> ... daß der Schwindel des Vermischens der klassischen Theorie und der Quantentheorie sich noch auf viele Weisen beim Aufspüren der Geheimnisse der Natur als fruchtbar erweisen wird.
> Bohr an Pauli, 11. Dez. 1924 [11]

Chapter 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.

Since a fully quantum dynamical description is by far beyond the scope of simulations, the requirement of approximations in the modelling of the physical systems as well as in the solution of the resulting equations is evident. Therefore, two mathematical topics have attracted considerable attention (see Fig. 1.1):

- the analysis and the construction of reduced models as approximations to full quantum dynamics. For example, *mixed quantum–classical* models have found growing interest in applications. These models 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 development of appropriate numerical algorithms — in the following also denoted as integrators — to solve the model equations. The construction of algorithms is challenged by *multiple scales in time and space*. To *efficiently* resolve the smallest scales, novel integration techniques have to be worked out.

At first glance, these topics seem to be almost unrelated and separately treatable. This is misleading, since especially the construction of numerical schemes relies heavily on results of the model analysis. Numerical analysis offers a great variety of approaches in the construction of integrators, but the selection of effective and appropriate schemes must be guided by a detailed knowledge of the model. Therefore, the manuscript at hand presents contributions and insights on both topics, mathematical modelling and numerical analysis, in a unified approach and gives an overview over the state of research revealing the links and their consequences.

Modelling One of the most popular quantum–classical models, the so-called QCMD model, consists of a Schrödinger equation nonlinearly coupled to classical Newtonian equations (see the foreword to the first part of this manuscript for a detailed introduction). Both, the QD and the QCMD model contain *singularly*

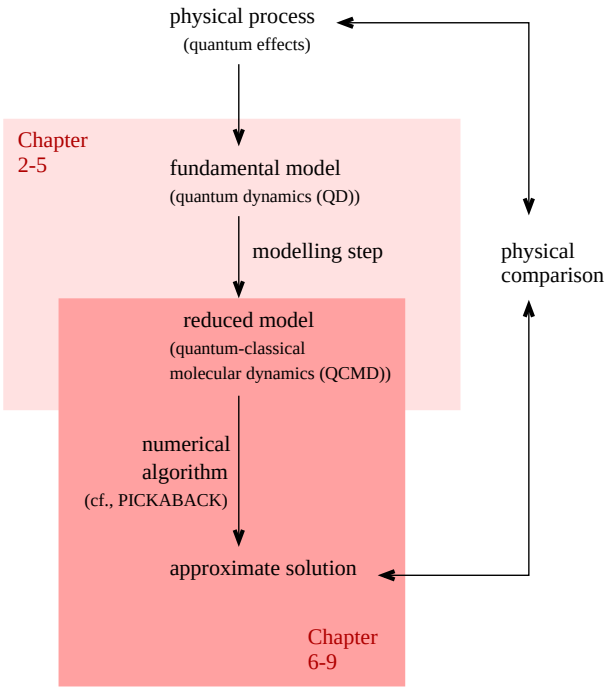

Figure 1.1. Connection between a physical process, the scientifically accepted model representation and a reduced model. The latter is approximately solved with a numerical algorithm. The boxes illustrate the dominating topics in this work.

perturbed Schrödinger equations. Their dynamics should be characterized with respect to the perturbation parameter ϵ ($0 < \epsilon \leq 1$). Therefore, we thoroughly have to distinguish between the case ϵ significantly larger than zero and the singular limit $\epsilon \to 0$.

The case of an ϵ significantly larger than zero was discussed by the author together with F.A. Bornemann and Ch. Schütte [15] resulting in a rigorous mathematical justification of the QCMD model.

The limit dynamics for $\epsilon \to 0$, i.e., the adiabatic dynamics, was analyzed using homogenization techniques in time by P. Gérard et. al. [34] for the full QD model and by F.A. Bornemann and Ch. Schütte [16, 13] for QCMD and externally driven QD models. The present manuscript compares this technique with the method of averaging transformations [68, 84, 64] in application to QCMD and the adiabatic theorem of QD. Furthermore, novel approaches to the justification of QCMD trajectory bundles for ϵ close to zero are discussed [104].

Numerical algorithms The numerical realization of the QCMD model must satisfy the specific requirements associated with the application problems under investigation. Thus, the construction of integrators follows the classification of the dynamics.
In the case of a smallness parameter ϵ significantly different from zero, a great variety of numerical methods exists:

- *Structure conserving methods* for long term simulations. Here, the author and his coworkers [87] derived a reliable symplectic algorithm. Symplectic multiple–time–stepping extensions were proposed by the author and S. Reich [89, 93] whereas symmetric multiple–time–stepping schemes were advocated by U. Schmitt and J. Brickmann [101].

- *Adaptive methods* for short term simulations. An adaptive stepsize control leading to efficient but accurate methods has been introduced by the author and Ch. Schütte [90].

- *Averaging integrators* for application problems with low regularity. For QCMD, this class of methods has first been presented by M. Hochbruck and Ch. Lubich [53, 54] and is based on an averaging over the highly oscillatory parts of the solution.

For $\epsilon \to 0$, appropriate numerical methods require prohibitively small stepsizes. A discussion of strategies leading to large–stepsize integrators for the singular limit is firstly presented in detail in this manuscript. In order to understand the intriguing robustness of averaging integrators with respect to $\epsilon \to 0$, we introduce and analyze an appropriate test equation. Based on this and on the insights gained in the modelling approach, a novel technique is proposed which, for the first time, allows for a systematic construction of averaging integrators.

Considering the described properties of suitable numerical integrators, the advantage of a thorough model analysis becomes evident: the dominant mathematical structure of the QCMD solution depending on the given application problem is passed to the numerical approximation. For long term simulations, energy conservation is of primary importance. This requirement can be satisfied by the use of symplectic maps as integrators. Thus, the propagator inherits the symplectic structure of the analytic flow. Another example of the close interaction between numerical analysis and modelling is given in the case $\epsilon \to 0$. Here, model analysis identifies the asymptotical limit system. Again, integration schemes which satisfy (inherit) the same asymptotical behavior as the QCMD solution have a major advantage: they allow for large stepsizes in time. Only a unified approach to mathematical modelling and numerical simulation, as first presented in this manuscript, can meet the requirements of a systematic construction of integrators of this kind.

Acknowledgments

I would like to express my deep gratitude to P. Deuflhard for his continuing support and encouragement. Forecasting the challenging requirement of efficient numerical techniques for the simulation of bio–molecules, he initiated and later pushed forward the research in this field. I thank him for giving me the opportunity to work in this uniquely stimulating research atmosphere at the Konrad–Zuse–Center (ZIB).

Especially, I would like to thank Ch. Schütte for sharing with me his considerable insight in the connections between physical application, mathematical modelling and numerical analysis. Instructing me in the appropriate means of analyzing the particular quantum–classical case, he essentially influenced the

accomplishment of this work. I greatly appreciate numerous times of motivating me when I discovered problems, and his friendly criticism.

Special thanks go to the staff of the ZIB, in particular to my colleagues W. Huisinga, F. Cordes, B. Schmidt, M. Weiser, A. Fischer, L. Zschiedrich, J. Schmidt-Ehrenberg, D. Runge, R. Beck and Th. Schneider for giving lots of advises and sometimes criticism. It was always a pleasure to share time with them.

Out of the many others to whom I am especially thankful are M. Hochbruck, Ch. Lubich and F.A. Bornemann for their fruitful and stimulating discussions.

Last but not least, I would like to thank Anja for doing more than her fair share of housework and child–minding during the last years and also for always "being there" and providing emotional support whenever needed.