EDITED BY
PRATIM KUMAR CHATTARAJ
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ELECTRON DENSITY

CONCEPTS, COMPUTATION AND DFT APPLICATIONS

WILEY

Electron Density

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Concepts, Computation and DFT Applications

Edited by

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Preface

Electron density or the single particle density is a 3D function even for a many-electron system. Electron density contains all information regarding the ground state and also about some excited states of an atom or a molecule. All the properties can be written as functionals of electron density, and the energy attains its minimum value for the true density. Moreover, it is an experimental observable. It brings out a drastic reduction in computational labor due to its reduced dimensionality. Electron density helps build up various models that in turn make the understanding of complicated chemical, physical, or biological problems simpler. As we live and perceive in a 3D classical world, visualization of different systems and processes becomes much easier as opposed to that using the many-body wavefunction. Accordingly, it helps develop a classical interpretation of quantum mechanics.

This book aims to outline fundamental as well as applied aspects of state-of the-art developments in the domain of density functional theory. It is well known in the scientific literature that density functional theory constitutes the work horse for modern computational chemistry and physics. Density functional theory has been very successful in analyzing and rationalizing numerous physicochemical processes. However, there are also challenging situations where density functional theory fails to predict and/or analyze several experimentally observed phenomena. Moreover, the application of density functional theory is difficult in case of very large systems such as biological systems due to the limitation in the available computational resources. To this end, various methodological and conceptual aspects related to density functional theory have been discussed in this book. In particular, conceptual density functional theory-based reactivity descriptors are discussed in detail. Areas in which density functional theory has been successfully applied have also been discussed to give a broad overview of the field to the reader.

On the methodological and fundamental aspects, this book aims to discuss the Levy–Perdew–Sahni equation and the Kohn–Sham inversion problem within the premise of density functional theory. Several key concepts related to conceptual density functional theory-based local and global reactivity descriptors have been discussed. The relativistic treatment of many-electron systems within the premise of density functional theory has been explained in detail. In addition, the properties and applications of relativistic reduced density matrices have been discussed herein. Utilizing the Coulomb Green's function, recipes for performing many-body multiconfigurational calculations have been explored. Furthermore, application of catastrophe theory in understanding the Diels–Alder cycloaddition reaction pathways have been discussed. On the other hand, muti-scale simulation techniques have been discussed in the context of the modeling of excited-state electronic structures of biomolecules.

On the applied aspects of density functional theory, this book comprises several interesting applications. The designing principles for ultrashort H$\cdots$H nonbonded contacts and ultralong

C–C bonds have been explored. Application of density functional theory in the context of analyzing the properties of materials has been discussed. The emerging topic of mechanochemistry has been explored by taking help from density-based quantum chemical formalism. Electrostatic potential and their applications in the context of analyzing several physicochemical processes are discussed. The role of electron spin density in dictating molecular magnetism has been explored via considering several diradical systems. Interesting and novel bonding scenarios have been explored and discussed via several density functional theory formalisms. Applications of density functional theory in predicting radiative efficiencies and global warming potential of some selected organic molecules are also discussed. Finally, the properties of several natural products are explored via the application of density functional theory.

Thus, this book intends to cover both fundamental and applied aspects on the state-of the-art status of density functional theory. The book would help practicing and aspiring theoretical and computational chemists/physicists to obtain a clear-cut overview on the status of density functional theory.

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Levy–Perdew–Sahni Equation and the Kohn–Sham Inversion Problem

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1.1 Introduction

Density functional theory (DFT) [1–9] is a rigorous formulation for studying the ground-state of a many-electron system in terms of the corresponding density. This theory is complementary to other formulations of many-electron problems, such as those based on field-theoretic techniques [10, 11] or the model Hamiltonian approaches [12–15]. However, because of the ease of its implementation, DFT has become the de facto electronic structure theory with the ongoing development of highly accurate energy functionals. Starting with the earliest local density approximation (LDA) [2] based on the energy of homogeneous electron gas, these functionals have been developed, [16–27] guided by the various exact properties [28] they should satisfy. Obtaining these exact properties and their further investigation for different systems is thus of fundamental importance for understanding DFT well and making it applicable with high accuracy for various electronic systems. The question is this: How does one go about performing such studies? We address this in the following paragraph.

Let us start by recalling that DFT is a reformulation of quantum-mechanical many-electron problem in terms of the ground-state density. Therefore in this theory, any quantity is expressed as a functional of density. This is done by transforming the expectation value of the operator corresponding to a quantity into an expression in terms of the density. This transformation can sometimes be made exactly; however for a majority of quantities, it is not possible to do so. As a result, performing density-based calculations necessitates developing approximate expressions for such quantities in terms of the density. The best-known example of such an approximation is the exchange–correlation energy functional and the corresponding exchange–correlation potential, which is the mainstay of Kohn–Sham (KS) DFT calculations. Beginning with the LDA, a lot of effort has been put into developing approximations for better and better exchange–correlation (XC) energy functionals since the inception of DFT. This research activity is evidently vital for practical applications of theory, and continuous development of new XC energy functional has made DFT the most widely used electronic structure theory. On the other hand, to gain fundamental insights into DFT one needs to explore the connection between a density functional and its wavefunctional counterpart without necessarily expressing relevant quantities in terms of the density [29]. In such cases, one can employ the formal expression of a density functional in terms of the exact many-body wavefunction. For example, to study energy density functional for fractional numbers of electrons, a statistical mixture of pure states is used [30] to obtain the corresponding energy.

From among various exact results of DFT, our focus in this chapter is on obtaining the exact Kohn–Sham potential for a given ground-state density. This falls under the category of the inverse

problems [31–33] with the direct problem being the calculation of density from a given potential. Over the years, various methods have been proposed and employed [34–66] for doing such a calculation. We will show in this chapter that all the density-based inversion methods can be obtained using the Euler equation [67–69]

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{eff}}(\mathbf{r}) \right] \sqrt{\rho} = \mu \sqrt{\rho} \tag{1.1}$$

for the density. We will begin by using this equation for the inversion and then go on to generalize it. This generalization shows the universal nature of these methods and opens the door to devising a method of one's choice suitable for a given density. In Eq. (1.1) $v_{\text{ext}}(\mathbf{r})$ is the potential in which electrons are moving; $v_{\text{eff}}(\mathbf{r})$ comprises the Pauli potential, the Hartree potential, and the exchange–correlation potential with μ being the chemical potential of the system. The expression for $v_{\text{eff}}(\mathbf{r})$ in terms of the exact wavefunction of a system has been derived by Levy–Perdew–Sahni (LPS) [67]. In the rest of this chapter, we will therefore refer to Eq. (1.1) as the LPS equation.

After demonstrating the universal nature of all density-based inversion methods, we next discuss how this understanding also leads to a general penalty method to obtain the Kohn–Sham potential for a ground-state density. Finally, using the expression of $v_{\text{eff}}(\mathbf{r})$ in terms of the wavefunction, we throw light on why methods that employ approximate wavefunctions rather than the density obtained from the same wavefunction give Kohn–Sham potential free of pathological features that are seen when these densities are employed in density-to-potential inversion. In the following, we first present the universal nature of seemingly different density-based Kohn–Sham inversion methods using Eq. (1.1) and show how these can all be generated from a single algorithm based on the LPS equation. An exciting application based on understanding universal nature is using random numbers to carry out the density-to-potential inversion. We will discuss that as well. Next, we present the general penalty method to obtain the Kohn–Sham potential from a ground-state density. Finally, we discuss how expression for $v_{\text{eff}}(\mathbf{r})$ in terms of the wavefunction can be used to find the Kohn–Sham potential of a many-electron system from an approximate wavefunction. All the methods are demonstrated by applying them to spherical systems.

1.2 One Equation $\Longrightarrow$ Several Methods; Universal Nature of Different Density-Based Kohn–Sham Inversion Algorithms [70]

1.2.1 Generating Functional $S[\rho]$ of Density-Based Kohn–Sham Inversion

In this section, we show how Eq. (1.1) can be used to obtain several different algorithms to get the Kohn–Sham potential for a given density using a generating functional $S[\rho]$ of density $\rho(\mathbf{r})$. Since the Hartree potential is well known in terms of density, obtaining the exact Kohn–Sham potential boils down to getting the exchange–correlation potential for a given density. This is done using Eq. (1.1). For this, let us first see how this equation is obtained. We begin by writing the energy functional as

$$E[\rho] = \frac{1}{8} \int \frac{|\nabla \rho|^2}{\rho} d\mathbf{r} + T_{\text{P}}[\rho] + \int v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho] \tag{1.2}$$

where

$$E_{\text{H}}[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \tag{1.3}$$

is the Hartree energy, $T_{\text{P}}[\rho]$ is the Pauli kinetic energy, and $E_{\text{xc}}[\rho]$ is the exchange–correlation energy. Note that $(1/8) \int |\nabla \rho(\mathbf{r})|^2/\rho(\mathbf{r})d\mathbf{r} = (1/2) \int |\nabla \sqrt{\rho(\mathbf{r})}|^2 d\mathbf{r}$ is the ground-state kinetic energy