Richard M.Martin

Electronic Structure

Basic Theory and Practical Methods

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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.

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 a 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. 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* and *Physical Review Letters*, and has recently been made associate editor for condensed matter theory for the *Reviews of Modern Physics*.

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

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 to 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.

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.

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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 Festkorperforschung in Stuttgart, partially funded by the Alexander von Humboldt Foundation, and continued at the University of Illinois, the Aspen Center for Physics, and Lawrence Livermore National Laboratory. Appreciation is due to these institutions for their support.

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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
Ω	volume (to avoid confusion with V used for potential)
$P = -(\mathrm{d}E/\mathrm{d}\Omega)$	pressure
$B = \Omega(\mathrm{d}^2E/\mathrm{d}\Omega^2)$	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)
$\mathbf{F}_I = -(\mathrm{d}E/\mathrm{d}\mathbf{R}_I)$	force on nucleus I
$C_{IJ} = \mathrm{d}^2E/\mathrm{d}\mathbf{R}_I\mathrm{d}\mathbf{R}_J$	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
$\tau_s, s = 1, \ldots, S$	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

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," $i = 1, \ldots, N_{\text{states}}$
ε_i	independent-particle eigenvalue, $i = 1, \ldots, N_{\text{states}}$
$f_i = f(\varepsilon_i)$	occupation of state i where f is the Fermi function
$\psi_i^\sigma(\mathbf{r})$, ε_i^σ	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, $\alpha = 1, \ldots, N_{\text{basis}}$. 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 $\mathbf{T}$
$\chi^{\text{OPW}}(\mathbf{r})$, $\chi^{\text{APW}}(\mathbf{r})$, $\chi^{\text{LMTO}}(\mathbf{r})$	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)
$G(z, \mathbf{r}, \mathbf{r}')$ 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

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