

# Preface

Density functional theory (DFT) was developed to calculate the electronic states of solids containing huge numbers of electrons. In the earliest years, DFT was, therefore, used only for calculations of band structure and other properties of solids. However, DFT began to be used in quantum chemistry calculations in the 1990s, and today it has become the predominant method, accounting for more than 80 % of all quantum chemistry calculations, after only two decades. Quantum chemistry is aimed mainly at chemical reactions and properties. Because chemical reactions are usually associated with electron transfers between much different electronic states, highly sophisticated methods are required, incorporating high-level electron correlations of well-balanced dynamical and nondynamical correlations (see Sect. 3.2) to quantitatively reproduce the reactions. Quantum chemists have, therefore, focused on how to incorporate high-level electron correlations efficiently for several decades. So far, various methods have been developed with the difference mainly in the approaches for sorting out electron configurations to incorporate electron correlations efficiently. Prior to DFT, conventional methods have required much computational time, making it difficult to calculate the electronic states of large molecules, even for those containing several dozen atoms in the 1990s. The appearance of DFT altered this situation. Because DFT incorporates high-level electron correlations of well-balanced dynamical and nondynamical correlations simply in exchange-correlation functionals of electron density (see Sect. 4.5), it enables us to calculate chemical reaction energy diagrams quantitatively, with computational times equivalent or less than those for the Hartree–Fock method.

In this book, the fundamentals of DFT are reviewed from the point of view of quantum chemistry. The fundamentals of DFT have so far been described in many reference books. However, most DFT books explain the fundamentals of conventional DFT methods used in solid state calculations, which are not necessarily the same as those used in quantum chemistry calculations. In order to figure out how to use DFT to approach quantum chemistry, it is necessary to know the meaning of electron correlation and the strategies to incorporate high-level electron correlations. Molecular orbital energy is one of the most reliable indicators to test the balance of the electron correlations, which are mostly included in

exchange-correlation functionals. Based on this concept, this book first introduces the history and fundamentals of quantum chemistry calculations, then explains exchange-correlation functionals and their corrections especially for incorporating high-level electron correlations, and finally describes highly sophisticated DFT methods to provide correct orbital energies.

The objectives and outlines of each chapter are as follows:

*In Chap. 1, DFT is placed in the history of quantum chemistry, and then the Schrödinger equation and the quantizations of molecular motions are reviewed.* First, the history of quantum chemistry is overviewed to place DFT in the history of quantum chemistry. This chapter then reviews the backgrounds and fundamentals of the Schrödinger equation with the meaning of the wavefunction, in accord with the history. As the first applications in quantum chemistry, the quantizations of the three fundamental molecular motions are discussed using simple models, especially for the meanings of the Schrödinger equation solutions.

*According to the history of quantum chemistry, the Hartree–Fock method and its computational algorithms are introduced in Chap. 2.* First, the Hartree method and molecular orbital theory are briefly reviewed as the foundations of molecular electronic state theories. Based on these, the Slater determinant for the wavefunction and the Hartree–Fock method based thereon are then explained. As the computational algorithms of the Hartree–Fock method in quantum chemistry calculations, this chapter also describes the Roothaan method, basis functions centering on Gaussian-type functions, and high-speed computation algorithms of the Coulomb and exchange integrals. The unrestricted Hartree–Fock method for open-shell system calculations is also surveyed. This chapter also explains the electronic configurations of the elements in the periodic table, confirmed by the Hartree–Fock method to a considerable extent.

*Chapter 3 reviews electron correlation, to which the highest importance has been attached in quantum chemistry, for the meaning and previous approaches to incorporate it.* After describing the main cause for electron correlation, dynamical and nondynamical electron correlations are introduced to clarify the details of electron correlation. As the calculation methods for these electron correlations, this chapter briefly reviews the configuration interaction and perturbation methods for dynamical correlations and the multiconfigurational self-consistent field (SCF) method for nondynamical correlations. This chapter also mentions advanced electron correlation calculation methods to incorporate high-level electron correlations.

*In Chap. 4, the Kohn–Sham equation, which is the fundamental equation of DFT, and the Kohn–Sham method using this equation are described for the basic formalisms and application methods.* This chapter first introduces the Thomas–Fermi method, which is conceptually the first DFT method. Then, the Hohenberg–Kohn theorem, which is the fundamental theorem of the Kohn–Sham method, is clarified in terms of its basics, problems, and solutions, including the constrained-search method. The Kohn–Sham method and its expansion to more general cases are explained on the basis of this theorem. This chapter also reviews the constrained-search-based method of exchange-correlation potentials from electron densities and

the expansions of the Kohn–Sham method to time-dependent and response property calculations.

*Exchange-correlation functionals, which determine the reliability of Kohn–Sham calculations, are compared in terms of the basic concepts in their development, and for their features and problems, in Chap. 5.* This chapter uses as examples the major local density approximation (LDA) and generalized gradient approximation (GGA) exchange-correlation functionals and meta-GGA, hybrid GGA, and semi-empirical functionals to enhance the degree of approximation in terms of their concepts, applicabilities, and problems.

*Chapter 6 reviews physically meaningful corrections for the exchange-correlation functionals, including their formulations and applications.* As the specific types of corrections, this chapter covers long-range corrections, enabling us to calculate orbital energies and exchange integral kernels correctly; self-interaction corrections, improving the descriptions of core electronic states; van der Waals corrections, which are required in calculating van der Waals interactions; relativistic corrections, which are needed in the electronic state calculations of heavy atomic systems; and vector-potential corrections, which play a significant role in magnetic calculations.

*Chapter 7 focuses on orbital energy, which is the solution of the Kohn–Sham equation and one of the best indicators to evaluate incorporated electron correlations, including the various approaches to reproduce accurate orbital energies.* The physical meaning of orbital energy is first explained on the basis of the Koopmans and Janak theorems. Then, this chapter summarizes previous discussions on the causes of poor-quality orbital energies given in Kohn–Sham calculations and shows highly sophisticated exchange-correlation potentials, which have been developed to calculate accurate orbital energies. Finally, the long-range corrected Kohn–Sham method, which reproduces accurate occupied and unoccupied orbital energies simultaneously, is discussed, revealing the path to obtain accurate orbital energies.

This book has as its target readership the following groups: graduate students who are beginning their study of quantum chemistry, experimental researchers who intend to study DFT calculations from the beginning, theoretical researchers from different fields who become attracted to DFT studies in quantum chemistry, and quantum chemists who wish to brush up their fundamentals of quantum chemistry and DFT or wish to have a reference book for their lectures. Therefore, this book was designed to be useful in studying the fundamentals, not only of DFT but of quantum chemistry itself. Unlike representative DFT books such as Parr and Yang’s *Density-Functional Theory of Atoms and Molecules* (Oxford Press) and Dreizler and Gross’s *Density Functional Theory: An Approach to the Quantum Many-Body Problem* (Springer), this book explains DFT in practical quantum chemistry calculations using the terminology of chemistry. Because this book focuses on quantum chemistry, it basically omits DFT topics unrelated directly to quantum chemistry calculations. The detailed derivations of formulations are also neglected in this book, unlike many DFT books in physics, because this book is intended to instill the comprehension of DFT fundamentals. For the details required in the

development of specific theories and computational programs, the reader is directed to the relevant papers that are cited.

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