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 provides a unified exposition of the basic theory and methods of electronic structure, together with instructive examples of practical computational methods and real-world applications. The book is appropriate for both graduate students and practicing scientists. It 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.

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Electronic Structure
Basic Theory and Practical Methods

Richard M. Martin
To Beverly
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 MgB2: bands, phonons, and superconductivity 47
   2.13 The continuing challenge: electron correlation 50
       Select further reading 51
3 Theoretical background
  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
  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
  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
  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
## Contents

### 10.7 Atomic sphere approximation in solids
Select further reading
Exercises

### 11 Pseudopotentials
Summary
11.1 Scattering amplitudes and pseudopotentials
11.2 Orthogonalized plane waves (OPWs) and pseudopotentials
11.3 Model ion potentials
11.4 Norm-conserving pseudopotentials (NCPPs)
11.5 Generation of l-dependent norm-conserving pseudopotentials
11.6 Unscreening and core corrections
11.7 Transferability and hardness
11.8 Separable pseudopotential operators and projectors
11.9 Extended norm conservation: beyond the linear regime
11.10 Ultrasoft pseudopotentials
11.11 Projector augmented waves (PAWs): keeping the full wavefunction
11.12 Additional topics
Select further reading
Exercises

---

### Part IV Determination of electronic structure: the three basic methods

### 12 Plane waves and grids: basics
Summary
12.1 The independent-particle Schrödinger equation in a plane wave basis
12.2 The Bloch theorem and electron bands
12.3 Nearly-free-electron approximation
12.4 Form factors and structure factors
12.5 Approximate atomic-like potentials
12.6 Empirical pseudopotential method (EPM)
12.7 Calculation of density: introduction of grids
12.8 Real-space methods
Select further reading
Exercises

### 13 Plane waves and grids: full calculations
Summary
13.1 “Ab initio” pseudopotential method
13.2 Projector augmented waves (PAWs)
13.3 Simple crystals: structures, bands, . . .
13.4 Supercells: surfaces, interfaces, phonons, defects
13.5 Clusters and molecules
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Select further reading</td>
<td>270</td>
</tr>
<tr>
<td>Exercises</td>
<td>271</td>
</tr>
<tr>
<td>14 Localized orbitals: tight-binding</td>
<td></td>
</tr>
<tr>
<td>Summary</td>
<td>272</td>
</tr>
<tr>
<td>14.1 Localized atom-centered orbitals</td>
<td>273</td>
</tr>
<tr>
<td>14.2 Matrix elements with atomic orbitals</td>
<td>274</td>
</tr>
<tr>
<td>14.3 Slater–Koster two-center approximation</td>
<td>278</td>
</tr>
<tr>
<td>14.4 Tight-binding bands: illustrative examples</td>
<td>279</td>
</tr>
<tr>
<td>14.5 Square lattice and CuO$_2$ planes</td>
<td>282</td>
</tr>
<tr>
<td>14.6 Examples of bands: semiconductors and transition metals</td>
<td>283</td>
</tr>
<tr>
<td>14.7 Electronic states of nanotubes</td>
<td>285</td>
</tr>
<tr>
<td>14.8 Total energy, force, and stress in tight-binding</td>
<td>289</td>
</tr>
<tr>
<td>14.9 Transferability: non-orthogonality and environment dependence</td>
<td>291</td>
</tr>
<tr>
<td>Select further reading</td>
<td>293</td>
</tr>
<tr>
<td>Exercises</td>
<td>294</td>
</tr>
<tr>
<td>15 Localized orbitals: full calculations</td>
<td></td>
</tr>
<tr>
<td>Summary</td>
<td>298</td>
</tr>
<tr>
<td>15.1 Solution of Kohn–Sham equations in localized bases</td>
<td>298</td>
</tr>
<tr>
<td>15.2 Analytic basis functions: gaussians</td>
<td>300</td>
</tr>
<tr>
<td>15.3 Gaussian methods: ground state and excitation energies</td>
<td>302</td>
</tr>
<tr>
<td>15.4 Numerical orbitals</td>
<td>304</td>
</tr>
<tr>
<td>15.5 Localized orbitals: total energy, force, and stress</td>
<td>307</td>
</tr>
<tr>
<td>15.6 Applications of numerical local orbitals</td>
<td>309</td>
</tr>
<tr>
<td>15.7 Green’s function and recursion methods</td>
<td>310</td>
</tr>
<tr>
<td>15.8 Mixed basis</td>
<td>310</td>
</tr>
<tr>
<td>Select further reading</td>
<td>311</td>
</tr>
<tr>
<td>Exercises</td>
<td>311</td>
</tr>
<tr>
<td>16 Augmented functions: APW, KKR, MTO</td>
<td></td>
</tr>
<tr>
<td>Summary</td>
<td>313</td>
</tr>
<tr>
<td>16.1 Augmented plane waves (APWs) and “muffin tins”</td>
<td>313</td>
</tr>
<tr>
<td>16.2 Solving APW equations: examples</td>
<td>318</td>
</tr>
<tr>
<td>16.3 The KKR or multiple-scattering theory (MST) method</td>
<td>323</td>
</tr>
<tr>
<td>16.4 Alloys and the coherent potential approximation (CPA)</td>
<td>329</td>
</tr>
<tr>
<td>16.5 Muffin-tin orbitals (MTOs)</td>
<td>331</td>
</tr>
<tr>
<td>16.6 Canonical bands</td>
<td>333</td>
</tr>
<tr>
<td>16.7 Localized “tight-binding” MTO and KKR formulations</td>
<td>338</td>
</tr>
<tr>
<td>16.8 Total energy, force, and pressure in augmented methods</td>
<td>341</td>
</tr>
<tr>
<td>Select further reading</td>
<td>342</td>
</tr>
<tr>
<td>Exercises</td>
<td>342</td>
</tr>
<tr>
<td>17 Augmented functions: linear methods</td>
<td></td>
</tr>
<tr>
<td>Summary</td>
<td>345</td>
</tr>
</tbody>
</table>

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## Contents

17.1 Energy derivative of the wavefunction: $\psi$ and $\dot{\psi}$ 346  
17.2 General form of linearized equations 348  
17.3 Linearized augmented plane waves (LAPWs) 350  
17.4 Applications of the LAPW method 351  
17.5 Linear muffin-tin orbital (LMTO) method 355  
17.6 “Ab initio” tight-binding 358  
17.7 Applications of the LMTO method 360  
17.8 Beyond linear methods: NMTO 362  
17.9 Full potential in augmented methods 364  
Select further reading 365  
Exercises 366  

### Part V Predicting properties of matter from electronic structure – recent developments

18 Quantum molecular dynamics (QMD) 371  
Summary 371  
18.1 Molecular dynamics (MD): forces from the electrons 371  
18.2 Car–Parrinello unified algorithm for electrons and ions 373  
18.3 Expressions for plane waves 376  
18.4 Alternative approaches to density functional QMD 377  
18.5 Non-self-consistent QMD methods 378  
18.6 Examples of simulations 379  
Select further reading 383  
Exercises 384  

19 Response functions: phonons, magnons, . . . 387  
Summary 387  
19.1 Lattice dynamics from electronic structure theory 388  
19.2 The direct approach: “frozen phonons,” magnons, . . . 390  
19.3 Phonons and density response functions 394  
19.4 Green’s function formulation 395  
19.5 Variational expressions 396  
19.6 Periodic perturbations and phonon dispersion curves 398  
19.7 Dielectric response functions, effective charges, . . . 399  
19.8 Electron–phonon interactions and superconductivity 401  
19.9 Magnons and spin response functions 402  
Select further reading 403  
Exercises 404  

20 Excitation spectra and optical properties 406  
Summary 406  
20.1 Dielectric response for non-interacting particles 407
# Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.2 Time-dependent density functional theory and linear response</td>
<td>408</td>
</tr>
<tr>
<td>20.3 Variational Green’s function methods for dynamical linear response</td>
<td>411</td>
</tr>
<tr>
<td>20.4 Explicit real-time calculations</td>
<td>412</td>
</tr>
<tr>
<td>20.5 Beyond the adiabatic local approximation</td>
<td>416</td>
</tr>
<tr>
<td>Select further reading</td>
<td>416</td>
</tr>
<tr>
<td>Exercises</td>
<td>417</td>
</tr>
<tr>
<td>21 Wannier functions</td>
<td>418</td>
</tr>
<tr>
<td>Summary</td>
<td>418</td>
</tr>
<tr>
<td>21.1 Definition and properties</td>
<td>418</td>
</tr>
<tr>
<td>21.2 “Maximally projected” Wannier functions</td>
<td>421</td>
</tr>
<tr>
<td>21.3 Maximally localized Wannier functions</td>
<td>422</td>
</tr>
<tr>
<td>21.4 Non-orthogonal localized functions</td>
<td>428</td>
</tr>
<tr>
<td>21.5 Wannier functions for “entangled bands”</td>
<td>429</td>
</tr>
<tr>
<td>Select further reading</td>
<td>431</td>
</tr>
<tr>
<td>Exercises</td>
<td>432</td>
</tr>
<tr>
<td>22 Polarization, localization, and Berry’s phases</td>
<td>434</td>
</tr>
<tr>
<td>Summary</td>
<td>434</td>
</tr>
<tr>
<td>22.1 Polarization: the fundamental difficulty</td>
<td>436</td>
</tr>
<tr>
<td>22.2 Geometric Berry’s phase theory of polarization</td>
<td>439</td>
</tr>
<tr>
<td>22.3 Relation to centers of Wannier functions</td>
<td>442</td>
</tr>
<tr>
<td>22.4 Calculation of polarization in crystals</td>
<td>442</td>
</tr>
<tr>
<td>22.5 Localization: a rigorous measure</td>
<td>444</td>
</tr>
<tr>
<td>22.6 Geometric Berry’s phase theory of spin waves</td>
<td>446</td>
</tr>
<tr>
<td>Select further reading</td>
<td>447</td>
</tr>
<tr>
<td>Exercises</td>
<td>447</td>
</tr>
<tr>
<td>23 Locality and linear scaling O(N) methods</td>
<td>450</td>
</tr>
<tr>
<td>Summary</td>
<td>450</td>
</tr>
<tr>
<td>23.1 Locality and linear scaling in many-particle quantum systems</td>
<td>451</td>
</tr>
<tr>
<td>23.2 Building the hamiltonian</td>
<td>454</td>
</tr>
<tr>
<td>23.3 Solution of equations: non-variational methods</td>
<td>455</td>
</tr>
<tr>
<td>23.4 Variational density matrix methods</td>
<td>463</td>
</tr>
<tr>
<td>23.5 Variational (generalized) Wannier function methods</td>
<td>466</td>
</tr>
<tr>
<td>23.6 Linear-scaling self-consistent density functional calculations</td>
<td>469</td>
</tr>
<tr>
<td>23.7 Factorized density matrix for large basis sets</td>
<td>470</td>
</tr>
<tr>
<td>23.8 Combining the methods</td>
<td>472</td>
</tr>
<tr>
<td>Select further reading</td>
<td>472</td>
</tr>
<tr>
<td>Exercises</td>
<td>473</td>
</tr>
<tr>
<td>24 Where to find more</td>
<td>475</td>
</tr>
</tbody>
</table>

## Appendix A Functional equations

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary</td>
<td>476</td>
</tr>
</tbody>
</table>
## Contents

A.1 Basic definitions and variational equations 476  
A.2 Functionals in density functional theory including gradients 477  
   Select further reading 478  
   Exercises 478

Appendix B LSDA and GGA functionals 479  
   Summary 479

B.1 Local spin density approximation (LSDA) 479
B.2 Generalized gradient approximation (GGAs) 480
B.3 GGAs: explicit PBE form 480  
   Select further reading 481

Appendix C Adiabatic approximation 482  
   Summary 482

C.1 General formulation 482
C.2 Electron–phonon interactions 484  
   Select further reading 484  
   Exercises 484

Appendix D Response functions and Green’s functions 485  
   Summary 485

D.1 Static response functions 485
D.2 Response functions in self-consistent field theories 486
D.3 Dynamic response and Kramers–Kronig relations 487
D.4 Green’s functions 489  
   Select further reading 491  
   Exercises 491

Appendix E Dielectric functions and optical properties 492  
   Summary 492

E.1 Electromagnetic waves in matter 492
E.2 Conductivity and dielectric tensors 494
E.3 The $f$ sum rule 494
E.4 Scalar longitudinal dielectric functions 495
E.5 Tensor transverse dielectric functions 496
E.6 Lattice contributions to dielectric response 496  
   Select further reading 497  
   Exercises 498

Appendix F Coulomb interactions in extended systems 499  
   Summary 499

F.1 Basic issues 499
F.2 Point charges in a background: Ewald sums 500  
F.3 Smeared nuclei or ions 505
F.4 Energy relative to neutral atoms 506
Contents

F.5 Surface and interface dipoles 507
F.6 Reducing effects of artificial image charges 508
  Select further reading 510
  Exercises 510

Appendix G Stress from electronic structure 512
  Summary 512
G.1 Macroscopic stress and strain 512
G.2 Stress from two-body pair-wise forces 514
G.3 Expressions in Fourier components 515
G.4 Internal strain 516
  Select further reading 517
  Exercises 518

Appendix H Energy and stress densities 519
  Summary 519
H.1 Energy density 520
H.2 Stress density 523
H.3 Applications 524
  Select further reading 527
  Exercises 527

Appendix I Alternative force expressions 530
  Summary 530
I.1 Variational freedom and forces 532
I.2 Energy differences 532
I.3 Pressure 532
I.4 Force and stress 533
I.5 Force in APW-type methods 534
  Select further reading 534

Appendix J Scattering and phase shifts 536
  Summary 536
J.1 Scattering and phase shifts for spherical potentials 536
  Select further reading 538

Appendix K Useful relations and formulas 539
  Summary 539
K.1 Bessel, Neumann, and Hankel functions 539
K.2 Spherical harmonics and Legendre polynomials 539
K.3 Real spherical harmonics 540
K.4 Clebsch–Gordon and Gaunt coefficients 541
K.5 Chebyshev polynomials 542

Appendix L Numerical methods 543
  Summary 543
xvi

Contents

L.1 Numerical integration and the Numerov method 543
L.2 Steepest descent 544
L.3 Conjugate gradient 545
L.4 Quasi-Newton–Raphson methods 547
L.5 Pulay DIIIS full-subspace method 547
L.6 Broyden Jacobian update methods 548
L.7 Moments, maximum entropy, kernel polynomial method, and random vectors 549
Select further reading 551
Exercises 551

Appendix M Iterative methods in electronic structure 553
Summary 553
M.1 Why use iterative methods? 553
M.2 Simple relaxation algorithms 554
M.3 Preconditioning 555
M.4 Iterative (Krylov) subspaces 556
M.5 The Lanczos algorithm and recursion 557
M.6 Davidson algorithms 559
M.7 Residual minimization in the subspace – RMM–DIIS 559
M.8 Solution by minimization of the energy functional 560
M.9 Comparison/combination of methods: minimization of residual or energy 563
M.10 Exponential projection in imaginary time 564
M.11 Algorithmic complexity: transforms and sparse hamiltonians 564
Select further reading 568
Exercises 569

Appendix N Code for empirical pseudopotential and tight-binding 570
N.1 Calculations of eigenstates: modules common to all methods 570
N.2 Plane wave empirical pseudopotential method (EPM) 570
N.3 Slater–Koster tight-binding (TB) method 571
N.4 Sample input file for TBPW 571
N.5 Two-center matrix elements: expressions for arbitrary angular momentum l 572

Appendix O Units and conversion factors 575

References 576
Index 618
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 work 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
Preface

Theory, are an increasing part of electronic structure theory for realistic problems. Yet many fundamental ideas and the most useful approaches at present are based upon independent-particle approximations. 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. A planned second volume will be devoted to many-body methods that are applicable to realistic problems in condensed matter and molecules.

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.
Outline

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 \textit{ab initio} 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.

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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

\[ \Omega \]
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

\[ \mu_{\alpha\beta} = -(1/\Omega)(\partial E/\partial u_{\alpha\beta}) \]
stress tensor (symmetrized form of \( \epsilon_{\alpha\beta} \))

\[ \sigma_{\alpha\beta} = -(1/\Omega)(\partial E/\partial u_{\alpha\beta}) \]
stress tensor (note the sign convention)

\[ F_I = -(dE/dR_I) \]
force on nucleus I

\[ C_{IJ} = d^2E/dR_IdR_J \]
force constant matrix

\[ n(r) \]
density of electrons

Notation for crystals

\[ \Omega_{\text{cell}} \]
volume of primitive cell

\[ \mathbf{a}_i \]
primitive translation vectors

\[ \mathbf{T} \text{ or } \mathbf{T}(\mathbf{n}) \equiv \mathbf{T}(n_1, n_2, n_3) \]
lattice translations

\[ = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \]

\[ \tau_s, s = 1, \ldots, S \]
positions of atoms in the basis

\[ \mathbf{b}_I \]
primitive vectors of reciprocal lattice

\[ \mathbf{G} \text{ or } \mathbf{G}(\mathbf{m}) \equiv \mathbf{G}(m_1, m_2, m_3) \]
reciprocal lattice vectors

\[ = m_1\mathbf{b}_1 + m_2\mathbf{b}_2 + m_3\mathbf{b}_3 \]

\[ \mathbf{k} \]
wavevector in first Brillouin zone (BZ)

\[ \mathbf{q} \]
general wavevector (\( \mathbf{q} = \mathbf{k} + \mathbf{G} \))
List of notation

**Hamiltonian and eigenstates**

$\hat{H}$

Hamiltonian for either many particles or a single particle

$\Psi(|r_i|)$

Many-body wavefunction of a set of particle positions $r_i, \; i = 1, N_{\text{particle}}$; spin is assumed to be included in the argument $r_i$ unless otherwise specified

$E_i$

energy of many-body state

$\Phi(|r_i|)$

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 $m'$

$\psi_i(r)$

independent-particle wavefunction or “orbital,” $i = 1, \ldots, N_{\text{states}}$

$\epsilon_i$

independent-particle eigenvalue, $i = 1, \ldots, N_{\text{states}}$

$f_i = f(\epsilon_i)$

occupation of state $i$ where $f$ is the Fermi function

$\psi_i^\sigma (r), \epsilon_i^\sigma$

used when spin is explicitly indicated

$\alpha_i(\sigma_j)$

spin wavefunction for particle $j; i = 1, 2$

$\phi_i(j, \sigma_j)$

single particle “spin-orbitals” ($= \psi_i^\sigma(r_j) \times \alpha_i(\sigma_j)$)

$\psi_i(r)$

single-body radial wavefunction

$(\psi_{i,m}(r) = \psi_i(r)Y_{lm}(\theta, \phi))$

$\phi_i(r)$

single-body radial wavefunction $\phi_i(r) = r \psi_i(r)$

$\eta(\sigma)$

phase shift

$\psi_{i,k}(r) = e^{ik \cdot r}u_{i,k}(r)$

Bloch function in crystal, with $u_{i,k}(r)$ periodic

$\epsilon_{i,k}$

eigenvalues that define bands as a function of $k$

$\hat{H}(k)$

“gauge transformed” hamiltonian given by Eq. (4.37); eigenvectors are the periodic parts of the Bloch functions $u_{i,k}(r)$

$\chi_\alpha(r)$

single-body basis function, $\alpha = 1, \ldots, N_{\text{basis}}$. Orbital $i$ is expanded in basis functions $\alpha$, i.e.

$\psi_i(r) = \sum_\alpha c_{i,\alpha} \chi_\alpha(r)$

$\chi_{\alpha}(r - (\tau + T))$

localized orbital basis function on atom at position $\tau$ in cell labelled by translation vector $T$

$\chi_{\alpha}^{\text{OPW}}(r), \chi_{\alpha}^{\text{APW}}(r), \chi_{\alpha}^{\text{LMO}}(r)$

Basis function for orthogonalized, augmented or muffin-tin orbital basis functions

$\tilde{w}_i(r - T)$

Wannier function $i$ associated with band $i$ and cell $T$

$\tilde{w}_i(r - T)$

Non-orthogonal transformation of Wannier functions

**Density functional theory**

$F[f]$ 

General notational for $F$ a functional of the function $f$

$E_{\text{xc}}[\sigma]$ 

exchange–correlation energy in Kohn–Sham theory

$\varepsilon_{\text{xc}}(r)$ 

exchange–correlation energy per electron

$V_{\text{xc}}(r)$ 

exchange–correlation potential in Kohn–Sham theory

$V_{\text{xc}}^{\text{spin}}(r)$ 

exchange–correlation potential with spin explicitly indicated
Response function and correlation functions

$\chi(\omega)$ \quad general response function

$\chi_0(\omega)$ \quad general response function for independent particles

$\varepsilon(\omega)$ \quad frequency dependent dielectric function

$n(r, \sigma; r', \sigma')$ \quad pair distribution

$g(r, \sigma; r', \sigma')$ \quad normalized pair distribution (often omitting the spin indices)

$G(z, r, r')$ or $G_{m,m'}(z)$ \quad Green's function of complex frequency $z$

$\rho(r, \sigma; r', \sigma')$ \quad density matrix

$\rho_{\sigma}(r, r')$ \quad density matrix diagonal in spin for independent-particles