

O. Madelung

Introduction to

# Solid-State Theory

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Translated by B. C. Taylor

With 144 Figures

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## Preface

This book is intended for graduate students of physics, materials science, and electrical engineering as a textbook in solid-state theory. In addition, it should provide the theoretical background needed by research physicists in solid-state physics and in the solid-state areas of electrical engineering.

The content of this book and the level of presentation are determined by the needs of its intended audience. The field of solid-state physics has grown so large that some selection of topics has to be made. In a book on solid-state *physics* it is still possible to survey the full range of solid-state phenomena and to connect them by a qualitative presentation of theoretical concepts. However, in a text introducing solid-state *theory*, a presentation of *all* theoretical concepts and methods seemed inappropriate. For this reason I have tried to develop the fundamentals of solid-state theory starting from a single unifying point of view—the description by *delocalized* (extended) and *localized states* and by *elementary excitations*. The development of solid-state theory within the last ten years has shown that by a systematic introduction of those concepts large parts of the theory can be described in a unified way. At the same time this form of description gives a “pictorial” formulation of many elementary processes in solids which facilitates their understanding.

Admittedly the attempt to present solid-state physics under one unifying aspect has its shortcomings. Not all parts of solid-state theory fit naturally into this frame. But the limitations imposed by such organization of the book seemed to me justified for several reasons. First, because there are only a few topics which do not fit into this type of description, the range covered is representative of the predominant part of solid-state theory. Secondly, the manner of description chosen seems especially suited for those areas of solid-state physics which are dominant in the application to solid-state electronics. Finally, since so many valuable textbooks and monographs on solid-state theory are available, a new book should intend to complement them rather than to compete.

I have tried to offer a general framework of solid-state theory which the reader can fill in from the more specialized material provided by monographs, review articles, and original papers. In this book, some fields are described in detail and some fields are treated more briefly. Topics which have been covered by comprehensive monographs are in some cases presented here only from the viewpoint of elementary excitations. Thus, spin-waves are emphasized in the chapter on magnetism. The electron-electron interaction by exchange of virtual phonons is the central topic in the chapter on superconductivity, whereas other important aspects of this field are only

mentioned briefly. In every case, however, I have tried to inform the reader as completely as possible about additional available literature.

It was not my intention to write a book on solid-state theory for the prospective solid-state *theorist*. I therefore intentionally refrained from using the abstract methods of quantum field theory, important as they are in many-body problems. The general use of these methods seems to me inappropriate for the broad audience to whom this book is directed. On the other hand, some prior knowledge of elementary quantum mechanics as well as of the most important solid-state phenomena is required and assumed. Because of the close connection of all fields of solid-state physics, from the basic theoretical concepts to the technical applications, I have made use of SI-units (Système International) throughout, in contrast to most other textbooks in this field. To each chapter some problems are added. Most of them are not intended to train the reader in theoretical methods but to direct his attention to applications and additional questions which arise from the respective sections. Many of the problems have already been discussed in other monographs or review articles. I have indicated such sources in the Bibliography.

This book is a revised and partly rewritten translation of three pocket books "Festkörpertheorie I-III"<sup>1</sup>. The present version has been prepared to meet the requirements of the extended market. Two appendices in the former texts—on group theory and on Green's functions—have been omitted.

I would like to express my gratitude to many colleagues and friends who helped me in the various stages of the preparation of the manuscript. Herbert Kroemer made the first suggestion to prepare an English version. Brian Taylor carried out the translation in exemplary fashion. He also gave me many suggestions for improving the text. I received helpful comments and support from Manuel Cardona, Peter Fulde, and Hans-Joachim Queisser and from my present and former co-workers K. Maschke, B. Movaghar, H. Overhof, U. Rössler, W. Schirmacher, P. Thomas, and J. Treusch. I gratefully acknowledge the cooperation of the publisher, Springer-Verlag, especially Mr. K. Koch, Mrs. J. Long and Dr. H. K. V. Lotsch.

Marburg, April 1978

*Otfried Madelung*

<sup>1</sup> Heidelberger Taschenbücher, Vols. 104, 109, and 126 (Springer, Berlin, Heidelberg, New York 1972 and 1973)

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# 1. Fundamentals

## 1.1 Introduction

Solids are composed of atoms held together by chemical bonds. Solid-state physics is therefore concerned with those physical properties which are the collective properties of this atomic arrangement. The characteristic properties of free atoms do, of course, determine the nature of the solid they make up, but, when embedded in a crystal lattice, these properties are greatly influenced by the surroundings. Electrical conductivity, ferromagnetism, specific heat, and phase transitions are, moreover, examples of concepts which can be defined for the solid but not for an individual atom. A theoretical description of the properties of solids must therefore use methods appropriate to many-body systems.

The characteristic feature of all solids (as with all *condensed matter*) is their order, i.e., the correlation in the positions of neighbouring atoms. This can be *short-range order* and restricted to a more or less limited volume surrounding an atom. Short-range order can diminish with increasing distance, as in amorphous semiconductors, or it can be restricted to microcrystals which are connected one to another in disjointed fashion. However the majority of all solids has *long-range order*, i.e., a regular *lattice* extending over considerable distances. The great number of structures able to satisfy lattice geometry and bonding criteria is one of the main reasons for the abundance of different solid-state phenomena.

Real crystals always show departures from an ideal structure. Every solid is of finite extent, so crystals are bounded by *surfaces* or *inner boundaries*. This is a trivial observation, but one which is important for many physical phenomena. *Lattice defects*, the presence of impurity atoms, dislocations, and local disturbances of lattice periodicity can never be completely absent in any real crystal.

Even the thermal motion of the lattice atoms constitutes a departure from strict periodicity. The periodic lattice is formed not by the atoms themselves but by their equilibrium positions. The atoms remain at these positions permanently only at the temperature of absolute zero, i.e., when the crystal is in its *ground state*. Departures from this ground state lead to deviations from order. At normal temperatures, however, the deviations are mostly so small that order remains the distinctive feature of a crystal.

Problems in solid-state physics can be related to two basic questions:

- 1) What is the ground state of a given solid? Why is it stable? What sort of forces hold the atoms in the lattice together?
- 2) How does the solid behave under external influences?

The first group of questions is characterized by concepts like crystal structure, chemical bonding, cohesion, and binding energy. This group appears at first to take precedence over the second which is concerned with the effect of external influences, but in fact the questions in the first group can only be answered *through* the answers to the second. *For every experiment means intervention, and a disturbance of the ground state.* Only by examining the consequences of such interventions, for example the effects produced by application of an electric field, or a temperature gradient, or by exposure to light, is it possible to also determine the properties of the solid in its ground state.

The phenomena of interest are characterized by the experimental tools available. These are

1) *Electric fields.* The object under investigation is charge transport, i.e., electric current. The phenomenological division of solids into metals, semiconductors, and insulators follows from these investigations, as does the division into electronic and ionic conductors, depending on the mechanism of electrical conduction. Superconductivity also belongs to this topic.

2) *Magnetic fields.* The various types of magnetism—dia- and para-, ferro-, antiferro-, and ferrimagnetism—are phenomena which a solid, depending upon its structure, shows in a magnetic field. A magnetic field is often used as an additional means to increase the variety of the observed effects. An example might be magnetic field as a parameter in investigating charge transport under the influence of an electric field. In this way more information and a greater insight into the characteristics of solids is obtained.

3) *Temperature gradients* lead to the transfer of thermal energy from hot to cold areas. Energy transport is possible along with charge transport.

4) *Optical phenomena*, absorption, reflection, and dispersion of photons provide information on the interaction between electromagnetic waves and solids.

5) *Electrons, neutrons*, and other corpuscular rays can be used to probe solid-state characteristics.

6) One can also obtain useful information about crystals by deliberately disturbing the crystal lattice, e.g., by doping with *impurity atoms*, or by producing *lattice disorder* or *dislocations*.

This list of experimental possibilities could be extended. But only the most important ones need to be mentioned here.

It is not possible to devise a single theoretical model to account for all these phenomena. The many-body system of the solid is too complicated for that. Appropriate, simplified models are deduced for particular areas of interest. Any true solid-state theory must, however, aim to bring these individual aspects together under some unifying *concepts*. There are several ways of achieving this.

The concept which has come increasingly to the fore in recent years is that of *elementary excitations*. This concept can be explained as follows:

As is clear from the above, the solid under investigation is usually in an excited state. The energy producing the excitation can be thermal, it can be imposed externally, or it can come from a deliberate disturbance of the lattice structure. It can be fed to various subsystems of the solid. It can be taken up by the valence electrons or by the lattice, it can appear as kinetic energy in the lattice ions, or it can reside in the coupled spins of the lattice ions.

Even for a very weak, local excitation the energy supplied does not usually remain localized at a single lattice particle. There are interactions between the lattice particles (ions and electrons) and these serve to distribute energy from one particle to the others.

From the mechanics of a system of point masses we know how to describe complex modes of oscillation in simple terms. For a system with  $s$  degrees of freedom, one introduces  $s$  new generalized coordinates (normal coordinates) in such a way that the Hamiltonian—for small oscillations a positive definite quadratic function—is diagonalized. That is, the complex equations of motion are split in normal coordinates into  $s$  independent equations representing the motions of free oscillators. In this approach, excited states close to the ground state can be described by the excitation of just a few of these free oscillators. This method of description is used in lattice dynamics to describe the (small) oscillations of lattice ions about their equilibrium positions. The complex, collective oscillation of the lattice is divided into a number of independent normal modes. These normal modes are quantized, and the associated quanta are called *phonons*. Phonons are an example of an *elementary excitation*. In many ways they are equivalent to *photons*, the elementary excitations of the electromagnetic field.

Besides these *collective excitations* there is a second example of how collective interactions in a many-particle system can formally be greatly simplified. If a charged particle moves through a "gas" of similarly charged particles, it will repel the other particles from its path. This can be described *formally* by a model in which no interactions occur; instead the particle is accompanied by a compensating cloud of charges of opposite sign. The interaction, i.e., the effect of the other particles on the one observed, is in fact replaced by the inertia of the charge-cloud that the particle has to carry with it. Here again we have replaced a system of interacting particles by an equivalent system of noninteracting particles, in which the dynamics of the original particles is now replaced by the (different) dynamics of new *quasi-particles*. These quasi-particles are a further example of elementary excitations.

In characterizing the behaviour of solids we find many opportunities to introduce such elementary excitations. Similarly to the phonons or quanta of the lattice vibrations, *plasmons* are introduced to describe collective oscillations of the valence electrons in metals. The spin system of lattice atoms can be represented in terms of spin waves, with *magnons* as the associated quanta.

A further example are the *excitons* used to describe excitations of the valence electrons in semiconductors.

The definition of a quasi-particle is not clear cut. Electrons can be subjected to a variety of interactions as they move through a crystal. Depending on the extent to which these interactions are included in the electron dynamics, i.e., on the approximation used, the electron can appear as a different quasi-particle (free electron, Hartree-Fock-electron, Bloch-electron, screened electron). This is an often overlooked fact and can on occasion give rise to misunderstandings.

To a first approximation, elementary excitations of a similar type are independent. But in higher approximations mutual interactions have to be taken into account. However even in the latter case the concept of elementary interactions can still remain useful. Only interactions which are weak compared to the original interaction have to be taken into account, and these can often be dealt with by perturbation theory.

We shall return to these questions in Sections 3.1.1 and 3.1.5, where we take a closer look at the concept of quasi-particles.

We may often be able to neglect interactions between excitations of a given kind, but interactions between different kinds are always important. It is these interactions which mainly account for the rich variety of solid-state phenomena. Even the setting up of an equilibrium state in the solid demands an interaction, i.e., an energy exchange between the various excitations.

Within the limits of this concept we can now ask the questions: What elementary excitations arise if a given solid is subjected to a small external disturbance? What energy do the quanta of the collective excitations and the quasi-particles have? What interactions should be considered? And finally: How are the elementary excitations affected by external forces? The answers to these questions then give us the answers to the questions on the physical properties of the solid and on its behaviour in an experiment.

Collective excitations like phonons are excitations of the entire solid. A phonon has a definite wave vector and a definite energy, whereas its location is completely undetermined. The same is true for the quasi-particles whose energy and wave vectors are precisely given. The description of excited states of a solid in terms of such *extended* or *delocalized* states is possible only if the solid can be considered as an infinite undisturbed medium. It has the advantage that the elementary processes leading to the excitation can be simply described: By external inputs of energy and momentum, by exchange of energy and momentum between different subsystems, quasi-particles change their state, and quanta of collective excitations are absorbed and emitted. The adoption of the concept of elementary excitations makes both the "pictorial" interpretation of the elementary processes and the mathematical formulation of many problems in solid-state theory relatively simple.

As with every theoretical concept, the concept of elementary excitations has only limited validity and applicability.



First it is clear that the concept is only reasonable for small deviations from the ground state, for when the number of collective excitations and quasi-particles becomes large, when the coupling between them becomes too strong, we again burden the theoretical picture with the many details from which we wanted to free ourselves by this very concept. One set of problems which can therefore certainly not be handled by this model is that of phase transitions.

In addition we must recognize that the description in terms of *extended states* is only one limiting case for the description of physical phenomena in an infinite undistorted solid. The description can also start from *localized states*, e.g., from states concentrated at individual lattice sites. Depending on the nature of the solid but also on the physical question posed, one or other limiting case will be chosen. We shall discuss these alternatives in more detail in Section 8.1.

In a *distorted lattice* a description based on localized states or at least a combination of both limiting cases will always be necessary. Localized point defects, impurity lattice atoms, or other imperfections lead to localized states in addition to the extended states of the host lattice. The catalogue of questions started above can then be extended by questions like: What isolated imperfections are possible in a given crystal? What localized states do occur? What interactions do they have with each other and with the elementary excitations? The answers to these provide the answer to the question on the effect of lattice imperfections on the physical properties of solids.

If the distortion of the lattice is very large, the concept of extended states is only of limited value and a description based on localized states becomes more important. This is the case for alloys and amorphous solids, for example.

The way we plan to present the material in this book is the following. First of all we shall attempt as far as possible to use the extended state description. This means we shall limit our attention to the perfect, infinite crystal and its physical properties. Within this theoretical framework an important role is played by the *one-electron approximation*. As long as we can neglect the interaction between the electrons in the solid or as soon as we can introduce noninteracting quasi-electrons, the description of many solid-state phenomena reduces to describing the behaviour of individual electrons under external influences. The fundamentals of the one-electron approximation will be discussed in Chapter 2.

In Chapter 3 we consider the various elementary excitations which form an important part of the description of solid-state phenomena. We shall also take a closer look at the theoretical basis for the concept of elementary excitations.

The following chapters are then dedicated, respectively, to important interactions between various elementary excitations. Each interaction leads to an important branch of solid-state physics: transport phenomena, superconductivity, optics, thermal properties. At first all these areas will be looked at from the point of view of the particular interaction. The content of the chapters will not, however, be limited to this.