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Quantum-classical molecular dynamics as an approximation to full quantum dynamics

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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 wave function and short wave asymptotics for its ''classical'' part. *Both* steps can be rigorously justified under the *same* smallness assumptions. This throws some light on the time-dependent self-consistent-field method and on mixed quantum-semiclassical models, which also depend on the separation step. On the other hand, the theory leads to a characterization of the critical situations in which the QCMD model is in danger of largely deviating from the solution of full Schrödinger equation. These critical situations are exemplified in an illustrative numerical simulation: the collinear collision of a classical particle with a harmonic quantum oscillator. © *1996 American Institute of Physics.* [S0021-9606(96)00727-1]

I. 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 Fig. 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, semiclassically, 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. Refs. 12 and 15 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 semiclassical models for most of the parts with a quantum description for the particularly interesting part, usually called *quantum-semiclassical* (QSCMD) models (see Ref. 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 Refs. 2, 5, and 6; more references may be found in studies for van der Waals molecules, e.g., Refs. 13 and 20).

Unfortunately enough, essentially *two* basic QCMD models are proposed in the literature[4,5] 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 they require significantly larger computational effort. We propose that a model selection should be guided by a rigorous 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 semiclassical approximations are usually applied to the *entire* quantum system, either using Gaussians (as Refs. 21 and 22, or the mathematical investigation[17]) or the WKB method (as many textbooks like Refs. 10 and 23 or mathematical investigations like Refs. 1 and 25). As pointed out in Ref. 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 rigorous analysis of any time-dependent ''partial classical

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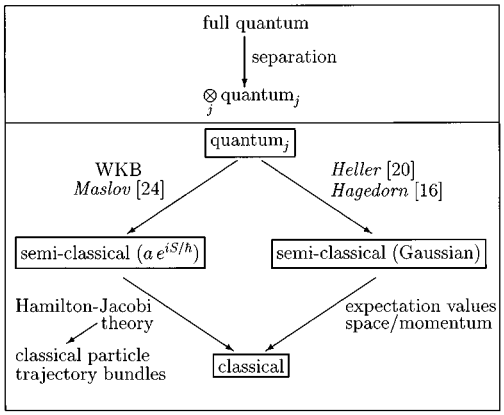

FIG. 1. Different approaches to quantum-(semi) classical models. In mixed approaches the full quantum system is first separated via the tensor product ansatz into parts j with coupled quantum description. Then, the evolution of each part j can be modeled on different levels: quantally, semiclassically, 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.

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 Gerber and collaborators (cf. Refs. 15, or 16): 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 rigorous 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 the less complicated of both models may directly be derived from the full quantum approach. Third, in Sec. IV, this motivation is mathematically justified. This implies a characterization of the possibly problematic scenarios for QCMD models, which is exemplified in Sec. V. 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.

II. QCMD MODELS

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

Let the two particles have space coordinates $x \in \mathbb{R}^d$ and $q \in \mathbb{R}^d$ 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 wave function $\psi = \psi(x,t)$ 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 parametrized 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 Eq. (2) are the so-called Hellman–Feynman forces. Together, Eqs. (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 Eq. (1) together with Eq. (2) constitutes a closed system of equations. This choice is used, e.g., in Ref. 13 or in Refs. 5 and 6, where, in addition, the Schrödinger equation is replaced by the Liouville–von Neumann equation.

(2) In Ref. 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 Eq. (1). This means, $\mu = q(t_0)$ is considered as *parameter* in Eq. (1) and the wave function $\psi = \psi(\mu,t)$ as in $[t_0, t_0+\Delta t]$ explicity depending on this pa-

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rameter. After this, the classical position q has to be updated via Eq. (2). The dependence of ψ on μ has to be taken into account yielding the derivative

$$\nabla_q U = (\langle \psi, \nabla_\mu V(\cdot,\mu)\psi\rangle + \langle \nabla_\mu \psi, V(\cdot,q)\psi\rangle + \langle \psi, V(\cdot,q)\nabla_\mu \psi\rangle)|_{\mu=q}, \tag{5}$$

which, in turn, leads to the necessity of evaluating $\nabla_\mu \psi$ in addition. An algorithmic realization of this approach is presented in Ref. 4, resulting in a simulation method which causes much more computational effort in real life applications than the simple choice Eq. (4). For test simulations using this model see Refs. 2 and 3.

We will show in this paper that the *first* model is naturally related 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 two-particle wave function $\Psi(t)=\Psi(x,q,t)$ lives in the state space $\mathscr{H}=L^2(\mathbb{R}^{2d})$. We will accomplish such a relation via two different approaches: A motivation via the Ehrenfest theorem (Sec. III) and a rigorous mathematical justification (Sec. IV).

III. MOTIVATION OF QCMD FROM FULL QUANTUM MODEL

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

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

We are interested in the time dependency of 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 Eq. (6). The Ehrenfest theorem[28] yields

$$\frac{d}{dt}\langle q\rangle = M^{-1}\langle P\rangle, \qquad \frac{d}{dt}\langle P\rangle = -\langle \nabla_q V\rangle, \tag{7}$$

with

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

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, Eq. (7) is a pure quantum theoretical equation. But Eq. (8) shows that, already on this level, the gradient is *inside* the expectation value, thus uniquely leading us to model Eq. (4) *without* need for correction terms. Indeed, one arrives at exactly the same result by switching into the Heisenberg picture (cf. Ref. 19).

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 wave functions 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.,

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

with $\epsilon(t)\leqslant\epsilon\ll 1$. Inserting this into Eq. (8) we get via Taylor expansion:

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

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 Eq. (2) and choice Eq. (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 defined in the Appendix—but on the smallness of its variance or location uncertainty $\epsilon(t)^2\ll 1$. Since ''small'' is a relative notion, we will relate ϵ to a typical length L, which is characteristic for the molecular system under investigation, e.g., the width of a potential well or its radius of curvature.

IV. MATHEMATICAL DERIVATION OF QCMD

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

(1) ϵ^2, the variance of the probability density for the particle of mass M at time zero (cf. the previous section),
(2) $\sqrt{m/M}$, 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 now works in two steps:

(1) *Separation*. This yields to an $\mathscr{O}(\epsilon/L)$ perturbation of the wave function.
(2) *Short wave asymptotics*. This yields an additional error term for the QCMD model of order $\mathscr{O}[(\epsilon/L)^2 + \sqrt{m/M}]$.

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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,

$$\epsilon/L \quad and \sqrt{m/M} \quad sufficiently\ small\ and\ t<t_{\max}.$$

These restrictions will be discussed later on.

Remark. Traditionally, the short wave asymptotics is presented as an $\mathcal{O}(\hbar)$ approximation, i.e., classical mechanics is understood as the limit $\hbar\to 0$ of quantum mechanics. Since this limit can only be applied to the full system, the procedure has to be changed for a *partial limit*. However, a simple scaling argument shows that the term $\sqrt{m/M}$ can be used instead of $\hbar$, cf. Refs. 7 and 18.

A. First approximation step: Separation

We start with the TDSCF equations, i.e., the following system of two coupled one-particle Schrödinger equations:

$$\begin{aligned} i\hbar\dot{\psi} &= \left(-\frac{\hbar^2}{2m}\Delta_x + \langle\phi, V(x,\cdot)\phi\rangle\right)\psi, \quad \psi(x,0)=\psi_0(x), \\ i\hbar\dot{\phi} &= \left(-\frac{\hbar^2}{2M}\Delta_q + \langle\psi, V(\cdot,q)\psi\rangle\right)\phi, \quad \phi(q,0)=\phi_0(q). \end{aligned} \tag{12}$$

This nonlinear system is uniquely solvable as can be proven by Galerkin approximation and energy based compactness arguments. Following Ref. 22, Eq. (4.4)[7] we construct the full space wave function

$$\Psi_\otimes = \exp\left(\frac{i}{\hbar}\int_0^t \langle(\psi\otimes\phi)(s), V(\psi\otimes\phi)(s)\rangle ds\right)\cdot\psi\otimes\phi, \tag{13}$$

which is the solution of the following *modified full Schrödinger equation*:

$$i\hbar\frac{d}{dt}\Psi_\otimes = \left(-\frac{\hbar^2}{2m}\Delta_x - \frac{\hbar^2}{2M}\Delta_q + V_\otimes(x,q,t)\right)\Psi_\otimes,$$
$$\Psi_\otimes|_{t=0} = \psi_0\otimes\phi_0,$$

with the modified potential

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

Note that up to phase factors this modified full Schrödinger equation is completely equivalent to the TDSCF system [see Eq. (12)]. Now, we investigate whether the wave function $\Psi_\otimes$ constitutes an approximation of the solution Ψ of the full Schrödinger Eq. (6) with the special initial data

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

To this end, we make the following assumption:

(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:

$$\operatorname{diamsupp}\phi(\cdot,t) = \mathcal{O}(\epsilon/L).$$

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

Assumption (A) implies that the wave packet ϕ is concentrated along some particle path $q(t)$. This assumption will be simplified in Sec. IV B.

Exploiting the properties of the approximate δ function ϕ via Taylor expansion, it can be shown that for $q\in\operatorname{supp}\phi(\cdot,t)^2$:

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

By standard results from perturbation theory this gives us our main approximation result for the separation step (for the details of a proof see Ref. 7):

Theorem 4.1

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

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

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

Since the system (12) is the basis of the so-called *time-dependent self-consistent field* (TDSCF) calculations (cf. Ref. 15), we have thus given some justification of this approach. It should be emphasized that this justification only requires that *one* of the wave functions in Eq. (12) is an approximate δ function while the form of the other one is not restricted. We should also 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.

B. Second approximation step: Short-wave asymptotics

Now, we will give a further simplification of the separated system (12) 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 semiclassical approximation in the literature, one can prove the validity of the following *asymptotic expansion*:

$$\phi(q,t) = a(q,t)\exp\left(i\frac{S(q,t)}{\hbar}\right) + \mathcal{O}\left(\sqrt{\frac{m}{M}}\right). \tag{14}$$

See Ref. 7 for details like the dependence of the $\mathcal{O}$ term on the ratio of the masses.

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

$$\frac{\partial S}{\partial t} + \frac{1}{2M}(\nabla_q S)^2 + \langle\psi, V(\cdot,q)\psi\rangle = 0 \tag{15}$$

and a continuity equation for a^2,

$$\frac{\partial a^2}{\partial t} + \operatorname{div}_q\left(a^2\frac{\nabla_q S}{M}\right) = 0. \tag{16}$$

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Now, Eq. (15) 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

$$\begin{aligned}&\dot{q}=M^{-1}p, \quad q(0)=q_0,\\ &\dot{p}=-\langle\psi,\nabla_q V(\cdot,q)\psi\rangle, \quad p(0)=\nabla_q S(q_0,0),\end{aligned} \tag{17}$$

satisfies throughout the relation

$$p(t)=\nabla_q S[q(t),t]. \tag{18}$$

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 (17) at time t, i.e.,

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

is one-to-one. At times t, where at least two *different* particle paths meet, the phase function S gets multivalued and the *asymptotic expansion (14) 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.,

$$\det D_q\Phi^t q|_{q=q_0}=0. \tag{19}$$

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 (16) 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 $W\subset\mathbb{R}^d$, cf. Ref. 9. This implies in particular that an initially concentrated wave-packet

$$a^2(q,0)=\chi_\epsilon(q-q_0)\approx\delta(q-q_0) \quad \text{for } \epsilon\ll L \tag{20}$$

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 $m/M\to 0$. 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

$$\begin{aligned}&i\hbar\dot{\psi}_{\mathrm{QC}}=\left(-\frac{\hbar^2}{2m}\,\Delta_x+V(x,q)\right)\psi_{\mathrm{QC}}, \quad \psi_{\mathrm{QC}}|_{t=0}=\psi_0,\\ &M\dot{q}=p, \quad q(0)=q_0,\\ &\dot{p}=-\langle\psi_{\mathrm{QC}},\nabla_q V\psi_{\mathrm{QC}}\rangle, \quad p(0)=p_0\end{aligned} \tag{21}$$

serves as an approximation of the system (12).

Theorem 4.2

Assumption (B) implies that the QCMD system (21) satisfies

$$\psi_{\mathrm{QC}}=\psi+\mathcal{O}[(\epsilon/L)^2+\sqrt{m/M}]$$

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

$$q(t)=\langle\phi,q\phi\rangle+\mathcal{O}[(\epsilon/L)^2+\sqrt{m/M}]$$

for all $t<t_{\max}$. Moreover, assumption (A) of Theorem 4.1 is fulfilled for these t in the limit $m/M\to 0$.

For a proof see again Ref. 7. It is again based on an exploitation of the properties of the approximate δ function a^2 via Taylor expansion and on arguments of perturbation theory.

The advantage of the WKB derivation of the QCMD model (21) 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, in nonharmonic potentials, the Schrödinger equation tends to disintegrate wave-packets because of dispersion.

(3) If the Hamilton–Jacobi equation forms caustics, i.e., if $t>t_{\max}$, the asymptotic expansion (14) 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 Sec. V 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 paths. Using this multivalued solution one can extend the WKB method in a way that up to errors of $\mathcal{O}(\sqrt{m/M})$ the wave function ϕ is concentrated on these particle paths. As indicated at the end of Sec. IV A this yields a justification of the TDSCF method even in this case for large M/m. Since the WKB method cannot be extended

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as an asymptotic expansion in $\sqrt{m/M}$ in the vicinity of focal points, the validity of the TDSCF method at a focal point remains to be doubtful.

C. Conservation of energy and canonical structure

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

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

with the time-dependent Hamilton operator

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

and the semiclassical wave function

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

Remember, that $a^2(\cdot,t)$ is an approximate δ-function at position $q(t)$ and that the relation (18) gives us $\nabla_q S(q(t),t)=p(t)$. This allows to derive (see Ref. 7 for details)

$$\begin{aligned}E(\Psi)&=\langle\psi_{\mathrm{QC}},H(t)\psi_{\mathrm{QC}}\rangle+\frac{1}{2M}|p(t)|^2\\&\quad+\Delta E(t)+\mathcal{O}(\epsilon/L+\sqrt{m/M}),\end{aligned}\tag{22}$$

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

$$\Delta E_0=\Delta E(0)=\frac{d\hbar^2}{8M\epsilon^2}.\tag{23}$$

Since ΔE is part of the quantum mechanical description of the ''classical'' particle with mass M, it is reasonable to view the function

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

as the natural total energy for the QCMD system (21). This energy is easily seen to be a *conserved* quantity. Now, comparing the energy expression (22) at time $t>0$ and at time $t=0$, we obtain by conservation of $E(\Psi)$ and of E_{QC} that the self energy ΔE remains nearly constant in time,

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

In consequence the quantum mechanical energy decomposes up to small terms into the energy E_{QC} of the QCMD model and the *initial* self energy of the ''classical'' particle,

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

Any numerical simulation of the QCMD model should reproduce the conservation of E_{QC}.

For the construction of such numerical methods, it is extremely helpful to note that the QCMD system (21) constitutes a canonical system with respect to the energy E_{QC}, i.e., that the evolution of Eq. (21) is *symplectic*. To this end we decompose the Hamilton operator

$$H=H_s+iH_a$$

into the selfadjoint and skewadjoint part and the wave function

$$\psi_{\mathrm{QC}}=\frac{1}{\sqrt{2\hbar}}(q_\psi+ip_\psi)\tag{24}$$

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

$$\begin{aligned}E_{\mathrm{QC}}&=E_{\mathrm{QC}}(Q,P)\\&=\frac{1}{2\hbar}(\langle q_\psi,H_s q_\psi\rangle+\langle p_\psi,H_s p_\psi\rangle\\&\quad+2\langle p_\psi,H_a q_\psi\rangle)+\frac{1}{2M}|p|^2.\end{aligned}$$

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

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

are just another form of writing the QCMD system (21).

Remark. The scaled decomposition (24) 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 Refs. 8 and 24.

V. DISCUSSION AND EXAMPLES

We shall now illustrate the potential dangers of the QCMD method as discussed at the end of Sec. IV B. Since the first two of the mentioned problems, i.e., mass M too small and the disintegration of the wave packet for larger

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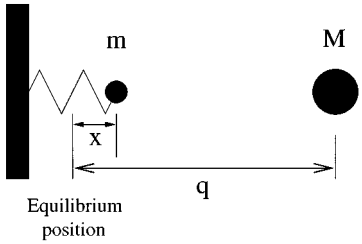

FIG. 2. Scheme of the collinear test system.

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. Fig. 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. Refs. 3 and 5). Using the notation of Sec. IV, the Hamiltonian of the system in question is given by

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

with masses $M=40$ u and $m=1$ u. For the interaction potential U we have taken the form (cf. Refs. 3 and 5)

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

with $A=1.654\times10^3$ kcal/mol and $b=2.438$ Å^{-1}. The frequency ψ of the undisturbed oscillator corresponds to a wave number of 1000 cm^{-1} or to an energy of $\hbar\psi=2.86$ kcal/mol. The initial wave packet 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 $\langle q\rangle_0=5$ 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 $\epsilon=0.075$ Å.

We have performed full quantum (QD), QCMD, and TDSCF calculations using the well-known Fourier-collocation technique as the space discretization and suitable second order *symplectic* time-discretizations based on operator splitting.[26] We have applied uniform time steps $\tau=0.01$ 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 256×1024 meshpoints. Fortunately, for the QCMD calculations only the 256 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

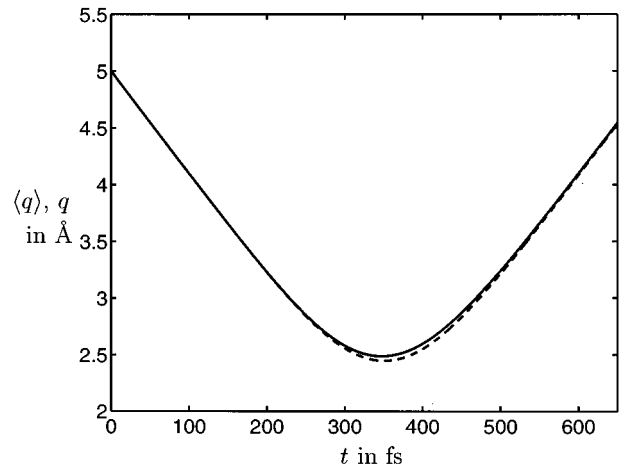

FIG. 3. Results of QD and QCMD calculations. The position expectation $\langle q\rangle$ (solid line) of the classical particle and its classical QCMD-trajectory q (dashed line) are shown vs time.

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 (Fig. 4), which reflects the analytical conservation of energy as discussed in Sec. IV C. This should be contrasted with some observations in Ref. 3, where a *nonsymplectic* numerical scheme was used.

Remark. Obviously, the *energy exchange* between the quantum and the classical part is of main importance for the dynamical process. Hence, an accurate reproduction of the energies in the system is an urgent requirement for all discretization schemes. However, there are no efficient schemes which conserve the energy *exactly*. For all practical reasons

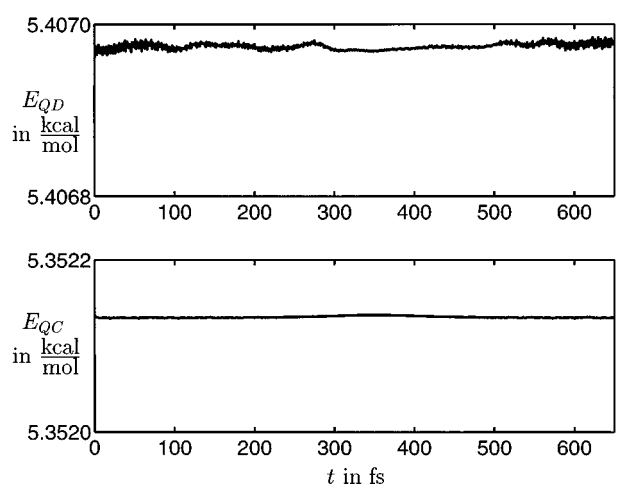

FIG. 4. Conservation of energy in the QD simulation (top) and the QCMD simulation (bottom). The difference between both values is caused by the zero-point energy $\Delta E_0=\hbar^2/8M\epsilon^2=0.0548$ kcal/mol of the ''classical'' particle as discussed in Sec. IV C. In both cases the maximal energy deviation is below 0.001%; compare the remark below.

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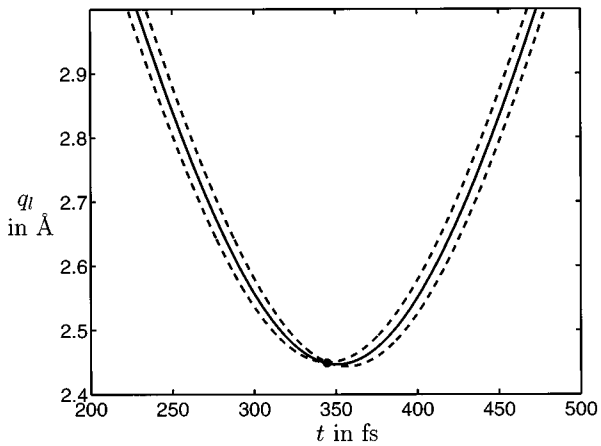

FIG. 5. Crossing of different paths q_l in the focal point (circle). The solid line represents the QCMD-trajectory q, the dashed lines the neighboring trajectories q_{-1} and q_1 started from a slightly different initial position. Notation as explained in the text.

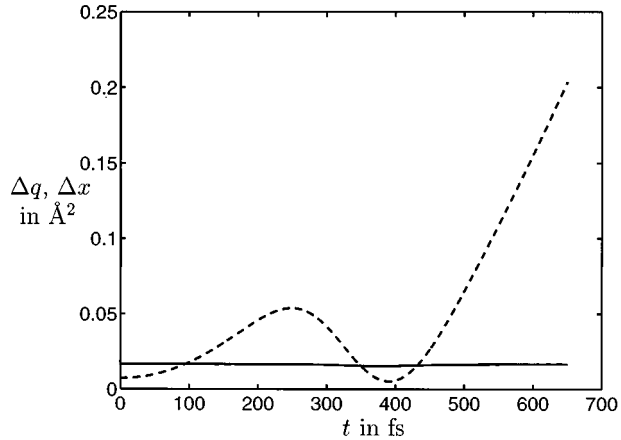

FIG. 6. Evolution of variances Δq (dashed) and Δx (solid) of the full QD wave packet. Note the disintegration of the wave packet in q direction in which no attractive potential is present. It is increasing as long as the particle is moving ''free'' and decreasing during the collision.

it is sufficient to use so called *symplectic* discretizations, which conserve the energy within a *very accurate* deviation range even for *long time simulations*, cf. Ref. 27. In contrast to this, ad hoc schemes typically cause an *energy drift* which increases in time—thus being not appropriate for our problem.

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 Fig. 5, which shows that two nearby starting particle paths $q_l = q_l(t)$, $l = -1,1$, cross the particle path $q(t)$ at this critical point. The q_l are solutions of

$$M\dot{q}_l = p_l,$$

$$\dot{p}_l = -\langle \psi, \nabla_q V(\cdot, q_l)\psi \rangle,$$

with initial states

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

with $\delta q = 0.01$ 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 (19), which defines a focal point.

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

$$\Delta_q = (\Psi, q^2\Psi) - \langle \Psi, q\Psi \rangle^2 = \langle q^2 \rangle - \langle q \rangle^2,$$

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 wave packet.

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 (12). 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→QCMD) fits

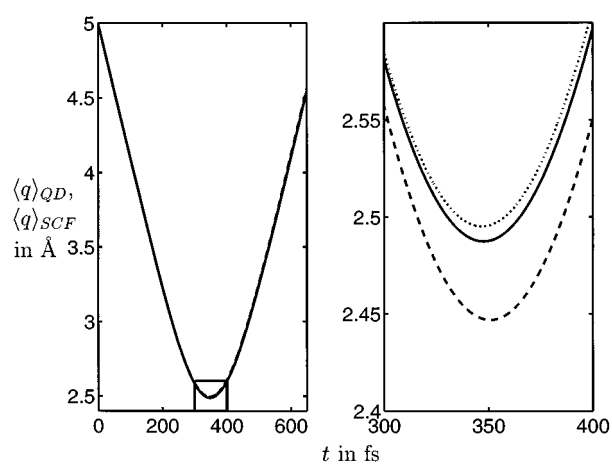

FIG. 7. Results of QD and TDSCF calculations. The picture on the left-hand side shows the corresponding position expectations $\langle q \rangle_{\mathrm{QD}}$ (solid line) and $\langle q \rangle_{\mathrm{SCF}}$ (dashed line) vs time. The region of the turning point (box) is magnified on the right-hand 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.

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the real situation: The approximation quality of TDSCF and thus of separation decreases near the problematic point of the QCMD approach.

VI. 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. This differs conceptually from all approaches which are interested in a description of the system *entirely* on a quantal, semiclassical, or classical level.

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 wave packet representing the ''classical'' particle and $\sqrt{m/M}$ corresponding to its mass. Our approximation result is twofold:

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

(R2) The classical trajectory computed from Eq. (17) approximates the position expectation of the classical part up to the error $\mathcal{O}[(\epsilon/L)^2+\sqrt{m/M}]$.

Thus, the total approximation error of QCMD is of order $\mathcal{O}(\epsilon/L+\sqrt{m/M})$. 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 Sec. V.

Concerning result (R2) the following should be noted: We have chosen semiclassical limits according to the WKB method as represented by the left methodical branch of Fig. 1. We could as well apply semiclassical limits via Gaussian wave packets as represented by the right methodical branch of Fig. 1. We would then arrive at the following alternative result (cf. Ref. 17):

(R2′) The semiclassical approximation of the classical particle by Gaussian wave packets is accurate up to $\mathcal{O}[(m/M)^{1/4}]$.

This avoids the ϵ dependence in this part of the approximation but leads to a slower asymptotic error rate in m/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 $\mathcal{O}[\epsilon/L+(m/M)^{1/4}]$ 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 wave function 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 the amplitudes of single frequencies may be completely wrong.

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

(i) The given error analysis of the separation step, on which all the mentioned models like TDSCF, QSCMD, and QCMD are based, requires the smallness of the uncertainty for at least one particle for all times. This can be concluded from the smallness of the *initial* uncertainty, if we are able to take the classical limit for this particle, i.e., if m/M is small. Thus our justification of TDSCF and QSCMD covers exactly the situation, for which QCMD is applicable.

(ii) 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 wave function will jump at each of these transitions by a shift of $\pi/2$ (see Ref. 25). This effect may explain some corresponding experimental observations (cf. Ref. 13, Sec. II).

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

(iv) Our results do not allow to decide the problem of whether QSCMD leads to a ''better'' representation of the influence of the potential curvature, as is expected in Ref. 22. However, we note that the QSCMD should also fail in detecting caustics and should get problems in this case, e.g., if the wave packet splits into several subpackets.

Conclusively, a better understanding of the separation step seems to be the bottleneck for a better approximation theory and 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., Ref. 14), but—as far as the authors know—a corresponding mathematical justification is still missing.

ACKNOWLEDGMENTS

It is a pleasure to thank P. Bala and B. Lesyng for intensive discussions on the subject and for providing background information on their work.[2–4] We thank B. Schmidt for pointing out Ref. 15 and S. Reich for insisting on the canonical structure of QCMD and for Ref. 24.

APPENDIX

We herein give a definition of the notion ''approximate δ function'': Let $\chi\in C^\infty(\mathbb{R}^d)$ be a smooth function, which is normalized according to the following three conditions:

(i) $$\int_{\mathbb{R}^d}\chi(x)\,dx=1,$$

(ii) $$\int_{\mathbb{R}^d}x\chi(x)\,dx=0,$$

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(iii) $$\int_{\mathbb{R}^d} (x \otimes x)\chi(x)\,dx = I,$$

where $I \in \mathbb{R}^{d\times d}$ 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 $\mathscr{D}'$ 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.

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