

Eric Cancès • Gero Friesecke
Editors

Density Functional Theory

Modeling, Mathematical Analysis,
Computational Methods, and Applications

 Springer

Editors

Eric Cancès
CERMICS
Ecole des Ponts and Inria Paris
Marne-la-Vallée, France

Gero Friesecke
Department of Mathematics
Technische Universität München
Garching bei München, Germany

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Preface

Density functional theory (DFT) provides the most widely used models for simulating molecules and materials based on the fundamental laws of quantum mechanics. It earned its main inventor Walter Kohn a Nobel prize, and nowadays plays a central role in a huge spectrum of applications in chemistry, physics, and materials science. DFT has become an interdisciplinary field as testified by the list of authors of this book, coming from chemistry, physics, materials science, mathematics, and scientific computing.

Quantum mechanics describes a system of N interacting particles in the physical three-dimensional space by a partial differential equation in $3N$ spatial variables. Hence, standard numerical methods incur an exponential increase of computational effort with N , a phenomenon known as the curse of dimensionality; in practice these methods already fail beyond $N = 2$. DFT overcomes this problem by (1) reformulating the N -body problem involving functions of $3N$ variables in terms of the electronic density, a function of 3 variables, (2) approximating it by a pioneering hybrid approach which keeps important ab initio contributions and re-models the remainder in a data-driven way.

In fact many different types of data were used by different researchers to parameterize the remainder, ranging from numerical results for reference systems over experimental properties of atoms and small molecules to exact constraints in asymptotic regimes.

Kohn–Sham DFT models a molecular system with N electrons as follows. For simplicity we describe the common case of a spin-unpolarized system. The quantum state of the electrons is described by a set of $N/2$ doubly occupied spatial orbitals $\{\varphi_i\}_{i=1,\dots,N/2}$, which are functions on the physical space \mathbb{R}^3 that are orthonormal with respect to the L^2 inner product. The total electronic energy is

$$E[\{\varphi_i\}] = \sum_{i=1}^{N/2} \int_{\mathbb{R}^3} |\nabla \varphi_i(\mathbf{r})|^2 d\mathbf{r} + \int_{\mathbb{R}^3} v_{\text{ne}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + E_{\text{Hxc}}[\rho]. \quad (1)$$

The first term models the kinetic energy of the electrons, v_{ne} is the electrostatic potential generated by the nuclei, and E_{Hxc} is the so-called Hartree-exchange-correlation functional which models the electron-electron interactions and interaction-induced corrections to the kinetic energy by some explicit functional of the density. The density ρ is expressed in terms of the orbitals as

$$\rho(\mathbf{r}) = 2 \sum_{i=1}^{N/2} |\varphi_i(\mathbf{r})|^2. \quad (2)$$

The Kohn–Sham ground state is obtained by minimizing the energy functional E over $\{\varphi_i\}$ subject to the orthonormality constraints $\int_{\mathbb{R}^3} \varphi_i^* \varphi_j = \delta_{ij}$. The Euler–Lagrange equations (stationarity conditions) are the *Kohn–Sham equations* [1]

$$\left(-\frac{1}{2} \nabla^2 + v_{\text{ne}}(\mathbf{r}) + v_{\text{Hxc}}(\mathbf{r}) \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}), \quad (3)$$

where the ε_i are Lagrange multipliers and $v_{\text{Hxc}}(\mathbf{r})$ is the Hartree-exchange-correlation potential defined as the functional derivative of $E_{\text{Hxc}}[\rho]$ with respect to $\rho(\mathbf{r})$. The orbitals satisfying Eq. (3) are called the Kohn–Sham orbitals. Mathematically, the Kohn–Sham equations are a system of nonlinear elliptic eigenvalue problems, since the potential v_{Hxc} depends on the φ_i 's through the density ρ .

There are a great many challenges associated with this system, touching upon different areas of physical and chemical modeling, mathematical analysis, and scientific computing, such as:

- Design of accurate yet computationally practical Hartree-exchange-correlation functionals, going beyond the local density approximation (LDA) introduced in Kohn and Sham's seminal 1965 paper [1] and the—currently widely used—semilocal and hybrid functionals and remaining applicable in strongly correlated regimes (stretched chemical bonds, transition metal oxides, Mott insulators).
- Design of effective numerical methods to solve the Kohn–Sham equations for large molecular systems, possibly coupled to an environment (linear scaling methods, coarse-graining, quantum-mechanics/molecular-mechanics (QM/MM), and other multilayer approaches).
- Theoretical understanding of the errors incurred both by the modeling and the numerical treatment (comparison to exact many-body quantum mechanics in scaling limits, choice of discretization or background basis, iterative algorithms with stopping criteria, adaptive floating-point arithmetic, massive parallelization for hybrid CPU/GPU, and future exascale architectures).
- Unearthing the intrinsic mathematical properties of different Kohn–Sham models in important basic situations such as bond dissociation, dispersion forces, or defects in crystals.

These challenges give rise to a variety of exciting and difficult problems for mathematicians and computational scientists, and bring one immediately to the edge of current knowledge in variational methods, nonlinear partial differential equations, large-scale numerical optimization and linear algebra, or model reduction. This book introduces and reviews the main models of DFT, covering their derivation and mathematical properties, numerical treatment, and selected applications. It intends to be an accessible yet state-of-art text on DFT for graduate students and researchers in applied and computational mathematics, physics, chemistry, and materials science. We hope that it helps to attract mathematicians and computer scientists willing to contribute to a very lively research topic and an essential tool to meet many scientific challenges of the twenty-first century, such as computer-aided drug design or computational materials engineering for green energy production and storage. We also hope that this volume will be useful to computational chemists and physicists seeking to better understand the mathematical foundations of DFT, and the state-of-the-art numerical methods used to solve the Kohn–Sham equations.

This book is organized as follows. This preface is followed by a prologue on the early days of DFT by Mel Levy, one of the pioneers of the field, who—among other things—introduced the celebrated concept of constrained search. The 11 chapters of the book can be classified into two groups:

- DFT models and their derivation, mathematical justification and analysis: Chaps. [1](#) (J. Toulouse), [2](#) (A. Savin), [3](#) (M. Lewin, E.H. Lieb, R. Seiringer), [4](#) (G. Friesecke, A. Gerolin, P. Gori-Giorgi), [5](#) (S. Kvaal), [6](#) (D. Gontier, J. Lu, C. Ortner);
- Numerical methods and applications: Chaps. [7](#) (E. Cancès, A. Levitt, Y. Maday, C. Yang), [8](#) (L. Lin, J. Lu, L. Ying), [9](#) (H. Chen, R. Schneider), [10](#) (X. Dai, A. Zhou), [11](#) (L. Genovese, T. Deutsch), [12](#) (K. Bhattacharya, V. Gavini, M. Ortiz, M. Ponga, P. Suryanarayana).

The chapters are self-contained and can be read independently, but we advise readers with mathematical or scientific computing backgrounds unfamiliar with DFT to get in shape with Sects. [1.1](#) and [1.3.1](#) in Chap. [1](#) (basics of DFT) and the first three sections of Chap. [7](#) (mathematical formulation and discretization methods), and consult the first three sections of Chap. [3](#) for a mathematical justification of the LDA.

Let us finally mention that this book focuses on Kohn–Sham DFT methods for electronic ground-state calculation within the Born–Oppenheimer (clamped nuclei) approximation. It does not cover time-dependent DFT (computation of excited states, linear response theory...), orbital-free DFT (simulation of warm dense matter...), nor classical DFT (classical statistical mechanics of the liquid state). Likewise, post-DFT methods (e.g., Green’s function methods such as GW or Bethe–Salpeter), coupling of DFT with finer but computationally more expensive electronic structure methods for strongly correlated electrons (e.g., DFT+DMFT), coupling of DFT with molecular dynamics and implicit solvent models (multilayer models such as QM/MM), or machine learning methods trained on data generated by DFT calculations lie beyond the scope of this book. So are the other two

most popular families of methods to compute ground-state electronic structures of molecules and materials, namely post-Hartree–Fock wave function methods (coupled-cluster, multiconfiguration methods, tensor network methods,...) and Monte Carlo methods. Each of these topics would be worth a book of their own in this series.

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Munich, Germany
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Eric Cancès
Gero Friesecke

Reference

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Prologue: Early Days of Modern DFT (1964–1979)

Mel Levy

It is a pleasure to write about the early days of modern DFT from a personal perspective.

At that time, the local density approximation dominated in approximating exchange-correlation for calculations. In basic theory, there was intense interest in the definition of $F[\rho]$, the universal functional of the density for the kinetic energy plus the electron-electron repulsion energy, where, of course,

$$E_0 = \min_{\rho} \left\{ \int_{\mathbb{R}^3} \rho(\mathbf{r}) v_{\text{ne}}(\mathbf{r}) \, d\mathbf{r} + F[\rho] \right\}.$$

Along these lines, on a chalkboard at a special session of a theoretical chemistry conference in Boulder, Colorado, in the summer of 1975, Walter Kohn wrote out the proof, by contradiction, of the 1964 Hohenberg–Kohn theorem. As I recall, the audience applauded enthusiastically. Then there was a lively discussion about the $F[\rho]$ in this HK paper of 1964, because this functional, born by this proof by contradiction, was identified specifically for only each trial density that is a non-degenerate ground state of some extremal potential (non-degenerate v -representable). There were questions. What happens when the trial density is not some ground state? What happens when the trial density is a ground state, but is a degenerate one? These questions were in my thoughts when I began the serious study of DFT in 1978.

Then, in looking through a 1978 issue of IJQC, I noticed a long paper by Jeremy Percus. In it he derived a number of interesting Legendre transform-type bounds, but, almost as an aside, he also happened to identify a noninteracting kinetic energy functional that was expressed as the minimum kinetic energy of all ensembles of idempotent density matrices that yield a noninteracting v -representable density. Influenced by this paper, it suddenly occurred to me a couple of weeks later that the original HK functional could be identified as a constrained search. Moreover, it

could also be generalized by using this constrained search. Namely,¹

$$F[\rho] = \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{T} + \hat{W}_{ee} | \Psi \rangle \quad (1)$$

because

$$E_0 = \min_{\rho} \min_{\Psi \rightarrow \rho} \langle \Psi | \hat{H} | \Psi \rangle \quad (2)$$

and because the same expectation value, involving v_{ne} , must be given by all wave functions that yield $\rho(\mathbf{r})$.

I remember finding expressions (1) and (2) a bit frightening as I wrote them down and stared at them, because they were so simply expressed and because I knew that they generalized DFT to include densities that are degenerate and to densities that are not necessarily v -representable. I also realized that they led to a deeper understanding of DFT. For instance, I soon realized that the philosophy behind Eqs. (1) and (2) could be applied to generalize Gilbert's functional of the electron-electron repulsion energy, as a functional of the one-matrix, to include a larger class of trial one matrices. All this appears in my 1979 paper.

Yes, the 15-year period from 1964 to 1979 was important indeed. Kohn–Sham theory and the thermal DFT of Mermin were formulated in 1965. Then von Barth and Hedin and Rajagopal and Calloway formulated spin-density functional theory in 1972 and 1973. In the mid-1970s, the adiabatic connection formula was derived by Langreth and Perdew and Gunnarsson and Lundqvist. This formula is, of course, important for the development of approximate exchange-correlation functionals. The concept of electronegativity was elucidated through DFT by Parr, Donnelly, Levy, and Palke in the 1978 paper that launched conceptual DFT. Then the time-independent ensemble theory for the density functional treatment of excited states was formulated by Theophilou in 1979.

Forty years ago, those of us immersed in DFT knew that we were gambling on a new field, especially since there were influential vocal skeptics. But we felt that there just might be good times ahead. . .

Mel Levy
 Department of Chemistry and Quantum Theory Group
 Tulane University
 New Orleans, LA, USA

¹ See Sect. 1.1.1 for a precise definition of the notation.

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Contributors

Kaushik Bhattacharya California Institute of Technology, Pasadena, CA, USA

Eric Cancès CERMICS, Ecole des Ponts and Inria Paris, Marne-la-Vallée, France

Huajie Chen School of Mathematical Sciences, Beijing Normal University, Beijing, China

Xiaoying Dai LSEC, Institute of Computational Mathematics and Scientific/Engineering Computing, Academy of Mathematics and Systems Science, Chinese Academy of Sciences, Beijing, China

Thierry Deutsch Univ. Grenoble Alpes, CEA, IRIG-MEM, Grenoble, France

Gero Friesecke Department of Mathematics, Technische Universität München, Garching bei München, Germany

Vikram Gavini University of Michigan, Ann Arbor, MI, USA

Luigi Genovese Univ. Grenoble Alpes, CEA, IRIG-MEM, Grenoble, France

Augusto Gerolin Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, ON, Canada

Department of Mathematics and Statistics, University of Ottawa, Ottawa, ON, Canada

David Gontier CEREMADE, Université Paris-Dauphine, PSL University, Paris, France

Paola Gori-Giorgi Department of Theoretical Chemistry, Vrije Universiteit Amsterdam, Amsterdam, The Netherlands

AI4Science Microsoft Research, Amsterdam, The Netherlands

Simen Kvaal Hylleraas Centre for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, Oslo, Norway

Antoine Levitt CERMICS, Ecole des Ponts and Inria Paris, Marne-la-Vallée, France

Mel Levy Department of Chemistry and Quantum Theory Group, Tulane University, New Orleans, LA, USA

Mathieu Lewin CNRS & CEREMADE, Université Paris-Dauphine, PSL University, Paris, France

Elliott H. Lieb Departments of Mathematics and Physics, Jadwin Hall, Princeton University, Princeton, NJ, USA

Lin Lin Department of Mathematics, University of California, Berkeley and Applied Mathematics and Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Jianfeng Lu Departments of Mathematics, Physics, and Chemistry, Duke University, Durham, NC, USA

Yvon Maday Sorbonne Université, Université Paris-Cité, CNRS, Laboratoire Jacques-Louis Lions (LJLL), Paris, France
Institut Universitaire de France, Paris, France

Michael Ortiz California Institute of Technology, Pasadena, CA, USA

Christoph Ortner Department of Mathematics, University of British Columbia, Vancouver, BC, Canada

Mauricio Ponga University of British Columbia, Vancouver, BC, Canada

Andreas Savin Laboratoire de Chimie Théorique, CNRS and Sorbonne University, Paris, France

Reinhold Schneider Institut für Mathematik, Technische Universität Berlin, Berlin, Germany

Robert Seiringer IST Austria (Institute of Science and Technology Austria), Klosterneuburg, Austria

Phanish Suryanarayana Georgia Institute of Technology, Atlanta, GA, USA

Julien Toulouse Laboratoire de Chimie Théorique (LCT), Sorbonne Université and CNRS, Paris, France
Institut Universitaire de France, Paris, France

Chao Yang Computational Research Division, Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Lexing Ying Department of Mathematics and Institute for Computational and Mathematical Engineering, Stanford University, Stanford, CA, USA

Aihui Zhou LSEC, Institute of Computational Mathematics and Scientific/Engineering Computing, Academy of Mathematics and Systems Science, Chinese Academy of Sciences, Beijing, China

List of Symbols

Parameters of the Electronic Problem

N	Number of electrons or electron pairs
N_{occ}	Number of electron occupied one-body electronic states
$M, N_{\text{nuc}}, N_{\text{n}}$	Number of nuclei
Z_m, \mathbf{R}_m	Nuclear charges, positions
β	Inverse temperature

Electron Coordinates

\mathbf{r}	Single-electron position coordinate vector
r_α	Cartesian components of single-electron position coordinate vector
$r_{ij} = \mathbf{r}_i - \mathbf{r}_j $	Euclidean distance between electrons i and j
$\mathbf{x}_i = (\mathbf{r}_i, s_i)$	Space-spin coordinates of i th electron

Wavefunctions, Density Matrices, Densities, Orbitals

$\Psi, \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$	Many-particle wavefunction
Γ	Many-particle density matrix
Γ_k	k -particle reduced density matrix
γ	Single-particle density matrix/1-particle reduced density matrix
$\rho, \rho(\mathbf{r})$	Single-particle density
$\rho_2, \rho_2(\mathbf{r}_1, \mathbf{r}_2)$	Pair density
Φ	Kohn–Sham wavefunction

φ_i, φ_a	Occupied/unoccupied Kohn–Sham orbitals or spin-orbitals
i, j, a, b	Summation indices: i, j for occupied orbitals, a, b for unoccupied orbitals
Φ_I	With $I = (i_1, \dots, i_N)$, or $ \varphi_{i_1} \dots \varphi_{i_N}\rangle$ or $\varphi_{i_1} \wedge \dots \wedge \varphi_{i_N}$: Slater determinant built from orbitals $\varphi_{i_1}, \dots, \varphi_{i_N}$

Functionals

$F, F[\rho]$	General functional
E_H	Hartree energy functional
E_{Hxc}	Hartree-exchange-correlation energy functional
E_{xc}	Exchange-correlation energy functional
E_x	Exchange energy functional
E_c	Correlation energy functional
T	Kinetic energy functional
T_S	Non-interacting kinetic energy functional
F_{LL}	Levy–Lieb constrained-search functional
F_{HK}	Hohenberg–Kohn functional
F_{DM}	Constrained-search density matrix functional

Energy Levels, Eigenvalues, Energy Densities, Fermi–Dirac Function

E_0	Ground state energy
$\varepsilon_i, \varepsilon_a$	Kohn–Sham eigenvalues
μ	Chemical potential, Fermi level
e_{xc}	Exchange-correlation energy per unit volume
ϵ_{xc}	Exchange-correlation energy per particle
f_β	Fermi–Dirac function

Potentials and Kernels

v	General (single-particle) potential
v_{ext}	External potential
$v_s, v_{\text{eff}}, v_{\text{KS}}$	Kohn–Sham effective potential
v_H	Hartree potential $v_H = \rho_0 \cdot ^{-1}$
$v_x, v_c, v_{\text{xc}}, v_{\text{Hxc}}$	Exchange, correlation, exchange-correlation, Hxc potentials
$f_x, f_c, f_{\text{xc}}, f_{\text{Hxc}}$	Exchange, correlation, exchange-correlation, Hxc kernels

Operators

A or \widehat{A}	Generic linear operators
A^* or A^\dagger	Adjoint of A
H	Many-body Hamiltonian operators
h	General single-particle Hamiltonian
h_ρ or h_γ	Kohn–Sham Hamiltonian
v_C	Coulomb operator
$\Delta = \nabla^2$	Laplace operator
χ	Reducible polarizability operator
χ_0	Irreducible polarizability operator
\mathcal{F}	Fourier transform
\mathcal{F}_{KS}	Kohn–Sham map

Matrices

A^\top	Transpose of A
A^*	Conjugate transpose of A

Discretization Parameters, Basis Functions, Discretized Models

N_b	Number of basis functions
N_g	Number of grid points
ξ_μ	Localized orbital (Gaussian, Slater, numerical,...)
Ξ	Set of localized orbitals
C, X	Coefficient matrices (of discretized KS orbitals in localized basis sets)
P	Discretized one-body density matrix
S	Overlap matrix
H	Hamiltonian matrices
V	Generic matrix
V_H	Hartree matrix
V_X	Exchange matrix
V_C	Correlation matrix
V_{xc}, V_{Hxc}	xc, Hxc matrices