Atomic and Electronic Structure of Solids

This text is a modern treatment of the theory of solids. The core of the book deals with the physics of electron and phonon states in crystals and how they determine the structure and properties of the solid.

The discussion uses the single-electron picture as a starting point and covers electronic and optical phenomena, magnetism and superconductivity. There is also an extensive treatment of defects in solids, including point defects, dislocations, surfaces and interfaces. A number of modern topics where the theory of solids applies are also explored, including quasicrystals, amorphous solids, polymers, metal and semiconductor clusters, carbon nanotubes and biological macromolecules. Numerous examples are presented in detail and each chapter is accompanied by problems and suggested further readings. An extensive set of appendices provides the necessary background for deriving all the results discussed in the main body of the text.

The level of theoretical treatment is appropriate for first-year graduate students of physics, chemistry and materials science and engineering, but the book will also serve as a reference for scientists and researchers in these fields.

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Atomic and Electronic Structure of Solids

Efthimios Kaxiras
I dedicate this book to three great physics teachers: Evangelos Anastassakis, who inspired me to become a physicist, John Joannopoulos, who taught me how to think like one, and Lefteris Economou, who vastly expanded my physicist’s horizon.
## Contents

*Preface*  
*Acknowledgments*  

**I Crystalline solids**  

1 Atomic structure of crystals  
  1.1 Building crystals from atoms  
    1.1.1 Atoms with no valence electrons  
    1.1.2 Atoms with $s$ valence electrons  
    1.1.3 Atoms with $s$ and $p$ valence electrons  
    1.1.4 Atoms with $s$ and $d$ valence electrons  
    1.1.5 Atoms with $s$, $d$ and $f$ valence electrons  
    1.1.6 Solids with two types of atoms  
    1.1.7 Hydrogen: a special one-$s$-valence-electron atom  
    1.1.8 Solids with many types of atoms  
  1.2 Bonding in solids  
  Further reading  
  Problems  

2 The single-particle approximation  
  2.1 The hamiltonian of the solid  
  2.2 The Hartree and Hartree–Fock approximations  
    2.2.1 The Hartree approximation  
    2.2.2 Example of a variational calculation  
    2.2.3 The Hartree–Fock approximation  
  2.3 Hartree–Fock theory of free electrons  
  2.4 The hydrogen molecule  
  2.5 Density Functional Theory  

*Preface*  

title* xv  

*Acknowledgments*  

title xix  

1 Crystalline solids  

1 Atomic structure of crystals  

1.1 Building crystals from atoms  

1.1.1 Atoms with no valence electrons  

1.1.2 Atoms with $s$ valence electrons  

1.1.3 Atoms with $s$ and $p$ valence electrons  

1.1.4 Atoms with $s$ and $d$ valence electrons  

1.1.5 Atoms with $s$, $d$ and $f$ valence electrons  

1.1.6 Solids with two types of atoms  

1.1.7 Hydrogen: a special one-$s$-valence-electron atom  

1.1.8 Solids with many types of atoms  

1.2 Bonding in solids  

Further reading  

Problems  

2 The single-particle approximation  

2.1 The hamiltonian of the solid  

2.2 The Hartree and Hartree–Fock approximations  

2.2.1 The Hartree approximation  

2.2.2 Example of a variational calculation  

2.2.3 The Hartree–Fock approximation  

2.3 Hartree–Fock theory of free electrons  

2.4 The hydrogen molecule  

2.5 Density Functional Theory  

42  

42  

44  

44  

46  

47  

49  

54  

58
Contents

2.6 Electrons as quasiparticles 65
  2.6.1 Quasiparticles and collective excitations 68
  2.6.2 Thomas–Fermi screening 69
2.7 The ionic potential 72
Further reading 78
Problems 78

3 Electrons in crystal potential 82
  3.1 Periodicity – Bloch states 82
  3.2 $\mathbf{k}$-space – Brillouin zones 87
  3.3 Dynamics of crystal electrons 94
  3.4 Crystal electrons in an electric field 97
  3.5 Crystal symmetries beyond periodicity 101
  3.6 Groups and symmetry operators 104
  3.7 Symmetries of the band structure 105
  3.8 Symmetries of 3D crystals 111
  3.9 Special $\mathbf{k}$-points 117
Further reading 119
Problems 120

4 Band structure of crystals 121
  4.1 The tight-binding approximation 121
    4.1.1 Example: 1D linear chain with $s$ or $p$ orbitals 125
    4.1.2 Example: 2D square lattice with $s$ and $p$ orbitals 129
    4.1.3 Generalizations of the TBA 136
  4.2 General band-structure methods 140
  4.3 Band structure of representative solids 145
    4.3.1 A 2D solid: graphite – a semimetal 145
    4.3.2 3D covalent solids: semiconductors and insulators 148
    4.3.3 3D metallic solids 153
Further reading 157
Problems 157

5 Applications of band theory 160
  5.1 Density of states 160
  5.2 Tunneling at metal–semiconductor contact 165
  5.3 Optical excitations 167
  5.4 Conductivity and dielectric function 169
Contents

5.5 Excitons 177
5.6 Energetics and dynamics 185
  5.6.1 The total energy 186
  5.6.2 Forces and dynamics 194
Further reading 200
Problems 201

6 Lattice vibrations 203
  6.1 Phonon modes 203
  6.2 The force-constant model 207
    6.2.1 Example: phonons in 2D periodic chain 209
    6.2.2 Phonons in a 3D crystal 213
  6.3 Phonons as harmonic oscillators 216
  6.4 Application: the specific heat of crystals 218
    6.4.1 The classical picture 218
    6.4.2 The quantum mechanical picture 219
    6.4.3 The Debye model 221
    6.4.4 Thermal expansion coefficient 225
  6.5 Application: phonon scattering 227
    6.5.1 Phonon scattering processes 228
    6.5.2 The Debye–Waller factor 232
    6.5.3 The Mössbauer effect 234
Problems 237

7 Magnetic behavior of solids 238
  7.1 Magnetic behavior of insulators 239
  7.2 Magnetic behavior of metals 246
    7.2.1 Magnetization in Hartree–Fock free-electron gas 247
    7.2.2 Magnetization of band electrons 251
  7.3 Heisenberg spin model 254
    7.3.1 Ground state of the Heisenberg ferromagnet 255
    7.3.2 Spin waves in the Heisenberg ferromagnet 258
    7.3.3 Heisenberg antiferromagnetic spin model 262
  7.4 Magnetic order in real materials 265
  7.5 Crystal electrons in an external magnetic field 268
    7.5.1 de Haas–van Alphen effect 270
    7.5.2 Classical and quantum Hall effects 273
Further reading 279
Problems 279
## Contents

### 8 Superconductivity

- 8.1 Overview of superconducting behavior 282
- 8.2 Thermodynamics of the superconducting transition 289
- 8.3 BCS theory of superconductivity 293
  - 8.3.1 Cooper pairing 293
  - 8.3.2 BCS ground state 297
  - 8.3.3 BCS theory at finite temperature 307
  - 8.3.4 The McMillan formula for $T_c$ 308
- 8.4 High-temperature superconductors 310

Further reading 312
Problems 312

### II Defects, non-crystalline solids and finite structures

- 9 Defects I: point defects 317
  - 9.1 Intrinsic point defects 317
    - 9.1.1 Energetics and electronic levels 317
    - 9.1.2 Defect-mediated diffusion 320
  - 9.2 Extrinsic point defects 325
    - 9.2.1 Impurity states in semiconductors 325
    - 9.2.2 Effect of doping in semiconductors 331
    - 9.2.3 The p–n junction 338
    - 9.2.4 Metal–semiconductor junction 345

Further reading 347
Problems 348

- 10 Defects II: line defects 350
  - 10.1 Nature of dislocations 350
  - 10.2 Elastic properties and motion of dislocations 355
    - 10.2.1 Stress and strain fields 356
    - 10.2.2 Elastic energy 360
    - 10.2.3 Peierls–Nabarro model 365
  - 10.3 Brittle versus ductile behavior 370
    - 10.3.1 Stress and strain under external load 371
    - 10.3.2 Brittle fracture – Griffith criterion 374
    - 10.3.3 Ductile response – Rice criterion 376
    - 10.3.4 Dislocation–defect interactions 378

Further reading 381
Problems 382
## Contents

11 Defects III: surfaces and interfaces 385
  11.1 Experimental study of surfaces 386
  11.2 Surface reconstruction 394
    11.2.1 Dimerization: the Si(001) surface 398
    11.2.2 Relaxation: the GaAs(110) surface 400
    11.2.3 Adatoms and passivation: the Si(111) surface 403
  11.3 Growth phenomena 408
  11.4 Interfaces 419
    11.4.1 Grain boundaries 419
    11.4.2 Hetero-interfaces 421

Further reading 427
Problems 428

12 Non-crystalline solids 430
  12.1 Quasicrystals 430
  12.2 Amorphous solids 436
    12.2.1 Continuous random network 437
    12.2.2 Radial distribution function 440
    12.2.3 Electron localization due to disorder 443
  12.3 Polymers 447
    12.3.1 Structure of polymer chains and solids 448
    12.3.2 The glass and rubber states 451

Further reading 456
Problems 457

13 Finite structures 459
  13.1 Clusters 460
    13.1.1 Metallic clusters 460
    13.1.2 Carbon clusters 462
    13.1.3 Carbon nanotubes 476
    13.1.4 Other covalent and mixed clusters 481
  13.2 Biological molecules and structures 483
    13.2.1 The structure of DNA and RNA 484
    13.2.2 The structure of proteins 498
    13.2.3 Relationship between DNA, RNA and proteins 504
    13.2.4 Protein structure and function 509

Further reading 510
Problems 510
Appendices

Appendix A Elements of classical electrodynamics 515
A.1 Electrostatics and magnetostatics 515
A.2 Fields in polarizable matter 518
A.3 Electrodynamics 520
A.4 Electromagnetic radiation 524
Further reading 529

Appendix B Elements of quantum mechanics 530
B.1 The Schrödinger equation 530
B.2 Bras, kets and operators 533
B.3 Solution of the TISE
B.3.1 Free particles 539
B.3.2 Harmonic oscillator potential 540
B.3.3 Coulomb potential 543
B.4 Spin angular momentum 549
B.5 Stationary perturbation theory 554
B.5.1 Non-degenerate perturbation theory 554
B.5.2 Degenerate perturbation theory 556
B.6 Time-dependent perturbation theory 557
B.7 The electromagnetic field term 559
Further reading 560
Problems 560

Appendix C Elements of thermodynamics 564
C.1 The laws of thermodynamics 564
C.2 Thermodynamic potentials 567
C.3 Application: phase transitions 570
Problems 578

Appendix D Elements of statistical mechanics 579
D.1 Average occupation numbers 580
D.1.1 Classical Maxwell–Boltzmann statistics 580
D.1.2 Quantum Fermi–Dirac statistics 582
D.1.3 Quantum Bose–Einstein statistics 583
D.2 Ensemble theory 584
D.2.1 Definition of ensembles 585
D.2.2 Derivation of thermodynamics 589
Contents xiii

D.3 Applications of ensemble theory 591
  D.3.1 Equipartition and the Virial 591
  D.3.2 Ideal gases 592
  D.3.3 Spins in an external magnetic field 603

Further reading 617
Problems 617

Appendix E Elements of elasticity theory 622
  E.1 The strain tensor 622
  E.2 The stress tensor 624
  E.3 Stress-strain relations 626
  E.4 Strain energy density 627
  E.5 Applications of elasticity theory 629
    E.5.1 Isotropic elastic solid 629
    E.5.2 Plane strain 632
    E.5.3 Solid with cubic symmetry 634

Further reading 636
Problems 636

Appendix F The Madelung energy 638
  F.1 Potential of a gaussian function 639
  F.2 The Ewald method 640
  Problems 642

Appendix G Mathematical tools 644
  G.1 Differential operators 644
  G.2 Power series expansions 646
  G.3 Functional derivatives 648
  G.4 Fourier and inverse Fourier transforms 649
  G.5 The δ-function and its Fourier transform 650
    G.5.1 The δ-function and the θ-function 650
    G.5.2 Fourier transform of the δ-function 654
    G.5.3 The δ-function sums for crystals 654
  G.6 Normalized gaussians 655

Appendix H Nobel prize citations 657

Appendix I Units and symbols 659

References 660
Index 667
Preface

This book is addressed to first-year graduate students in physics, chemistry, materials science and engineering. It discusses the atomic and electronic structure of solids. Traditional textbooks on solid state physics contain a large amount of useful information about the properties of solids, as well as extensive discussions of the relevant physics, but tend to be overwhelming as introductory texts. This book is an attempt to introduce the single-particle picture of solids in an accessible and self-contained manner. The theoretical derivations start at a basic level and go through the necessary steps for obtaining key results, while some details of the derivations are relegated to problems, with proper guiding hints. The exposition of the theory is accompanied by worked-out examples and additional problems at the end of chapters.

The book addresses mostly theoretical concepts and tools relevant to the physics of solids; there is no attempt to provide a thorough account of related experimental facts. This choice was made in order to keep the book within a limit that allows its contents to be covered in a reasonably short period (one or two semesters; see more detailed instructions below). There are many sources covering the experimental side of the field, which the student is strongly encouraged to explore if not already familiar with it. The suggestions for further reading at the end of chapters can serve as a starting point for exploring the experimental literature. There are also selected references to original research articles that laid the foundations of the topics discussed, as well as to more recent work, in the hope of exciting the student’s interest for further exploration. Instead of providing a comprehensive list of references, the reader is typically directed toward review articles and monographs which contain more advanced treatments and a more extended bibliography.

As already mentioned, the treatment is mostly restricted to the single-particle picture. The meaning of this is clarified and its advantages and limitations are described in great detail in the second chapter. Briefly, the electrons responsible for the cohesion of a solid interact through long-range Coulomb forces both with the
nuclei of the solid and with all the other electrons. This leads to a very complex many-electron state which is difficult to describe quantitatively. In certain limits, and for certain classes of phenomena, it is feasible to describe the solid in terms of an approximate picture involving “single electrons”, which interact with the other electrons through an average field. In fact, these “single-electron” states do not correspond to physical electron states (hence the quotes). This picture, although based on approximations that cannot be systematically improved, turns out to be extremely useful and remarkably realistic for many, but not all, situations. There are several phenomena – superconductivity and certain aspects of magnetic phenomena being prime examples – where the collective behavior of electrons in a solid is essential in understanding the nature of the beast (or beauty). In these cases the “single-electron” picture is not adequate, and a full many-body approach is necessary. The phenomena involved in the many-body picture require an approach and a theoretical formalism beyond what is covered here; typically, these topics constitute the subject of a second course on the theory of solids.

The book is divided into two parts. The first part, called Crystalline solids, consists of eight chapters and includes material that I consider essential in understanding the physics of solids. The discussion is based on crystals, which offer a convenient model for studying macroscopic numbers of atoms assembled to form a solid. In this part, the first five chapters develop the theoretical basis for the single-electron picture and give several applications of this picture, for solids in which atoms are frozen in space. Chapter 6 develops the tools for understanding the motion of atoms in crystals through the language of phonons. Chapters 7 and 8 are devoted to magnetic phenomena and superconductivity, respectively. The purpose of these last two chapters is to give a glimpse of interesting phenomena in solids which go beyond the single-electron picture. Although more advanced, these topics have become an essential part of the physics of solids and must be included in a general introduction to the field. I have tried to keep the discussion in these two chapters at a relatively simple level, avoiding, for example, the introduction of tools like second quantization, Green’s functions and Feynman diagrams. The logic of this approach is to make the material accessible to a wide audience, at the cost of not employing a more elegant language familiar to physicists.

The second part of the book consists of five chapters, which contain discussions of defects in crystals (chapters 9, 10 and 11), of non-crystalline solids (chapter 12) and of finite structures (chapter 13). The material in these chapters is more specific than that in the first part of the book, and thus less important from a fundamental point of view. This material, however, is relevant to real solids, as opposed to idealized theoretical concepts such as a perfect crystal. I must make here a clarification on why the very last chapter is devoted to finite structures, a topic not traditionally discussed in the context of solids. Such structures are becoming increasingly important, especially in the field of nanotechnology, where the functional components may be
measured in nanometers. Prime examples of such objects are clusters or tubes of car-
bon (the fullerenes and the carbon nanotubes) and biological structures (the nucleic
acids and proteins), which are studied by ever increasing numbers of traditional
physicists, chemists and materials scientists, and which are expected to find their
way into solid state applications in the not too distant future. Another reason for in-
cluding a discussion of these systems in a book on solids, is that they do have certain
common characteristics with traditional crystals, such as a high degree of order.

After all, what could be a more relevant example of a regular one-dimensional
structure than the human DNA chain which extends for three billion base-pairs with
essentially perfect stacking, even though it is not rigid in the traditional sense?

This second part of the book contains material closer to actual research topics
in the modern theory of solids. In deciding what to include in this part, I have
drawn mostly from my own research experience. This is the reason for omitting
some important topics, such as the physics of metal alloys. My excuse for such
omissions is that the intent was to write a modern textbook on the physics of solids,
with representative examples of current applications, rather than an encyclopedic
compilation of research topics. Despite such omissions, I hope that the scope of
what is covered is broad enough to offer a satisfactory representation of the field.

Finally, a few comments about the details of the contents. I have strived to make
the discussion of topics in the book as self-contained as possible. For this reason,
I have included unusually extensive appendices in what constitutes a third part of the
book. Four of these appendices, on classical electrodynamics, quantum mechanics,
thermodynamics and statistical mechanics, contain all the information necessary
to derive from very basic principles the results of the first part of the book. The
appendix on elasticity theory contains the background information relevant to the
discussion of line defects and the mechanical properties of solids. The appendix
on the Madelung energy provides a detailed account of an important term in the
total energy of solids, which was deemed overly technical to include in the first
part. Finally, the appendix on mathematical tools reviews a number of formulae,
techniques and tricks which are used extensively throughout the text. The material
in the second part of the book could not be made equally self-contained by the
addition of appendices, because of its more specialized nature. I have made an
effort to provide enough references for the interested reader to pursue in more
detail any topic covered in the second part. An appendix at the end includes Nobel
prize citations relevant to work mentioned in the text, as an indication of how vibrant
the field has been and continues to be. The appendices may seem excessively long
by usual standards, but I hope that a good fraction of the readers will find them
useful.

Some final comments on notation and figures: I have made a conscious effort to
provide a consistent notation for all the equations throughout the text. Given the
breadth of topics covered, this was not a trivial task and I was occasionally forced
to make unconventional choices in order to avoid using the same symbol for two different physical quantities. Some of these are: the choice of $\Omega$ for the volume so that the more traditional symbol $V$ could be reserved for the potential energy; the choice of $\Theta$ for the enthalpy so that the more traditional symbol $H$ could be reserved for the magnetic field; the choice of $Y$ for Young’s modulus so that the more traditional symbol $E$ could be reserved for the energy; the introduction of a subscript in the symbol for the divergence, $\nabla_r$ or $\nabla_k$, so that the variable of differentiation would be unambiguous even if, on certain occasions, this is redundant information. I have also made extensive use of superscripts, which are often in parentheses to differentiate them from exponents, in order to make the meaning of symbols more transparent. Lastly, I decided to draw all the figures “by hand” (using software tools), rather than to reproduce figures from the literature, even when discussing classic experimental or theoretical results. The purpose of this choice is to maintain, to the extent possible, the feeling of immediacy in the figures as I would have drawn them on the blackboard, pointing out important features rather than being faithful to details. I hope that the result is not disagreeable, given my admittedly limited drawing abilities. Exceptions are the set of figures on electronic structure of metals and semiconductors in chapter 4 (Figs. 4.6–4.12), which were produced by Yannis Remediakis, and the figure of the KcsA protein in chapter 13 (Fig. 13.30), which was provided by Pavlos Maragakis.

The book has been constructed to serve two purposes. (a) For students with adequate background in the basic fields of physics (electromagnetism, quantum mechanics, thermodynamics and statistical mechanics), the first part represents a comprehensive introduction to the single-particle theory of solids and can be covered in a one-semester course. As an indication of the degree of familiarity with basic physics expected of the reader, I have included sample problems in the corresponding appendices; the readers who can tackle these problems easily can proceed directly to the main text covered in the first part. My own teaching experience indicates that approximately 40 hours of lectures (roughly five per chapter) are adequate for a brisk, but not unreasonable, covering of this part. Material from the second part can be used selectively as illustrative examples of how the basic concepts are applied to realistic situations. This can be done in the form of special assignments, or as projects at the end of the one-semester course.

(b) For students without graduate level training in the basic fields of physics mentioned above, the entire book can serve as the basis for a full-year course. The material in the first part can be covered at a more leisurely pace, with short introductions of the important physics background where needed, using the appendices as a guide. The material of the second part of the book can then be covered, selectively or in its entirety as time permits, in the remainder of the full-year course.
Acknowledgments

The discussion of many topics in this book, especially the chapters that deal with symmetries of the crystalline state and band structure methods, was inspired to a great extent by the lectures of John Joannopoulos who first introduced me to this subject. I hope the presentation of these topics here does justice to his meticulous and inspired teaching.

Acknowledgments

John Smith, Klaus Kern, Oliver Leifeld, Lefteris Economou, Nikos Flytzanis, Stavros Farantos, George Tsironis, Grigoris Athanasiou, Panos Tzanetakis, Kostas Fotakis, George Theodorou, José Soler, Thomas Frauenheim, Riad Manaa, Doros Theodorou, Vassilis Pontikis and Sauro Succi. Certain of these individuals played not only the role of a colleague or collaborator, but also the role of a mentor at various stages of my career: they are, John Joannopoulos, Kosal Pandey, Dimitri Papaconstantopoulos, Henry Ehrenreich, Bert Halperin and Sidney Yip; I am particularly indebted to them for guidance and advice, as well as for sharing with me their deep knowledge of physics.

I was also very fortunate to work with many talented graduate and undergraduate students, including Yumin Juan, Linda Zeger, Normand Modine, Martin Bazant, Noam Bernstein, Greg Smith, Nick Choly, Ryan Barnett, Sohrab Ismail-Beigi, Jonah Erlebacher, Melvin Chen, Tim Mueller, Yuemin Sun, Joao Justo, Maurice de Koning, Yannis Remediakis, Helen Eisenberg, Trevor Bass, and with a very select group of Postdoctoral Fellows and Visiting Scholars, including Daniel Kandel, Laszlo Barabási, Gil Zumbach, Umesh Waghmare, Ellad Tadmor, Vasily Bulatov, Kyeongjae Cho, Marcus Elstner, Ickjin Park, Hanchul Kim, Olivier Politano, Paul Maragakis, Dionisios Margetis, Daniel Orlikowski, Qiang Cui and Gang Lu. I hope that they have learned from me a small fraction of what I have learned from them over the last dozen years.

Last but not least, I owe a huge debt of gratitude to my wife, Eleni, who encouraged me to turn my original class notes into the present book and supported me with patience and humor throughout this endeavor.

The merits of the book, to a great extent, must be attributed to the generous input of friends and colleagues, while its shortcomings are the exclusive responsibility of the author. Pointing out these shortcomings to me would be greatly appreciated.

Cambridge, Massachusetts, October 2001