Solid State Physics

SECOND EDITION

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固体物理学 第2版

Solid State Physics
Second Edition

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Solid State Physics Second Edition

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Preface to the second edition

These last years have witnessed a continuous progress in the traditional areas of solid state physics, as well as the emergence of new areas of research, rich of results and promises. The countless novelties appeared in the literature with the beginning of this century are one of the main motivations of the second edition of "Solid State Physics." Besides the inclusion of new material, the content has been greatly rationalized and the manuscript appears now in a widely renewed dress. Furthermore, this second edition is accompanied and enriched by the presence of numerous Appendices, containing better in-depth treatment of specific topics, or containing significant solved problems, for the readers willing to increase the proper technical abilities.

The chapters of "Solid State Physics" are in large part self-contained, and can be chosen with great flexibility and split in two semesters to cover an annual course for the degree in physics, or also for the degree in material science and electrical engineering. The volume is also suited for the graduate students, who have not followed similar in-depth courses in their curricula. From a didactical point of view, it is a steady characteristics of this book to enhance gradually the level of difficulty starting from the initial models and leading as near as possible to the frontier science. The purpose is to provide within the reasonable length of a textbook the general cultural baggage needed for all researchers, whose activity is oriented, or is going to be oriented, in the fascinating field of solid state physics.

We wish to express our deepest gratitude to our colleagues for their valuable suggestions, and to our students for their challenging questions; in their own way, they have made the most relevant contribution to improve and inspire this textbook. Many warm thanks are due to Donna de Weerd-Wilson for her encouragement in pursuing this project, and to Paula Callaghan, to Anita Koch, to Sharmila Vadivelan, and to Jessica Vaughan for their assistance and professionalism in the preparation of the manuscript.

Pavia and Pisa, May 2013
Giuseppe Grosso and Giuseppe Pastori Parravicini

Preface to the first edition

This textbook has developed from the experience of the authors in teaching the course of Solid State Physics to students in physics at the Universities of Pavia and Pisa. The book is addressed to students at the graduate and advanced level, both oriented toward theoretical and experimental activity. No particular prerequisite is required, except for the ordinary working knowledge of wave mechanics. The degree of difficulty increases somewhat as the book progresses; however, the contents develop always in very gradual steps.

The material presented in the book has been assembled to make as economical as possible the didactical task of teaching, or learning, the various subjects. The general organization in chapters, and groups of chapters, is summarized in the synoptic table of contents. The first three chapters have a propaedeutic nature to the main entries of the book. Chapter IV starts with the analysis of the electronic structure of crystals, one of the most traditional subjects in solid state physics; Chapters V and VI concern the band theory of solids and a number of specific applications; the concepts of excitons and plasmons are given in Chapter VII. Then, in Chapters VIII and IX, the adiabatic principle and the interdependence of electronic states and lattice dynamics are studied. Having established the electronic and vibrational structure of crystals, the successive chapters from X to XIV describe several investigative techniques of crystalline properties; these include scattering of particles, optical spectroscopy, and transport measurements. Chapters XV, XVI, and XVII concern the electronic magnetism of tendentially delocalized or localized electronic systems, and cooperative magnetic effects. The final chapter is an introduction to the world of superconductivity.

From a didactical point of view, an effort is made to remain as rigorous as possible, while keeping the presentation at an accessible level. In this book, on one hand we aim to give a clear presentation of the basic physical facts, on the other hand we wish to describe them by rigorous theoretical and mathematical tools. The technical side is given the due attention and is never considered optional; in fact, a clear supporting theoretical formalism (without being pedantic) is essential to establish the limits of the physical models, and is basic enough to allow the reader eventually to move on his or her own legs, this being the ultimate purpose of a useful book.

The various chapters are organized in a self-contained way for the contents, appendixes (if any), references, and have their own progressive numeration for tables, figures, and formulae (the chapter number is added when addressing items in chapters differing from the running one). With regard to the references, these are intended only as indicative, since it is impossible to mention, let alone to comment on, all the relevant contributions of the wide literature. Since the chapters are presented in a (reasonably) self-contained way, the lecturers and readers are not compelled to follow the

order in which the various subjects are discussed; the chapters, or group of chapters, can be taken up with great flexibility, selecting those topics that best fit personal tastes or needs. We will be very interested and very pleased to receive (either directly or by correspondence) comments and suggestions from lecturers and readers.

The preparation of a textbook, although general in nature, requires also a great deal of specialized information. We consider ourselves fortunate for the generous help of the colleagues and friends at the Physics Departments of the University of Pavia, University of Pisa, and Scuola Normale Superiore of Pisa; they have contributed to making this textbook far better by sharing their expertise with us. Very special thanks are due to Emilio Doni, who survived the task of reading and commenting on the whole preview-manuscript. Several other colleagues helped with their critical reading of specific chapters; we are particularly grateful to Lucio Claudio Andreani, Antonio Barone, Pietro Carretta, Alberto Di Lieto, Giorgio Guizzetti, Franco Marabelli, Liana Martinelli, Attilio Rigamonti. Many heartfelt thanks are due to Saverio Moroni for his right-on-target comments.

Before closing, we wish to thank all contributors and publishers, who gave us permission to reproduce their illustrations; their names and references are indicated adjacent each figure. We wish also to express our gratitude to Gioia Ghezzi for her encouragement, to Serena Bureau, Manjula Goonawardena, Cordelia Sealy, and Bridget Shine for their assistance in the preparation of the manuscript. Last, but always first, we thank our families for their never ending trust that the manuscript would eventually be completed and would be useful to somebody.

Pavia and Pisa, May 1999
Giuseppe Grosso and Giuseppe Pastori Parravicini

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1 Electrons in One-Dimensional Periodic Potentials

Chapter Outline head

Low dimensionality offers a unique opportunity to introduce some relevant concepts of solid state physics, keeping the treatment at a reasonably simple level. In the early days of solid state physics, just this desire for technical simplicity was the motivation for the studies on one-dimensional periodic potentials. More recently, with the restless developments in the world of nanoscience and nanotechnology, low-dimensional models have had a renaissance for the understanding of a number of realistic situations. At the same time a note of warning is necessary: the features of one-dimensional systems that have any relevance beyond dimensionality must be assessed situation by situation; cavalier extensions of one-dimensional results to actual three-dimensional crystals may be misleading or even completely unreliable.

The material of this chapter is organized and presented so that it can also be embodied in standard courses of "Structure of Matter" or "Quantum Mechanics"; in fact no previous knowledge is needed other than elementary ideas about wave mechanics.

This chapter begins with the presentation of the Bloch theorem for one-dimensional periodic lattices. A peculiar aspect of the energy spectrum of an electron in a periodic potential is the presence of allowed and forbidden energy regions. One-dimensional approaches are particularly suited to show from different points of view (weak binding, tight-binding, quantum tunneling, continued fractions) the mechanism of formation of energy bands in solids. The semiclassical dynamics of electrons in energy bands is then

considered; together with the Pauli exclusion principle for occupation of states, it gives a qualitative distinction between metals, semiconductors, and insulators.

Before beginning our trip among the one-dimensional models of primary interest in the field of solid state, we wish to notice the frequent "trespassings" that have occurred, in the course of the years, among areas quite different from the original context. For instance the Kronig-Penney model, originally suggested to justify qualitatively the formation of electronic energy bands in periodic materials, is often encountered as a precious tool in the study of electronic states in artificial superlattices, or of the propagation of electromagnetic waves in photonic crystals. Similarly, the concept of Bloch oscillations of electrons in periodic potentials and external electric fields, experimentally rather elusive even for semiconducting superlattices, has been well verified for atomic condensates in optical lattices, where gravity takes the role played by electric fields in semiconductors. Bloch oscillations of light waves have also been observed in dielectric superlattices, where a refractive index gradient plays the optical analog of the external force. Although the focus of this chapter is on one-dimensional periodic potentials, with traditional contributions going back to the early times of the foundation of quantum mechanics, it is worthwhile to be aware of the cross-fertilization of concepts and techniques between this historical area of solid state and other much younger and very active areas of research, which include for instance artificial structures and superlattices, organic crystals, photonic crystals, atomic condensates.

1.1   The Bloch Theorem for One-Dimensional Periodicity

Consider an electron in a one-dimensional potential energy $V(x)$ and the corresponding Schrödinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x). \tag{1.1}$$

The solutions of Eq. (1.1) for several typical forms of $V(x)$ are well known; familiar models include the free-electron case: $V(x) = 0$, the harmonic oscillator: $V(x) = (1/2)Kx^2$, the case of a uniform electric field: $V(x) = eFx$, quantum wells, and others. We focus here on the general properties of Eq. (1.1) in the case $V(x)$ is the periodic potential of a one-dimensional crystal of lattice constant a.

A potential $V(x)$, of period a, satisfies the relation

$$V(x) = V(x + ma), \tag{1.2}$$

with m arbitrary integer. The Fourier transform of a periodic potential $V(x)$ includes only plane waves of wavenumbers $h_n = n2\pi/a$, and $V(x)$ can be expressed in the form

$$V(x) = \sum_{n=-\infty}^{+\infty} V(h_n)e^{ih_n x}. \tag{1.3}$$

In general, if $V(x)$ is not periodic, it can still have a continuous Fourier transform $V(q)$ such that

$$V(x) = \int_{-\infty}^{+\infty} V(q)e^{iqx}dq. \tag{1.4}$$

We wish to analyze the implications on the eigenfunctions and eigenvalues of Eq. (1.1) brought about by the fact that the potential $V(x)$ is periodic, and hence its Fourier spectrum is discrete, according to Eq. (1.3).

Let us start considering Eq. (1.1) in the particular case that the periodic potential $V(x)$ vanishes (empty lattice). In the free-electron case, the wavefunctions are simply plane waves and can be written in the form

$$W_k(x) = \frac{1}{\sqrt{L}}e^{ikx}. \tag{1.5}$$

The normalization constant has been chosen such that $W_k(x)$ is normalized to 1 in the interval $0 \le x \le L$ (and the length L of the crystal is understood in the limit $L \to \infty$ whenever necessary). The wavenumbers k are real and the eigenvalues are $E(k) = \hbar^2k^2/2m$. The plane waves (1.5) constitute a complete set of orthonormal functions, that can be conveniently used as an expansion set.

Let us now consider the eigenvalue problem (1.1), when the potential $V(x)$ is periodic and thus satisfies Eq. (1.3). If we apply the operator $H = (p^2/2m) + V(x)$ to the plane wave $W_k(x)$, we see that $H|W_k(x)\rangle$ belongs to the subspace S_k of plane waves of wavenumbers $k + h_n$:

$$S_k \equiv \{W_k(x), W_{k+h_1}(x), W_{k-h_1}(x), W_{k+h_2}(x), W_{k-h_2}(x) \ldots\}.$$

We also notice that the subspace S_k is *closed* under the application of the operator H to any of its elements; thus the diagonalization of the Hamiltonian operator within the subspace S_k provides eigenfunctions of H that can be labeled as $\psi_k(x)$. Notice that two subspaces S_k and $S_{k'}$ are different if k and k' are *not* related by integer multiples (positive, negative or zero) of $2\pi/a$; on the contrary, if $k \equiv k' + n2\pi/a$, then the two subspaces S_k and $S_{k'}$ coincide. This allows us to define a fundamental region of k-space, limited by $-\pi/a < k \le \pi/a$, which includes all the different k labels giving independent S_k subspaces; this fundamental region, of length $2\pi/a$, is named *first Brillouin zone* (or simply *Brillouin zone*).

Any generic wavefunction $\psi_k(x)$, obtained by diagonalization of H within the subspace S_k, can be expressed as an appropriate linear combination of the type

$$\psi_k(x) = \sum_n c(k + h_n)\frac{1}{\sqrt{L}}e^{i(k+h_n)x}. \tag{1.6}$$

It is convenient to denote by $u_k(x)$ the function

$$u_k(x) = \sum_n c(k + h_n)\frac{1}{\sqrt{L}}e^{ih_nx} = \sum_n c(k + h_n)\frac{1}{\sqrt{L}}e^{in(2\pi/a)x}.$$

It is evident that $u_k(x)$ is a function with the same periodicity, a, as $V(x)$. Equation (1.6) then takes the form

$$\boxed{\psi_k(x) = e^{ikx} u_k(x)} \quad \text{with} \quad \boxed{u_k(x+a) = u_k(x)}. \tag{1.7}$$

This expresses the Bloch theorem: *any physically acceptable solution of the Schrödinger equation in a periodic potential takes the form of a traveling plane wave modulated on the microscopic scale by an appropriate function with the lattice periodicity.*

The Bloch theorem, summarized by Eq. (1.7), can also be written in the equivalent form

$$\boxed{\psi_k(x + t_n) = e^{ikt_n} \psi_k(x)}, \tag{1.8}$$

where $t_n = na$ is any translation in the direct lattice. It is easy to verify that Eq. (1.7) implies Eq. (1.8), and vice versa [to demonstrate the latter case, multiply both members of Eq. (1.8) by $\exp(-ikx - ikt_n)$ and denote by $u_k(x)$ the resulting periodic function]. The Bloch theorem, in the form of Eq. (1.8), shows that the values of the wavefunction $\psi_k(x)$ in any two points of the real space differing by a translation t_n are related by the phase $\exp(ikt_n)$.

We can finally notice that, in the case of a generic potential of type (1.4), the discretized expansion of Eq. (1.6) does not hold any more; in general the expansion of $\psi(x)$ includes all plane waves in the form

$$\psi(x) = \int_{-\infty}^{+\infty} c(q) e^{iqx} dq. \tag{1.9}$$

Nothing specific and general can be inferred from Eq. (1.9) about the properties of the wavefunctions and the energy spectrum of H: in fact, for aperiodic potentials, it is possible to find localized wavefunctions for the whole spectrum, itinerant ones, both types (separated by mobility edges), or even solutions belonging to fractal regions of the spectrum.

The Bloch theorem plays a central role in the physics of periodic systems; not only it characterizes the *itinerant form of the wavefunctions* summarized by Eqs. (1.7) and (1.8), but also entails the fact that the energy spectrum consists, in general, of *allowed energy regions separated by energy gaps* (as discussed in the forthcoming sections). The eigenvalues $E = E(k)$ of the Schrödinger equation (1.1), when plotted as a function of k within the first Brillouin zone, describe the band structure of the crystal; notice that $E(k) = E(-k)$, as can be seen from direct inspection of Eq. (1.1) under complex conjugate operation (or in a more formal way by use of group theory analysis of time reversal symmetry of the electronic Hamiltonian).

A feature of one-dimensional periodic potentials is that the allowed energy bands *cannot cross* each other; in fact for any allowed energy E there are only two linearly independent solutions of the differential Eq. (1.1), and the degeneracy $E(k) = E(-k)$ rules out any degeneracy at a given k. Thus, for any allowed energy band the dispersion relation $E(k)$ is a monotonic function of k for $0 \leq k \leq \pi/a$; the extremal energies occur only at $k = 0$ and π/a, where dE/dk in general vanishes. (The non-crossing of

one-dimensional bands is confirmed also by group theory analysis; in one dimension the group of symmetry operations (neglecting spin) is too small to imply degeneracy of bands; on the contrary, in two- and three-dimensional crystals crossing of energy bands is possible at high symmetry points or lines in the Brillouin zone.)

So far we have considered Eq. (1.1) in the infinite interval $-\infty \leq x \leq \infty$; it is essentially equivalent from a physical point of view to consider Eq. (1.1) in the macroscopic region $0 \leq x \leq L \equiv Na$ where N is a very large but finite number (N is the number of unit cells of the crystal and is of order 10^8 for $L = 1$ cm). The reason to consider a very large macroscopic region, rather than an infinite one, is simply a matter of convenience, mainly for counting states and distributing electrons in the energy bands. In order not to affect the physics by boundary effects we use cyclic or Born-von Karman boundary conditions for the wavefunctions. This consists in the requirement

$$\psi(x + Na) \equiv \psi(x), \tag{1.10a}$$

i.e. the points x and $x + Na$ are considered as physically equivalent.

The wavefunction $\psi(x)$ must be a Bloch function of wavenumber k; then the boundary condition (1.10a) restricts the acceptable values of k to the ones that satisfy

$$e^{ikNa} = 1 \implies k = \frac{2\pi}{Na}n \quad (n = 0, \pm1, \pm2, \ldots). \tag{1.10b}$$

The density-of-states in k space is equal to $L/2\pi$, and is proportional to the length of the crystal. When the macroscopic length $L = Na$ is very large, the variable k must be thought of as a dense (although discrete) variable; notice that the first Brillouin zone contains *a number of uniformly distributed k points, equal to the number N of cells of the lattice.*

1.2 Energy Levels of a Single Quantum Well and of a Periodic Array of Quantum Wells

One of the most elementary problems in quantum mechanics is the study of the energy levels of a particle in a single quantum well. Similarly, one of the most elementary applications of the Bloch theorem is the study of the energy bands of a particle moving in a periodic array of quantum wells. The periodically repeated quantum well model was introduced by Kronig and Penney in 1931 to replace the actual crystal potential with a much more manageable piecewise constant potential; in this way, in each well (or in each barrier) the linearly independent solutions of the Schrödinger equation are simple trigonometric (or exponential) functions. Standard boundary conditions of continuity of wavefunctions and currents, combined with Bloch conditions required by periodicity, easily lead to an analytic compatibility equation for the eigenvalues of the crystal Hamiltonian. Successively, the Kronig-Penney model, with appropriate generalizations, has found a revival in the very active field of research of the electronic states of layered structures and superlattices [superlattices are artificial materials, obtained by growing on a substrate a controlled number of layers of two or more chemically

similar crystals, in an appropriate periodic sequence]. Applications also include other models of field propagation, such as mechanical waves in phononic crystals and electromagnetic waves in photonic crystals.

Energy Levels of a Single Quantum Well

Before considering the one-dimensional motion of a particle in a periodic sequence of potential wells, we begin with the model of a single one-dimensional well of finite height V_0 and width w. The energy potential profile $V(x)$ is indicated in Figure 1.1; the potential is zero for $-w/2 < x < +w/2$ and equals a positive constant V_0 elsewhere. The potential has inversion symmetry around the center of the well; thus the eigenfunctions of Eq. (1.1) must be either even or odd under spatial inversion.

The general *even* solution $\psi(x) = \psi(-x)$ for bound states $(E < V_0)$ takes the form

$$\psi(x) = \begin{cases} A\cos qx & \text{if } |x| < \frac{w}{2}; \quad q(E) = \sqrt{\frac{2mE}{\hbar^2}}; \qquad q_0 = \sqrt{\frac{2mV_0}{\hbar^2}}, \\ Be^{-\beta|x|} & \text{if } |x| > \frac{w}{2}; \quad \beta(E) = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}; \quad \beta^2 + q^2 = q_0^2, \end{cases}$$

(1.11)

where $q(E)$ is the propagation wavenumber in the well and $\beta(E)$ is the damping of the wavefunction in the barrier; A and B are two arbitrary coefficients.
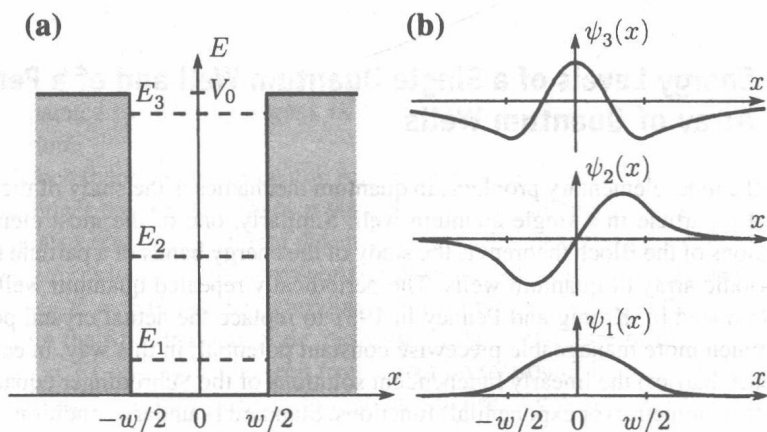

Figure 1.1 (a) Potential energy profile of a symmetric finite quantum well. In the case $V_0 = 1$ eV and $w = 14$ Å ($\approx 26\,a_B$) there are three bound states of energy $E_1 = 0.120$ eV, $E_2 = 0.464$ eV, and $E_3 = 0.936$ eV. Notice that the lowest energy levels of a quantum well in an infinite barrier $V_0 \to \infty$ of the same width are $E_1^\infty = 0.2$ eV, $E_2^\infty = 0.8$ eV, and $E_3^\infty = 1.8$ eV. (b) Normalized wavefunctions corresponding to the bound states of the finite quantum well under attention.