description level can be realized, as indicated, on two different ways. On each way both steps can be justified strictly mathematically in the context of appropriate asymptotic expansions. The simultaneous justification of the separation step remains the crucial point.

Unfortunately enough, essentially *two* basic QCMD-models are proposed in the literature [5][4] for biomolecular systems, which *differ* in a crucial point and result in essentially different *numerical problems.* Moreover, it is claimed that QSCMD-models are a better approximation of the full quantum behavior, but require significantly larger computational effort. We propose that a model selection should be guided by a strict analysis of approximation properties with respect to the solution of the full Schrödinger equation in a context in which a classical description of most of the atoms is required and allowed. Hence, we are looking for the "partial classical limit" of the full quantum dynamics. It should be noted, that semi-classical approximations are usually applied to the *entire* quantum system, either using Gaussians (as [21][20] or the mathematical investigation [16]) or the WKB method (as many textbooks like [23][10] or in mathematical investigations like [1][25]). As pointed out in [15], the separation ansatz (and with it TDSCF) occurs as an intermediate step in a derivation of QCMD *and* QSCMD from the full Schrödinger equation. Thus, we simultaneously ask for the validity of separation in this "partial limit". As far as the authors know there is no strict analysis of any time-dependent "partial classical limit" which — in turn — explains the conceptual differences in the QCMD-models proposed.

The herein presented approach tries to bridge this gap. Its mathematical results allow to *decide* which of the two above mentioned models for QCMD can be derived from a full quantum model by specifying the sense and order of approximation. On the other hand, the results lead to a characterization of the situations in which the models are in danger of largely deviating from the solution of full Schrödinger equation.

The mathematical argumentation follows the red thread of an approach proposed by [15]: It starts with a separation ansatz for the full Schrödinger equation, leading to the TDSCF-equations. Then, it is shown via short wave asymptotics or WBK-approximation that these TDSCF-equations imply a certain QCMD-model under some smallness assumptions which specify what is meant by "partial classical limit". The essential point now is that these mathematical results for QCMD also lead to a strict justification of the separation ansatz in this limit.

The text is organized in five steps: First, we introduce the two basic QCMD-models of the literature and explain their crucial difference. In a second, motivating step it is shown that *only one* of both models, interestingly the less complicated one, may be derived from the full quantum approach. Third, in Section 4, this motivation is mathematically justified. This implies a characterization of the possibly problematic scenarios for QCMD-models, which is exemplified in Section 5. The fifth and last step leads us to the discussions of our results and their implications for QSCMD-models.

For simplicity of notation we herein restrict the discussion to the case of only two interacting particles. However, one should note that all the following considerations can be extended to arbitrary many particles or degrees of freedom.

2 QCMD Models

In this section we give an intuitive formulation of the basic QCMD models, preparing for Sections 3 and 4 in which we show how they fit into the framework of full quantum models.

Let the two particles have space coordinates $x \in \mathbf{R}^d$ and $q \in \mathbf{R}^d$ and masses m and M respectively. Moreover, let the interaction potential between them be $V = V(x,q)$. The basic assumption of QCMD is that the masses differ significantly: $m \ll M$, and that, therefore, the heavier particle can be modeled classically while the lighter one remains a "quantum particle". That is, the quantum particle is described by a wavefunction $\psi = \psi(x,t)$ which obeys Schrödinger's equation

$$i\hbar\,\dot{\psi} \;=\; \left(-\frac{\hbar^2}{2m}\,\Delta_x \,+\, V(x,\mu)\right)\Bigg|_{\mu=q(t)} \psi \tag{1}$$

with a parameterized potential which depends on the location $q(t)$ of the "classical" particle, thus being time-dependent. The location $q = q(t)$ is the solution of a classical Hamiltonian equation of motion

$$\begin{aligned} M\,\dot{q} &= p \\ \dot{p} &= -\nabla_q U, \end{aligned} \tag{2}$$

in which the time-dependent potential U is given as the original one V weighted with the probability of finding the quantum particle:

$$U(q,\psi,t) \;=\; \langle \psi\,,\, V(\cdot,q)\,\psi\rangle \;=\; \int V(x,q)\,|\psi(x,t)|^2\,dx. \tag{3}$$

Thus, the forces in (2) are the so-called Hellmann-Feynman forces. Together, (1) and (2) are the basic equations of motion of QCMD. But one question is still unaddressed in this *intuitive* approach: What kind of q-dependence underlies the potential U in order to compute the partial derivative $\nabla_q U$? There are two answers discussed in the literature:

1. The arguments (q,ψ) of U are *independent* unknowns and therefore we get
$$\nabla_q U \;=\; \langle \psi\,,\, \nabla_q V(\cdot,q)\,\psi\rangle. \tag{4}$$

This can be evaluated directly and (1) together with (2) constitutes a closed system of equations. This choice is used, e.g., in [5],[6], where, in addition, the Schrödinger equation is replaced by the Liouville-von Neumann equation.

2. In [4], QCMD is seen as an extension of the Born-Oppenheimer approximation to our time-dependent situation: the heavier particle may be fixed for a short instant $[t_0, t_0+\Delta t]$ in which the quantum particle behaves according to its Schrödinger equation (1). This means, $\mu = q(t_0)$ is considered as *parameter* in (1) and the wavefunction $\psi = \psi(\mu, t)$ as in $[t_0, t_0 + \Delta t]$ explicitly depending on this parameter. After this, the classical position q has to be updated via (2). However this may be realized, the dependence of ψ on μ has to be taken into account yielding the derivative
$$\begin{aligned} \nabla_q U \;&=\; \Big(\langle \psi \,,\, \nabla_\mu V(\cdot, \mu)\, \psi \rangle \\ &\quad + \langle \nabla_\mu \psi \,,\, V(\cdot, q)\, \psi \rangle + \langle \psi \,,\, V(\cdot, q)\, \nabla_\mu \psi \rangle \Big)\Big|_{\mu=q}, \end{aligned} \tag{5}$$
which, in turn, leads to the necessity of evaluating $\nabla_\mu \psi$ in addition. An algorithmic realization of this approach is presented in [4], resulting in a simulation method which causes much more computational effort in real life applications than the simple choice (4). The Born-Oppenheimer approximation is understood as being static and the terms containing $\nabla_\mu \psi$ are interpreted as corrections caused by fast motions of the heavy particle. For test simulations using this model see [2][3].

Which of the two different approaches can be derived from the full quantum model? This means that we would like to relate a QCMD model to the full Schrödinger equation for both particles:
$$i\hbar\, \dot{\Psi} \;=\; \left(-\frac{\hbar^2}{2m}\, \Delta_x \;-\; \frac{\hbar^2}{2M}\, \Delta_q \;+\; V(x, q) \right) \Psi, \tag{6}$$
in which the 2-particle wavefunction $\Psi(t) = \Psi(x, q, t)$ lives in the state space $\mathcal{H} = L^2(\mathbf{R}^{2d})$. We will accomplish such a relation via two approaches: A motivation via the Ehrenfest theorem (Section 3) and a mathematical justification (Section 4). Both will indeed result in the intuitive QCMD model (1) and (2). However they give favor to the gradient evaluation (4), thus showing that the correction term $\nabla_\mu \psi$ of (5) cannot be based on the full quantum model.

3 Motivation of QCMD from full Quantum Model

Let the expectation value of an time-independent observable $A : L^2(\mathbf{R}^{2d}) \to L^2(\mathbf{R}^{2d})$ with respect to state $\Psi(\cdot, t) \in L^2(\mathbf{R}^{2d})$ be denoted

$$\langle A\rangle(t) \;=\; \langle \Psi(t), A\Psi(t)\rangle \;=\; \int \bar{\Psi}(x,q,t)\, A\Psi(x,q,t)\, dx\, dq.$$

Then the Ehrenfest theorem [27] states

$$\frac{d}{dt}\langle A\rangle \;=\; \frac{i}{\hbar}\langle [H, A]\rangle$$

if Ψ is the solution of the Schrödinger equation $i\hbar\dot{\Psi} = H\Psi$. One should note, that this is correct even in the case of a time-dependent Hamilton operator.

We are interested in the location expectation $\langle q\rangle$ and in the expectation values $\langle P\rangle$ of the conjugated momentum operator $P = -i\hbar\nabla_q$ for the solution $\Psi = \Psi(t)$ of (6). The Ehrenfest theorem yields

$$\begin{aligned} \frac{d}{dt}\langle q\rangle &= M^{-1}\langle P\rangle \\ \frac{d}{dt}\langle P\rangle &= -\langle \nabla_q V\rangle. \end{aligned} \tag{7}$$

with

$$\langle \nabla_q V\rangle \;=\; \int \Big(\nabla_q V(x,q)\Big)\, |\Psi(x,q,t)|^2\, dx\, dq, \tag{8}$$

which can only be evaluated if Ψ is known. Remember that $\langle q\rangle$ and $\langle P\rangle$ correspond to space coordinate and momentum of our "classical" particle. Still, (7) is a pure quantum theoretical equation. But (8) shows that, already on this level, that the gradient is *inside* the expectation value, thus uniquely leading us to model (4) *without* need for correction terms. Indeed, one arrives at exactly the same result by switching into the Heisenberg picture (cf. [18]).

The system (7) gets the form of the classical equation of motion (2) if we construct a relation

$$\langle \nabla_q V\rangle \;=\; \nabla_q U(\langle q\rangle, t).$$

This can be done if we give an explicit formulation of our assumption that the heavier particle "behaves classically": Ψ is a product of the wavefunctions

ψ for the quantum particle and ϕ for the classical one, whose probability distribution is "classical", i.e., with very small uncertainty in space. In other words, we separate $\Psi(x,q,t) = \psi(x,t)\cdot\phi(q,t)$ and assume that ϕ is an approximate δ-function, e.g.:

$$\phi(x,q,t) \;=\; \frac{1}{(\epsilon(t)\,\sqrt{2\pi})^{d/2}}\;\exp\left(-\,\frac{|q-\langle q\rangle|^2}{4\epsilon(t)^2}\right)\;\exp\left(i\,\frac{\langle P\rangle}{\hbar}\,q\right). \tag{9}$$

with $\epsilon(t)\le\epsilon\ll 1$. Inserting this into (8) we get (cf. appendix, Lemma 7.1):

$$\langle\nabla_q V\rangle \;=\; \langle\psi\,,\,\nabla_q V(\cdot,\langle q\rangle)\,\psi\rangle \;+\; \mathcal{O}(\epsilon^2) \tag{10}$$

and, thus, in the limit $\epsilon\to 0$:

$$\langle\nabla_q V\rangle \;=\; \langle\psi\,,\,\nabla_q V(\cdot,\langle q\rangle)\,\psi\rangle, \tag{11}$$

i.e., we end up with (2) and choice (4). There is no need for considering the term $\nabla_\mu\psi$.

It should be noted that this argument does *not* depend on the Gaussian form of ϕ — we may use any approximate δ-function as we will see in the next section — but that it depends on the smallness of its variance or location uncertainty $\epsilon(t)^2\ll 1$.

However, there is some need for a discussion of whether our two assumptions:

(A1) Ψ is separable,

(A2) ϕ is a moving approximate δ-function, its variance remains uniformly small $\epsilon(t)^2<\epsilon^2\ll 1$

may lead to an *appropriate approximation* of the total wavefunction Ψ. Indeed, the above approach can be mathematically refined in a way which yields an asymptotic expansion of Ψ in terms of two smallness parameters: For appropriate initial conditions the solution of the QCMD-model using gradient evaluation (4) approximates the full quantum dynamics up to an error $\mathcal{O}(\epsilon+\hbar/\sqrt{M})$. In particular, our assumptions (A1) and (A2) are justified if ϵ is small and M large enough. The range of validity of the asymptotic expansion gives us criteria to decide about the applicability of the QCMD approach. Moreover, the analysis of the separation step also leads to a justification of TDSCF-approaches, since those methods depend on the separation ansatz only.

4 Mathematical Derivation of QCMD

In this section we present a methodology to derive the QCMD model from the full Schrödinger equation (6) as an approximation in a quite strict sense, i.e., including the asymptotic size of the error terms. To be specific, we introduce the following two smallness parameters:

- ϵ^2, the variance of the probability density for the particle of mass M at time zero,
- $\hbar/\sqrt{M}$, measuring the effect of $m \ll M$.

The smallness of these two parameters will specify the meaning of "classical" behavior of the particle with mass M. The approximation procedure works now in two steps:

- Separation. This yields to an $\mathcal{O}(\epsilon)$-perturbation of the wavefunction.
- Short wave asymptotics. This yields an additional error term for the QCMD model of order $\mathcal{O}(\epsilon^2 + \hbar/\sqrt{M})$.

The procedure works within the restriction that the time t under consideration is smaller than a certain maximal value $t_{\max}$. Thus, we end up with a rather precise setup for the validity of the QCMD model, namely

$$\epsilon \textit{ and } \hbar/\sqrt{M} \textit{ sufficiently small and } t < t_{\max}.$$

These restrictions will be discussed later on.

4.1 First Approximation Step: Separation

We consider the solution Ψ of the full Schrödinger equation (6) with *separated* initial data

$$\Psi|_{t=0} = \psi_0 \otimes \phi_0, \quad \text{i.e.,} \quad \Psi(x,q,0) = \psi_0(x) \cdot \phi_0(q). \tag{12}$$

In general, we cannot expect that this initial separation persists in time. However, to begin with, we *assume* that the solution Ψ has the form of a separated wavefunction $\Psi_\otimes$ defined by

$$\Psi_\otimes = \psi \otimes \phi, \quad \text{i.e.,} \quad \Psi_\otimes(x,q,t) = \psi(x,t) \cdot \phi(q,t), \tag{13}$$

i.e., we assume that $\Psi = \Psi_\otimes$. For this specific case an alternative way of computing $\Psi_\otimes$ will be derived, which we will use to approximate Ψ in the general case $\Psi \neq \Psi_\otimes$.

Under the assumption $\Psi = \Psi_\otimes$ the full Schrödinger equation (6) can be separated into two coupled 1-particle Schrödinger equations. Namely, multiplication of (6) by $\bar{\phi}$ and integration with respect to q, respectively multiplication by $\bar{\psi}$ and integration with respect to x, yields:

$$\begin{aligned} i\hbar\dot{\psi} &= \left(-\frac{\hbar^2}{2m}\Delta_x + \langle \phi, V(x,\cdot)\phi\rangle + \gamma_\phi(t)\right)\psi, \\ i\hbar\dot{\phi} &= \left(-\frac{\hbar^2}{2M}\Delta_q + \langle \psi, V(\cdot,q)\psi\rangle + \gamma_\psi(t)\right)\phi \end{aligned} \tag{14}$$

with the time-dependent functions

$$\begin{aligned} \gamma_\phi(t) &= -i\hbar\langle \phi, \dot{\phi}\rangle - \frac{\hbar^2}{2M}\langle \phi, \Delta_q \phi\rangle, \\ \gamma_\psi(t) &= -i\hbar\langle \psi, \dot{\psi}\rangle - \frac{\hbar^2}{2m}\langle \psi, \Delta_x \psi\rangle. \end{aligned} \tag{15}$$

The system (14) can be put to a more suitable form, if we note, that the time-dependent function γ_ϕ and γ_ψ are responsible for a phase shift only. To be specific, the relations

$$\psi(x,t) = \exp\left(-\frac{i}{\hbar}\int_0^t \gamma_\phi(s)\,ds\right)\psi_*(x,t)$$

and

$$\phi(x,t) = \exp\left(-\frac{i}{\hbar}\int_0^t \gamma_\psi(s)\,ds\right)\phi_*(x,t)$$

hold, where ψ_* and ϕ_* are the solutions of the simplified system

$$\begin{aligned} i\hbar\dot{\psi}_* &= \left(-\frac{\hbar^2}{2m}\Delta_x + \langle \phi_*, V(x,\cdot)\phi_*\rangle\right)\psi_*, \\ i\hbar\dot{\phi}_* &= \left(-\frac{\hbar^2}{2M}\Delta_q + \langle \psi_*, V(\cdot,q)\psi_*\rangle\right)\phi_*. \end{aligned} \tag{16}$$

This nonlinear system is uniquely solvable as can be proven by Galerkin approximation and energy based compactness arguments. Thus, we may solve this system instead of (14) whenever the explicit knowledge of the phase is of no importance. For instance all expectation values are invariant under phase shift. Inserting the expression for ψ and ϕ into the definition (15) of γ_ϕ and γ_ψ we get

$$\gamma_\phi + \gamma_\psi = -\langle \psi_* \otimes \phi_*, V\psi_* \otimes \phi_*\rangle$$

and therefore the following reconstruction of $\Psi_\otimes$:

$$\Psi_\otimes = \exp\left(\frac{i}{\hbar}\int_0^t \langle \Psi_\otimes^*(s), V\Psi_\otimes^*(s)\rangle\, ds\right)\Psi_\otimes^*, \qquad \Psi_\otimes^* = \psi_* \otimes \phi_*, \tag{17}$$

a relation which may also be found as formula (4.4) in [21]. In this way the simplified system (16) *defines* via (17) a separated wavefunction $\Psi_\otimes$ which respects the initial data (12) — independently of whether the solution Ψ of the full Schrödinger equation is separated ($\Psi = \Psi_\otimes$) or not ($\Psi \neq \Psi_\otimes$).

Now, we have to investigate for the case $\Psi \neq \Psi_\otimes$, in which sense $\Psi_\otimes$ as defined by (17) can nevertheless be viewed as an approximation $\Psi_\otimes \approx \Psi$. To this end we differentiate the expression (17) with respect to the time t, use the equations of the system (16) and get the following *modified full Schrödinger equation*:

$$i\hbar\frac{d}{dt}\Psi_\otimes = \left(-\frac{\hbar^2}{2m}\Delta_x - \frac{\hbar^2}{2M}\Delta_q + V_\otimes(x,q,t)\right)\Psi_\otimes$$

with the modified potential

$$V_\otimes(x,q,t) = \langle \phi, V(x,\cdot)\phi\rangle + \langle \psi, V(\cdot,q)\psi\rangle - \langle \Psi_\otimes, V\Psi_\otimes\rangle.$$

A simple calculation shows that the expectation value of the potential remains unchanged, i.e.,

$$\langle \Psi_\otimes, V\Psi_\otimes\rangle = \langle \Psi_\otimes, V_\otimes\Psi_\otimes\rangle.$$

Thus, the new potential $V_\otimes$ appears to be somewhat the right separation of the original potential V.

We now make the following assumption additionally to the initial condition (12):

(A) The probability density $|\phi|^2$ is an *approximate δ-function* as defined in the appendix, i.e.,

$$|\phi(q,t)|^2 = \chi_{\epsilon(t)}(q - q(t), t).$$

Further we assume that for $t < t_{\max}$ this approximate δ-function has uniformly small support:

$$\operatorname{diam}\operatorname{supp}\phi(\cdot,t) = \mathcal{O}(\epsilon).$$

This means that $|\phi(\cdot,t)|^2 \to \delta(\cdot - q(t))$ for $\epsilon \to 0$.

Assumption (A) implies that the wavepacket ϕ is concentrated along some particle path $q(t)$. This assumption will be simplified in Section 4.2. Our main approximation result for the separation step is now

Theorem 4.1 *Assumption (A) implies that the asymptotic error of separation is given by*

$$\Psi_{\otimes} = \Psi + \mathcal{O}(\epsilon)$$

in the space $L^2(\mathbf{R}^{2d})$.

Proof. Lemma 7.1 of the appendix shows

$$\langle \phi, V(x, \cdot)\phi \rangle = V(x, q(t)) + \mathcal{O}(\epsilon^2),$$

thus giving

$$V_{\otimes}(x, q, t) = V(x, q(t)) + \langle \psi, (V(\cdot, q) - V(\cdot, q(t)))\psi \rangle + \mathcal{O}(\epsilon^2).$$

Now one easily shows that only the values of $V_{\otimes}(x, q, t)$ for $q \in \operatorname{supp} \phi(\cdot, t)^2$ determine the solution $\Psi_{\otimes}$. Taylor expansion yields for these values of q

$$V_{\otimes}(x, q, t) = V(x, q) + \mathcal{O}(\epsilon).$$

The desired result is now implied by standard results from perturbation theory as for instance Theorem IX.2.19 in [22]. □

Since the system (16) is the basis of the so called *time–dependent self–consistent field* (TDSCF) calculations (cf. [15]), we have thus given some justification of this approach. We should note, that Theorem 4.1 remains even valid, if the probability density $|\phi|^2$ supports *several* particle traces with a variance of ϵ^2. This will be a possible advantage of the TDSCF approach over the QCMD model, which constitutes a further approximation step relying on just *one* particle trace.

4.2 Second Approximation Step: Short Wave Asymptotics

Now, we will give a further simplification of the separated system (16) for large masses $M \gg m$. As a by-product we will be able to simplify assumption (A).

Using short wave asymptotics [1][23][25], also called WKB method or semi-classical approximation in the literature, one can prove the validity of the following *asymptotic expansion*:

$$\phi_*(q, t) = a(q, t) \exp\left(i \frac{S(q, t)}{\hbar} \right) + \mathcal{O}(\hbar/\sqrt{M}). \tag{18}$$

Remark. The reader should note, that we explicitly state the dependence on M of the $\mathcal{O}(\hbar)$ error term, which usually can be found in the literature. A simple argument for this particular dependence will be given in the appendix. Since we apply short wave asymptotics to only part of the system (16) the limit $\hbar \to 0$ would not make sense.

The phase function S and the real amplitude a obey the following equations: A nonlinear Hamilton-Jacobi equation for S

$$\frac{\partial S}{\partial t} + \frac{1}{2M}\left(\nabla_q S\right)^2 + \langle\psi, V(\cdot, q)\psi\rangle = 0 \tag{19}$$

and a continuity equation for a^2

$$\frac{\partial a^2}{\partial t} + \mathrm{div}_q\left(a^2 \frac{\nabla_q S}{M}\right) = 0. \tag{20}$$

Now, equation (19) for the phase S is a classical Hamilton–Jacobi equation for the *action* of a particle with respect to the time-dependent potential $\langle\psi, V(\cdot, q)\psi\rangle$. The Hamilton-Jacobi theory of classical mechanics [1] states that the solution of the canonical equations

$$\begin{array}{rclcrcl} \dot{q} & = & M^{-1}p, & \qquad & q(0) & = & q_0, \\ \dot{p} & = & -\langle\psi, \nabla_q V(\cdot, q)\psi\rangle, & & p(0) & = & \nabla_q S(q_0, 0), \end{array} \tag{21}$$

satisfies throughout the relation

$$p(t) = \nabla_q S(q(t), t). \tag{22}$$

This allows us to construct $S(\cdot, t)$ from a *fixed* initial phase $S(\cdot, 0)$ as long as the particle flow map Φ^t which maps the initial position q_0 to the solution $q(t)$ of the Hamiltonian system (21) at time t, i.e.,

$$\Phi^t q_0 = q(t),$$

is one-to-one. At times t, where at least two *different* particle pathes meet, the phase function S gets multi-valued and *the asymptotic expansion (18) ceases to be valid.* At those times there will be points $q_f = \Phi^t q_0$, for which the flow is even locally not one-to-one, i.e.,

$$\det D_q \Phi^t q|_{q=q_0} = 0. \tag{23}$$

Such a point q_f is called a *focal point* at time t and all focal points at a given time are called a *caustic*. However, there is a time $t_{\max}$ such that for $t < t_{\max}$ there are no focal points at all.

The continuity equation (20) for the probability density $a^2 = |\phi|^2$ describes the transport of the initial probability density $a^2(q,0)$ along the flow Φ^t of the velocity field $\dot{q} = \nabla_q S/M$. A well known consequence of this transport is the following local conservation property of the probability density:

$$\int_{\Phi^t W} a^2(q,t)dq = \int_W a^2(q,0)dq$$

for all domains $W \subset R^d$, cf. [8]. This implies in particular that an initially concentrated wave packet

$$a^2(q,0) = \chi_\epsilon(q-q_0) \approx \delta(q-q_0), \qquad \text{for } \epsilon \ll 1, \tag{24}$$

remains in the limit $\epsilon \to 0$ concentrated at the classical trajectory $q(t) = \Phi^t q_0$, i.e.,

$$a^2(q,t) \to \delta(q - q(t)).$$

Thus assumption (A) is satisfied for $t < t_{\max}$ if it is satisfied initially for $t = 0$ in the context of short wave asymptotics $M \to \infty$. We collect our new assumption:

(B) The initial preparation ϕ_0 is given as

$$\phi_0(q) = a_0(q) \exp\left(\frac{i}{\hbar} p_0 \cdot q\right),$$

where the probability density $a_0^2 = |\phi_0|^2$ is an *approximate δ-function* as defined in the appendix, i.e.,

$$a_0(q)^2 = \chi_\epsilon(q - q_0),$$

where χ has compact support.

We are now able to state in which sense the QCMD model

$$\begin{aligned} i\hbar\dot{\psi}_{QC} &= \left(-\frac{\hbar^2}{2m}\Delta_x + V(x,q)\right)\psi_{QC}, & \psi_{QC}|_{t=0} &= \psi_0, \\ M\dot{q} &= p, & q(0) &= q_0, \\ \dot{p} &= -\langle\psi_{QC}, \nabla_q V \psi_{QC}\rangle, & p(0) &= p_0 \end{aligned} \tag{25}$$

serves as an approximation of the system (16).

Theorem 4.2 *Assumption (B) implies that the QCMD system (25) satisfies*

$$\psi_{QC} = \psi_* + \mathcal{O}(\epsilon^2 + \hbar/\sqrt{M})$$

in the space $L^2(\mathbf{R}^d)$ *and*

$$q(t) = \langle \phi_*, q\phi_* \rangle + \mathcal{O}(\epsilon^2 + \hbar/\sqrt{M})$$

for all $t < t_{\max}$. *Moreover, assumption (A) of Theorem 4.1 is fulfilled for these* t *in the limit* $M \to \infty$.

Proof. The asymptotic expansion (18) together with Lemma 7.2 of the appendix yields the position expectation value

$$\langle \phi_*, q\phi_* \rangle = q(t) + \mathcal{O}(\epsilon^2 + \hbar/\sqrt{M})$$

and the following approximation of the potential for ψ_*:

$$\langle \phi_*, V(x, \cdot)\phi_* \rangle = V(x, q(t)) + \mathcal{O}(\epsilon^2 + \hbar/\sqrt{M}),$$

which implies the error between ψ_{QC} and ψ_* by arguments of perturbation theory, cf. [22]. □

Technical Aside. The detailed statement of the asymptotic expansion (18) as given in Theorem 7.3 of the appendix shows that the statement of assumption (A) concerning the support is in fact only valid *up to any power* of $\hbar/\sqrt{M}$. However, this decrease is rapidly enough to justify Theorem 4.1.

The advantage of the WKB derivation of the QCMD model (25) is the statement of assumptions under which it can be regarded as a good approximation. Conversely, if these assumptions are not fulfilled the QCMD model is in danger of largely deviating from the full quantum model. We stress this important point by collecting the central assumptions in the converse as *potential dangers*:

1. If the mass M of the classical particle becomes small, the approximation may be bad.

2. If the variance ϵ^2 is not small enough, thus allowing a certain initial uncertainty in space, we must face the effect that the "width" of the probability density a^2 increases with time due to the divergence of the velocity flow field. This is related to the fact that the Schrödinger equation disintegrates wave packets because of dispersion.

3. If the Hamilton-Jacobi equation forms caustics, i.e., if $t > t_{\max}$, the asymptotic expansion (18) is *not valid* even for very large masses M. Caustics may appear in the neighborhood of quantum mechanical diffraction of the heavier particle.

All these points indicate that a long term validity of the QCMD model cannot be expected. In Section 5 these potential dangers will be exemplified.

Remark. If the solution of the Hamilton-Jacobi equation gets *multivalued* after passing a focal point, the particle of M somewhat splits into several pathes. Using this multivalued solution one can extend the WKB method in a way that up to errors of $\mathcal{O}(\hbar/\sqrt{M})$ the wavefunction ϕ is concentrated on these particle pathes. As indicated at the end of Section 4.1 this yields a justification of the TDSCF method even in this case for $M \to \infty$. Since the WKB method cannot be extended as an asymptotic expansion in $\hbar/\sqrt{M}$ in the vicinity of focal points, the validity of the TDSCF method *at* a focal point remains to be doubtful.

4.3 Conservation of Energy

The total energy of the full quantum system (6) in the state Ψ is given by

$$E(\Psi) = -\frac{\hbar^2}{2m}\langle \Psi, \Delta_x \Psi\rangle - \frac{\hbar^2}{2M}\langle \Psi, \Delta_q \Psi\rangle + \langle \Psi, V\Psi\rangle.$$

Inserting the two approximation steps (separation and WKB limit), we get

$$\begin{aligned} E(\Psi) &= E(\Psi_\otimes) + \mathcal{O}(\epsilon) \\ &= \langle \psi_{QC}, H(t)\psi_{QC}\rangle - \frac{\hbar^2}{2M}\langle \phi_S, \Delta_q \phi_S\rangle + \mathcal{O}(\epsilon + \hbar/\sqrt{M}) \end{aligned}$$

with the time-dependent Hamilton operator

$$H = -\frac{\hbar^2}{2m}\Delta_x + V(\cdot, q(t))$$

and the semi-classical wavefunction

$$\phi_S(q,t) = a(q,t)\exp\left(\frac{iS(q,t)}{\hbar}\right).$$

Exploiting

$$\nabla_q \phi_S = \left(\nabla_q a + \frac{i}{\hbar} a \nabla_q S \right) \exp\left(\frac{iS}{\hbar} \right)$$

and Lemma 7.2 of the appendix, we get the following asymptotics for the kinetic energy of ϕ_S:

$$\begin{aligned} -\frac{\hbar^2}{2M} \langle \phi_S, \Delta_q \phi_S \rangle &= \frac{\hbar^2}{2M} \langle \nabla_q \phi_S, \nabla_q \phi_S \rangle \\ &= \frac{1}{2M} |p(t)|^2 + \frac{\hbar^2}{2M} \langle \nabla_q a, \nabla_q a \rangle + O(\epsilon^2). \end{aligned}$$

Remember, that $a^2(\cdot, t)$ is an approximate δ-function at position $q(t)$ and the relation (22) gives us $\nabla_q S(q(t), t) = p(t)$. Summarizing, we get

$$E(\Psi) = \langle \psi_{QC}, H(t) \psi_{QC} \rangle + \frac{1}{2M} |p(t)|^2 + \Delta E(t) + \mathcal{O}(\epsilon + \hbar/\sqrt{M}), \tag{26}$$

where the term

$$\Delta E(t) = \frac{\hbar^2}{2M} \langle \nabla_q a(\cdot, t), \nabla_q a(\cdot, t) \rangle$$

represents the *zero-point energy* or *self energy* of the "classical" particle with mass M.

Remark. Note that we do not have $|p(t)|^2/2M = \mathcal{O}(\hbar^2/M)$. The reason is that the asymptotic expansion (18), as stated in Theorem 7.3 of the appendix, is even valid for a kinetic energy bounded away from zero in the limit $M \to \infty$, i.e., it allows any initial momentum

$$|p_0|^2 \leq c\, M,$$

where c is some constant independent of M.

This self energy $\Delta E(t)$ deserves special attention: Its dependence on the variance ϵ^2 of the wavepacket is like $\mathcal{O}(\epsilon^{-2})$. If we choose for instance at the initial time $t = 0$ a Gaussian wavepacket ϕ_0 with the amplitude

$$a_0(q) = \frac{1}{(\epsilon\sqrt{2\pi})^{d/2}} \exp\left(-\frac{|q - q_0|^2}{4\epsilon^2} \right),$$

we obtain an initial self energy of

$$\Delta E_0 = \Delta E(0) = \frac{d\,\hbar^2}{8M\epsilon^2}. \tag{27}$$

As we will see, this self energy remains nearly constant in time. Since ΔE is part of the quantum mechanical description of the "classical" particle with mass M, it is reasonable to view the function

$$E_{QC}(t) = \langle \psi_{QC}, H(t)\psi_{QC} \rangle + \frac{1}{2M}|p(t)|^2$$

as the natural total energy for the QCMD system (25). This energy is easily seen to be a *conserved* quantity:

$$\begin{aligned}
\frac{dE_{QC}}{dt} &= \langle \psi_{QC}, \dot{H}\psi_{QC} \rangle + \frac{p}{M}\dot{p} + \underbrace{\langle \dot{\psi}_{QC}, H\psi_{QC} \rangle + \langle \psi_{QC}, H\dot{\psi}_{QC} \rangle}_{=0} \\
&= \langle \psi_{QC}, \nabla_q V \psi_{QC} \rangle \dot{q} + \dot{q}\dot{p} \\
&= 0.
\end{aligned}$$

Now, comparing the energy expression (26) at time $t > 0$ and at time $t = 0$, we obtain by conservation of $E(\Psi)$ and of E_{QC} that

$$\Delta E(t) = \Delta E_0 + \mathcal{O}(\epsilon + \hbar/\sqrt{M})$$

and

$$E(\Psi) = E_{QC} + \Delta E_0 + \mathcal{O}(\epsilon + \hbar/\sqrt{M}).$$

Thus, the quantum mechanical energy decomposes up to small terms into the energy of the QCMD model and the *initial* self energy of the "classical" particle.

For the purpose of numerical simulations, it is extremely helpful to note that the QCMD system (25) constitutes a canonical system with respect to the energy E_{QC}. To this end we decompose the Hamilton operator

$$H = H_s + iH_a$$

into the selfadjoint and skewadjoint part and the wavefunction

$$\psi_{QC} = \frac{1}{\sqrt{2\hbar}}(q_\psi + ip_\psi) \tag{28}$$

into a scaled real and imaginary part. Now, introducing the generalized position

$$Q = (q_\psi, q)^T$$

and generalized momentum

$$P = (p_\psi, p)^T$$

the energy reads as

$$E_{QC} = E_{QC}(Q,P) = \frac{1}{2\hbar}\left(\langle q_\psi, H_s q_\psi\rangle + \langle p_\psi, H_s p_\psi\rangle + 2\langle p_\psi, H_a q_\psi\rangle\right) + \frac{1}{2M}|p|^2.$$

A simple *formal* calculation shows, that the corresponding canonical equations

$$\dot{Q} = \frac{\partial}{\partial P} E_{QC}, \qquad \dot{P} = -\frac{\partial}{\partial Q} E_{QC}$$

are just another form of writing the QCMD system (25). However, one should note that the partial derivatives have to be interpreted as *functional derivatives*. One can easily circumvent the functional analytic technicalities if one considers Ritz-Galerkin approximation in some orthonormal function system.

Remark. The scaled decomposition (28) is commonly used in the literature to give the Schrödinger equation a canonical Hamiltonian structure. A more intrinsic way of this argument in the setting of infinite Hamiltonian systems can be found in [7][24].

5 Discussion and Examples

We shall now illustrate the potential dangers of the QCMD method as discussed at the end of Section 4.2. Since the first two of the mentioned problems, i.e., mass M too small and the disintegration of the wavepacket for larger times, meet common understanding, we herein concentrate on the third problem, the formation of *caustics*.

This point can nicely be illustrated by the numerical simulation of a simple collinear collision of a "classical" particle with a harmonic quantum oscillator (cf. Figure 2), a model problem which has been treated extensively in the literature without explanation of the differences between the QCMD and the full quantum approach (cf. [5][3]). Using the notation of Section 4, the Hamiltonian of the system in question is given by:

$$H \;=\; -\frac{\hbar^2}{2m}\Delta_x \;-\; \frac{\hbar^2}{2M}\Delta_q \;+\; \underbrace{\frac{m}{2}\omega^2 x^2 \;+\; U(|x-q|)}_{=V(x,q)}$$

with masses $M = 40\mathrm{u}$ and $m = 1\mathrm{u}$, roughly representing Argon (Ar) and a HCl oscillator respectively. For the interaction potential U we have taken

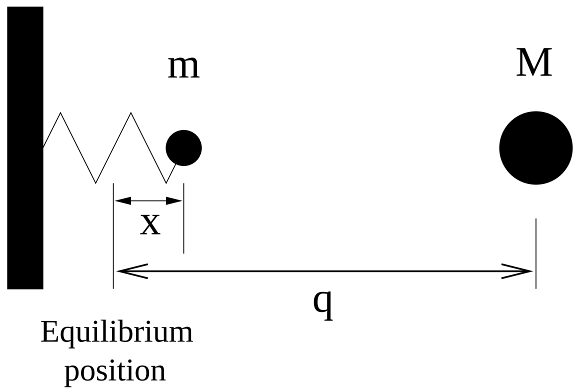

Figure 2: Scheme of the collinear test system.

the form (cf. [5][3])

$$U(r) \;=\; A \exp(-br)$$

with $A = 1.654 \cdot 10^3$ kcal/mol and $b = 2.438\text{Å}^{-1}$. The frequency ω of the undisturbed oscillator corresponds to a wavenumber of 1000cm^{-1} or to an energy of $\hbar\omega = 2.86$ kcal/mol. The initial wavepacket Ψ_0 is constructed as follows: $\Psi_0 = \psi_0 \otimes \phi_0$ is a tensor product of the ground state ψ_0 of the undisturbed oscillator and a Gaussian distribution for the "classical" particle:

$$\phi_0(q) \;=\; \frac{1}{(\epsilon\sqrt{2\pi})^{1/2}} \exp\left(-\frac{|q-\langle q\rangle_0|^2}{4\epsilon^2}\right) \exp\left(i\,\frac{\langle P\rangle_0}{\hbar}\,q\right)$$

with initial location $\langle q\rangle_0 = 5\text{Å}$, momentum $\langle P\rangle_0$ directed towards the oscillator's location in $x_0 = 0$ corresponding to an initial kinetic energy of 3.9 kcal/mol, and location uncertainty $\epsilon = 0.075\text{Å}$. We have performed full quantum (QD), QCMD- and TDSCF-calculations using the well-known Fourier-collocation technique as the space discretization and suitable *symplectic* time-discretizations based on operator splitting [26]. We have applied uniform time steps $\tau = 0.05$ fs over a total time interval $t/\text{fs} \in [0, 1000]$ and a spatial computation domain $x/\text{Å} \in [-1, 0.5]$ and $q/\text{Å} \in [1, 12]$ with 128×1024 meshpoints. Fortunately, for the QCMD-calculations only the 128 point x-grid is necessary — leading to a tremendous decrease in computational effort.

Figure 3 shows the expectation value $\langle q \rangle$ for the position of the classical particle computed via the full QD-simulation and the corresponding classical trajectory $q = q(t)$ of the QCMD-calculations. The results show, that the QCMD gives a very good approximation of the full quantum dynamics, however, with a small but clearly visible difference at the time $t = 350$fs of the reflection of the classical particle. Total energy is well-conserved in both cases by our numerical schemes (Figure 4), which perfectly reflects the analytical conservation of energy as discussed in Section 4.3. This should be contrasted with the observations in [3], where a *non-symplectic* numerical scheme was used.

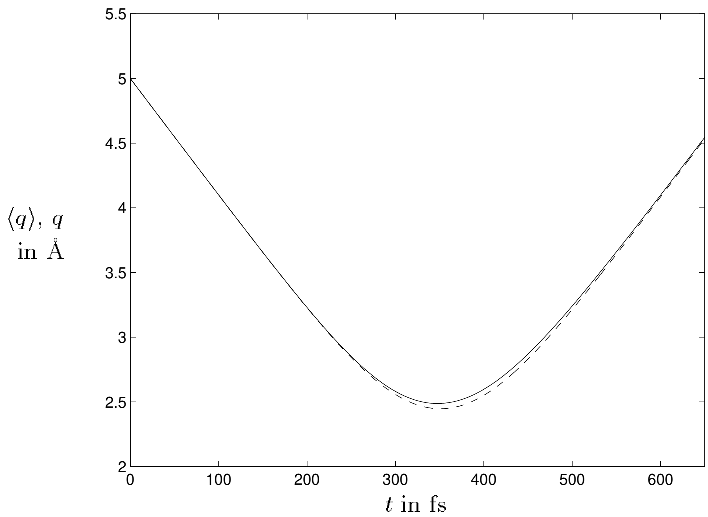

Figure 3: Results of QD- and QCMD-calculations. Shown is the position expectation $\langle q \rangle$ (solid line) of the classical particle and its classical QCMD-trajectory q (dashed line) versus time.

The difference between QD and QCMD in the neighborhood of the turning point are explained by identifying this point as a *focal point*. This is illustrated by Figure 5 which shows that two nearby starting particle pathes $q_l = q_l(t)$, $l = -1, 1$, cross the particle path $q(t)$ at this critical point. The q_l are solutions of

$$\begin{aligned} M\,\dot{q}_l &= p_l \\ \dot{p}_l &= -\langle \psi\,,\, \nabla_q V(\cdot, q_l)\, \psi \rangle, \end{aligned}$$

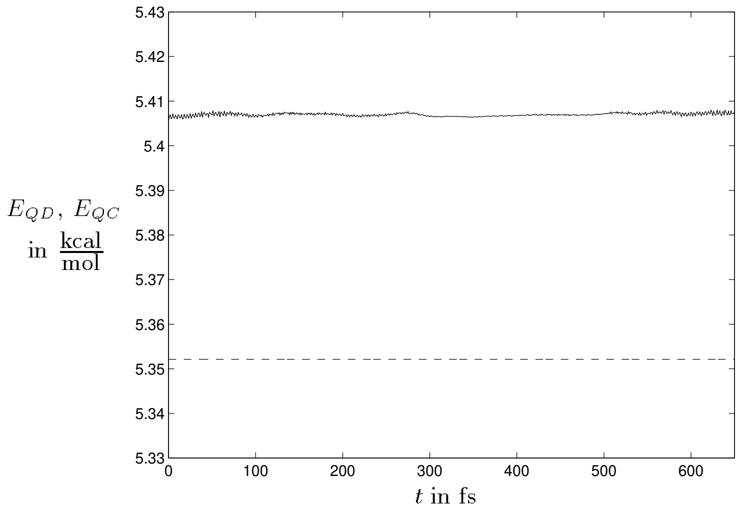

Figure 4: Conservation of energy in the QD-simulation (solid line) and the QCMD-simulation (dashed line). The difference between both values is caused by the zero-point energy $\Delta E_0 = \hbar^2/8M\epsilon^2 = 0.0535\,\text{kcal/mol}$ of the "classical" particle as discussed in Section 4.3.

with initial states

$$q_l(0) \;=\; \langle q\rangle_0 + l\,\delta q \qquad \text{and} \qquad p_l(0) = \langle P\rangle_0$$

with $\delta q = 0.01\text{Å}$. ψ is *fixed* to be the solution of the QCMD-calculation. Thus, small perturbation of the initial data result in *no* difference of the position value at the critical point. Exactly this is the meaning of the condition (23), which defines a focal point.

Our simple test system can also be used in order to illustrate the disintegration of the wavepacket because of dispersion. This effect will always be significant if the total simulation time T is large enough (as in our case with $T = 1\text{ps}$), being less important for smaller time scales ($T < 100\text{fs}$). Figure 6 shows the evolution of the statistical variances

$$\Delta q \;=\; \langle \Psi, q^2\,\Psi\rangle \;-\; \langle \Psi, q\,\Psi\rangle^2 \;=\; \langle q^2\rangle \;-\; \langle q\rangle^2$$

and $\Delta x = \langle x^2\rangle - \langle x\,\rangle^2$ of position measurement for the full quantum system with state Ψ. It is well-known that these magnitudes are the correct measures for the position uncertainty in a quantum system, i.e., for the disintegration of its wavepacket.

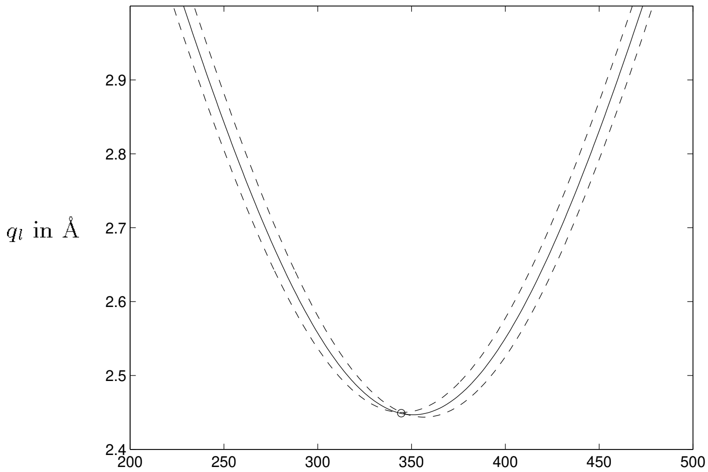

Figure 5: Crossing of different particle pathes q_l in the focal point (circle). The solid line represents the QCMD-trajectory q, the dashed lines the neighboring trajectories q_{-1} and q_1 started from a slightly different initial position. Notation as explained in the text.

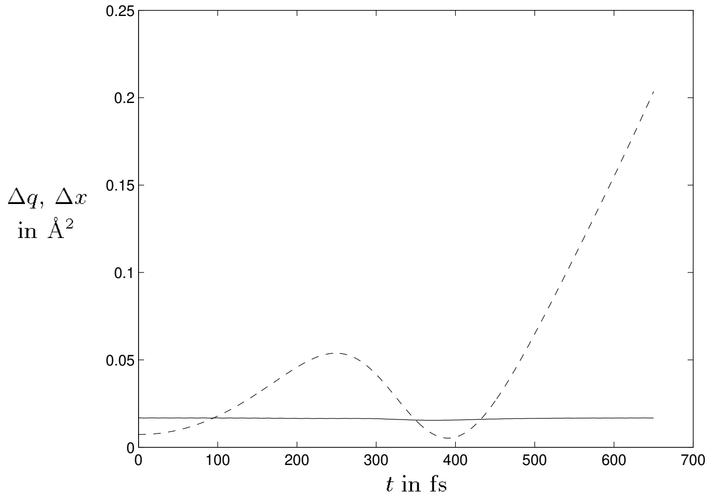

Figure 6: Evolution of variances Δq (dashed) and Δx (solid) of the full QD-wavepacket. Note the disintegration of the wavepacket in q-direction in which no attractive potential is present. It is increasing as long as the particle is moving "free" and decreasing during the collision.

The statistical variances Δq and Δx represent the variance ϵ^2 occurring in our approximation results. We know from the previous section that the separation step itself introduces an approximation error $\mathcal{O}(\epsilon)$. Therefore, we are interested in the error caused by separation in the test system. To that end, we compare the full quantum simulation with the corresponding TDSCF-calculations connected to the system (16). Figure 7 presents the two corresponding position expectations and a comparison with QCMD. Note, that *both*, TDSCF and QCMD, show deviations from the full quantum solution in the region of the focal point. This, indeed, illustrates that they are both subject to the same underlying approximation error caused by separation. Moreover, it exemplifies that the proposed analytical approach (justification of separation via the validity of the step TDSCF $\rightarrow$ QCMD) fits the real situation: The approximation quality of TDSCF and thus of separation decreases near the problematic point of the QCMD-approach.

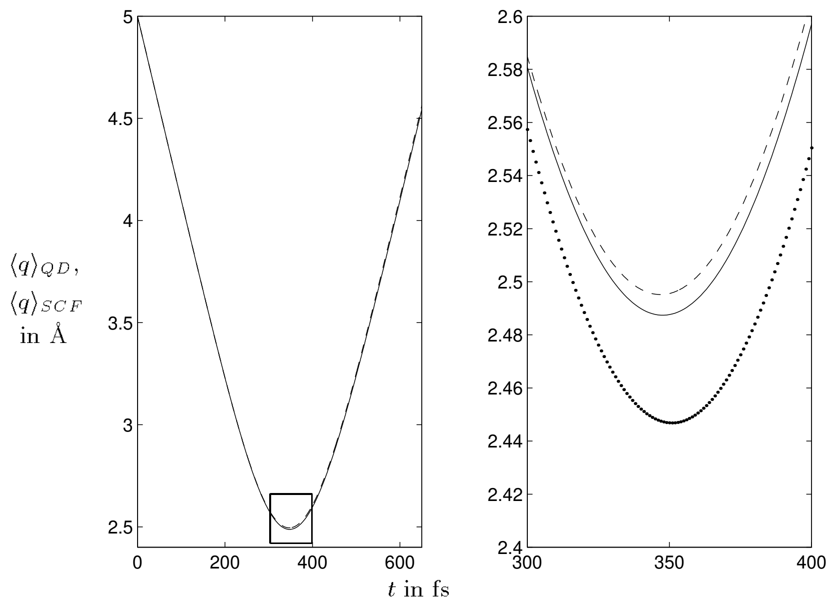

Figure 7: Results of QD- and TDSCF-calculations. The picture on the left hand side shows the corresponding position expectations $\langle q \rangle_{QD}$ (solid line) and $\langle q \rangle_{SCF}$ (dashed line) versus time. The region of the turning point (box) is magnified on the right hand side. Here, the additional dotted line represents the corresponding QCMD-trajectory q. Note, that this picture does *not* change, if we refine the stepsizes used.

6 Concluding Remarks

We have considered a *mixed quantum-classical* description of large (bio)molecular systems, which allows to describe most atoms by the means of classical mechanics but an important, small portion of the underlying system by the means of quantum mechanics. The starting point of our investigation has been to analyze how such a QCMD-model could be derived from the full Schrödinger equation and in which sense of approximation. That is, we were finally interested in a "partial classical limit" which has been established via the smallness of two parameters: variance ϵ^2 of the wavepacket representing the "classical" particle and $\hbar/\sqrt{M}$ corresponding to its mass. Our approximation result is two-fold:

(R1) Tensor product separation of the full wavefunction is accurate up to an error of $\mathcal{O}(\epsilon)$.

(R2) The classical trajectory computed from (21) approximates the position expectation of the classical part up to the error $\mathcal{O}(\epsilon^2 + \hbar/\sqrt{M})$.

Thus, the total approximation error of QCMD is of order $\mathcal{O}(\epsilon + \hbar/\sqrt{M})$. These results are valid under three *conditions*:

(C1) the mass M is large enough,

(C2) the initial variance $\epsilon^2(t_0)$ is small enough,

(C3) no caustics are present,

which on the other hand, if violated, are connected to scenarios of potential deficiencies of the QCMD as exemplified in Section 5.

Concerning result (R2) the following should be noted: We have chosen semi-classical limits according to the WKB method as represented by the left methodical branch of Figure 1. We could as well apply semi-classical limits via Gaussian wavepackets as represented by the right methodical branch of Figure 1. We would then arrive at the following alternative result (cf. [16]):

(R2') The semi-classical approximation of the classical particle by Gaussian wavepackets is accurate up to $\mathcal{O}(\sqrt{\hbar}/M^{1/4})$.

This avoids the ϵ-dependence in this part of the approximation but leads to a slower asymptotic error rate in $1/M$. But nevertheless, with regard to the total error as an approximation of the full Schrödinger equation, the

ϵ-dependence (R1) is again introduced by the underlying separation ansatz; resulting in the estimate $\mathcal{O}(\epsilon + \sqrt{\hbar}/M^{1/4})$ of the total approximation error, which is worse in comparison to our approach.

It should be emphasized, that we discuss the approximation of the full wavefunction Ψ in the L^2-norm. Thus, the results also hold for all expectation values of Ψ but not necessarily for "pointwise" quantities, which may be important. The Fourier spectrum of Ψ, e.g., is well-approximated in a L^2-average sense, but amplitudes of single frequencies may be completely wrong.

Note again that our *mixed* approach concerning a "partial classical limit" differs conceptually from approaches which are interested in a description of the system *entirely* on a quantal, semi-classical, or classical level.

Summarizing we shortly list some conclusions which are of particular importance for a comparison of the various models:

- If both conditions (C1) and (C3) are fulfilled, the QCMD does not seriously deteriorate the $\mathcal{O}(\epsilon)$-approximation already made by the separation ansatz. Thus, neither TDSCF nor QSCMD are "better" in this case and QCMD is the first choice for practical reasons.

- Using the presented approach, neither the QCMD nor the QSCMD nor even the TDSCF approach can be justified at caustics or focal points.

- The QCMD approximation *fails* at focal points. It eventually can again be a useful approximation after passing a focal point, but the complex phase of the wavefunction will jump at each of these transitions by a shift of $\pi/2$ (see [25]). This effect may explain some corresponding experimental observations (cf. [13], section II).

- The QCMD approximation can not even *detect* focal points or caustics. Focal points may be detected by a numerical solution of the Hamilton-Jacobi equation (19) for the phase S, e.g., using particle trajectory bundles (cf. [15]).

- Our results do not allow to decide the problem of whether QCSMD leads to a "better" representation of the influence of the potential curvature, as is expected in [21]. However, we note that the QSCMD also fails in detecting caustics and gets problems in this case, e.g., if the wavepacket splits into several subpackets.

Conclusively, the separation step seems to be the bottleneck for a better approximation theory or a more precise distinction between the various mixed quantum-(semi)classical models. Investigations concerning correction terms for the separation ansatz have already been presented in the literature (e.g., [14]), but — as far as the authors know — a corresponding mathematical justification is still missing.

7 Appendix

In this appendix we collect several mathematical details which we have omited in our previous discussions.

7.1 Approximate δ-Functions

Let $\chi \in C^\infty(\mathbf{R}^d)$ be a smooth function, which is normalized according to the following three conditions:

$$\begin{aligned} \text{i)} \qquad & \int_{\mathbf{R}^d} \chi(x)\, dx = 1, \\ \text{ii)} \qquad & \int_{\mathbf{R}^d} x\chi(x)\, dx = 0, \\ \text{iii)} \qquad & \int_{\mathbf{R}^d} (x \otimes x)\chi(x)\, dx = I, \end{aligned}$$

where $I \in \mathbf{R}^{d\times d}$ denotes the identity matrix. The scaled family

$$\chi_\epsilon(x) = \epsilon^{-d}\chi\left(\frac{x - x_0}{\epsilon}\right)$$

is called *an approximate δ-function* at position x_0, since

$$\chi_\epsilon \to \delta(\cdot - x_0)$$

for $\epsilon \to 0$ in the space $\mathcal{D}'$ of distributions. A simple example is given by the Gaussian distribution function

$$\chi_\epsilon(x) = \frac{1}{(\epsilon\sqrt{2\pi})^d} \exp\left(-\frac{|x - x_0|^2}{2\epsilon^2}\right)$$

of meanvalue x_0 and variance ϵ^2.

For technical reasons we impose the additional restriction, that χ is either Gaussian or has compact support.

Lemma 7.1 *For a given approximate δ-function χ_ϵ at position x_0 and a smooth function $f \in C^\infty(\mathbf{R}^d)$ of at most exponential growth we get*

$$\int_{\mathbf{R}^d} f(x)\chi_\epsilon(x)\,dx = f(x_0) + \frac{\epsilon^2}{2}\,\mathrm{trace}\, D^2 f(x_0) + \mathcal{O}(\epsilon^3).$$

Proof. Taylor expansion yields

$$\begin{aligned}
\int_{\mathbf{R}^d} f(x)\chi_\epsilon(x)\,dx &= \int_{\mathbf{R}^d} f(x_0+\epsilon x)\chi(x)\,dx \\
&= \int_{\mathbf{R}^d} \Bigg(f(x_0) + \epsilon\, Df(x_0)\cdot x + \frac{\epsilon^2}{2}\, D^2 f(x_0) : (x\otimes x) \\
&\qquad + \mathcal{O}(\epsilon^3)\Bigg)\,\chi(x)\,dx \\
&= f(x_0) + \frac{\epsilon^2}{2}\, D^2 f(x_0) : I + \mathcal{O}(\epsilon^3) \\
&= f(x_0) + \frac{\epsilon^2}{2}\,\mathrm{trace}\, D^2 f(x_0) + \mathcal{O}(\epsilon^3),
\end{aligned}$$

where we used the normalizations of χ. □

Now we apply this result to the solution ρ^ϵ of the continuity equation

$$\rho^\epsilon_t + \mathrm{div}(\rho^\epsilon v) = 0, \qquad \rho^\epsilon|_{t=0} = \chi_\epsilon, \tag{29}$$

with an approximate δ-function as initial data. The time-dependent velocity field $v : \mathbf{R}^d \times \mathbf{R} \to \mathbf{R}^d$ is supposed to be smooth and induces a flow map Φ^t by

$$\frac{d}{dt}\Phi^t x = v(\Phi^t x, t), \qquad \Phi^0 x = x.$$

We consider times $t \le t_{\max} < \infty$ for which Φ^t is a diffeomorphism onto $\mathbf{R}^d$, i.e.,

$$J(x,t) = \det D_x\Phi^t x \neq 0, \qquad t < t_{\max},\ x \in \mathbf{R}^d\,.$$

This is exactly the condition which precludes the existence of focal points in the WKB method of Section 4.2.

Lemma 7.2 *Given a smooth function $f \in C^\infty(\mathbf{R}^d)$ of at most exponential growth. If the initial data $\rho^\epsilon|_{t=0}$ of (29) constitute an approximate δ-function* *at position x_0, the asymptotic expansion*

$$\int_{\mathbf{R}^d} f(x)\rho^\epsilon(x,t)\,dx = f(\Phi^t x_0) + \frac{\epsilon^2}{2}\ \mathrm{trace}\, D_x^2 f(\Phi^t x)\Big|_{x=x_0} + \mathcal{O}(\epsilon^3),$$

is valid uniformly in $0 \le t \le t_{\max}$.

Proof. The solution ρ^ϵ of the continuity equation satisfies the transport relation

$$\rho^\epsilon(\Phi^t x, t) J(x,t) = \rho^\epsilon(x,0) = \chi_\epsilon(x),$$

which can be found for instance in [8]. Using the well known transformation formula of multiple integrals we thus get

$$\begin{aligned}\int_{\mathbf{R}^d} f(x)\rho^\epsilon(x,t)\,dx &= \int_{\mathbf{R}^d} f(\Phi^t x)\rho^\epsilon(\Phi^t x,t)\,J(x,t)\,dx \\ &= \int_{\mathbf{R}^d} f(\Phi^t x)\chi_\epsilon(x)\,dx.\end{aligned}$$

An application of Lemma 7.1 yields the desired result. □

7.2 Short Wave Asymptotics

Here we will give a mathematical rigorous statement of the short wave asymptotics. In the literature semi-classical approximations are usually stated for $\hbar \to 0$, which would not make much sense in our context. However, a simple trick translate the usual results to the limit $\kappa = \hbar/\sqrt{M} \to 0$. Asymptotics in this quantity κ appear for instance in the analysis of the Born-Oppenheimer adiabatic approximation — a setting where one also deals with some large mass ratio M/m. A discussion of the adiabatic approximation in the framework of semiclassical limits may be found in [9][17].

Theorem 7.3 *Given the solution $\psi \in C^\infty$ of the time-dependent Schrödinger equation*

$$i\hbar\dot{\psi} = -\frac{\hbar^2}{2M}\Delta\psi + V(x,t)\psi$$

to the initial data

$$\psi(x,0) = a_0(x)\exp\left(\frac{i}{\hbar}S_0^M(x)\right).$$

We assume that

i) $V \in C^\infty$ *is uniformly bounded from below:*

$$\inf_{x\in\mathbf{R}^d} V(x,t) \geq K > -\infty, \qquad \forall t \geq 0.$$

ii) $a_0 \in C^\infty$ *has compact support.*

iii) $S_0^M \in C^\infty$ *is depending on* M *in such a way, that* $S_0^M/\sqrt{M}$ *is bounded in* C^∞ *and the Hamilton-Jacobi equation (30) has no caustics for* $t \leq t_{\max}$ *uniformly in* M.

Then we get the asymptotic expansion

$$\psi(x,t) = a(x,t)\exp\left(\frac{i}{\hbar}S(x,t)\right) + R(x,t),$$

where the remainder satisfies the estimate

$$\|R\|_{C([0,t_{\max}],L^2(\mathbf{R}^d))} \leq c\frac{\hbar}{\sqrt{M}}$$

for $\hbar/\sqrt{M}$ *sufficiently small. The phase function* S *fulfills the Hamilton-Jacobi equation*

$$S_t + \frac{1}{2M}|\nabla S|^2 + V = 0, \qquad S|_{t=0} = S_0^M, \tag{30}$$

and the amplitude a *satisfies*

$$\frac{\partial}{\partial t}a^2 + \operatorname{div}\left(a^2\frac{\nabla S}{M}\right) = 0, \qquad a|_{t=0} = a_0.$$

Moreover we have outside the support of a

$$\|R(\cdot,t)\|_{L^2(\mathbf{R}^d\setminus\operatorname{supp} a(\cdot,t))} = \mathcal{O}\left((\hbar/\sqrt{M})^\infty\right)$$

uniformly in $t \in [0, t_{\max}]$.

Proof. We abbreviate $\kappa = \hbar/\sqrt{M}$ and introduce the new time variable $\tau = t/\sqrt{M}$. The Schrödinger equation transforms with $\hat{\psi}(x,\tau) = \psi(x,\tau\sqrt{M})$ to

$$i\kappa\frac{d}{d\tau}\hat{\psi} = -\frac{\kappa^2}{2}\Delta\hat{\psi} + V(x,\tau\sqrt{M})\hat{\psi}$$

with initial condition

$$\hat{\psi}(x,0) = a_0(x)\exp\left(\frac{i}{\kappa}\hat{S}_0(x)\right), \qquad \hat{S}_0 = S_0^M/\sqrt{M}.$$

Theorem 12.3 of Maslov and Fedoriuk [25] states that for some time $\tau_{\max}$ the asymptotic expansion

$$\hat{\psi}(x,\tau) = \hat{a}(x,\tau)\exp\left(\frac{i}{\kappa}\hat{S}(x,\tau)\right) + \hat{R}(x,\tau) \tag{31}$$

is valid with the remainder $\hat{R}$ bounded by

$$\|\hat{R}\|_{C([0,\tau_{\max}],L^2(\mathbf{R}^d))} \le c\kappa, \qquad \|\hat{R}(\cdot,\tau)\|_{L^2(\mathbf{R}^d \setminus \operatorname{supp}\hat{a}(\cdot,\tau))} = \mathcal{O}(\kappa^\infty) \tag{32}$$

for sufficiently small κ. Here the phase function fulfills

$$\hat{S}_\tau + \frac{1}{2}|\nabla\hat{S}|^2 + V = 0, \qquad \hat{S}|_{t=0} = \hat{S}_0,$$

and $\tau_{\max}$ may be chosen as large as necessary to prevent the first appearance of a caustic for $\hat{S}$. The amplitude $\hat{a}$ obeys

$$\frac{\partial}{\partial\tau}\hat{a}^2 + \operatorname{div}\left(\hat{a}^2\nabla\hat{S}\right) = 0, \qquad \hat{a}|_{t=0} = a_0. \tag{33}$$

Now we set

$$S(x,t) = \sqrt{M}\hat{S}(x,t/\sqrt{M}), \quad a(x,t) = \hat{a}(x,t/\sqrt{M})$$

and

$$R(x,t) = \hat{R}(x,t/\sqrt{M}).$$

A simple calculation shows that S fulfills the Hamilton-Jacobi equation (30) to the initial data S_0^M, which by definition of $\tau_{\max}$ has no caustics for $t \le \tau_{\max}\sqrt{M}$. However assumption (iii) precludes caustics prior to $t_{\max}$ which shows that we can choose at least

$$\tau_{\max} = t_{\max}/\sqrt{M}.$$

Thus we have the validity of the asymptotic expansion (31) within the required time interval. All other assertions are simple transformations of (32) and (33). $\square$

Remark. In many cases, like for the initial choice

$$S_0^M = \sqrt{M}\hat{S}_0$$

with a fixed $\hat{S}_0$, this proof shows that one even has

$$t_{\max} = \mathcal{O}(\sqrt{M}).$$

This means, that caustics appear the later the heavier our particle is — even if we fix the initial kinetic energy.

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