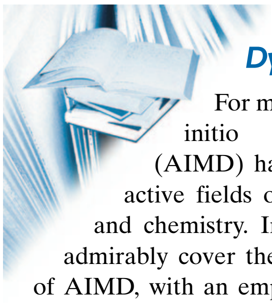


Ab Initio Molecular Dynamics

For more than two decades, ab initio molecular dynamics (AIMD) has been one of the most active fields of computational physics and chemistry. In this book the authors admirably cover the fundamental principles of AIMD, with an emphasis on the Car–Parrinello (CP) method and its implementation in the CPMD program. The target readers for this book are researchers and graduate students in computational chemistry and physics. Fairly advanced background knowledge of quantum mechanics, quantum chemistry, and molecular dynamics (MD) as well as solid-state and mathematical physics will be required to follow some of the discussions. As a stand-alone reference, the book is most appropriate for researchers wanting to gain a comprehensive understanding of the principles and technical aspects of AIMD. Beginning and intermediate graduate students will likely require supplementary reading (including references sited in the book) to follow parts of the text. However, the comprehensive nature of the book will make the effort put into it rewarding for serious students.

After the first chapter, which serves as an introduction and motivation, the book has three parts, Basic techniques, Advanced techniques, and Applications.

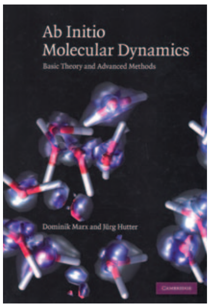
Part I consists of three chapters. Chapter 2 gives an introduction to deriving the coupled electronic and nuclear equations of AIMD starting from the time-dependent Schrödinger equation and the molecular Hamiltonian. The authors describe three approximate methods, namely Born–Oppenheimer, Ehrenfest, and Car–Parrinello MD for coupling of the time-dependences of the classical nuclear degrees of freedom and the quantum mechanical electronic degrees of freedom. The treatment of nuclear and electronic degrees of freedom in the three methods are compared and issues involved in solving the electronic part of the problem, such as dealing with electronic correlations and use of localized atom-centered or plane-wave basis sets, are discussed. This chapter provides an excellent conceptual background to AIMD and should be accessible to graduate students with a basic knowledge of quantum mechanics and electronic structure theory. It is highly recommended as an introduction for any student first approaching AIMD.

Chapter 3 focuses on implementing AIMD and begins with a discussion of the electronic component of the AIMD problem. The procedure for solving the density functional theory Kohn–Sham (KS) equation is adapted to the use of plane-wave basis sets and pseudopotentials. The energy and gradients from the KS-DFT are expressed in terms of expansions in the reciprocal space vectors **G** characterizing plane waves. A description of the time integration of the CP equations of motion follows.

From this chapter onwards, the book becomes more technical, which makes it useful for the researchers, but more difficult to follow for the beginner. Part of this problem stems from the large amount of background knowledge and terminology needed to understand the material. This always leaves authors with the difficult decision of what background material to include and what to leave out. For example, in Chapter 3, the authors write the KS orbitals $\phi_j(\mathbf{r},\mathbf{k})$ in general "Bloch form", $(\phi_j(\mathbf{r},\mathbf{k}) = \exp[i\mathbf{k}\cdot\mathbf{r}]\,u(\mathbf{r},\mathbf{k}))$. While writing orbitals for periodic systems in the Bloch form is standard in solid-state physics, it is difficult to judge whether the student reader of this text will be familiar with the concepts of Bloch orbitals and the Brillouin zone. Another example from Chapter 3 is quoting the "sampling theorem" for discrete Fourier transforms without further discussion.

Chapter 4 is an in-depth study of pseudo-orbitals and pseudopotentials (PPs) and their use in molecular electronic structure calculations. The general conditions a pseudo-orbital must satisfy are given and methodologies to generate PPs that give required pseudo-orbital properties are discussed. The discussion of different PP construction schemes with plane-wave basis sets is comprehensive. More detail in some parts could again have been helpful to the learner. For example, the reason for "unscreening" a pseudopotential is not described in detail and the reasoning behind the labels "local" or "nonlocal" for operators (in Section 4.3) is not discussed.

Chapter 5 describes generalizations to the adiabatic, ground electronic state, microcanonical AIMD calculations described in the previous chapters. The first generalization involves coupling external variables such as temperature and pressure to the molecular dynamics of the nuclear and electronic degrees of freedom. This discussion will be very useful to readers familiar to the implementations of thermostats and barostats in classical MD. Molecular dynamics is biased towards sampling low-energy parts of the phase space. The authors next describe sampling high-energy regions of the phase space with the history-dependent non-Markovian metadynamics method. This method is used for studying rare events with high energy barriers and calculating free energies. The abstract metadynamics method is clearly presented, however, a first-time reader would have greatly benefited from a specific example illustrating the concept of "collective coordinates". The next subsections discuss systems where excited electronic states are important in the dynamics, systems



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where quantum corrections have to be applied to nuclear motions in the simulations, and large systems where hybrid quantum-classical nuclear motions are used in the simulations. The description of these specialized topics shows the applicability of AIMD simulations to a variety of complex cases.

Chapter 6 gives a further discussion of PPs with an emphasis on non-normconserving ultrasoft PPs and the projector augmented-wave (PAW) method and their implementation in KS-DFT. Because of the widespread use of ultrasoft PPs and the PAW method, this chapter could have been logically incorporated into Chapter 4.

Chapter 7 describes how molecular properties are derived from the results of AIMD calculations. The first part of this chapter involves properties related to the interaction of the molecule with external fields. These properties are related to derivatives of the total molecular energy with respect to the field and are calculated by density functional perturbation theory. The details given are sufficient for the reader to follow, but a deeper understanding of all issues raised in the discussions may require further reading. The second part of the chapter discusses how the results of AIMD calculations, expressed in terms of nonlocalized plane-wave basis sets, can be used to describe localized molecular properties. This is achieved through the introduction of Wannier or localization functions which allow interpretation of AIMD results in terms of localized chemical bonding, molecular dipole moments, and atomic charges.

Part III consists of two chapters. Chapter 9 is an exhaustive catalog of systems which have been studied by AIMD methods, and Chapter 10 is a list of properties which have been calculated for some of these systems. Although a list of applications is useful, given the fast pace of research in this area, these chapters will quickly require updating and they are perhaps more appropriate for an on-line supplementary chapter. Some of the space allotted to these chapters could perhaps have been used to discuss the fundamentals in more detail.

In summary, this book is an excellent addition to the bookshelf of researchers and serious students of AIMD methods. The exposition is comprehensive, but at places the reader may need to refer to other resources for background material.

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