AB INITIO MOLECULAR DYNAMICS: BASIC THEORY AND ADVANCED METHODS

Ab initio molecular dynamics revolutionized the field of realistic computer simulation of complex molecular systems and processes, including chemical reactions, by unifying molecular dynamics and electronic structure theory. This book provides the first coherent presentation of this rapidly growing field, covering a vast range of methods and their applications, from basic theory to advanced methods.

This fascinating text for graduate students and researchers contains systematic derivations of various *ab initio* molecular dynamics techniques to enable readers to understand and assess the merits and drawbacks of commonly used methods. It also discusses the special features of the widely used Car–Parrinello approach, correcting various misconceptions currently found in the research literature.

The book contains pseudo-code and program layout for typical plane wave electronic structure codes, allowing newcomers to the field to understand commonly used program packages, and enabling developers to improve and add new features in their code.

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Preface

In this book we develop the rapidly growing field of *ab initio* molecular dynamics computer simulations from the underlying basic ideas up to the latest techniques, from the most straightforward implementation up to multilevel parallel algorithms. Since the seminal contributions of Roberto Car and Michele Parrinello starting in the mid-1980s, the unification of molecular dynamics and electronic structure theory, often dubbed "Car–Parrinello molecular dynamics" or just "CP", widened the scope and power of *both* approaches considerably. The forces are described at the level of the many-body problem of interacting electrons and nuclei, which form atoms and molecules as described in the framework of quantum mechanics, whereas the dynamics is captured in terms of classical dynamics and statistical mechanics. Due to its inherent virtues, *ab initio* molecular dynamics is currently an extremely popular and ever-expanding computational tool employed to study physical, chemical, and biological phenomena in a very broad sense. In particular, it is the basis of what could be called a "virtual laboratory approach" used to study complex processes at the molecular level, including the difficult task of the breaking and making of chemical bonds, by means of purely theoretical methods. In a nutshell, *ab initio* molecular dynamics allows one to tackle vastly different systems such as amorphous silicon, Ziegler-Natta heterogeneous catalysis, and wet DNA using the same computational approach, thus opening avenues to deal with molecular phenomena in physics, chemistry, and biology in a unified framework.

We now feel that the time has come to summarize the impressive developments of the last 20 years in this field within a unified framework at the level of an advanced text. Currently, any newcomer in the field has to face the problem of first working through the many excellent and largely complementary review articles or Lecture Notes that are widespread. Even worse, much of the significant development of the last few years is not even accessible at

that level. Thus, our aim here is to provide not only an introduction to the beginner such as graduate students, but also as far as possible a comprehensive and up-to-date overview of the entire field including its prospects and limitations. Both aspects are also of value to the increasing number of those scientists who wish only to apply *ab initio* molecular dynamics as a powerful problem-solving tool in their daily research, without having to bother too much about the technical aspects, let alone about method development. This is indeed possible, in principle, since several rather easy-to-use program packages are now on the market, mostly for free or at low cost for academic users.

In particular, different flavors of *ab initio* molecular dynamics methods are explained and compared in the first part of this book at an introductory level, the focus being on the efficient extended Lagrangian approach as introduced by Car and Parrinello in 1985. But in the meantime, a wealth of techniques that go far beyond what we call here the "standard approach", that is microcanonical molecular dynamics in the electronic ground state using classical nuclei and norm-conserving pseudopotentials, have been devised. These advanced techniques are outlined in Part II and include methods that allow us to work in other ensembles, to enhance sampling, to include excited electronic states and nonadiabatic effects, to deal with quantum effects on nuclei, and to treat complex biomolecular systems in terms of mixed quantum/classical approaches. Most important for the practitioner is the computation of properties during the simulations, such as optical, IR, Raman, or NMR properties, mostly in the context of linear response theory or the analysis of the dynamical electronic structure in terms of fragment dipole moments, localized orbitals, or effective atomic charges. Finally in Part III, we provide a glimpse of the wide range of applications, which not only demonstrate the enormous potential of *ab initio* molecular dynamics for both explaining and predicting properties of matter, but also serve as a compilation of pertinent literature for future reference and upcoming applications.

In addition to all these aspects we also want to provide a solid basis of technical knowledge for the younger generation such as graduate students, postdocs, and junior researchers beginning their career in a nowadays well-established field. For this very reason we also decided to include, as far as possible, specific references in the text to the original literature as well as to review articles. To achieve this, the very popular approach of solving the electronic structure problem in the framework of Kohn–Sham density functional theory as formulated in terms of plane waves and pseudopotentials is described in detail in Part I. Although a host of "tricks" can already

be presented at that stage, specific aspects can only be made clear when discussing them at the level of implementation. Here, the widely used and ever-expanding program package `CPMD` serves as our main reference, but we stress that the techniques and paradigms introduced apply analogously to many other available codes that are in extensive use. This needs to be supplemented with an introduction to the concept of norm-conserving pseudopotentials, including definitions of various widely used pseudopotential types. In Part I, the norm-conserving pseudopotentials are explained, whereas in Part II, the reader will be exposed to the powerful projector augmented-wave transformation and ultrasoft pseudopotentials. A crucial aspect for large-scale applications, given the current computer architectures and the foreseeable future developments, is how to deal with parallel platforms. We account for this sustainable trend by devoting special attention in Part II to parallel programming, explaining a very powerful hierarchical multilevel scheme. This paradigm allows one to use not only the ubiquitous Beowulf clusters efficiently, but also the largest machines available, viz. clustered shared-memory parallel servers and ultra-dense massively parallel computers.

Overall, our hope is that this book will contribute not only to strengthen applications of *ab initio* molecular dynamics in both academia and industry, but also to foster further technical development of this family of computer simulation methods. In the spirit of this idea, we will maintain the site `www.theochem.rub.de/go/aimd-book.html` where corrections and additions to this book will be collected and provided in an open access mode. We thus encourage all readers to send us information about possible errors, which are definitively hidden at many places despite our investment of much care in preparing this manuscript.

Last but not least we would like to stress that our knowledge of *ab initio* molecular dynamics has grown slowly within the realms of a fruitful and longstanding collaboration with Michele Parrinello, initially at IBM Zurich Research Laboratory in Rüschlikon and later at the Max-Planck-Institut für Festkörperforschung in Stuttgart, which we gratefully acknowledge on this occasion. In addition, we profited enormously from pleasant cooperations with too many friends and colleagues to be named here.