

SECOND EDITION

Solid State Physics

Giuseppe Grosso
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Second Edition

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Contents

Preface to the second edition	xi
Preface to the first edition	xiii
1 Electrons in One-Dimensional Periodic Potentials	1
1.1 The Bloch Theorem for One-Dimensional Periodicity	2
1.2 Energy Levels of a Single Quantum Well and of a Periodic Array of Quantum Wells	5
1.3 Transfer Matrix, Resonant Tunneling, and Energy Bands	12
1.4 The Tight-Binding Model	25
1.5 Plane Waves and Nearly Free-Electron Model	34
1.6 Some Dynamical Aspects of Electrons in Band Theory	38
Appendix A. Solved Problems and Complements	49
Further Reading	64
2 Geometrical Description of Crystals: Direct and Reciprocal Lattices	67
2.1 Simple Lattices and Composite Lattices	67
2.2 Geometrical Description of Some Crystal Structures	72
2.3 Wigner-Seitz Primitive Cells	83
2.4 Reciprocal Lattices	84
2.5 Brillouin Zones	88
2.6 Translational Symmetry and Quantum Mechanical Aspects	91
2.7 Density-of-States and Critical Points	99
Further Reading	104
3 The Sommerfeld Free-Electron Theory of Metals	107
3.1 Quantum Theory of the Free-Electron Gas	107
3.2 Fermi-Dirac Distribution Function and Chemical Potential	112
3.3 Electronic Specific Heat in Metals and Thermodynamic Functions	116
3.4 Thermionic Emission from Metals	118
Appendix A. Outline of Statistical Physics and Thermodynamic Relations	120
Appendix B. Fermi-Dirac and Bose-Einstein Statistics for Independent Particles	125
Appendix C. Modified Fermi-Dirac Statistics in a Model of Correlation Effects	131
Further Reading	133
4 The One-Electron Approximation and Beyond	135
4.1 Introductory Remarks on the Many-Electron Problem	136
4.2 The Hartree Equations	137
4.3 Identical Particles and Determinantal Wavefunctions	139
4.4 Matrix Elements Between Determinantal States	140
4.5 The Hartree-Fock Equations	144

4.6	Overview of Approaches Beyond the One-Electron Approximation	154
4.7	Electronic Properties and Phase Diagram of the Homogeneous Electron Gas	155
4.8	The Density Functional Theory and the Kohn-Sham Equations	163
	Appendix A. Bielectronic Integrals Among Spin Orbitals	171
	Appendix B. Outline of Second Quantization Formalism for Identical Fermions	172
	Appendix C. An Integral on the Fermi Sphere	175
	Further Reading	176
5	Band Theory of Crystals	179
5.1	Basic Assumptions of the Band Theory	180
5.2	The Tight-Binding Method (LCAO Method)	182
5.3	The Orthogonalized Plane Wave (OPW) Method	189
5.4	The Pseudopotential Method	197
5.5	The Cellular Method	204
5.6	The Augmented Plane Wave (APW) Method	207
5.7	The Green's Function Method (KKR Method)	211
5.8	Iterative Methods in Electronic Structure Calculations	217
	Appendix A. Matrix Elements of the Augmented Plane Wave Method	228
	Appendix B. Solved Problems and Complements	232
	Appendix C. Evaluation of the Structure Coefficients of the KKR Method with the Ewald Procedure	235
	Further Reading	240
6	Electronic Properties of Selected Crystals	243
6.1	Band Structure and Cohesive Energy of Rare-Gas Solids	244
6.2	Electronic Properties of Ionic Crystals	251
6.3	Covalent Crystals with Diamond Structure	263
6.4	Band Structures and Fermi Surfaces of Some Metals	266
6.5	Carbon-Based Materials and Electronic Structure of Graphene	272
	Appendix A. Solved Problems and Complements	277
	Further Reading	284
7	Excitons, Plasmons, and Dielectric Screening in Crystals	287
7.1	Exciton States in Crystals	288
7.2	Plasmon Excitations in Crystals	296
7.3	Static Dielectric Screening in Metals within the Thomas-Fermi Model	298
7.4	The Longitudinal Dielectric Function within the Linear Response Theory	301
7.5	Dielectric Screening within the Lindhard Model	304
7.6	Quantum Expression of the Longitudinal Dielectric Function in Crystals	312
7.7	Surface Plasmons and Surface Polaritons	314
	Appendix A. Friedel Sum Rule and Fumi Theorem	318
	Appendix B. Quantum Expression of the Longitudinal Dielectric Function in Materials with the Linear Response Theory	320
	Appendix C. Lindhard Dielectric Function for the Free-Electron Gas	325
	Appendix D. Quantum Expression of the Transverse Dielectric Function in Materials with the Linear Response Theory	328
	Further Reading	331

8	Interacting Electronic-Nuclear Systems and the Adiabatic Principle	333
8.1	Interacting Electronic-Nuclear Systems and Adiabatic Potential-Energy Surfaces	334
8.2	Non-Degenerate Adiabatic Surface and Nuclear Dynamics	337
8.3	Degenerate Adiabatic Surfaces and Jahn-Teller Systems	342
8.4	The Hellmann-Feynman Theorem and Electronic-Nuclear Systems	356
8.5	Parametric Hamiltonians and Berry Phase	359
8.6	The Berry Phase Theory of the Macroscopic Electric Polarization in Crystals	364
	Appendix A. Simplified Evaluation of Typical Jahn-Teller and Renner-Teller Matrices	371
	Appendix B. Solved Problems and Complements	377
	Further Reading	389
9	Lattice Dynamics of Crystals	391
9.1	Dynamics of Monoatomic One-Dimensional Lattices	391
9.2	Dynamics of Diatomic One-Dimensional Lattices	396
9.3	Dynamics of General Three-Dimensional Crystals	400
9.4	Quantum Theory of the Harmonic Crystal	407
9.5	Lattice Heat Capacity. Einstein and Debye Models	410
9.6	Considerations on Anharmonic Effects and Melting of Solids	412
9.7	Optical Phonons and Polaritons in Polar Crystals	415
	Appendix A. Quantum Theory of the Linear Harmonic Oscillator	430
	Further Reading	436
10	Scattering of Particles by Crystals	437
10.1	General Considerations	437
10.2	Elastic Scattering of X-rays from Crystals and the Thomson Approximation	440
10.3	Compton Scattering and Electron Momentum Density	455
10.4	Inelastic Scattering of Particles and Phonons Spectra of Crystals	459
10.5	Quantum Theory of Elastic and Inelastic Scattering of Neutrons	463
10.6	Dynamical Structure Factor for Harmonic Displacements and Debye-Waller Factor	467
10.7	Mössbauer Effect	474
	Appendix A. Solved Problems and Complements	476
	Further Reading	481
11	Optical and Transport Properties of Metals	483
11.1	Macroscopic Theory of Optical Constants in Homogeneous Materials	484
11.2	The Drude Theory of the Optical Properties of Free Carriers	490
11.3	Transport Properties and Boltzmann Equation	499
11.4	Static and Dynamic Conductivity in Metals	502
11.5	Boltzmann Treatment and Quantum Treatment of Intraband Transitions	508
11.6	The Boltzmann Equation in Electric Fields and Temperature Gradients	509
	Appendix A. Solved Problems and Complements	523
	Further Reading	527

12	Optical Properties of Semiconductors and Insulators	529
12.1	Transverse Dielectric Function and Optical Constants in Homogeneous Media	530
12.2	Quantum Theory of Band-to-Band Optical Transitions and Critical Points	534
12.3	Indirect Phonon-Assisted Transitions	539
12.4	Two-Photon Absorption	544
12.5	Exciton Effects on the Optical Properties	547
12.6	Fano Resonances and Absorption Lineshapes	553
12.7	Optical Properties of Vibronic Systems	559
	Appendix A. Transitions Rates at First and Higher Orders of Perturbation Theory	569
	Appendix B. Optical Constants, Green's Function and Kubo-Greenwood Relation	574
	Further Reading	575
13	Transport in Intrinsic and Homogeneously Doped Semiconductors	577
13.1	Fermi Level and Carrier Density in Intrinsic Semiconductors	577
13.2	Impurity Levels in Semiconductors	582
13.3	Fermi Level and Carrier Density in Doped Semiconductors	590
13.4	Non-Equilibrium Carrier Distributions	594
13.5	Generation and Recombination of Electron-Hole Pairs in Doped Semiconductors	599
	Appendix A. Solutions of Typical Transport Equations in Uniformly Doped Semiconductors	601
	Further Reading	608
14	Transport in Inhomogeneous Semiconductors	609
14.1	Properties of the p - n Junction at Equilibrium	609
14.2	Current-Voltage Characteristics of the p - n Junction	615
14.3	The Bipolar Junction Transistor	621
14.4	Semiconductor Heterojunctions	624
14.5	Metal-Semiconductor Contacts	627
14.6	Metal-Oxide-Semiconductor Structure	632
14.7	Metal-Oxide-Semiconductor Field-Effect Transistor (MOSFET)	637
	Further Reading	640
15	Electron Gas in Magnetic Fields	643
15.1	Magnetization and Magnetic Susceptibility	644
15.2	Energy Levels and Density-of-States of a Free Electron Gas in Magnetic Fields	646
15.3	Landau Diamagnetism and de Haas-van Alphen Effect	655
15.4	Spin Paramagnetism of a Free-Electron Gas	661
15.5	Magnetoresistivity and Classical Hall Effect	662
15.6	Quantum Hall Effects	668
	Appendix A. Solved Problems and Complements	686
	Further Reading	694
16	Magnetic Properties of Localized Systems and Kondo Impurities	697
16.1	Quantum Mechanical Treatment of Magnetic Susceptibility	698
16.2	Permanent Magnetic Dipoles in Atoms or Ions with Partially Filled Shells	701

16.3	Paramagnetism of Localized Magnetic Moments	704
16.4	Localized Magnetic States in Normal Metals	709
16.5	Dilute Magnetic Alloys and the Resistance Minimum Phenomenon	714
16.6	Magnetic Impurity in Normal Metals at Very Low Temperatures	724
	Further Reading	729
17	Magnetic Ordering in Crystals	731
17.1	Ferromagnetism and the Weiss Molecular Field	732
17.2	Microscopic Origin of the Coupling Between Localized Magnetic Moments	741
17.3	Antiferromagnetism in the Mean Field Approximation	748
17.4	Spin Waves and Magnons in Ferromagnetic Crystals	750
17.5	The Ising Model with the Transfer Matrix Method	756
17.6	The Ising Model with the Renormalization Group Theory	761
17.7	Itinerant Magnetism	769
	Appendix A. Solved Problems and Complements	775
	Further Reading	787
18	Superconductivity	789
18.1	Some Phenomenological Aspects of Superconductors	790
18.2	The Cooper Pair Idea	799
18.3	Ground State for a Superconductor in the BCS Theory at Zero Temperature	805
18.4	Excited States of Superconductors at Zero Temperature	813
18.5	Treatment of Superconductors at Finite Temperature and Heat Capacity	820
18.6	The Phenomenological London Model for Superconductors	824
18.7	Macroscopic Quantum Phenomena	828
18.8	Tunneling Effects	837
	Appendix A. The Phonon-Induced Electron-Electron Interaction	845
	Further Reading	848
Index		851

CONTENTS SYNOPSIS

Chapters 1, 2, 3	Introductory information
Chapters 4, 5, 6, 7	Electronic structure of crystals
Chapters 8, 9	Adiabatic principle and lattice vibrations
Chapters 10, 11, 12, 13, 14	Scattering; optical and transport properties
Chapters 15, 16, 17	Magnetic field effects and magnetism
Chapter 18	Superconductivity

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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

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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 tententially 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

1 Electrons in One-Dimensional Periodic Potentials

Chapter Outline head

1.1	The Bloch Theorem for One-Dimensional Periodicity	2
1.2	Energy Levels of a Single Quantum Well and of a Periodic Array of Quantum Wells	5
1.3	Transfer Matrix, Resonant Tunneling, and Energy Bands	12
1.3.1	Transmission and Reflection of Electrons from an Arbitrary Potential	13
1.3.2	Double Barrier and Resonant Tunneling	20
1.3.3	Electron Tunneling through a Periodic Potential	22
1.4	The Tight-Binding Model	25
1.4.1	Expansion in Localized Orbitals	25
1.4.2	Tridiagonal Matrices and Continued Fractions	27
1.5	Plane Waves and Nearly Free-Electron Model	34
1.5.1	Expansion in Plane Waves	34
1.5.2	The Mathieu Potential and the Continued Fraction Solution	37
1.6	Some Dynamical Aspects of Electrons in Band Theory	38
Appendix A. Solved Problems and Complements		49
Further Reading		64

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

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

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

$$V(x) = V(x + ma), \quad (1.2)$$

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

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

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

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

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

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

The normalization constant has been chosen such that $W_k(x)$ is normalized to 1 in the interval $0 \leq x \leq L$ (and the length L of the crystal is understood in the limit $L \rightarrow \infty$ whenever necessary). The wavenumbers k are real and the eigenvalues are $E(k) = \hbar^2 k^2 / 2m$. 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 $k + h_n$:

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

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 $-\pi/a < k \leq \pi/a$, 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

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

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

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

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

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

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

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

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

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

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

$$\psi(x + Na) \equiv \psi(x), \quad (1.10a)$$

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

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

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