Computational Materials Science: From Ab Initio to Monte Carlo Methods

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From Ab Initio to Monte Carlo Methods

With 77 Figures

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129 **Computational Materials Science**
From Ab Initio to Monte Carlo Methods
By K. Ohno, K. Esfarjani, and Y. Kawazoe

Volumes 1–125 are listed at the end of the book.

Preface

There has been much progress in the computational approaches in the field of materials science during the past two decades. In particular, computer simulation has become a very important tool in this field since it is a bridge between theory, which is often limited by its oversimplified models, and experiment, which is limited by the physical parameters. Computer simulation, on the other hand, can partially fulfill both of these paradigms, since it is based on theories and is in fact performing experiment but under any arbitrary, even unphysical, conditions.

This progress is indebted to advances in computational physics and chemistry. Ab initio methods are being used widely and frequently in order to determine the electronic and/or atomic structures of different materials. The ultimate goal is to be able to predict various properties of a material just from its atomic coordinates, and also, in some cases, to even predict the stable atomic positions of a given material. However, at present, the applications of ab initio methods are severely limited with respect to the number of particles and the time scale of dynamical simulation. This is one extreme of the methodology based on very accurate electronic-level calculations.

When one does not require such ab initio calculations, there are many alternative powerful semi-empirical techniques such as the tight-binding method. More empirical methods, e.g. classical molecular dynamics and Monte Carlo simulations, also offer powerful ways to treat even larger-scale systems. This is the other extreme where one uses methods such as the lattice gas model, which has a very simple interaction function with few parameters only.

How to build a bridge between these two completely different levels of calculations is also a major theme in the field of computational materials science, and we have addressed this issue in the fourth chapter.

The basic theories and their applications are thus quite diverse and not always very easy for students, scientists and engineers to survey and understand correctly. In particular, developments that represent recent progress in solid-state physics and chemistry are now already being used in materials research and even in biology.

Because of the very rapid progress in computational methods in materials research nowadays, there has been a strong demand for a comprehensive

and introductory book which covers most of the important computational methodologies and basic theories behind them, and ranges from very rigorous methods such as ab initio methods to more empirical methods such as those using classical potentials or lattice models. In this book, we have attempted to put together all these methods in a unified description and in a systematic fashion, from the basics to very advanced methods, so that students and researchers can acquire an overview of this quickly evolving field and its applications. Many references have also been supplied for those requiring a deeper insight into more advanced problems or details of implementations of some of the methods.

In recent years, physicists, chemists, materials scientists, and even biochemists have been using the same computational tools in order to solve their very different problems. Quantum chemistry, solid state physics, and materials science have shared recent progress in their fields. This book is intended to introduce many basic theories behind the recent methodologies adopted in computational materials science. We start from small scale behavior and highly accurate treatments and finish with very large scale behavior using simple models. This allows us to introduce different levels of methodology more systematically and more easily.

Some attention is also paid to points which are not fully established but promise to have important applications in the future. Such examples are the quantum Monte Carlo method which is the most accurate treatment of the many-fermion problem possible up to now, beyond the Born-Oppenheimer approximation, and the GW approximation. All these fields are becoming very active because of their intrinsic importance coupled with recent advances in computer hardware, which make simulations of these levels possible.

We would like to express our sincere thanks to Dr. Claus Ascheron for his suggesting and encouraging us to write this book from the very beginning until its publication as a new volume in Springer's Series in Solid-State Sciences and also for his very patient cooperation during completion of the book. We also would like to thank Douglas Meekison and Dr. Angela Lahee for their excellent assistance in improving the style and English of this book. We believe that this book would never have been appeared without their kind and patient cooperation.

Kaoru Ohno
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Contents

1. Introduction

1.1 Computer Simulation as a Tool for Materials Science

Although categorized as an engineering field which normally studies artificial materials, metallurgy has also treated natural objects in its long history. Metallurgy and Alchemy, which are the basis of present-day materials science, have also produced all the natural sciences, including chemistry and physics. The field of materials science is expanding rapidly to include amorphous, ceramic, polymer, and nanoscale materials. Alchemy was not successful, but its methods still contribute to industry, because they introduce new useful materials.

Since materials are complex in nature, it has never been possible to treat them directly by theory; experimental studies have always been the main method in materials research. In the past, physical concepts could only be applied to pure crystals, and real materials with defects and grain boundaries could not be treated theoretically. Recent progress in computer technology is now opening a new era in which one can treat real, complex materials as they are. The first dramatic change has happened in chemistry. In the past, the most important work of chemists has been to categorize chemicals, and for this purpose, computer databases have been used as a new tool. In the 1980s, molecular-orbital calculations were applied to calculate the properties of chemicals which were of interest in research and in industry. At present, chemicals, including drugs, are designed first by applying molecular-orbital calculations, and then experimental tests confirm the theoretical results, before the molecules are realized. This means new chemicals with desired properties can now be designed by using such calculations. The physical and chemical properties of large molecules such as DNA are also studied by using supercomputers.

In molecular orbital (MO) calculations, the MO is assumed to be a linear combination of atomic orbitals. Although it seems sufficient to express the molecular orbital in this way, a large number of basis functions might be needed in order to accurately represent the electronic wavefunction and, consequently, the charge density. In this case, usually, the Hartree-Fock approximation is used to describe electron-electron interaction effects. This approximation is known to be rough, since it does not include correlation effects. A better approximation, the local-density approximation (LDA), will

give ground-state properties almost perfectly and more efficiently. The LDA is, of course, an approximation, and cannot be applied to excited states and highly correlated systems. The latter are among the hot topics in theoretical physics.

The application of ab initio methods to real materials is still limited. At the moment, even if we employ the fastest supercomputer with the largest memory, we can treat at most a few hundred atoms, and it is not possible to compute all of the properties of real materials. Periodic boundary conditions serve in the study of crystals, but do not really increase the number of atoms included in the system. Therefore, other methods, such as the tight-binding method or classical molecular dynamics, are very important in order to overcome the complexities of some materials. In this case, we assume potential parameters that are extracted from experiment or ab initio calculations. The latter are, however, only valid in the region where they were fitted, and not beyond. It is, nevertheless, useful to study complex materials on the basis of these approximations. Popular potentials such as Lennard-Jones or Finnis-Sinclair are known to be good enough for computing some of the properties of various materials under various conditions.

The above treatments, ab initio molecular dynamics, tight binding, and classical molecular dynamics, are all "deterministic". The state of the system is determined completely by the initial condition. This approach to materials research is useful in understanding stable structures, vibrations, and growth at the atomistic level. Another method for treating complex systems is the Monte Carlo method. It assumes very idealized or simplified interaction parameters and can treat larger number of atoms. Physical and chemical properties of large systems can be obtained as a statistical average over randomly moved particles. It is, therefore, a "stochastic" method. In Chap. 5, we introduce the Monte Carlo method, starting with some concepts from statistical physics. The standard Ising model, classical spin systems, percolation and quantum Monte Carlo, all using this method, are described.

1.2 Modeling of Natural Phenomena

How do we understand Nature's behavior? Except for philosophical sayings such as "I think therefore I exist", we should consider the methods of human understanding. Philosophy, in each era, has been based on the physical understanding of that time. (This statement might be inverted by philosophers!) In the basic conceptual framework of physics, we try to understand the world by discarding metaphysical meanings. In other words, the science of physics expresses the complex world by numerical equations. For example, in Newtonian mechanics, the acceleration is proportional to the external force, and the proportionality constant is called the mass. It is an amazing fact that by only this equation, the motion of planets or the trajectory of the Space Shuttle can be computed very accurately. However, this approximation can-

not hold for very fast motions close to the light velocity. Einstein's principle of relativity is not even relevant to advanced technology in space, let alone daily life, but it predicts the motion of light or light particles passing close to a heavy object such as the sun.

Another standard method of modeling is "linearization". The Newtonian equation is the linear approximation of the relativistic equation of motion at speeds much smaller than the light velocity. Other well-known examples are Ohm's law and Hooke's law. For these, a moderate voltage or force is assumed. The reason why the linear approximation holds for complex systems is that the potential around the stable position can be expressed by a quadratic equation. It is also important to study the situation outside the range of linearity. It is not easy to solve nonlinear equations by analytic methods, and normally, numerical solutions are needed. One of the recent fields in which computer simulation has been applied recently is Chaos theory, where small variations of some parameters cause drastic changes in the solution.

Human knowledge has expanded greatly, and the "ultimate elements of matter" were found first to be protons and neutrons, and then quarks and gluons. However, in the 20th century, this reductionist approach of separating matter into small elements reached its end. As a typical example, the Superconducting Super Collider (SSC) project in the USA was stopped. It is not possible to make an accelerator surrounding the earth, either physically or economically. The search for the ultimate constituents of matter is still important, even though it may now be no more than the dream of the monkey removing the successive skins of an onion in a fruitless attempt to find what is inside.

The subject covered in this book is, fundamentally, the many-body problem, which has long been known to be difficult to solve analytically. The two-body equation in classical dynamics is reduced to a one-body equation as follows. The equations for two particles are expressed as

$$m_1\ddot{r}_1 = f(r_1 - r_2), \tag{1.1}$$

$$m_2\ddot{r}_2 = f(r_2 - r_1). \tag{1.2}$$

Introducing the relative coordinate

$$r = r_1 - r_2, \tag{1.3}$$

the reduced equation for r is obtained as

$$\frac{m_1 m_2}{m_1 + m_2}\ddot{r} = f(r). \tag{1.4}$$

This equation can be solved as a one-body equation. What will happen when we increase the number of particles? This reduction method can not be applied to systems of more than three particles. The study of three-body systems was established as a field of research long ago. Except for linear, or in general, symmetric systems where the number of degrees of freedom can be reduced, the following general three-body equation cannot be solved analytically:

$$m_1\ddot{r}_1 = f(r_1, r_2, r_3), \tag{1.5}$$

$$m_2\ddot{r}_2 = f(r_1, r_2, r_3), \tag{1.6}$$

$$m_3\ddot{r}_3 = f(r_1, r_2, r_3). \tag{1.7}$$

Numerical treatment is the only way to solve many-body problems in general. The basic equation in molecular dynamics is an extension of this scheme to include a large number of particles. It has been extended to quantum systems by Faddeev.

In solid-state physics, the term of "many-body problem" is used in a different way. That is to say, materials are assumed to be composed of an infinite number of atoms (actually 10^{23} for one mole) and such a material is referred to as "bulk". Because of the high degree of symmetry present in the system, namely the invariance under translations of the unit cell, it is possible to use powerful theorems such as Bloch's theorem to solve this many-(almost infinite) body system. The symmetry can be deduced from the observation of X-ray diffraction patterns; without actually seeing the atoms, it was possible to discover the periodicity of crystals!

Therefore, it is important to model the physical systems that occur in nature. The surface of water, like a mirror, is very rough at an atomistic level. Basically we can understand nature in relation to our size (in units of meters and seconds). It is not easy to recognize objects with different scales and they have no meaning in daily life. Amounts of water or electricity are not measured by their number of molecules or electrons. We measure these amounts in proper units such as litres or amperes. And even during a period of high inflation, we will not use money in units of 10^{23}!

How do we aim to understand nature by first-principles calculations? We will start with the categorization of forces. That is,

- (1) strong interaction (nuclear force)
- (2) Coulomb force
- (3) weak interaction (the force related to β decay)
- (4) gravitational force.

These are distinguished by their orders of magnitude. That is, the strength of the force is strongest for (1) and weakest for (4). In units of $\sqrt{\hbar c} = 1.778 \times 10^{13}\ J^{1/2}\ m^{1/2}$, their strengths are 10, 0.1, 10^{-3}, 10^{-19}, respectively. The interactions are long-ranged, as $1/r$ for (4); usually shielded with a range of molecular size, for (2); and very short-ranged, with a range of order 10^{-15} m, for (1) and (3). These are the four basic kinds of force, which characterize present-day science.

One of the main research areas in physics is the unification of these forces. For example, the magnetic force is unified with the Coulomb force in Maxwell's equations, and is expressed in terms of c(the speed of light) and e (the electron charge). The electromagnetic and weak interactions have already been unified by Weinberg and Salam. Although larger-scale unification is being studied by many researchers, it is a very difficult task to include all the forces into a single one. There are other considerations claiming that a fifth or even sixth category of force exists! These studies belong in the domain of elementary-particle physics.

The forces we talk about in this book originate from the Coulomb force only. Although people categorize them as ionic, covalent, molecular and van der Waals forces, they are all different manifestations of the Coulomb force. The material properties studied here for molecules, crystals and polymers are determined by the fundamental forces between their constituents. Since a complete ab initio calculation is not possible, determination of the properties is strongly dependent on the establishment of interaction potentials and on experimental observations. At present, materials cannot be directly designed by ab initio methods in a computer used as a virtual laboratory. However, because of the dramatic progress of computer power, it will be possible in the future to realize our dream of predicting new materials by computer. This is the reason why we study computer simulation methods such as molecular dynamics and Monte Carlo methods; the aim is to design materials with desired properties.