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Setting the stage: why *ab initio*
molecular dynamics?

Classical molecular dynamics using predefined potentials, force fields, either based on empirical data or on independent electronic structure calculations, is well established as a powerful tool serving to investigate many-body condensed matter systems, including biomolecular assemblies. The broadness, diversity, and level of sophistication of this technique are documented in several books as well as review articles, conference proceedings, lecture notes, and special issues [25, 120, 136, 272, 398, 468, 577, 726, 1189, 1449, 1504, 1538, 1539]. At the very heart of any molecular dynamics scheme is the question of how to describe – that is in practice how to approximate – the interatomic interactions. The traditional route followed in molecular dynamics is to determine these potentials in advance. Typically, the full interaction is broken up into two-body and many-body contributions, long-range and short-range terms, electrostatic and non-electrostatic interactions, etc., which have to be represented by suitable functional forms, see Refs. [550, 1405] for detailed accounts. After decades of intense research, very elaborate interaction models, including the nontrivial aspect of representing these potentials analytically, were devised [550, 1280, 1380, 1405, 1539].

Despite their overwhelming success – which will, however, not be praised in this book – the need to devise a fixed predefined potential implies serious drawbacks [1123, 1209]. Among the most significant are systems in which (i) many different atom or molecule types give rise to a myriad of different interatomic interactions that have to be parameterized and/or (ii) the electronic structure and thus the chemical bonding pattern changes qualitatively during the course of the simulation. Such systems are termed here “chemically complex”. An additional aspect (iii) is of a more practical nature: once a specific system is understood after elaborate development of satisfactory potentials, changing a single species provokes typically enormous efforts to

parameterize the new potentials needed. As a result, systematic studies are a *tour de force* if no suitable set of consistent potentials is already available.

The reign of traditional molecular dynamics *and* electronic structure methods was extended greatly by a family of techniques that is referred to here as “*ab initio* molecular dynamics” (AIMD). Apart from the widely used general notion of “Car–Parrinello” or just “CP simulations” as defined in the *Physics and Astronomy Classification Scheme*, PACS [1093], other names including common abbreviations that are currently in use for such methods are for instance first principles (FPMD), on-the-fly, direct, extended Lagrangian (ELMD), density functional (DFMD), quantum chemical, Hellmann–Feynman, Fock-matrix, potential-free, or just quantum (QMD) molecular dynamics amongst others. The basic idea underlying every *ab initio* molecular dynamics method is to compute the forces acting on the nuclei from electronic structure calculations that are performed “on-the-fly” as the molecular dynamics trajectory is generated, see Fig. 1.1 for a simplifying scheme. In this way, the electronic variables are not integrated out beforehand and represented by fixed interaction potentials, rather they are considered to be active and explicit degrees of freedom in the course of the simulation. This implies that, given a suitable approximate solution of the many-electron problem, also “chemically complex” systems, or those where the electronic structure changes drastically during the dynamics, can be handled easily by molecular dynamics. But this also implies that the approximation is shifted from the level of devising an interaction potential to the level of selecting a particular approximation for solving the Schrödinger equation, since it cannot be solved exactly for the typical problems at hand.

Applications of *ab initio* molecular dynamics are particularly widespread in physics, chemistry, and more recently also in biology, where the aforementioned difficulties (i)–(iii) are particularly severe [39, 934]. A collection of problems that have already been tackled by *ab initio* molecular dynamics, including the pertinent references, can be found in Chapter 9 of Part III. The power of this novel family of techniques led to an explosion of activity in this field in terms of the number of published papers, see the squares in Fig. 1.2 that can be interpreted as a measure of the activity in the area of *ab initio* molecular dynamics. This rapid increase in activity started in the mid to late 1980s. As a matter of fact the time evolution of the number of citations of a particular paper, the one by Car and Parrinello from 1985 entitled “Unified approach for molecular dynamics and density-functional theory” [222, 1216], initially parallels the growth trend of the entire field, see the circles in Fig. 1.2. Thus, the resonance evoked by this publication and, at its very heart, the introduction of the Car–Parrinello

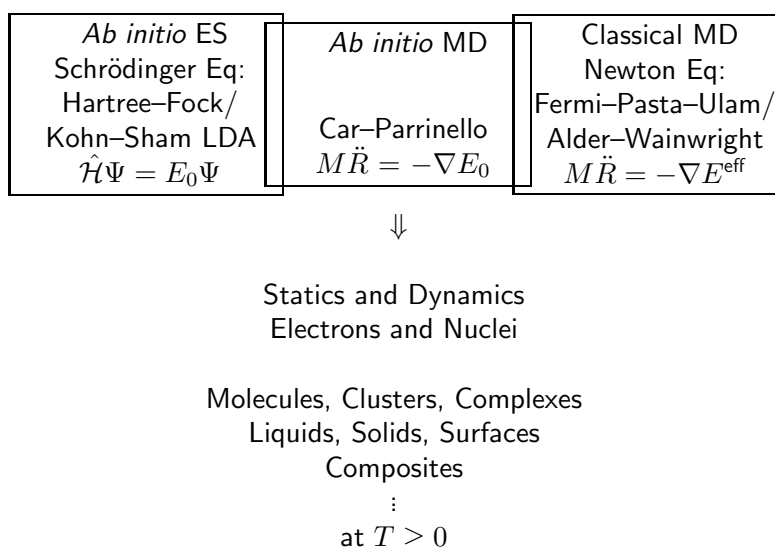


Fig. 1.1. *Ab initio* molecular dynamics unifies approximate *ab initio* electronic structure theory (i.e. solving Schrödinger’s wave equation numerically using, for instance, Hartree–Fock theory or the local density approximation within Kohn–Sham theory) and classical molecular dynamics (i.e. solving Newton’s equation of motion numerically for a given interaction potential as reported by Fermi, Pasta, Ulam, and Tsingou for a one-dimensional anharmonic chain model of solids [409] and published by Alder and Wainwright for the three-dimensional hard-sphere model of fluids [19]; see Refs. [33, 272, 308, 453, 652] for historic perspectives on these early molecular dynamics studies).

“Lagrangean” [995], has gone hand in hand with the popularity of the entire field over the last decade. Incidentally, the 1985 paper by Car and Parrinello is the last one included in the section “Trends and Prospects” in the reprint collection of “key papers” from the field of atomistic computer simulations [272]. Evidence that the entire field of *ab initio* molecular dynamics has matured is also provided by the separate PACS classification number (“71.15.Pd - Electronic Structure: Molecular dynamics calculations

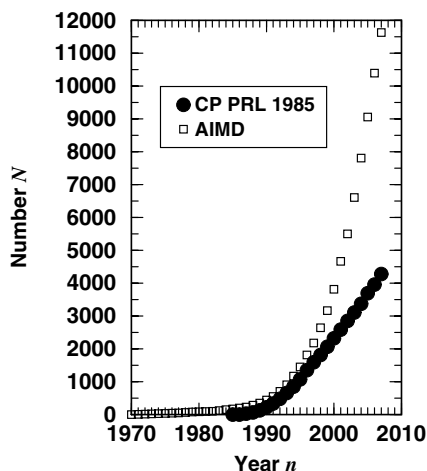


Fig. 1.2. Publication and citation analysis up to the year 2007. Squares: number of publications N which appeared up to the year n containing the keyword “ab initio molecular dynamics” (or synonyms such as “first principles MD”, “Car–Parrinello simulations” etc.) in title, abstract or keyword list. Circles: number of publications N which appeared up to the year n citing the 1985 paper by Car and Parrinello [222] (including misspellings of the bibliographic reference). Self-citations and self-papers are excluded, i.e. citations of Ref. [222] in their own papers and papers coauthored by R. Car and/or M. Parrinello are *not* considered in the respective statistics; note that this, together with the correction for misspellings, is probably the main reason for a slightly different citation number up to the year 2002 as given here compared to that (2819 citations) reported in Ref. [1216]. The analysis is based on Thomson/ISI Web of Science (WoS), literature file CAPLUS of the Chemical Abstracts Service (CAS), and INSPEC file (Physics Abstracts) as accessible under the database provider STN International. Earlier reports of these statistics [933, 934, 943] are updated as of March 13, 2008; the authors are most grateful to Dr. Werner Marx (Information Service for the Institutes of the Chemical Physical Technical Section of the Max Planck Society) for carrying out these analyses.

(Car–Parrinello) and other numerical simulations”) introduced in 1996 into the *Physics and Astronomy Classification Scheme* [1093].

Despite its obvious advantages, it is evident that a price has to be paid for putting molecular dynamics onto an *ab initio* foundation: the correlation lengths and relaxation times that are accessible are much smaller than what is affordable in the framework of standard molecular dynamics. More recently, this discrepancy was counterbalanced by the ever-increasing power of available computing resources, in particular massively parallel platforms [661, 662], which shifted many problems in the physical sciences right into the realm of *ab initio* molecular dynamics. Another appealing feature of standard molecular dynamics is less evident, namely the experimental

aspect of “playing with the potential”. Thus, tracing back the properties of a given system to a simple physical picture or mechanism is much harder in *ab initio* molecular dynamics, where certain interactions cannot easily be “switched off” like in standard molecular dynamics. On the other hand, *ab initio* molecular dynamics has the power to eventually map phenomena onto a firm basis in terms of the underlying electronic structure and chemical bonding patterns. Most importantly, however, is the fact that new phenomena, which were not foreseen before starting the simulation, can simply happen if necessary. All this lends *ab initio* molecular dynamics a truly predictive power.

Ab initio molecular dynamics can also be viewed from another perspective, namely from the field of classical trajectory calculations [1284, 1514]. In this approach, which has its origin in gas phase reaction dynamics, a *global* potential energy surface is constructed in a first step either empirically, semi-empirically or, more and more, based on high-level electronic structure calculations. After fitting it to a suitable analytical form in a second step (but without imposing additional approximations such as pairwise additivity, etc.), the dynamical evolution of the nuclei is generated in a third step by using classical mechanics, quantum mechanics, or semi/quasiclassical approximations of various sorts. In the case of using classical mechanics to describe the dynamics - which is the focus of the present book - the limiting step for large systems is the first one, why should this be so? There are $3N-6$ internal degrees of freedom that span the global potential energy surface of an unconstrained N -body system. Using, for simplicity, 10 discretization points per coordinate implies that of the order of 10^{3N-6} electronic structure calculations are needed in order to map such a global potential energy surface. Thus, the computational workload for the first step in the approach outlined above grows roughly like $\sim 10^N$ with increasing system size $\sim N$. This is what might be called the “curse of dimensionality” or “dimensionality bottleneck” of calculations that rely on *global* potential energy surfaces, see for instance the discussion on p. 420 in Ref. [551].

What is needed in *ab initio* molecular dynamics instead? Suppose that a useful trajectory consists of about 10^M molecular dynamics steps, i.e. 10^M electronic structure calculations are needed to generate one trajectory. Furthermore, it is assumed that 10^n independent trajectories are necessary in order to average over different initial conditions so that 10^{M+n} *ab initio* molecular dynamics steps are required in total. Finally, it is assumed that each single-point electronic structure calculation needed to devise the global potential energy surface and one *ab initio* molecular dynamics time step require roughly the same amount of CPU time. Based on this truly simplistic

order of magnitude estimate, the advantage of *ab initio* molecular dynamics vs. calculations relying on the computation of a global potential energy surface amounts to about $10^{3N-6-M-n}$. The crucial point is that for a given statistical accuracy (that is for M and n fixed and independent of N) and for a given electronic structure method, the computational advantage of “on-the-fly” approaches grows like $\sim 10^N$ with system size. Thus, Car–Parrinello methods always outperform the traditional three-step approaches *if the system is sufficiently large and complex*. Conversely, computing global potential energy surfaces beforehand and running many classical trajectories afterwards without much additional cost always pays off for a given system size N like $\sim 10^{M+n}$ *if the system is small enough* so that a global potential energy surface can be computed and parameterized.

Of course, considerable progress has been achieved in accelerating the computation of global potentials by carefully selecting the discretization points and reducing their number, choosing sophisticated representations and internal coordinates, exploiting symmetry and decoupling of irrelevant modes, implementing efficient sampling and smart extrapolation techniques and so forth. Still, these improvements mostly affect the prefactor but not the overall scaling behavior, $\sim 10^N$, with the number of active degrees of freedom. Other strategies consist of, for instance, reducing the number of active degrees of freedom by constraining certain internal coordinates, representing less important ones by a (harmonic) bath or by friction forces, or building up the global potential energy surface in terms of few-body fragments. All these approaches, however, invoke approximations beyond those of the electronic structure method itself. Finally, it is evident that the computational advantage of the “on-the-fly” approaches diminishes as more and more trajectories are needed for a given (small) system. For instance, extensive averaging over many different initial conditions is required in order to calculate scattering or reactive cross-sections quantitatively. Summarizing this discussion, it can be concluded that *ab initio* molecular dynamics is the method of choice to investigate large and “chemically complex” systems.

Quite a few reviews, conference articles, lecture notes, and overviews dealing with *ab initio* molecular dynamics have appeared since the early 1990s [38, 228, 338, 460, 485, 486, 510, 563, 564, 669, 784, 933, 934, 936–938, 943, 1099, 1103, 1104, 1123, 1209, 1272, 1306, 1307, 1498, 1512, 1544] and the interested reader is referred to them for various complementary viewpoints. This book originates from the Lecture Notes [943] “*Ab initio* molecular dynamics: Theory and implementation” written by the present authors on the occasion of the *NIC Winter School 2000* titled “Modern Methods and Algorithms of Quantum Chemistry”. However, it incorporates in addition

many recent developments as covered in a variety of lectures, courses, and tutorials given by the authors as well as parts from our previous review and overview articles. Here, emphasis is put on both the broad extent of the approaches and the depth of the presentation as demanded from both the practitioner's and newcomer's viewpoints.

With respect to the broadness of the approaches, the discussion starts in Part I, "Basic techniques", at the coupled Schrödinger equation for electrons and nuclei. Classical, Ehrenfest, Born–Oppenheimer, and Car–Parrinello molecular dynamics are derived in Chapter 2 from the time-dependent mean-field approach that is obtained after separating the nuclear and electronic degrees of freedom. The most extensive discussion is related to the features of the standard Car–Parrinello approach, however, all three *ab initio* approaches to molecular dynamics - Car–Parrinello, Born–Oppenheimer, and Ehrenfest - are contrasted and compared. The important issue of how to obtain the correct forces in these schemes is discussed in some depth. The two most popular electronic structure theories implemented within *ab initio* molecular dynamics, Kohn–Sham density functional theory but also the Hartree–Fock approach, are only touched upon since excellent textbooks [363, 397, 625, 760, 762, 913, 985, 1102, 1423] already exist in these well-established fields. Some attention is also given to another important ingredient in *ab initio* molecular dynamics, the choice of the basis set.

As for the depth of the presentation, the focus in Part I is clearly on the implementation of the basic *ab initio* molecular dynamics schemes in terms of the powerful and widely used plane wave/pseudopotential formulation of Kohn–Sham density functional theory outlined in Chapter 3. The explicit formulae for the energies, forces, stress, pseudopotentials, boundary conditions, optimization procedures, etc. are noted for this choice of method to solve the electronic structure problem, making particular reference to the CPMD software package [696]. One should, however, keep in mind that an *increasing* number of other powerful codes able to perform *ab initio* molecular dynamics simulations are available today (for instance ABINIT [2], CASTEP [234], CONQUEST [282], CP2k [287], CP-PAW [288], DACAPO [303], FHI98md [421], NWChem [1069], ONETEP [1085], PINY [1153], PWscf [1172], SIESTA [1343], S/PHI/nX [1377], or VASP [1559] amongst others), which are partly based on very similar techniques. An important ingredient in any plane wave-based technique is the usage of pseudopotentials to represent the core electrons, therefore enabling them not to be considered explicitly. Thus, Chapter 4 of Part I introduces the norm-conserving pseudopotentials up to the point of providing an overview about the different generation schemes and functional forms that are commonly used.

In Part II devoted to “Advanced techniques”, the standard *ab initio* molecular dynamics approach as outlined in Part I is extended and generalized in various directions. In Chapter 5, ensembles other than the microcanonical one are introduced and explained along with powerful techniques used to deal with large energetic barriers and rare events, and methods to treat other electronic states than the ground state, such as time-dependent density functional theory in both the frequency and time domains. The approximation of using classical nuclei is lifted by virtue of the path integral formulation of quantum statistical mechanics, including a discussion of how to approximately correct classical time-correlation functions for quantum effects. Various techniques that allow us to represent only part of the entire system in terms of an electronic structure treatment, the hybrid, quantum/classical, or “QM/MM” molecular dynamics simulation methods, are outlined, including continuum solvation models. Subsequently, advanced pseudopotential concepts such as Vanderbilt’s ultrasoft pseudopotentials and Blöchl’s projector augmented-wave (PAW) transformation are introduced in Chapter 6.

Modern techniques to calculate properties directly from the available electronic structure information in *ab initio* molecular dynamics, such as infrared, Raman or NMR spectra, and methods to decompose and analyze the electronic structure including its dynamical changes are discussed in Chapter 7. Last but not least, the increasingly important aspect of writing highly efficient parallel computer codes within the framework of *ab initio* molecular dynamics, which take as much advantage as possible of the parallel platforms currently available and of those in the foreseeable future, is the focus of the last section in Part II, Chapter 8.

Finally, Part III is devoted to the wealth of problems that can be addressed using state-of-the-art *ab initio* molecular dynamics techniques by referring to an extensive set of references. The problems treated are briefly outlined with respect to the broad variety of systems in Chapter 9 and to specific properties in Chapter 10. The book closes with a short outlook in Chapter 11. In addition to this printed version of the book corrections and additions will be provided at www.theochem.rub.de/go/aimd-book.html in an open access mode.

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Part I

Basic techniques

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