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.

Efthimios Kaxiras received his PhD in theoretical physics at the Massachusetts Institute of Technology, and worked as a Postdoctoral Fellow at the IBM T. J. Watson Research Laboratory in Yorktown Heights. He joined Harvard University in 1991, where he is currently a Professor of Physics and the Gordon McKay Professor of Applied Physics. He has worked on theoretical modeling of the properties of solids, including their surfaces and defects; he has published extensively in refereed journals, as well as several invited review articles and book chapters. He has co-organized a number of scientific meetings and co-edited three volumes of conference proceedings. He is a member of the American Physical Society, the American Chemical Society, the Materials Research Society, Sigma Xi-Scientific Research Society, and a Chartered Member of the Institute of Physics (London).

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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

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 carbon (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 including 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 Ω for the volume so that the more traditional symbol V could be reserved for the potential energy; the choice of Θ 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, $\nabla_{\mathbf{r}}$ or $\nabla_{\mathbf{k}}$, 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.

In my two-decade-long journey through the physics of solids, I had the good fortune to interact with a great number of colleagues, from all of whom I have learned a tremendous amount. In roughly chronological order in which I came to know them, they are: John Joannopoulos, Karin Rabe, Alex Antonelli, Dung-Hai Lee, Yaneer Bar-Yam, Eugen Tarnow, David Vanderbilt, Oscar Alerhand, Bob Meade, George Turner, Andy Rappe, Michael Payne, Jim Chelikowsky, Marvin Cohen, Jim Chadi, Steven Louie, Stratos Manousakis, Kosal Pandey, Norton Lang, Jerry Tersoff, Phaedon Avouris, In-When Lyo, Ruud Tromp, Matt Copel, Bob Hamers, Randy Feenstra, Ken Shih, Franz Himpsel, Joe Demuth, Sokrates Pantelides, Pantelis Kelires, Peter Blöchl, Dimitri Papaconstantopoulos, Barry Klein, Jeremy Broughton, Warren Pickett, David Singh, Michael Mehl, Koblar Jackson, Mark Pederson, Steve Erwin, Larry Boyer, Joe Feldman, Daryl Hess, Joe Serene, Russ Hemley, John Weeks, Ellen Williams, Bert Halperin, Henry Ehrenreich, Daniel Fisher, David Nelson, Paul Martin, Jene Golovchenko, Bill Paul, Eric Heller, Cynthia Friend, Roy Gordon, Howard Stone, Charlie Lieber, Eric Mazur, Mike Aziz, Jim Rice, Frans Spaepen, John Hutchinson, Michael Tinkham, Ike Silvera, Peter Pershan, Bob Westervelt, Venky Narayanamurti, George Whitesides, Charlie Marcus, Leo Kouwenhoven, Martin Karplus, Dan Branton, Dave Weitz, Eugene Demler, Uzi Landman, Andy Zangwill, Peter Feibelman, Priya Vashishta, Rajiv Kalia, Mark Gyure, Russ Cafflisch, Dimitri Vvedensky, Jenna Zink, Bill Carter, Lloyd Whitman, Stan Williams, Dimitri Maroudas, Nick Kioussis, Michael Duesbery, Sidney Yip, Farid Abraham, Shi-Yu Wu, John Wilkins, Ladislas Kubin, Rob Phillips, Bill Curtin, Alan Needleman, Michael Ortiz, Emily Carter, 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.

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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