The quantum–classical molecular dynamics model

In this chapter we introduce the fundamental quantum dynamics model as well as the QCMD model. 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.

Let the two particles have space coordinates $x \in \mathbb{R}^d$ and $q \in \mathbb{R}^d$ and masses m and M $(M > m)$, respectively. Moreover, let the interaction potential between them be $V = V(x, q)$.

§1   Full quantum dynamics

At first, let us consider the universally accepted quantum dynamics model.

Definition 2.1 *The state of a full quantum dynamical system (QD) is a 2-particle wave function $\Psi = \Psi(x, q, t)$ and lives in the state space $\Psi(\cdot, \cdot, t) \in L^2(\mathbb{R}^{2d})$. It obeys the time–dependent Schrödinger equation*

$$i\,\hbar\,\dot{\Psi} \; = \; \left(-\frac{\hbar^2}{2m}\,\Delta_x \; - \; \frac{\hbar^2}{2M}\,\Delta_q \; + \; V(x, q) \right)\,\Psi \qquad (2.1)$$

with initial condition $\Psi(\cdot, \cdot, t_0) = \Psi_*$.

Typically, a proper choice of the coordinate system allows the initial quantum state to be approximated by a product state (cf., [37], §IIb). Throughout the following, we might therefore assume that

(IP) the initial state Ψ_* has a product state representation

$$\Psi_*(x, q) \; = \; \phi_*(q) \, \cdot \, \psi_*(x). \qquad (2.2)$$

§2   QCMD

Now, we give an intuitive formulation of the QCMD model, preparing for Chap. 3 in which we show how it fits into the framework of other quantum and quantum–classical models.

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 $\psi_{\mathrm{QC}} = \psi_{\mathrm{QC}}(x, t)$ which obeys Schrödinger's equation

$$i\hbar\,\dot{\psi}_{\mathrm{QC}} \; = \; \left. \left(-\frac{\hbar^2}{2m}\,\Delta_x \; + \; V(x, \mu) \right) \right|_{\mu = q(t)} \psi_{\mathrm{QC}} \qquad (2.3)$$

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

$$
\begin{aligned}
M\,\dot{q} &= p \\
\dot{p} &= -\nabla_q U,
\end{aligned}
\tag{2.4}
$$

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

$$
U(q, \psi_{\mathrm{QC}}(t)) = \langle \psi_{\mathrm{QC}}(t)\,, V(\cdot, q)\,\psi_{\mathrm{QC}}(t)\rangle = \int V(x, q)\,|\psi_{\mathrm{QC}}(x, t)|^2\,dx. \tag{2.5}
$$

Thus, the forces in (2.4) are the so-called Hellmann-Feynman forces. Together, (2.3) and (2.4) are the basic equations of motion of QCMD.

In this approach, the arguments (q, ψ_{QC}) of U are naturally *independent* unknowns. Therefore we get

$$
\nabla_q U = \langle \psi_{\mathrm{QC}}\,, \nabla_q V(\cdot, q)\,\psi_{\mathrm{QC}}\rangle. \tag{2.6}
$$

Whenever the gradient of V is given, this can be evaluated directly and (2.3) together with (2.4) constitutes a closed system of equations:

Definition 2.2 *The* QCMD model dynamics *is given by the solution* $q, p : \mathbb{R} \to \mathbb{R}^d$ *and* $\psi(\cdot, t) \in L^2(\mathbb{R}^d)$ *of the equations of motion:*

$$
\begin{aligned}
i\hbar\,\dot{\psi}_{\mathrm{QC}} &= \underbrace{\left(-\frac{\hbar^2}{2m}\Delta_x + V(x, \mu) \right)\Big|_{\mu = q(t)}}_{H(q)}\psi_{\mathrm{QC}}, & \psi_{\mathrm{QC}}|_{t=t_0} &= \psi_*, \\
M\,\dot{q} &= p, & q(t_0) &= q_*, \\
\dot{p} &= -\langle \psi_{\mathrm{QC}}, \nabla_q V \psi_{\mathrm{QC}}\rangle, & p(t_0) &= p_*
\end{aligned}
\tag{2.7}
$$

where $H(q)$ *denotes the Hermitian Hamiltonian operator of the quantum subsystem.*

Remark. Our choice (2.6) of the partial derivative $\nabla_q U$ is used, e.g., in [33] or [6],[7], where, in addition, the Schrödinger equation is replaced by its density matrix representation, the Liouville-von Neumann equation.

Remark. In [4], $\mu = q(t_0)$ is considered as *parameter* in (2.3) and the wave function $\psi_{\mathrm{QC}} = \psi_{\mathrm{QC}}(\mu, t)$ as explicitly depending on this parameter. It is assumed that the dependence of ψ_{QC} on μ has then to be taken into account yielding the derivative

$$
\begin{aligned}
\nabla_q U = \Big(&\langle \psi_{\mathrm{QC}}\,, \nabla_\mu V(\cdot, \mu)\,\psi_{\mathrm{QC}}\rangle \\
&+ \langle \nabla_\mu \psi_{\mathrm{QC}}\,, V(\cdot, q)\,\psi_{\mathrm{QC}}\rangle + \langle \psi_{\mathrm{QC}}\,, V(\cdot, q)\,\nabla_\mu \psi_{\mathrm{QC}}\rangle \Big)\Big|_{\mu = q},
\end{aligned}
$$

which, in turn, leads to the necessity of evaluating $\nabla_\mu \psi_{\mathrm{QC}}$ 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 (2.6). For test simulations using this model see [2][3].

§3   Appropriate scaling

For ease of notation in our further analysis, we scale the time and potential in (2.1) and (2.7) by

$$\frac{\hbar t}{\sqrt{mM}} \to t, \qquad \frac{m}{\hbar^2} V \to V.$$

Furthermore, let us introduce the smallness parameter ϵ which denotes the mass ratio

$$\epsilon^2 = m/M.$$

Subsequently, we will often consider the case $M \to \infty$ which is equivalent to $\epsilon \to 0$. The full Schrödinger equation (2.1) transforms into the — with respect to ϵ — singularly perturbed equation

$$i\epsilon \, \partial_t \Psi \;=\; \left(-\frac{\epsilon^2}{2}\Delta_q \;-\; \tfrac{1}{2}\Delta_x \;+\; V(x,q) \right) \Psi. \tag{2.8}$$

Applying the same scaling, we obtain the following QCMD equations

$$
\begin{aligned}
i\epsilon \dot{\psi}_{\mathrm{QC}} &= \underbrace{\left(-\frac{1}{2}\Delta_x + V(x,q) \right)}_{H(q)} \psi_{\mathrm{QC}}, & \psi_{\mathrm{QC}}|_{t=t_0} &= \psi_*, \\
\dot{q} &= p, & q(t_0) &= q_*, \\
\dot{p} &= -\langle \psi_{\mathrm{QC}}, \nabla_q V \psi_{\mathrm{QC}} \rangle, & p(t_0) &= p_*.
\end{aligned}
\tag{2.9}
$$

§4   Spatial discretization

Since the Schrödinger equations in (2.8) and (2.9) are *partial differential equations* (PDE), any numerical solution must be based on a projection of the solution into a finite (N) dimensional subspace of the Hilbert state space $L^2(\mathbb{R}^{2d})$ or $L^2(\mathbb{R}^d)$, respectively. The construction of a suitably adapted subspace for the application problem is an essential task in the preparation of the physical model and requires a great deal of physical insight into the particular system.

However, we will subsequently assume, that this topic has already been addressed. This might have been done with either by *pseudo–spectral methods* [17, 66], collocation methods [67] or by using a particular basis set as, for example, a finite number of electronic orbitals or eigenstates of a given Hamiltonian. To exemplify these Galerkin methods, let us consider the Schrödinger-equation:

$$i\hbar \frac{\partial}{\partial t} u \;=\; H\,u \tag{2.10}$$

with Hermitian operator H. Now, take a finite number of trial functions $\phi_k = \phi_k(x)$ which span the chosen subspace. The projection of u can be expanded into these trial functions

$$u^N(x,t) \;=\; \sum_{k=0}^{N} a_k(t)\,\phi_k(x)$$

where a_k are time–dependent expansion coefficients. In the case of pseudo–spectral methods the ϕ_k have a global support and $\phi_k \in C^\infty(\mathbb{R})$. Fourier-Galerkin or Fourier–collocation methods use $\phi_k(x) = \exp(ikx)$. Now, methods of weighted residuals require

$$\int \psi_k(x) \left(i\hbar \frac{\partial}{\partial t} u^N - H\, u^N \right) dx \;=\; 0 \qquad\qquad (2.11)$$

for N test functions ψ_k. Galerkin methods demand additionally an orthogonality relation between ψ_k and ϕ_k

$$\int \psi_k(x)\, \phi_l(x)\, dx \;=\; \delta_{kl}$$

whereas collocation methods set $\psi_k = \delta(x - x_k)$ leading therefore to the exact solution on the N given points x_k. Formally, both kinds of methods result via (2.10) and (2.11) in the same structure of ordinary differential equation

$$i\hbar \frac{\partial}{\partial t} u_k \;=\; \sum_{l=0}^{N} H_{kl}^N u_l.$$

with a Hermitian matrix $H^N = (H_{kl}^N)$.

§5   Application problems

In the following, we will describe three classes of application problems for quantum–classical molecular dynamics. A classification in terms of the smallness parameter ϵ allows for an estimation of the character of the dynamics. Particular attention will be given to the limiting factors in the realization of simulations, as for example time and computer memory consuming properties. Later, the classification implies for every application problem appropriate model enhancements and restrictions as well as optimally adapted numerical algorithms (See Fig. 2.1).

Proton transfer reaction   A correct description of biochemical reactions necessarily requires the consideration of quantum effects. Thus, time–dependent quantum dynamical models play an important role in the analysis of enzyme catalysis, interactions of enzymes with chemotherapeutic agents, proton tunneling in biomolecular systems, photosynthesis and phosphorylation processes in biomolecular systems [2]. An elucidation of the enzymatic reactions can, for example, be done by the QCMD model describing the dynamics of the key protons quantum dynamically, whereas the remaining atoms are modeled classically [3].

An example is the enzyme Ribonuclease T1 which cleaves a single stranded RNA specifically at the base guanine. Fig. 2.2 illustrates schematically the reaction center of the enzyme and a possible path for the first step of the reaction. The enzyme aligns with its sidechains Arg77+ and His92+ the negatively charged phosphate group of the substrate. A proton transfer from the O2' hydroxy group of the substrate to the Glu58- sidechain of the enzyme will initiate a nucleophilic attack of the O2' oxygen on the phosphorus, which leads to a

	Proton transfer	Photo dissoziation in solvent	Electronic transitions
ε	$0 \ll \varepsilon < 1$	$0 \ll \varepsilon < 1$	$0 < \varepsilon \ll 1$
Dynamics	essentially non-adiabatic	essentially non-adiabatic	**almost adiabatic**
Simulation time spans	**large**	short	short
Dimension of quantum system after discretization	small	**large**	small
Number of occupied eigenstates of quantum Hamiltonian	small	**large**	small

Figure 2.1. Schematic representation of some application classes

pentacoordinated intermediate state of the reaction. Proton transfer and nucleophilic attack are processes, which can be described theoretically only on the basis of quantum dynamics.
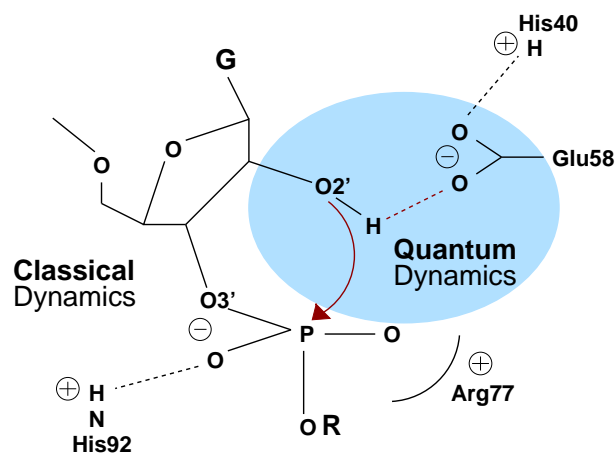

Figure 2.2. Example of a system to be described quantum–classically: an enzymatic reaction catalyzed by Ribonuclease T1

For proton transfer processes, the mass ratio between the classically modeled atoms and the proton is around one or two orders of magnitude. Such small differences in the masses result in an essentially non–adiabatic motion (see Chap. 5). The dynamics is determined by numerous eigenvalue crossings of all kind. The simulations are obstructed by the large number of classical atoms of realistic biomolecules which make the evaluation of the intra–classical inter-

action potentials very time–consuming. Furthermore, typical reaction processes take place on a very large time scale. The spatial discretization of the quantum system depends strongly on the analyzed application. It varies from collocation methods [3] with many grid points to expansions into only a few (≈ 5) proton orbitals [116].

Photodissociation of Hydrogen containing molecules The breaking of molecular bonds induced by light plays a major role in the understanding of photochemical reactions. The investigation of photodissociation reactions of simple molecules is at present a very active field of research [99]. A particular example is the dissociation dynamics of a small solute molecule embedded in a cluster or a matrix of solvent particles. Here, a so–called *cage–effect* of the solvent might delay or hinder the separation of the photo fragments. In fact, a direct cage exit where photo fragments escape from a solvent cage without notably deforming it competes with a delayed or even an indirect cage exit where just collision–induced cage deformations allow for an eventual cage exit. In this process, the quantum character of the light photo fragments crucially influence the kind of cage exit.

In cooperation with B. SCHMIDT and M. HOLZ, a photodissociation of HF in an Argon matrix was quantum–classically analyzed (cf., Fig. 2.3) [56]. Only the use of symmetry adapted basis functions in the Galerkin method made the solution of the corresponding QCMD equations in 3 quantum dimensions possible. For the first time, the dependence of the energy transfer to the argon matrix on the initial quantum state could be computed. The previously mentioned cage–effect was observed for certain rotationally excited initial states of the Hydrogen.

Since the mass ratio in these photodissociation processes is similar to proton transfer processes, the dynamics is also essentially non–adiabatic. Limiting factors in the computation are on the one hand given by the high dimension of the quantum system due to the fact, that the photodissociation process transforms the initially bounded Hydrogen into an unbounded state. This also leads an excitation of very high eigenvalues of the quantum Hamiltonian $H(q)$. On the other hand, the number of considered classical atoms usually makes the intra–classical potential evaluation very time–consuming.

Electronic problems Transitions in the electron structure of molecules determine chemical reactions, as it is in the photodissociation example, where light induced the breaking of a bond by excitation of the electron levels. Over the years many models and methods have been proposed to compute the electron dynamics of realistic models (see [78, 79, 80] and references herein).

The great mass difference between nuclei and electrons —three or four orders of magnitude— result in an almost adiabatic motion. This means, that the adiabatic limit $\epsilon \to 0$ is in many situations a good approximation to full QD. Nevertheless, the —often mildly— non–adiabatic effects have to be taken into account. This is, due to the smallness of ϵ possible via higher order expansion terms in ϵ.

The advantage of a small ϵ for the modelling question is meanwhile a problem when solving the time–dependent Schrödinger equation. Since the stepsize of the time discretization has to be adjusted to the highest frequencies in the system

$j = 0$ $\qquad\qquad\qquad\qquad$ $j = 6$

$t = 0$ fs $\qquad\qquad\qquad\qquad\qquad$ $t = 0$ fs

$t = 10$ fs $\qquad\qquad\qquad\qquad\qquad$ $t = 10$ fs

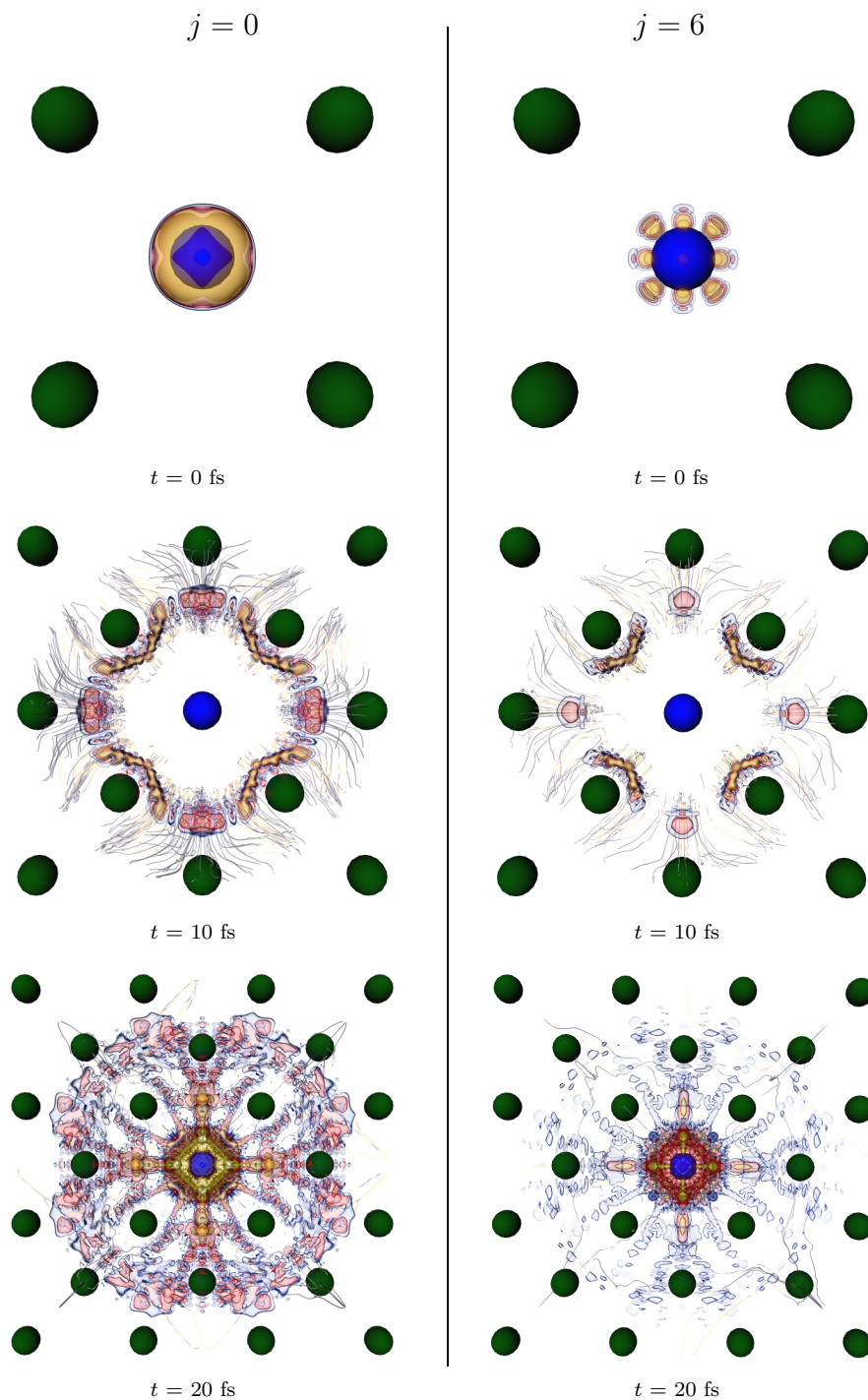$t = 20$ fs $\qquad\qquad\qquad\qquad\qquad$ $t = 20$ fs

FIGURE 2.3. Quantum–classical modeled photodissociation of HF in an Argon matrix. Shown is a cut plane of the model in three spatial dimensions. The classically modeled atoms are represented as spheres whereas the quantum probability density of the Hydrogen is shown via isosurfaces and probability density current stream lines [100]. The time evolution of initial quantum states corresponding to the rotational quantum numbers $j = 0$ and $j = 6$ are shown. Note, that the particular spatial expansion of the initial state for $j = 6$ results in a cage effect: most of the wave packet is repelled from the next neighbors and repercusses onto the Fluorine atom.

($\approx \epsilon^{-1}$) it might become prohibitively expensive for small ϵ. For that reason, many approaches circumvent an explicitly time–dependent description of the light particles. However, the dimension of the quantum system is in standard examples quite small: usually, the considered Hilbert subspace is spanned by only a few electronic orbitals.