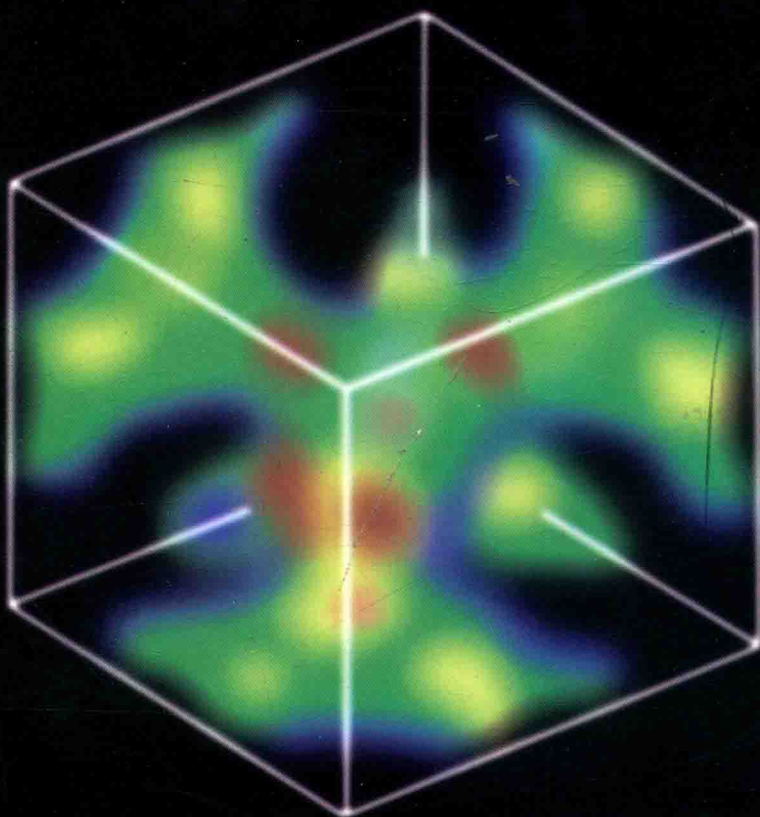


Richard M. Martin

Electronic Structure

Basic Theory and Practical Methods

电子结构



CAMBRIDGE

世界图书出版公司
www.wpcbj.com.cn

Elementary Basic Theorems and Methods

Richard M. Martin



CAMBRIDGE
UNIVERSITY PRESS

图书在版编目 (CIP) 数据

电子结构 = Electronic Structure : Basic Theory and Practical Methods :

英文 / (美) R. M. 马丁 (R. M. Martin) 著 . — 影印本 . —

北京 : 世界图书出版公司北京公司 , 2016.11

ISBN 978-7-5192-2087-7

I . ①电… II . ①马… III . ①电子结构—英文 IV . ① O552.5

中国版本图书馆 CIP 数据核字 (2016) 第 271861 号

著 者: Richard M. Martin

责任编辑: 刘 慧 高 蓉

装帧设计: 任志远

出版发行: 世界图书出版公司北京公司

地 址: 北京市东城区朝内大街 137 号

邮 编: 100010

电 话: 010-64038355 (发行) 64015580 (客服) 64033507 (总编室)

网 址: <http://www.wpcbj.com.cn>

邮 箱: wpcbjst@vip.163.com

销 售: 新华书店

印 刷: 三河市国英印务有限公司

开 本: 787mm × 1092mm 1/16

印 张: 40.5

字 数: 768 千

版 次: 2017 年 1 月第 1 版 2017 年 1 月第 1 次印刷

版权登记: 01-2016-6900

定 价: 129.00 元

版权所有 翻印必究

(如发现印装质量问题, 请与所购图书销售部门联系调换)

ELECTRONIC STRUCTURE

The study of the electronic structure of materials is at a momentous stage, with new algorithms and computational methods, and rapid advances in basic theory. Many properties of materials can now be determined directly from the fundamental equations for the electrons, providing new insights into critical problems in physics, chemistry, and materials science. This book is the first of two volumes that provide a unified exposition of the basic theory and methods of electronic structure, together with instructive examples of practical computational methods and real-world applications. These books are appropriate for both graduate students and practicing scientists. This volume describes the approach most widely used today – density functional theory – with emphasis upon understanding the ideas, practical methods, and limitations. Many references are provided to original papers, pertinent reviews, and widely available books. Included in each chapter is a short list of the most relevant references and a set of exercises that reveal salient points and challenge the reader.

RICHARD M. MARTIN received his Ph.D. from the University of Chicago in 1969, followed by post-doctoral research at Bell Laboratories. In 1971 he joined the Xerox Palo Alto Research Center in California where he became Principal Scientist and Consulting Professor at Stanford University. Since 1987 he has been Professor of Physics at the University of Illinois at Urbana-Champaign, where he has organized courses, workshops, and schools on electronic structure as well as founding the Materials Computation Center. In 2008 he was appointed again as Consulting Professor at Stanford University. He has made important contributions to many areas of modern electronic structure, with over 200 published papers. He is a fellow of the American Physical Society and the American Association for the Advancement of Science, and he is a recipient of the Alexander von Humboldt Senior Scientist Award. He has served on editorial boards of the American Physical Society, including *Physical Review*, *Physical Review Letters*, and *Reviews of Modern Physics* where he was associate editor for condensed matter theory.

Electronic Structure: Basic Theory and Practical Methods (978-0-521-53440-6) by Richard M. Martin first published by Cambridge University Press 2005

All rights reserved.

This reprint edition for the People's Republic of China is published by arrangement with the Press Syndicate of the University of Cambridge, Cambridge, United Kingdom.

© Cambridge University Press & Beijing World Publishing Corporation 2016

This book is in copyright. No reproduction of any part may take place without the written permission of Cambridge University Press or Beijing World Publishing Corporation.

This edition is for sale in the mainland of China only, excluding Hong Kong SAR, Macao SAR and Taiwan, and may not be bought for export therefrom.

此版本仅限中华人民共和国境内销售，不包括香港、澳门特别行政区及中国台湾。不得出口。



To Beverly

Preface

The field of electronic structure is at a momentous stage, with rapid advances in basic theory, new algorithms, and computational methods. It is now feasible to determine many properties of materials directly from the fundamental equations for the electrons and to provide new insights into vital problems in physics, chemistry, and materials science. Increasingly, electronic structure calculations are becoming tools used by both experimentalists and theorists to understand characteristic properties of matter and to make specific predictions for real materials and experimentally observable phenomena. There is a need for coherent, instructive material that provides an introduction to the field and a resource describing the conceptual structure, the capabilities of the methods, limitations of current approaches, and challenges for the future.

The purpose of this and a second volume in progress is to provide a unified exposition of the basic theory and methods of electronic structure, together with instructive examples of practical computational methods and actual applications. The aim is to serve graduate students and scientists involved in research, to provide a text for courses on electronic structure, and to serve as supplementary material for courses on condensed matter physics and materials science. Many references are provided to original papers, pertinent reviews, and books that are widely available. Problems are included in each chapter to bring out salient points and to challenge the reader.

The printed material is complemented by expanded information available on-line at a site maintained by the Electronic Structure Group at the University of Illinois (see Ch. 24). There one can find codes for widely used algorithms, more complete descriptions of many methods, and links to the increasing number of sites around the world providing codes and information. The on-line material is coordinated with descriptions in this book and will contain future updates, corrections, additions, and convenient feedback forms.

The content of this work is determined by the conviction that “electronic structure” should be placed in the context of fundamental issues in physics, while at the same time emphasizing its role in providing useful information and understanding of the properties of materials. At its heart, electronic structure is an interacting many-body problem that ranks among the most pervasive and important in physics. Furthermore, these are problems that must be solved with great accuracy in a vast array of situations to address issues relevant to materials. Indeed, many-body methods, such as quantum Monte Carlo and many-body perturbation

theory, are an increasing part of electronic structure theory for realistic problems. These methods are the subject of the second volume.

The subjects of this volume are fundamental ideas and the most useful approaches at present are based upon independent-particle approximations. *These methods address directly and quantitatively the full many-body problem because of the ingenious formulation of density functional theory and the Kohn–Sham auxiliary system.* This approach provides a way to approach the many-body problem, whereby certain properties can be calculated, in principle exactly, and in practice very accurately for many materials using feasible approximations and independent-particle methods. This volume is devoted to independent-particle methods, with emphasis on their usefulness and their limitations when applied to real problems of electrons in materials. In addition, these methods provide the starting point for much of the work described in the planned second volume. Indeed, new ideas that build upon the construction of an auxiliary system and actual independent-particle calculations are critical aspects of modern many-body theory and computational methods that can provide quantitative description of important properties of condensed matter and molecular systems.

It is a humbling experience to attempt to bring together the vast range of excellent work in this field. Many relevant ideas and examples are omitted (or given short shrift) due to lack of space, and others not covered because of the speed of progress in the field. Feedback on omissions, corrections, suggestions, examples, and ideas are welcome in person, by e-mail, or on-line.

Outline

Part I consists of the first five chapters, which include introductory material. Chapter 1 provides historical background and early developments of the theoretical methods that are foundations for more recent developments. Chapter 2 is a short summary of characteristic properties of materials and modern understanding in terms of the electronic structure. Examples are chosen to illustrate the goals of electronic structure theory and a few of the achievements of the last decades. Further details and applications are included in later chapters. Chapters 3–5 present background theoretical material: Ch. 3 summarizes basic expressions in quantum mechanics needed later; Ch. 4 provides the formal basis for the properties of crystals and establishes notation needed in the following chapters; and Ch. 5 is devoted to the homogeneous electron gas, the idealized system that sets the stage for electronic structure of condensed matter.

Part II, Chs. 6–9, is devoted to density functional theory upon which is based much of the present-day work in the theory of electronic structure. Chapter 6 presents the basic existence theorems of Hohenberg, Kohn, and others; and Ch. 7 describes the Kohn–Sham approach, which is the theoretical basis for approximate inclusion of many-body effects in practical independent-particle equations. This approach has proven to be very successful in many problems and is by far the most widely used technique for quantitative calculations. Chapter 8 covers examples of functionals; although the primary emphasis here is the use of the functionals, selected material is included on the many-body effects implicitly incorporated

into the functionals. This is required for appreciation of the limitations of widely used approximate functionals and avenues for possible improvements. Finally, general aspects of the solution of the Kohn–Sham equations are in Ch. 9, with further details and specific applications given in later chapters.

Part III, Chs. 10 and 11, addresses the solution of mean-field Hartree–Fock and Kohn–Sham equations in the simplest case, the spherical geometry of an atom, and the generation of pseudopotentials. Atomic calculations illustrate the theory and are used directly as essential parts of the methods described later. Pseudopotentials are widely used in actual calculations on real materials and, in addition, their derivation brings out beautiful theoretical issues.

Part IV, Chs. 12–17, is devoted to the three core methods for solution of independent-particle equations in solids. The goal is to describe the methods in enough detail to show key ideas, their relationships, and relative advantages in various cases. But it is not the goal to give all details needed to construct working algorithms fully. Many noteworthy aspects are placed in appendices.

Part V, Chs. 18–23, represents the culmination of present-day electronic structure, which has flowered to produce ideas and methods that enable prediction of many properties of real materials. Probably the most important single development in recent years is the “Car–Parrinello” method (Ch. 18) that has revolutionized the field of electronic structure, making possible calculations on previously intractable problems such as solids at finite temperature, liquids, molecular reactions in solvents, etc. New developments in the understanding and use of response functions and time-dependent density functional theory have proved practical methods for computing spectra for phonons and spin excitations (Ch. 19) and optical excitations (Ch. 20). New developments in the understanding and use of Wannier functions and the theory of polarization and localization in solids (Chs. 21 and 22) have led to new understanding of issues resolved only in the last decade. Finally, satisfying local descriptions of electronic properties and potentially useful linear-scaling, “order- N ” methods are described in Ch. 23.

The short chapter, Ch. 24, “Where to find more” replaces a summary; instead of attempting to summarize, it is more appropriate to point to further developments in a way that will be updated in the future, namely an online site where there is further information coordinated with this volume, computer codes, and links to many other sites.

The appendices are devoted to topics that are too detailed to include in the main text and to subjects from different fields that have an important role in electronic structure.

Acknowledgments

Four people and four institutions have played the greatest role in shaping the author and this work: the University of Chicago and my advisor Morrel H. Cohen, who planted the ideas and set the level for aspirations; Bell Labs, where the theory group and interactions with experimentalists provided diversity and demanded excellence; Xerox Palo Alto Research Center (PARC), in particular, my stimulating collaborator J. W. (Jim) Allen and my second mentor W. Conyers Herring; and the University of Illinois at Urbana-Champaign, especially my close collaborator David M. Ceperley. I am indebted to the excellent colleagues and students in the Department of Physics, the Frederick Seitz Materials Research Laboratory, and the Beckman Institute.

The actual writing of this book started at the Max Planck Institut für Festkörperforschung in Stuttgart, partially funded by the Alexander von Humboldt Foundation, and continued at the University of Illinois, the Aspen Center for Physics, Lawrence Livermore National Laboratory, and Stanford University. Their support is greatly appreciated.

Funding from the National Science Foundation, the Department of Energy, the Office of Naval Research, and the Army Research Office during the writing of this book is gratefully acknowledged.

Appreciation is due to countless people who cannot all be named. Many colleagues who provided figures are specifically acknowledged in the text. Special thanks are due to David Drabold, Beverly Martin, and Richard Needs for many comments and criticisms on the entire volume. Others who contributed directly in clarifying the arguments presented here, correcting errors, and critical reading of the manuscript are: V. Akkiseni, O. K. Andersen, V. P. Antropov, E. Artacho, S. Baroni, P. Blöchl, M. Boero, J. Chelikowsky, X. Cheng, T. Chiang, S. Chiesa, M. A. Crocker, D. Das, K. Delaney, C. Elliott, G. Galli, O. E. Gunnarsson, D. R. Hamann, V. Heine, L. Hoddeson, V. Hudson, D. D. Johnson, J. Junquera, J. Kim, Y.-H. Kim, E. Koch, J. Kübler, K. Kunc, B. Lee, X. Luo, T. Martinez, J. L. Martins, N. Marzari, W. D. Mattson, I. I. Mazin, A. K. McMahan, V. Natoli, O. H. Nielsen, J. E. Northrup, P. Ordejon, J. Perdew, W. E. Pickett, G. Qian, N. Romero, D. Sanchez-Portal, S. Satpathy, S. Savrossov, E. Schwegler, G. Scuseria, E. L. Shirley, L. Shulenburger, J. Soler, I. Souza, V. Tota, N. Trivedi, A. Tsolakidis, D. H. Vanderbilt, C. G. Van de Walle, M. van Schilfhaarde, I. Vasiliev, J. Vincent, T. J. Wilkens. For corrections in 2008, I am indebted to K. Belashchenko, E. K. U. Gross, I. Souza, A. Torralba, C. G. Van de Walle, and J.-X. Zhu.

Notation

Abbreviations

BZ	first Brillouin zone
wrt	with respect to
+c.c.	denotes adding the complex conjugate of the preceding quantity

General physical quantities

E	energy
Ω	volume (to avoid confusion with V used for potential)
$P = -(dE/d\Omega)$	pressure
$B = \Omega(d^2E/d\Omega^2)$	bulk modulus (inverse of compressibility)
$H = E + P\Omega$	enthalpy
$u_{\alpha\beta}$	strain tensor (symmetrized form of $\epsilon_{\alpha\beta}$)
$\sigma_{\alpha\beta} = -(1/\Omega)(\partial E/\partial u_{\alpha\beta})$	stress tensor (note the sign convention)
$\mathbf{F}_I = -(dE/d\mathbf{R}_I)$	force on nucleus I
$C_{IJ} = d^2E/d\mathbf{R}_I d\mathbf{R}_J$	force constant matrix
$n(\mathbf{r})$	density of electrons

Notation for crystals

Ω_{cell}	volume of primitive cell
\mathbf{a}_i	primitive translation vectors
\mathbf{T} or $\mathbf{T}(\mathbf{n}) \equiv \mathbf{T}(n_1, n_2, n_3)$ $= n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$	lattice translations
$\tau_s, s = 1, \dots, S$	positions of atoms in the basis
\mathbf{b}_i	primitive vectors of reciprocal lattice
\mathbf{G} or $\mathbf{G}(\mathbf{m}) \equiv \mathbf{G}(m_1, m_2, m_3)$ $= m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3$	reciprocal lattice vectors
\mathbf{k}	wavevector in first Brillouin zone (BZ)
\mathbf{q}	general wavevector ($\mathbf{q} = \mathbf{k} + \mathbf{G}$)

Hamiltonian and eigenstates

\hat{H}	hamiltonian for either many particles or a single particle
$\Psi(\{\mathbf{r}_i\})$	Many-body wavefunction of a set of particle positions \mathbf{r}_i , $i = 1, N_{\text{particle}}$; spin is assumed to be included in the argument \mathbf{r}_i unless otherwise specified
E_i	energy of many-body state
$\Phi(\{\mathbf{r}_i\})$	single determinant uncorrelated wavefunction
$H_{m,m'}$	matrix element of hamiltonian between states m and m'
$S_{m,m'}$	overlap matrix elements of states m and m'
$\psi_i(\mathbf{r})$	independent-particle wavefunction or “orbital,” $i = 1, \dots, N_{\text{states}}$
ε_i	independent-particle eigenvalue, $i = 1, \dots, N_{\text{states}}$
$f_i = f(\varepsilon_i)$	occupation of state i where f is the Fermi function
$\psi_i^\sigma(\mathbf{r}), \varepsilon_i^\sigma$	used when spin is explicitly indicated
$\alpha_i(\sigma_j)$	spin wavefunction for particle j ; $i = 1, 2$
$\phi_i(\mathbf{r}_j, \sigma_j)$	single particle “spin-orbitals” ($= \psi_i^\sigma(\mathbf{r}_j) \times \alpha_i(\sigma_j)$)
$\psi_l(r)$	single-body radial wavefunction $(\psi_{l,m}(\mathbf{r}) = \psi_l(r)Y_{lm}(\theta, \phi))$
$\phi_l(r)$	single-body radial wavefunction $\phi_l(r) = r\psi_l(r)$
$\eta_l(\varepsilon)$	phase shift
$\psi_{i,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{i,\mathbf{k}}(\mathbf{r})$	Bloch function in crystal, with $u_{i,\mathbf{k}}(\mathbf{r})$ periodic
$\varepsilon_{i,\mathbf{k}}$	eigenvalues that define bands as a function of \mathbf{k}
$\hat{H}(\mathbf{k})$	“gauge transformed” hamiltonian given by Eq. (4.37); eigenvectors are the periodic parts of the Bloch functions $u_{i,\mathbf{k}}(\mathbf{r})$
$\chi_\alpha(\mathbf{r})$	single-body basis function, $\alpha = 1, \dots, N_{\text{basis}}$. Orbital i is expanded in basis functions α , i.e. $\psi_i(\mathbf{r}) = \sum_\alpha c_{i\alpha} \chi_\alpha(\mathbf{r})$
$\chi_\alpha(\mathbf{r} - (\tau + \mathbf{T}))$	localized orbital basis function on atom at position τ in cell labelled by translation vector \mathbf{T}
$\chi^{\text{OPW}}(\mathbf{r}), \chi^{\text{APW}}(\mathbf{r}), \chi^{\text{LMT0}}(\mathbf{r})$	Basis function for orthogonalized, augmented or muffin-tin orbital basis functions
$w_i(\mathbf{r} - \mathbf{T})$	Wannier function i associated with band i and cell \mathbf{T}
$\tilde{w}_i(\mathbf{r} - \mathbf{T})$	Non-orthogonal transformation of Wannier functions

Density functional theory

$F[f]$	General notational for F a functional of the function f
$E_{\text{xc}}[n]$	exchange–correlation energy in Kohn–Sham theory
$\epsilon_{\text{xc}}(\mathbf{r})$	exchange–correlation energy per electron
$V_{\text{xc}}(\mathbf{r})$	exchange–correlation potential in Kohn–Sham theory
$V_{\text{xc}}^\sigma(\mathbf{r})$	exchange–correlation potential for spin σ
$f_{\text{xc}}(\mathbf{r}, \mathbf{r}')$	Response $\delta^2 E_{\text{xc}}[n]/\delta n(\mathbf{r})\delta n(\mathbf{r}')$

Response function and correlation functions

$\chi(\omega)$	general response function
$\chi_0(\omega)$	general response function for independent particles
$K(\omega)$	Kernel in self-consistent response function $\chi^{-1} = [\chi^0]^{-1} - K$
$\epsilon(\omega)$	frequency dependent dielectric function
$n(\mathbf{r}, \sigma; \mathbf{r}', \sigma')$	pair distribution
$g(\mathbf{r}, \sigma; \mathbf{r}', \sigma')$	normalized pair distribution (often omitting the spin indices)
$G(z, \mathbf{r}, \mathbf{r}') \text{ or } G_{m,m'}(z)$	Green's function of complex frequency z
$\rho(\mathbf{r}, \sigma; \mathbf{r}', \sigma')$	density matrix
$\rho_\sigma(\mathbf{r}, \mathbf{r}')$	density matrix diagonal in spin for independent-particles

Contents

Preface	page xvii
Acknowledgments	xx
Notation	xxi

Part I Overview and background topics

1	Introduction	1
	Summary	1
1.1	Quantum theory and the origins of electronic structure	1
1.2	Emergence of quantitative calculations	5
1.3	The greatest challenge: electron correlation	8
1.4	Recent developments	9
	Select further reading	10
2	Overview	11
	Summary	11
2.1	Electronic ground state: bonding and characteristic structures	12
2.2	Volume or pressure as the most fundamental variable	16
2.3	Elasticity: stress–strain relations	21
2.4	Magnetism and electron–electron interactions	22
2.5	Phonons and displacive phase transitions	24
2.6	Thermal properties: solids, liquids, and phase diagrams	28
2.7	Atomic motion: diffusion, reactions, and catalysis	31
2.8	Surfaces, interfaces, and defects	32
2.9	Nanomaterials: between molecules and condensed matter	36
2.10	Electronic excitations: bands and band gaps	40
2.11	Electronic excitations: heat capacity, conductivity, and optical spectra	44
2.12	Example of MgB_2 : bands, phonons, and superconductivity	47
2.13	The continuing challenge: electron correlation	50
	Select further reading	51

3	Theoretical background	52
	Summary	52
3.1	Basic equations for interacting electrons and nuclei	52
3.2	Coulomb interaction in condensed matter	56
3.3	Force and stress theorems	56
3.4	Statistical mechanics and the density matrix	60
3.5	Independent-electron approximations	61
3.6	Exchange and correlation	65
3.7	Perturbation theory and the “ $2n + 1$ theorem”	68
	Select further reading	70
	Exercises	71
4	Periodic solids and electron bands	73
	Summary	73
4.1	Structures of crystals: lattice + basis	73
4.2	The reciprocal lattice and Brillouin zone	81
4.3	Excitations and the Bloch theorem	85
4.4	Time reversal and inversion symmetries	89
4.5	Point symmetries	91
4.6	Integration over the Brillouin zone and special points	92
4.7	Density of states	96
	Select further reading	96
	Exercises	97
5	Uniform electron gas and simple metals	100
	Summary	100
5.1	Non-interacting and Hartree–Fock approximations	102
5.2	The correlation hole and energy	107
5.3	Binding in sp-bonded metals	112
5.4	Excitations and the Lindhard dielectric function	113
	Select further reading	116
	Exercises	116

Part II Density functional theory

6	Density functional theory: foundations	119
	Summary	119
6.1	Thomas–Fermi–Dirac approximation: example of a functional	120
6.2	The Hohenberg–Kohn theorems	121
6.3	Constrained search formulation of density functional theory	125
6.4	Extensions of Hohenberg–Kohn theorems	126
6.5	Intricacies of exact density functional theory	129
6.6	Difficulties in proceeding from the density	131
	Select further reading	132
	Exercises	133

7	The Kohn–Sham auxiliary system	135
	Summary	135
7.1	Replacing one problem with another	135
7.2	The Kohn–Sham variational equations	138
7.3	E_{xc} , V_{xc} , and the exchange–correlation hole	139
7.4	Meaning of the eigenvalues	144
7.5	Intricacies of exact Kohn–Sham theory	145
7.6	Time-dependent density functional theory	147
7.7	Other generalizations of the Kohn–Sham approach	148
	Select further reading	149
	Exercises	149
8	Functionals for exchange and correlation	152
	Summary	152
8.1	The local spin density approximation (LSDA)	152
8.2	Generalized-gradient approximations (GGAs)	154
8.3	LDA and GGA expressions for the potential $V_{xc}^{\sigma}(\mathbf{r})$	157
8.4	Non-collinear spin density	159
8.5	Non-local density formulations: ADA and WDA	160
8.6	Orbital-dependent functionals I: SIC and LDA + U	160
8.7	Orbital-dependent functionals II: OEP and EXX	162
8.8	Hybrid functionals	165
8.9	Tests of functionals	166
	Select further reading	169
	Exercises	170
9	Solving Kohn–Sham equations	172
	Summary	172
9.1	Self-consistent coupled Kohn–Sham equations	172
9.2	Total energy functionals	174
9.3	Achieving self-consistency	179
9.4	Force and stress	182
	Select further reading	184
	Exercises	184

Part III Important preliminaries on atoms

10	Electronic structure of atoms	187
	Summary	187
10.1	One-electron radial Schrödinger equation	187
10.2	Independent-particle equations: spherical potentials	189
10.3	Open-shell atoms: non-spherical potentials	190
10.4	Relativistic Dirac equation and spin–orbit interactions	193
10.5	Example of atomic states: transition elements	195
10.6	Delta-SCF: electron addition, removal, and interaction energies	198

10.7	Atomic sphere approximation in solids	199
	Select further reading	201
	Exercises	202
11	Pseudopotentials	204
	Summary	204
11.1	Scattering amplitudes and pseudopotentials	204
11.2	Orthogonalized plane waves (OPWs) and pseudopotentials	207
11.3	Model ion potentials	211
11.4	Norm-conserving pseudopotentials (NCPPs)	212
11.5	Generation of l -dependent norm-conserving pseudopotentials	215
11.6	Unscreening and core corrections	218
11.7	Transferability and hardness	219
11.8	Separable pseudopotential operators and projectors	220
11.9	Extended norm conservation: beyond the linear regime	221
11.10	Ultrasoft pseudopotentials	222
11.11	Projector augmented waves (PAWs): keeping the full wavefunction	225
11.12	Additional topics	227
	Select further reading	228
	Exercises	229

Part IV Determination of electronic structure: the three basic methods

12	Plane waves and grids: basics	236
	Summary	236
12.1	The independent-particle Schrödinger equation in a plane wave basis	236
12.2	The Bloch theorem and electron bands	238
12.3	Nearly-free-electron approximation	239
12.4	Form factors and structure factors	240
12.5	Approximate atomic-like potentials	242
12.6	Empirical pseudopotential method (EPM)	243
12.7	Calculation of density: introduction of grids	246
12.8	Real-space methods	248
	Select further reading	251
	Exercises	251
13	Plane waves and grids: full calculations	254
	Summary	254
13.1	“ <i>Ab initio</i> ” pseudopotential method	255
13.2	Projector augmented waves (PAWs)	258
13.3	Simple crystals: structures, bands, ...	259
13.4	Supercells: surfaces, interfaces, phonons, defects	265
13.5	Clusters and molecules	269