

Mathematical Derivation of QCMD

In this section, we present a methodology to derive the QCMD model from the full Schrödinger equation (2.8) 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:

- δ^2 , the variance of the probability density for the particle of mass M at time zero,
- $\epsilon^2 = m/M$, 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:

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

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

$$\delta \text{ and } \epsilon \text{ sufficiently small and } t < t_{\max}.$$

These restrictions will be discussed later on.

§1 First Approximation Step: Separation

We consider the solution Ψ of the full Schrödinger equation (2.8) with *separated* initial data (2.2) according to assumption (IP) on page 8. 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 wave function Ψ_{\otimes} defined by

$$\Psi_{\otimes} = \psi \otimes \phi, \quad \text{i.e.,} \quad \Psi_{\otimes}(x, q, t) = \psi(x, t) \cdot \phi(q, t), \quad (3.1)$$

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

Definition 3.1 *Under the assumption $\Psi = \Psi_{\otimes}$ the full Schrödinger equation (2.8) can be separated into two coupled 1-particle Schrödinger equations:*

$$\begin{aligned} i\epsilon\dot{\psi}_{\text{SCF}} &= \left(-\frac{1}{2}\Delta_x + \langle \phi_{\text{SCF}}, V(x, \cdot)\phi_{\text{SCF}} \rangle \right) \psi_{\text{SCF}}, \\ i\epsilon\dot{\phi}_{\text{SCF}} &= \left(-\frac{\epsilon^2}{2}\Delta_q + \langle \psi_{\text{SCF}}, V(\cdot, q)\psi_{\text{SCF}} \rangle \right) \phi_{\text{SCF}}. \end{aligned} \quad (3.2)$$

This nonlinear system is uniquely solvable as can be proven by Galerkin approximation and energy based compactness arguments. In chemical literature it is known as time-dependent self-consistent field (TDSCF) model (cf. [36]).

To be specific: Detailed computations show (cf. [50] or [14]) that the solutions ψ_{SCF} and ϕ_{SCF} from (3.2) allow the following reconstruction of Ψ_{\otimes} :

$$\Psi_{\otimes} = \exp\left(\frac{i}{\epsilon} \int_*^t \langle \Psi_{\otimes}^*(s), V\Psi_{\otimes}^*(s) \rangle ds\right) \Psi_{\otimes}^*, \quad \Psi_{\otimes}^* = \psi_{\text{SCF}} \otimes \phi_{\text{SCF}}, \quad (3.3)$$

which shows that Ψ_{\otimes}^* computed due to (3.2) differs from Ψ_{\otimes} by a phase factor only. Hence, we may solve the system (3.2) in order to compute Ψ_{\otimes} whenever the explicit knowledge of the phase is of no importance. For instance all expectation values are invariant under phase shift. In this way the simplified system (3.2) defines via (3.3) a separated wave function Ψ_{\otimes} which respects the initial data (2.2) — 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 Ψ_{\otimes} as defined by (3.3) can nevertheless be viewed as an approximation $\Psi_{\otimes} \approx \Psi$. To this end we differentiate the expression (3.3) with respect to the time t , use the equations of the system (3.2) and get the following *modified full Schrödinger equation*:

$$i\epsilon \frac{d}{dt} \Psi_{\otimes} = \left(-\frac{1}{2} \Delta_x - \frac{\epsilon^2}{2} \Delta_q + V_{\otimes}(x, q, t) \right) \Psi_{\otimes}$$

with the modified potential

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

Before we make an assumption in addition to the initial condition (2.2) we give a definition of the notion “approximate δ -function”:

Definition 3.2 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) $\int_{\mathbb{R}^d} x \chi(x) dx = 0,$
- iii) $\int_{\mathbb{R}^d} (x \otimes x) \chi(x) dx = \mathbb{I},$

where $\mathbb{I} \in \mathbb{R}^{d \times d}$ 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

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

for $\epsilon \rightarrow 0$ in the space \mathcal{D}' of distributions.

A simple example is given by the Gaussian distribution function

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

of meanvalue x_0 and variance δ^2 .

Let us now assume:

(ID) the probability density $|\phi|^2$ is an *approximate δ -function* as defined in Definition 3.2, i.e.,

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

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

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

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

Assumption (ID) implies that the wave packet ϕ is concentrated along some particle path $q(t)$. This assumption will be simplified in Sec. §2.

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

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

By standard results from perturbation theory this gives us our main approximation result for the separation step (for the details of a proof see [14]):

Theorem 3.3 *Assumption (ID) implies that the asymptotic error of separation is given by*

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

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

Since the system (3.2) is the basis of the so called *time-dependent self-consistent field* (TDSCF) calculations (cf. [36]), 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 (3.2) is an approximate δ -function while the form of the other one is not restricted. We should also note, that Thm. 3.3 remains even valid, if the probability density $|\phi|^2$ supports *several* particle traces with a variance of δ^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.

§2 Second Approximation Step: Short Wave Asymptotics

Now, we will give a further simplification of the separated system (3.2) for large masses $M \gg m$, that is, for small ϵ . As a by-product we will be able to simplify assumption (ID).

Using short wave asymptotics [1][71][76], also called WKB method or semi-classical approximation in the literature, one can prove the validity of the following *asymptotic expansion*:

$$\phi_{\text{SCF}}(q, t) = a(q, t) \exp\left(i \frac{S(q, t)}{\epsilon}\right) + \mathcal{O}(\epsilon). \quad (3.4)$$

See [14] 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

$$\frac{\partial S}{\partial t} + \frac{1}{2} (\nabla_q S)^2 + \langle \psi, V(\cdot, q) \psi \rangle = 0 \quad (3.5)$$

and a continuity equation for a^2

$$\frac{\partial a^2}{\partial t} + \text{div}_q (a^2 \nabla_q S) = 0. \quad (3.6)$$

Now, equation (3.5) 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

$$\begin{aligned} \dot{q} &= p, & q(t_0) &= q_*, \\ \dot{p} &= -\langle \psi, \nabla_q V(\cdot, q) \psi \rangle, & p(t_0) &= \nabla_q S(q_*, t_0), \end{aligned} \quad (3.7)$$

satisfies throughout the relation

$$p(t) = \nabla_q S(q(t), t). \quad (3.8)$$

This allows us to construct $S(\cdot, t)$ from a *fixed* initial phase $S(\cdot, t_0)$ as long as the particle flow map Φ^t which maps the initial position q_* to the solution $q(t)$ of the Hamiltonian system (3.7) at time t , i.e.,

$$\Phi^t q_* = q(t),$$

is one-to-one. At times t , where at least two *different* particle paths meet, the phase function S gets multi-valued and *the asymptotic expansion (3.4) ceases to be valid*. At those times there will be points $q_f = \Phi^t q_*$, for which the flow is even locally not one-to-one, i.e.,

$$\det D_q \Phi^t q|_{q=q_*} = 0. \quad (3.9)$$

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 $t < t_{\text{max}}$ there are no focal points at all (see Fig. 3.1). The continuity equation (3.6) for the probability density $a^2 = |\phi|^2$ describes the transport of the initial probability density $a^2(q, t_0)$ along the flow Φ^t of the velocity field $\dot{q} = \nabla_q S$. A well known consequence of this transport is the following local conservation property of the probability density:

$$\int_{\Phi^t W} a^2(q, t) dq = \int_W a^2(q, t_0) dq$$

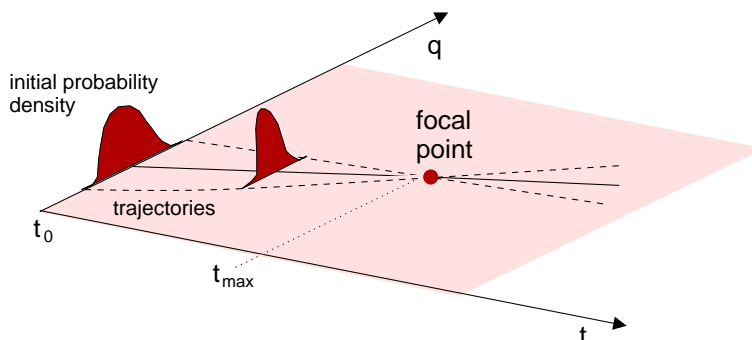


FIGURE 3.1. Illustration of a focal point. Different trajectories sample the probability distribution. If they cross each other in position space, the transport or probability density is not longer unique and the approximation might break down.

for all domains $W \subset \mathbb{R}^d$, cf. [20]. This implies in particular that an initially concentrated wave packet

$$a^2(q, t_0) = \chi_\delta(q - q_*) \approx \delta(q - q_*), \quad \text{for } \delta \ll L, \quad (3.10)$$

remains in the limit $\delta \rightarrow 0$ concentrated at the classical trajectory $q(t) = \Phi^t q_*$, i.e.,

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

Thus assumption (ID) is satisfied for $t < t_{\max}$ if it is satisfied initially for $t = t_0$ in the context of short wave asymptotics $\epsilon \rightarrow 0$. We collect our new assumption:

(IP2) The initial preparation ϕ_* is given as

$$\phi_*(q) = a_*(q) \exp\left(\frac{i}{\epsilon} p_* \cdot q\right), \quad (3.11)$$

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

$$a_*(q)^2 = \chi_\delta(q - q_*),$$

where χ has compact support.

We are now able to state in which sense the QCMD model (2.9) serves as an approximation of the system (3.2).

Theorem 3.4 *Assumption (IP2) implies that the QCMD system (2.9) satisfies*

$$\psi_{\text{QC}} = \psi_{\text{SCF}} + \mathcal{O}(\delta^2 + \epsilon)$$

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

$$q(t) = \langle \phi_{\text{SCF}}, q \phi_{\text{SCF}} \rangle + \mathcal{O}(\delta^2 + \epsilon)$$

for all $t < t_{\max}$. Moreover, assumption (ID) of Thm. 3.3 is fulfilled for these t in the limit $\epsilon \rightarrow 0$.

For a proof see again [14]. It is 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 (2.9) 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 δ^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 (3.4) 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. §3 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 $\mathcal{O}(\epsilon)$ the wave function ϕ is concentrated on these particle paths. As indicated at the end of Sec. §1 this yields a justification of the TDSCF method even in this case for $\epsilon \rightarrow 0$. Since the WKB method cannot be extended as an asymptotic expansion in ϵ in the vicinity of focal points, the validity of the TDSCF method *at a focal point* remains to be doubtful.

§3 Discussion and Examples

We shall now illustrate the potential dangers of the QCMD method as discussed. Since the first two of the mentioned problems, i.e., mass M too small and the disintegration of the wave packet 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. Fig. 3.2), 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. [6][2]). Using the notation of Chap. 2, the Hamiltonian operator of the system in question is given by:

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

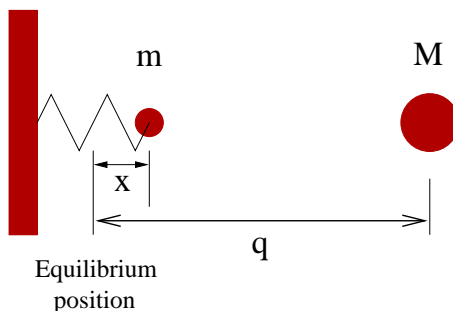


FIGURE 3.2. Scheme of the collinear test system.

with masses $M = 40\text{u}$ and $m = 1\text{u}$. For the interaction potential U we have taken the form (cf. [6][2]) $U(r) = A \exp(-br)$ with $A = 1.654 \cdot 10^3 \text{ kcal/mol}$ and $b = 2.438 \text{ \AA}^{-1}$. The frequency ω of the undisturbed oscillator corresponds to a wavenumber of 1000 cm^{-1} or to an energy of $\hbar\omega = 2.86 \text{ kcal/mol}$. 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:

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

with initial location $\langle q \rangle_0 = 5 \text{ \AA}$, 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 $\delta = 0.075 \text{ \AA}$. We have performed 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 (see 6.§3). We have applied uniform time steps $\tau = 0.01 \text{ fs}$ over a total time interval $t/\text{fs} \in [0, 1000]$ and a spatial computation domain $x/\text{ \AA} \in [-1, 0.5]$ and $q/\text{ \AA} \in [1, 12]$ 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.

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 $t = 350 \text{ fs}$ of the reflection of the classical particle. Total energy is well-conserved in both cases by our numerical schemes, which reflects the analytical conservation of energy as discussed in Sec. 6.§1.1. This should be contrasted with some observations in [2], where a *non-symplectic* numerical scheme was used.

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. 3.3 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

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

with initial states

$$q_l(t_0) = \langle q \rangle_0 + l \delta q \quad \text{and} \quad p_l(t_0) = \langle P \rangle_0$$

with $\delta q = 0.01\text{\AA}$. 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 (3.9), which defines a focal point.

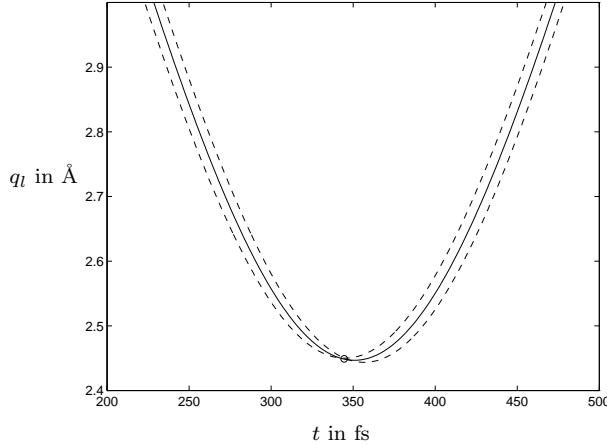


FIGURE 3.3. Crossing of different particle paths q_l in the focal point (circle). The solid line represents the QCMD-trajectory q , the dashed lines the neighboring trajectories q_{-1} and q_1 started from a slightly different initial position. Notation as explained in the text.

We know from the previous section that the separation step itself introduces an approximation error $\mathcal{O}(\delta)$. 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 (3.2). Fig. 3.4 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.

§4 Concluding Remarks

The “partial classical limit” leads us to a two-fold approximation result:

- (R1) Tensor product separation of the full wave function is accurate up to an error of $\mathcal{O}(\delta)$.
- (R2) The classical trajectory computed from (3.7) approximates the position expectation of the classical part up to the error $\mathcal{O}(\delta^2 + \epsilon)$.

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

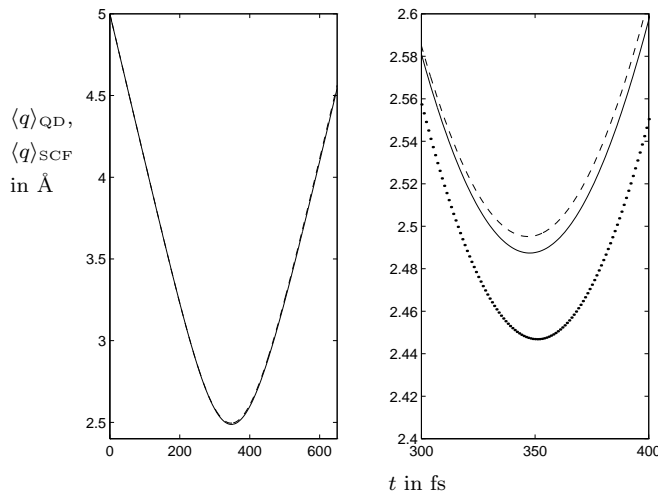


FIGURE 3.4. Results of QD- and TDSCF-calculations. The picture on the left hand side shows the corresponding position expectations $\langle q \rangle_{\text{QD}}$ (solid line) and $\langle q \rangle_{\text{SCF}}$ (dashed line) versus time. The region of the turning point is magnified on the RHS. Here, the additional dotted line represents the corresponding QCMD-trajectory q . Note, that this picture does *not* change, if we refine the stepsizes used.

(C1) the mass ratio $\epsilon^2 = m/M$ is small enough,

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

(C3) no caustics are present.

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 Fig. 3.5. We could as well apply semi-classical limits via Gaussian wave packets as represented by the right methodical branch of Fig. 3.5. We would then arrive at the following alternative result (cf. [39]):

(R2') The semi-classical approximation of the classical particle by Gaussian wave packets is accurate up to $\mathcal{O}(\sqrt{\epsilon})$.

But note, [39] is based on the assumption that δ and ϵ are coupled via $\delta = \sqrt{\epsilon}$. Therefore, both approaches yield under this assumption the same $\mathcal{O}(\sqrt{\epsilon})$ -estimate for the total approximation error.

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.

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:

- The given error analysis of the separation step, on which all the mentioned models like TDSCF, quantum-semiclassical molecular dynamics

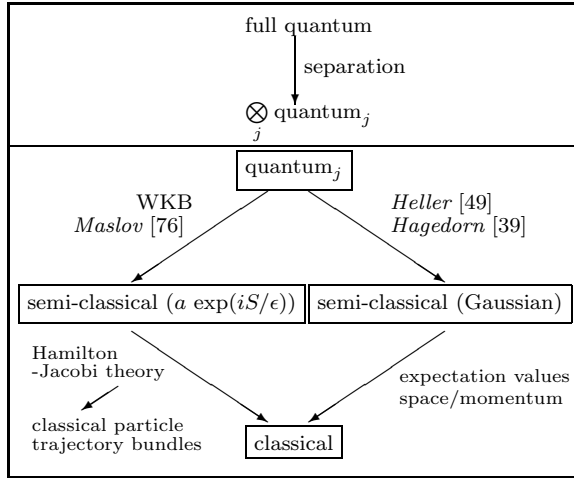


FIGURE 3.5. Different approaches to quantum-(semi-)classical models. In mixed approaches the full quantum system is first separated via the tensor product ansatz into parts j with coupled quantum description. Then, the evolution of each part j can be modeled on different levels: quantumly, semi-classically, 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.

(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.

- 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 wave function will jump at each of these transitions by a shift of $\pi/2$ (see [76]). This effect may explain some corresponding experimental observations (cf. [33], Sec. 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 (3.5) for the phase S , e.g., using particle trajectory bundles (cf. [36]).
- 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 [50]. However, we note that the QSCMD also fails in detecting caustics and gets problems in this case, e.g., if the wave packet 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., [35]), but — as far as the authors know — a corresponding mathematical justification is still missing.