1 Introduction

The longstanding goal of computer simulation of materials is gaining accurate knowledge on structural and electronic properties of realistic condensed-matter systems. Since materials are complex in nature, past theoretical investigations were restricted mostly to simple models. Recent progress in computer technology made a realistic description of a wide range of materials possible. Since then the computational material science has rapidly developed and expanded into new fields in science and technologies, and computer simulations have become an important tool in many areas of academic and industrial research, such as physics, chemistry, biology and nanotechnology. This book focuses on the foundations and practical aspects of computational physics.

Most of the methods in computational physics are based on the density functional theory (DFT). The density functional theory deals with inhomogeneous systems of electrons. This approach is based on the theorem of Hohenberg and Kohn which states that the ground state properties of a many-particle system can be exactly represented in terms of the ground state density. This allows to replace the many-particle wave function by the particle density or the current density of the system. The desired ground state quantities can be obtained by minimization of an unique energy functional, which is decomposed into one-electron contributions and the so-called exchange-correlation energy functional, which contains all many-body effects. In practical applications it is usually approximated by some model density functionals. The variational problem can be reduced to an effective one-electron Kohn-Sham equation describing non-interacting electrons in an effective potential and in principle reproducing exact ground-state density. One of the most popular functionals is the local density approximation (LDA), in which all many-body effects are included on the level of the homogeneous electron gas. Such approach enables one to carry out the so-called *"first-principles"* or *"ab-initio"* calculations (direct calculations of material properties from fundamental quantum mechanical theory). Many fundamental properties, for example bond strength and reaction energies, can be estimated from first principles.

By construction the stationary density functional theory is designed for the ground state and can not be expected to describe excited state properties. A classical tool for this problem is the Green's function formalism which

is an important technique for studying correlations in many-body systems. The Green's function provides spectral densities for occupied and unoccupied states and its poles can be interpreted as single-particle excitations. To calculate the Green's function is in general a non-trivial task and it requires to solve the Dyson equation which involves a non-interacting Green's function and a self-energy operator. In practice, it is necessary to make approximations for the self-energy which can be handled. In most first-principles methods the self-energy is approximated by a local exchange-correlation potential. In this case the Kohn-Sham eigenvalues are interpreted as excitation energies. This simple approach works surprisingly well in many applications and is widely used in a variety of methods on the first-principles level. However, the electron correlations and many-body effects are not adequately represented by the local Kohn-Sham approximation which fails to describe, for example, band gaps in semiconductors or lifetime in spectroscopies. At an *ab-initio* level the self-energy can be implemented e.g. within the random-phase approximation (RPA). This approximation treats the electron correlations on the basis of many-particle theory and is much more accurate but also much more time-consuming then the Kohn-Sham approach.

The development of first-principles methods is a difficult and challenging task. Firstly, an *"ab-inito"* method should be constructed as general as possible to be applicable to a wide class of problems. Usually, a first principles code consists of many thousand lines. Secondly, a development of such programs requires a deep knowledge of numerical methods and programming tools. Since the majority of physical systems exhibit intrinsic symmetries, one should use a symmetry analysis and the group theory to optimize and to speed up computational process. The group theory as a mathematical tool plays an important role to classify the solutions within the context of the underlying symmetries. Extensive use of group theory has been made to simplify the study of electronic structure or vibrational modes of solids or molecules. The group theory is especially useful in understanding the degeneracy of electronic energy levels and also photonic energy bands.

First-principles methods enable to describe fundamental processes in biology, chemistry and physics as accurately as possible with moderate computational effort. Nevertheless, the application of first-principles methods to study the real-time evolution of complex systems is strongly limited. This can be done by using first-principles molecular-dynamics (MD) methods, which can simulate the evolution of atomic and electronic motions without assuming empirical parameters. Molecular dynamics has proved to be an optimal numerical recipe applicable to problems with many degrees of freedom from quite different fields of science. The knowledge of the energy or potential landscape of interacting particles, like electrons and atoms, enables one to calculate the forces acting on the particles and to study the evolution of the system with time. Overall, first-principles molecular dynamics appears as a convincing method to corroborate experimental work and make reliable predictions based on well-established electronic structure techniques.

Due to of similarities between the Schrödinger equation and the Maxwell's equations, the concept of electronic structure methods can be adopted for the study of photonic nano-materials, which have important applications in micro- and nano-electronics. Such computer simulations help to understand quantum dots or photonic crystals that act as new source of a coherent radiation, cages or guided pathways, operating on smaller and smaller scales at steadily increasing speed.

In this book the above-mentioned aspects of computational physics will be discussed from frameworks to practical applications. The general organization of this book is as follows (see the table of Contents). Part I gives a basic description of electrons and photons in crystals. Part II reviews the various techniques of simulations of nanoscopic and macroscopic materials. Some practical aspects of parallel computing and multi-grid methods will be presented in Part III. The interested reader can find references of several other works in the bibliography sections at the end of each chapter.