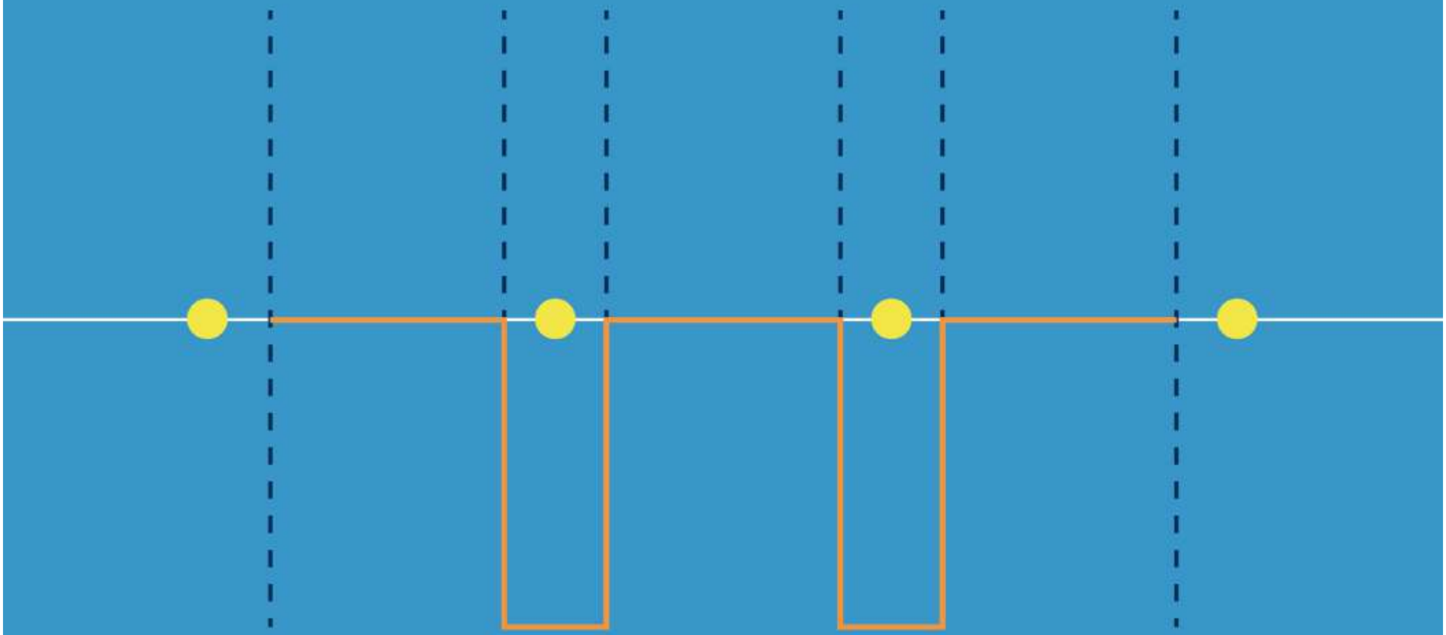
Solid State Physics

A primer

Luciano Colombo



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Luciano Colombo
University of Cagliari, Italy

IOP Publishing, Bristol, UK

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ISBN 978-0-7503-2265-2 (ebook)
ISBN 978-0-7503-2262-1 (print)
ISBN 978-0-7503-2263-8 (myPrint)
ISBN 978-0-7503-2264-5 (mobi)

DOI 10.1088/978-0-7503-2265-2

Version: 20210301

IOP ebooks

British Library Cataloguing-in-Publication Data: A catalogue record for this book is available from the British Library.

Published by IOP Publishing, wholly owned by The Institute of Physics, London

IOP Publishing, Temple Circus, Temple Way, Bristol, BS1 6HG, UK

US Office: IOP Publishing, Inc., 190 North Independence Mall West, Suite 601, Philadelphia, PA 19106, USA

To my students.

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Foreword

When Professor Colombo approached me to write the preface of this book, I was both surprised and honoured. Surprised because there are many eminent scholars out there that could 'do the job', and honoured because I have the greatest respect for Professor Colombo and his work. I have known Professor Colombo for many years—we interacted on several occasions (often at the MRS Fall Meeting in Boston), he visited me in Montréal, I visited him in Cagliari (invited to give a short course on models of laser ablation). I have always been impressed by the clarity and rigour of his mind, his knowledge of various topics in physics, his desire to not only do the 'best physics' but also to communicate it with clarity and passion. He has been a model for me and I tried my best, over the years, to imitate his style.

Professor Colombo told me once that writing a book was some sort of 'romantic' adventure. I was not too sure what he meant (and I did not dare to ask!), but the idea remained in my head. I suspect that he sees this as some sort of an idealised accomplishment, because as a professor, you teach and you need (and love!) the students to understand. This requires clarity and pedagogical aptitudes, and this is precisely what one finds in this excellent book: a text written for students. Having myself taught solid-state physics, in particular recently as an introductory course to undergraduate students (one semester, three credits), this book would have been perfect for my class, both with the material covered and with the level of knowledge in quantum physics, statistical physics and molecular physics expected from students. The amount of material covered is perhaps a bit large for a one-semester course, but some more advanced topics may be left for personal reading. This book fills a gap that is largely unoccupied. There are not many texts that address this topic in such a comprehensive way, and at the beginner level.

I admit that the title of the book, *Solid State Physics*, surprised me a bit at first, as it seems to me that 'condensed-matter physics' is perhaps more modern and inclusive. But I thought 'What's in a name? That which we call a rose, by any other name would smell as sweet' (William Shakespeare, *Romeo and Juliet*). We exchanged on this issue with Professor Colombo and I fully adhere to his views. The solid state is somehow a subset of the condensed state, one that is idealised and can be described using the fabulous mathematical toolbox that applies to periodic systems, including periodic boundary conditions. And this is relatively easy for students to understand and visualise. While the ideal solid state really does not exist in nature (just as a circle does not exist), it provides a reference for understanding more complex systems found in the real world. From a pedagogical viewpoint, further, understanding the basics of the discipline, i.e. solid-state physics, is a prerequisite to dealing with more complex situations, i.e. condensed-matter physics, e.g. with such problems as amorphous systems (lack of periodic order), nanomaterials (importance of boundary effects), etc. To cite Professor Colombo, this primer and the others in this series 'are my personal battle to promote the need to train students, especially at undergraduate level, by passing a strong, robust, general and universally applicable set of fundamentals'. This statement, I would say, is the clear act of faith of a remarkable professor, fully dedicated to his art: kudos to Professor Colombo.

The book is organised in three parts, each divided in several chapters. The first part, 'Preliminary concepts', presents the basic basics. Chapter 1, 'The overall picture', is clever: it answers first the necessary question 'what are we talking about?' (crystalline solids, which are approached from the point of view of diffusion—very nice!), then moves on to discuss, upfront, concepts that percolate throughout the various topics which will be addressed in subsequent chapters. The late George K Horton (Rutgers), who was an authority in the area of dynamical properties of solids, told me once that writing a paper (or, for that matter, a book chapter or a book) is not like writing a novel: one should not keep the 'punch' for the end but say early where one is going, and this will serve to light the route that one follows. This is precisely what this first chapter does (and I wish I had followed George Horton's advice more often myself!). The connection between the atomic structure and the complicated many-body electronic structure is introduced right at the outset (semi-classical approximation, frozen-core approximation, Born–Oppenheimer approximation, etc). Chapter 2 goes into the 'heart of the matter' and discusses in detail the crystalline structure, both in direct and in reciprocal space (including an introduction to the Bloch theorem and one-electron wavefunctions), and inevitable deviations from the ideal picture (defects). The stage is set.

The second part, 'Vibrational, thermal, and elastic properties', emerges naturally from chapter 2. Once again, Professor Colombo excels in communicating his message effectively. As it should, the first chapter in this section, chapter 3, deals with lattice dynamics: modes of vibration, dispersion relations (acoustic and optic modes), dynamical matrix and, evidently, phonons. The presentation of phonons as a gas of pseudo-particles within the framework of the quantum theory of the harmonic crystal, is simple, direct and effective. From a communications viewpoint, and this diffuses throughout the book, the author is clearly 'speaking' to the reader—the student—just as if he was standing in front of the class. I would have loved to have been one of his students (I have been on a few occasions)! Chapter 3 continues with a clever discussion of the experimental determination of the dispersion relations—an exercise that is not *a priori* simple and one that is, in my view, essential (and sometimes overlooked)—and of the vibrational density of states, which saves one from having to count the modes one by one! Chapter 4 is concerned with the thermal properties of solids—heat capacity (including the Debye model and the quantum framework that underlies the theory) and the very important anharmonic effects, including a very nice section on phonon–phonon interactions for the most avid readers (with an excellent discussion of the crystal momentum and normal/Umklapp processes), and thermal transport (Boltzmann equation). The second part closes with chapter 5 on a discussion of elastic properties (strain, stress, elastic constants), moving from a discrete, atomic description of the crystal to a continuous description of it. This topic allows one to connect to the real world: you *know* that solids are made of atoms, but you *see* how they react to pressure or temperature, for example. I would not normally cover this subject in my undergraduate course—but perhaps I should!

The third part, ‘Electronic structure’, is where ‘the beef is’. It consists of five chapters and begins with a general discussion of electrons in crystals (chapter 6), more precisely methods for constructing the electronic structure, namely free-electron, tight-binding and density-functional theory, all of which are developed in detail in subsequent chapters. This chapter also reviews Fermi–Dirac statistics and revisits in detail the Bloch theorem and Bloch wavefunctions. It ends with a thorough discussion of the Kronig–Penney model which provides a simple, clear introduction to the concept of band structure with its allowed regions and forbidden regions (gaps). Chapter 7 is devoted to the free-electron theory of metals, and includes a very nice discussion of the Drude model (and the reasons of its failure) and of the Sommerfeld theory of conduction. This is one occasion to introduce the electronic density of states, both at zero (ground-state) and at finite temperature, showing very nicely the contributions of electrons and phonons to the specific heat, and how the latter dominates at high temperatures. The chapter closes on a discussion of relaxation times and scattering, and limitations of the Sommerfeld theory. The latter topic provides a natural transition to chapter 8 (‘The band theory’) that conveys many important concepts, notably the nearly-free electron gas (weak potential) which permits the author to introduce such important ideas as energy bands and energy gaps, hence explaining the difference between insulators, semiconductors and metals. Further to this, Professor Colombo discusses in detail the tight-binding approach (and he is famous for his work in this area, among others) and its success in describing the electronic structure. A thorough description of the band structure follows—with such topics as electron dynamics, field effects, electrons and holes, etc—and the chapter closes with a short overview of other approaches to the band structure. Chapter 9, ‘Semiconductors’, is dedicated to the theoretical framework underlying the physics of semiconductors—important for applications—and, in particular, to electron transport. It introduces such important concepts as doping, charge transport, carrier statistics and populations, optical (photon) absorption and related carrier transitions and excitons. Finally, chapter 10 introduces the now ubiquitous density-functional theory—Hohenberg–Kohn and Kohn–Sham theorems and practical implementation of the method; this is a great idea, not common in solid-state physics books, as it allows students to connect to topical research and shows them that quantum mechanics is a ‘practical tool’!

A few more notes; in line with the logic of ‘tell them what you are going to tell them’, each chapter starts by a summarising ‘syllabus’. This is extremely useful and helps give a direction to the reader. Further, the book includes several appendices where specific and useful topics are discussed (like, for instance, ‘Essential thermodynamics’, ‘The tight-binding theory’). Finally, the text contains many illustrations that are very well done and very informative; graphical representations of complex (or abstract) concepts that describe real-world objects is extremely useful for students to develop their intuition.

This book is a ‘primer’ and, in that respect, cannot cover the subject matter in an exhaustive manner. Yet, I find it to be remarkably complete, in particular for a book intended to undergraduate students. And all of this in 250 pages is a genuine *tour de force*. True, there are some topics that could have been covered (e.g. superconductivity), but there is already a lot of material for a one-semester course. I would have loved to have this book for my class. Thanks to Professor Colombo for this excellent addition to the literature. I predict that it will become a 'classic'.

Laurent J Lewis
Département de physique
Université de Montréal
September 2020

Presentation of the ‘primer series’

This is the second volume of a series of three books that, as a whole, account for an introduction to the huge field usually referred to as ‘condensed matter physics’: they are respectively addressed to atomic and molecular physics, to solid state physics, and to statistical methods for the description of classical or quantum ensembles of particles. They are based on my 20 year experience of teaching undergraduate courses on these topics for bachelor-level programs in physical and engineering sciences at the University of Cagliari (Italy).

The volumes are called ‘Primers’ to underline that the pedagogical aspects have been privileged over those of completeness. In particular, I selected the contents of each volume so as to keep limited its number of pages and so that the topics actually covered correspond to the *syllabus* of a typical one-semester course.

More important, however, was the choice of the style of presentation: I wanted to avoid an excessively formal treatment, preferring instead the exploration of the underlying physical features and always placing phenomenology at the centre of the discussion. More specifically, the main characteristics of this book series are:

- emphasis is always given to the physical content, rather than to formal proofs, i.e. mathematics is kept at the minimum level possible, without affecting rigour or clear thinking;
- an in-depth analysis is presented about the merits and faults of any approximation used, incorporating also a thorough discussion of the conceptual framework supporting any adopted physical model;
- prominence is always on the underlying physical basis or principle, rather than to applications;
- when discussing the proposed experiments, the focus is given to their conceptual background, rather than to the details of the instrumental setup.

Despite the tutorial approach, I nevertheless wanted to follow the Italian academic tradition, which provides even the elementary introduction to condensed matter physics at a quantum level. I hope that my efforts have optimally combined ease-of-access and rigour, especially conceptually.

The intentionally non-encyclopaedic content and the tutorial character of these ‘Primers’ should facilitate their use even for students not specifically enrolled in a university *curriculum* in physics. I hope, in particular, that my textbooks could be accessible to students in chemistry, materials science and also of many engineering branches. In view of this, I have included a brief outline of non-relativistic quantum mechanics in the first ‘Primer’, a subject that does not appear in the typical engineering *curricula*. For the rest, classical mechanics, elementary thermodynamics and Maxwell theory of electromagnetism are used, to which all students of natural and engineering sciences are normally exposed.

Each ‘Primer’ is organised in parts, divided into chapters. This structure is tailored to facilitate the planning of a one-semester course: these volumes aim at being their main teaching tool. More specifically, each part identifies an independent teaching module, while each chapter corresponds to about two weeks of lecturing.

I cannot conclude this general introduction without thanking the many students who, over the years, have attended my courses in condensed matter physics at the University of Cagliari. Through the continuous exchange of ideas with them I have gradually understood how best to organise my teaching and the corresponding study material. As a matter of fact, the contents that I have collected in these volumes were born from this very fruitful dialogue.

Luciano Colombo
Cagliari, June 2019

Acknowledgements

I am really indebted to Ms C Mitchell—Commissioning Editor of IOP Publishing—and Mr Daniel Heatley—ebooks Editorial Assistant of IOP Publishing—for their great enthusiasm in accepting my initial proposal and for shaping it into a suitable editorial product. I also warmly acknowledge Ms Emily Tapp—Commissioning Editor of IOP Publishing—and Mr R Trevelyan—Editorial Assistant of IOP Publishing—for supporting my writing efforts of the second Primer with great professionalism, always promptly replying to my queries and clarifying my doubts. Overall, their assistance has been really precious.

Introduction to: 'Solid state physics: a primer'

In my view the 'solid state' is an idealised state of condensed matter where translational invariance rules most physical phenomena. By 'idealised' I simply mean that real solid materials are in fact not at all perfectly periodic: they contain defects, either point-like and extended, as imposed by thermodynamics; they are contaminated or doped, as result of natural or intentional processes randomly altering their pristine chemistry; they have a finite size, that is they have surfaces. While all these phenomena are indeed fascinating topics of condensed matter physics, a first pedagogical approach to solids is in my opinion better framed within the idealisation of a surface-free and periodically invariant system, namely a crystal. This allows one to develop a simple formalism—in several important cases analytically workable—which leads to quite a few important achievements like, for instance, understanding the difference between metals and insulators or describing the thermal transport in terms of the corpuscular phonon language.

A modern approach to the fundamental physics of crystalline solids does require the use of quantum mechanics, which is the language adopted in any chapter, although classical physics is often used in order to set up the first approach to a problem or, through the manifestation of its inadequacy, to remark the real need of a full quantum treatment. Furthermore, despite the tutorial approach, some robust basic notion on atomic physics is nevertheless needed in order to fully appreciate the physics discussed in this book.

A possible subtitle for this Primer could have been: 'a first introduction to the physics of phonons and electrons in crystalline systems'. As a matter of fact, these are the only two topics—treated separately in view of the fundamental adiabatic approximation—here discussed, among many other important ones which are simply omitted, since this textbook is primarily intended as the study material for a first undergraduate course in condensed matter physics. Despite this somewhat narrow perspective, I believe that the focus on the physics of phonons and electrons in periodic crystals is enough to define the minimal-complexity framework needed to understand the fundamentals of condensed matter physics. It is understood that, in order to complete the student's background in this field, a more advanced course on dielectric, optical, magnetic ordering, and many-body properties is mostly needed, including topics like the physics of defects and surfaces, the mechanical properties of solids, and superconductivity.

This Primer is divided in three parts: the first one provides, at first, a careful account of the hierarchy of approximations adopted to treat the solid state and, next, the formal tools to describe the crystalline atomic structures; the second part deals with the vibrational, thermal, and elastic properties of crystal solids; the third part is addressed to their electronic structure. A short presentation of the density functional theory—which is nowadays considered the 'standard model' to treat condensed matter systems—is offered in the last chapter. Nine appendices are added to the text, each focussed on some technical development which, at first reading, can be skipped without compromising the general understanding of the arguments developed in the main text. A bibliography is added to each chapter as a guideline for further reading.

The volume contains many figures, most of which are ‘conceptual’, that is: they are basically intended to provide a graphical representation of the main ideas and concepts developed in the written part. Tables with numerical values of important physical properties are included as well, in the attempt to provide the reader with information useful to ‘quantify’ the physical results presented. Finally, a list of all the mathematical symbols used in the volume is given at the beginning as an orientation guide while reading.

Luciano Colombo
Cagliari, February 2021

Acknowledgements

I am really indebted with many friends who helped me by critically reading (in part or totally) the pre-editorial version of the book (for this special thanks go to Dr G Malloci and Professor C Melis, both at the Department of Physics, University of Cagliari, Italy, and to Dr S Giordano, CNRS and University of Lille, France) or by providing me with the output of their calculations used to plot some figures (Dr G Fugallo, CNRS and University of Nantes, France and Dr A Antidormi, ICN2, Barcelona, Spain) or for suggesting updated bibliographic entries. Finally, Professor C Melis is once again warmly thanked for assisting me in generating several figures reporting experimental data taken from literature. The care these friends have taken in checking my original manuscript has corrected several unclear passages and many misprints, thus greatly improving my presentation. If there are still errors or omissions they should be attributed solely to me.

Author biography

Luciano Colombo

Luciano Colombo received his doctoral degree in physics from the University of Pavia (I) in 1989 and then he was a post-doc at the École polytechnique fédérale de Lausanne (CH) and at the International School for Advanced Studies (I). He became assistant professor (tenured) at the University of Milano (I) in 1990, next moving to the University of Milano-Bicocca (I) in 1996 for an equivalent position. Since 2002 he has been full professor of theoretical condensed matter physics at the University of Cagliari (I) and since 2015 fellow of the 'Istituto Lombardo—Accademia di Scienze e Lettere' (Milano, I). He has been the principal investigator of several research projects addressed to solid-state and materials physics problems, the supervisor of more than 80 students (at bachelor, master, and PhD level), and the mentor of about 20 post-docs. He is the author, or coauthor, of more than 276 scientific articles and 9 books (this included). More about him can be found at: http://people.unica.it/lucianocolombo.

Symbols

α	optical absorption coefficient
α_T	isothermal compressibility
β	thermal expansion coefficient
γ	weighted Grüneisen parameter
$\gamma_{s\mathbf{q}}$	Grüneisen parameter for $(s\mathbf{q})$ phonon mode
$\Delta^2 R(t)$	atomic mean square displacement
ϵ_0	vacuum permittivity
ϵ_{ij}	*ij*th component of the second-rank strain tensor
$\epsilon_{\mathrm{r}}(\omega)$	frequency-dependent relative permittivity of a material
κ_{e}	thermal conductivity of electrons (generic)
$\kappa_{\mathrm{e}}^{\mathrm{Drude}}$	thermal conductivity of electrons, calculated according to the Drude theory
$\kappa_{\mathrm{e}}^{\mathrm{Sommerfeld}}$	thermal conductivity of electrons, calculated according to the Sommerfeld theory
κ_{l}	lattice thermal conductivity
κ_{tot}	total thermal conductivity
λ	first Lame’ coefficient
λ_{e}	electron mean free path
$\lambda_{s\mathbf{q}}$	mean free path of the $(s\mathbf{q})$ phonon mode
μ	second Lame’ coefficient
μ_{c}	chemical potential
μ_{e}	electron mobility
μ_{h}	hole mobility
μ_{B}	electron Bohr magneton
μ_{N}	nuclear magneton
μ_{x}	exciton effective mass
$\rho(\mathbf{r})$	electron density
$\rho_{\mathrm{GS}}(\mathrm{r})$	ground-state electron density
ρ^{HEG}	electron density in a homogeneous electron gas
σ_{e}	direct-current electron conductivity
σ_{h}	direct-current hole conductivity
σ_{tot}	direct-current total conductivity
τ_{e}	electron relaxation time
τ_{h}	hole relaxation time
$\tau_{s\mathbf{q}}$	relaxation time (lifetime) of the $(s\mathbf{q})$ phonon mode
$\varphi_{\mathrm{KS}}(\mathbf{r})$	Kohn–Sham orbital
$\Phi(\mathbf{r}, \mathbf{R})$	total crystalline wavefunction
Φ_{e}	flux of electrons
Φ_{h}	flux of holes
Φ_{ph}	flux of photons
$\Psi_{\mathrm{e}}^{(\mathbf{R})}(\mathbf{r})$	total electron wavefunction (when ions are clamped in the $\mathbf{R}$ configuration)
$\Psi_{\mathrm{n}}(\mathbf{r})$	total ion wavefunction
ζ	atomic valence
ω_{p}	plasma frequency
ω_{E}	Einstein frequency
ω_{D}	Debey frequency

a_{CB}	deformation potential for the conduction band
a_{H}	Bohr radius
a_{VB}	deformation potential for the valence band
a_0	lattice constant of cubic crystals
$\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$	translation vectors of the direct lattice
A	atomic mass number
$\{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\}$	translation vectors of the reciprocal lattice
B	bulk modulus
$\mathbf{B}$	externally applied magnetic field
$\mathbf{B}_{\mathrm{d}}$	Burgers vector of a dislocation
c	speed of light
c_V^{e}	constant-volume specific heat (electron contribution)
c_V^{l}	constant-volume specific heat (lattice contribution)
c_V^{tot}	total constant-volume specific heat
C_{ij}	*ij*th component of the elastic stiffness tensor in the compact Voigt notation
C_{ijkh}	*ijkh*th component of the fourth rank elastic stiffness tensor
$\mathcal{C}_V^{\mathrm{Drude}}(T)$	constant-volume heat capacity (Drude interpolation scheme)
$\mathcal{C}_V^{\mathrm{Einstein}}(T)$	constant-volume heat capacity (Einstein model)
$\mathcal{C}_V^{\mathrm{quantum}}(T)$	constant-volume heat capacity (full quantum expression)
$\mathbb{C}^{\mathrm{Voigt}}$	matrix representation of the elastic stiffness tensor in the compact Voigt notation
D_{e}	electron diffusivity
D_{h}	hole diffusivity
D_{ij}	*ij*th component of the elastic compliance tensor in the compact Voigt notation
D_{ijkh}	*ijkh*th component of the fourth rank elastic compliance tensor
e	electron charge (absolute value)
e_{cohesive}	cohesive energy per atom of a crystal
$\mathbf{E}$	externally applied electric field
E_{c}	energy at the bottom of the conduction band
$E_{\mathrm{c}}^{\mathrm{HEG}}$	correlation energy of a homogeneous electron gas
$E_{\mathrm{c}}^{\mathrm{LDA}}$	correlation energy in the local density approximation
E_{cohesive}	cohesive energy of a crystal
$E_{\mathrm{e}}^{(\mathbf{R})}$	total electron energy (when ions are clamped in the configuration $\mathbf{R}$)
E_{v}	energy at the top of the valence band
$E_{\mathrm{x}}^{\mathrm{HEG}}$	exchange energy of a homogeneous electron gas
$E_{\mathrm{x}}^{\mathrm{LDA}}$	exchange energy in the local density approximation
E_{F}	Fermi energy
$E_{\mathrm{CB}}(\mathbf{k})$	dispersion relation for the conduction band
$E_{\mathrm{VB}}(\mathbf{k})$	dispersion relation for the valence band
E_T	total energy of the crystal
E_{x}	exciton binding energy
$E_{\mathrm{x},n}$	exciton discrete energy spectrum
$E_{\mathrm{xc}}[\rho(\mathbf{r})]$	exchange-correlation energy functional
$E_{\mathrm{xc}}^{\mathrm{LDA}}$	exchange-correlation energy in the local density approximation
$F[\rho(\mathbf{r})]$	electron total energy functional

$g(r)$	pair correlation function
$g_n(E)$	electronic density of states per unit volume for the band n of a semiconductor
$\bar{g}_{CB}(E)$	$g_n(E)$ for the conduction band in parabolic bands approximation
$\bar{g}_{VB}(E)$	$g_n(E)$ for the valence band in parabolic bands approximation
$\mathbf{G}$	lattice vector (reciprocal lattice)
$\mathcal{G}$	Gibbs free energy
$\mathtt{G}$	carrier generation rate
$G(E)$	electronic density of states (eDOS) of a metal
$G(\omega)$	vibrational density of states (vDOS) or phonon density of states
$G_n(E)$	electronic density of states for the band n of a semiconductor
$G_{\mathrm{D}}(\omega)$	vibrational density of states (Drude interpolation scheme)
h	Planck constant
$\hbar$	$\hbar = h/2\pi$
$\mathcal{H}$	enthalpy
$\hat{\mathtt{i}}$	unit vector of the x-axis
$\hat{\mathtt{j}}$	unit vector of the y-axis
$\mathbf{J}_{\mathrm{CB}}$	electron charge density current (conduction band)
$\mathbf{J}_{\mathrm{VB}}$	hole charge density current (valence band)
$\mathbf{J}_{\mathrm{q,tot}}$	total charge density current
$\mathbf{J}_{\mathrm{h}}$	heat density current
$\hat{\mathtt{k}}$	unit vector of the z-axis
$\mathbf{k}$	electron wavevector
k_{B}	Boltzmann constant
k_{F}	Fermi wavevector
$\mathbf{L}_{\mathrm{d}}$	line vector of a dislocation
m_{e}	electron rest mass
m_{e}^*	electron effective mass
m_{h}^*	hole effective mass
m_{n}	neutron rest mass
m_{p}	proton rest mass
$\hat{\mathrm{n}} = (\mathrm{n}_1, \mathrm{n}_2, \mathrm{n}_3)$	unit vector of a generic direction in space
$\mathcal{N}_{\mathrm{A}}$	Avogadro number
$n_{\mathrm{BE}}(s\mathbf{q}, T)$	Bose–Einstein distribution for (population of) the ($s\mathbf{q}$) phonon mode
$n_{\mathrm{FD}}(E, T)$	Fermi–Dirac distribution for (population of) the electron level with energy E
$\bar{n}(s\mathbf{q}, T)$	non-equilibrium population of the ($s\mathbf{q}$) phonon mode
$\mathcal{N}_{\mathrm{c}}$	effective density of states in conduction band
$\mathcal{N}_{\mathrm{v}}$	effective density of states in valence band
P	pressure
$\mathbf{q}$	phonon wavevector (or wavevector of a lattice vibrational wave)
$\mathbf{r}$	generic electron position within a crystal
r_{x}	electron–hole orbital radius (exciton size)
$\mathbf{R}$	generic ion position within a crystal
$\mathtt{R}$	carrier recombination rate
$\mathbf{R}_{\mathrm{b}}$	ion position within the basis
$\mathcal{R}_{\mathrm{H}}$	Rydberg constant for hydrogen
$\mathbf{R}_{\mathrm{l}}$	lattice vector (direct lattice)
S	entropy

T	temperature
T_D	Debye temperature
T_F	Fermi temperature
T_{ij}	*ij*th component of the second rank stress tensor
$\hat{T}_{\mathbf{R}_\mathrm{l}}$	translation operator such that $\hat{T}_{\mathbf{R}_\mathrm{l}} f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R}_\mathrm{l})$
u	elastic energy density
$\mathbf{u}$	ionic displacement vector
$\mathcal{U}$	internal energy
$U(\mathbf{R})$	crystalline ion energy (for ions in configuration $\mathbf{R}$)
$\mathbf{v}_\mathrm{d}$	electron drift velocity in a weak field regime
$\mathbf{v}_\mathrm{e}^\mathrm{th}$	electron thermal velocity
$\mathbf{v}_\mathrm{F}$	electron Fermi velocity
$\mathbf{v}_\mathrm{sat}$	electron saturation velocity in a strong field regime
$\mathbf{v}_\mathrm{CB}(\mathbf{k})$	velocity of an electron in the conduction band
$\mathbf{v}_\mathrm{VB}(\mathbf{k})$	velocity of an electron in the valence band
V	volume (generic)
V_c	volume of the primitive unit cell (direct lattice)
V_cfp	crystal field potential
V_ee	electron–electron Coulomb interaction potential
V_Hartree	Hartree potential
V_ne	nucleus–electron Coulomb interaction potential
V_nn	nucleus–nucleus Coulomb interaction potential
V_xc	exchange-correlation potential
w	atomic weight
Z	atomic number

Part I

Preliminary concepts

IOP Publishing

Solid State Physics

A primer

Luciano Colombo

Chapter 1

The overall picture

Syllabus—*After defining what condensed matter (and, in particular, the crystalline solid state) is, we build the theoretical framework of minimum complexity able to deal with the corresponding atomic-scale physics. Proceeding from a limited set of basic definitions, a hierarchy of approximations is introduced, like, e.g. the separation between the nuclear and the electronic degrees of freedom and the single-particle picture.*

1.1 Basic definitions

The first task we must accomplish is defining the physical system we are actually interested in. This semantic exercise is quite important, since it will properly define the topic treated in this textbook: *the physics of crystalline solids*.

A fruitful constitutive hypothesis to start from is embodied by the *atomistic picture* [1, 2] which, relying on robust experimental evidence, states that *ordinary matter is made by elementary constituents known to be atoms*[1]. We agree that *condensed matter* forms whenever a *very large number of such atoms* (belonging to just one or more chemical species) *tightly bind together* by electrostatic interactions. Both features are indeed necessary in order to sharply define the state of aggregation we are interested in: (i) the fact that the number of atoms is very large allows us to exclude single molecules[2] from the horizon of our interest, while (ii) the strong character of their mutual interactions allows us to neglect the case of gaseous systems.

The definition just given is actually very generic and it does not allow us to distinguish between two paradigmatically different situations. In order to clarify and resolve this ambiguity, let us consider a sample of condensed matter and let us label

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[1] By ‘ordinary’ we mean matter as typically organised in materials found on Earth.

[2] A single molecule may have as many as thousands of atoms, like e.g. RNA or DNA nucleic acids: this is still a comparatively smaller number than found in a material specimen with any dimension from the micro- to the macro-scale.

doi:10.1088/978-0-7503-2265-2ch1

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by $\mathbf{R}_\alpha(t)$ the position of its αth atom at time t. We define the *mean square atomic displacement* $\Delta^2 R(t)$ as

$$\Delta^2 R(t) = \frac{1}{N}\sum_{\alpha=1}^{N} |\mathbf{R}_\alpha(t) - \mathbf{R}_\alpha(0)|^2, \tag{1.1}$$

where $\mathbf{R}_\alpha(0)$ represents the initial position of the αth atom and N is the total number of particles in the system. It is understood that the system is in equilibrium at temperature T. The calculation of $\Delta^2 R(t)$ for a silicon sample is reported in figure 1.1 at two different temperatures, respectively, above and below its melting temperature $T_\mathrm{m}^\mathrm{Si} = 1685$ K. If, according to atomic diffusion theory [3], we now link such a quantity to the corresponding diffusion coefficient $D(T)$

$$D(T) = \lim_{t\to+\infty}\frac{1}{6}\frac{\Delta^2 R(t)}{t}, \tag{1.2}$$

we immediately realise that below T_m^Si the sample does not show any self-diffusion characteristics[3] while above T_m^Si it flows. In other words, the definition of condensed matter given above allows *both solid and liquid systems* to be called *condensates*, despite their physics being largely different. Therefore, we make it clear that from now on we will focus our attention only on the *solid state*, i.e. only on *condensed matter systems that do not show any diffusive behaviour* (an introduction to the fascinating physics of liquids can be found elsewhere [4]).

The description just given of solid state is still inconveniently too general, since it is compatible with atomic arrangements showing quite unalike structural order

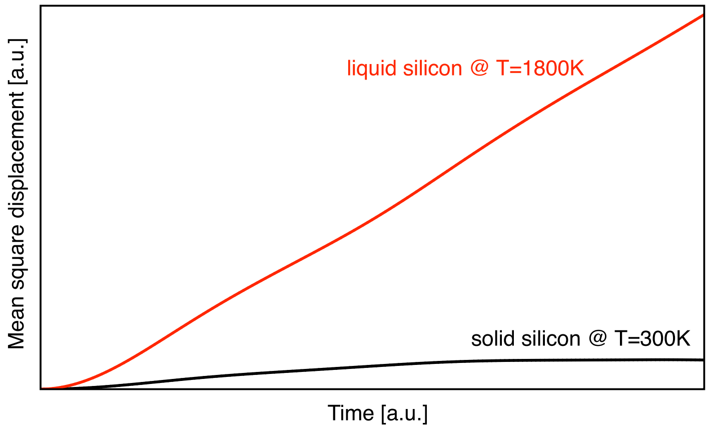

Figure 1.1. The mean square displacement of silicon at $T = 300$ K (black) and at $T = 1800$ K (red). Data are calculated by molecular dynamics simulations. Arbitrary units (a.u.) are used in both axes.

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[3] The phenomenological Fick law of diffusion $\mathbf{J}(T) = -D(T)\nabla C$ links the amount of matter $\mathbf{J}$ flowing through a unit area in a unit time interval to the concentration gradient ∇C across that unit area. Accordingly, zero-diffusivity systems do not flow.

features: we must duly refine this notion. To this aim let us consider a monoatomic solid state system and let us introduce its *pair correlation function*[4] $g(r)$ which at a generic position $\mathbf{r}$ is defined as

$$g(r) = \frac{1}{N\rho}\left\langle \sum_{\alpha\neq\beta=1}^{N} \delta(\mathbf{r} - \mathbf{R}_{\alpha\beta}) \right\rangle, \tag{1.3}$$

where $\rho = N/V$ is the average number density in the system and $\mathbf{R}_{\alpha\beta} = \mathbf{R}_\beta - \mathbf{R}_\alpha$ is the distance vector between atoms α and β. The $\langle\cdots\rangle$ brackets indicate that the sum is time- and direction-averaged by keeping constant the number of particles in the system as well as its volume and temperature, while the δ-symbol is defined usually as: it is worth one if its argument is null, otherwise it is worth zero.

Equation (1.3) describes how the number density varies within the system: more specifically, it provides the probability of finding a pair of (α, β) particles at a distance $r = R_\beta - R_\alpha$ apart, relative to the corresponding probability calculated for a uniform (random) distribution of similar atoms at the same density. In figure 1.2 we report the pair correlation function for two solid state silicon systems, both at room temperature. The peaks of the $g(r)$ function indicate *local densifications* of matter, while its minima indicate *local rarefactions*, in both cases referred to the

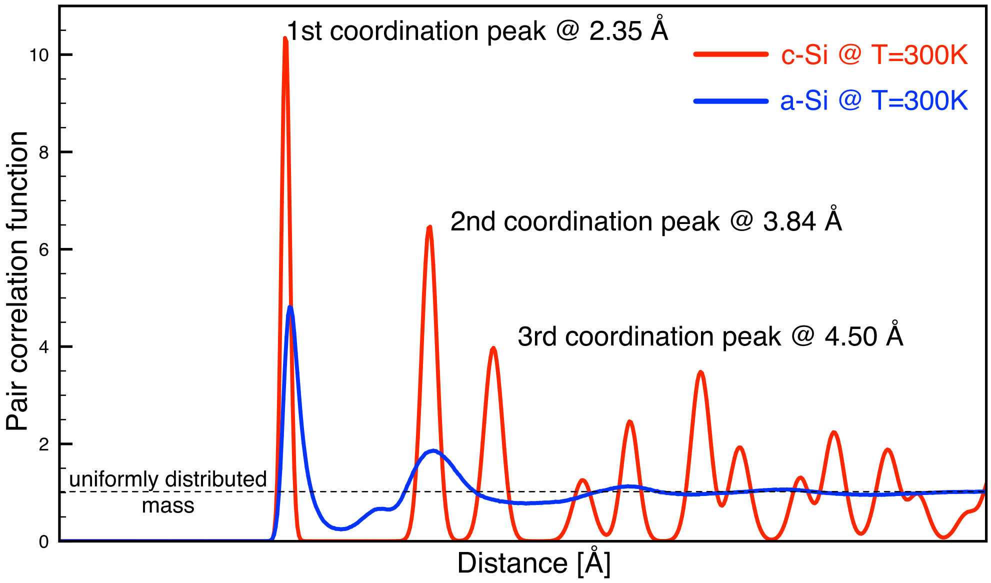

Figure 1.2. Pair correlation function for a crystalline (c-Si, red) and an amorphous (a-Si, blue) silicon sample with same density and both kept at room temperature. The actual position of the first-, second-, and third-coordination peak is reported in the case of c-Si. The dashed line represents the case of a uniformly distributed mass with the very same density. Data are calculated by molecular dynamics simulations.

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[4] A thorough discussion of the pair correlation function is found elsewhere [3, 4].

normalised value $g(r) = 1$ corresponding, as anticipated above, to a uniformly distributed mass. These peaks *are precise markings of the discrete distribution of the atoms forming the solid*. For instance, the first peak reveals the position of the first coordination shell, i.e. the average distance at which the first nearest neighbours are found. Furthermore, because of the very definition of pair correlation function, we argue that the integral of each peak represents the *average number of neighbours found at that distance*.

It is apparent from figure 1.2 that there is a striking difference between the two samples, namely: while a persistent pattern is found in one case, no structure at all is observed beyond ~4.5 Å in the other one. We conclude that figure 1.2 allows us to distinguish between a discrete distribution of atoms characterised by a *regular repeated pattern* and a discrete distribution of atoms showing *no regularity above the shell of second-next-neighbours*. Solid state systems corresponding to the first situation are characterised by *long-range structural order* and are named *crystals*; on the other hand, solids showing just a *short-range structural order* are referred to as *amorphous systems*. We state that from now on we will focus our attention only on *solid state crystalline materials*.

In order to conclude the task of unambiguously defining the material systems to be studied, we still have to address a last important issue. It is trivial to observe that any object has a size, possibly even very large (especially when compared with typical interatomic spacings or even molecular sizes), but in any case finite. In short: *a material system has boundary surfaces*. This implies that the set of atoms forming any condensed matter system can be divided into two categories: *bulk atoms* and *surface atoms*. They feel a vastly different physics, as intuitively understood by considering that surface atoms (i) are under-coordinated with respect to bulk ones and that (ii) they are exposed to external perturbations (or, equivalently, they interact with the environment surrounding the system). A primary consequence is that *surfaces usually show a lower degree of crystallinity than the bulk regions*: this is an annoying issue, in view of the above comfortable definition of crystalline state. Furthermore, *a large number of phenomena only occur at surfaces*, like growth, catalysis, or chemical bond reconstruction to name just a few. Surface physics is, therefore, an industry with many specifics and it represents a very lively and rapidly expanding sub-discipline of modern condensed matter physics [5–9]; nevertheless, we will not deal with it because it largely falls beyond the scope of this primer. Rather, *we are primarily interested in bulk properties* and we will focus on them by invoking the following justification: by assuming a nearly constant number density ρ, the number of bulk and surface atoms, respectively, scales as $\sim\rho V$ and $\sim\rho V^{2/3}$ for a system of volume V. This implies that *for a 'large enough' specimen, the number of surface atoms becomes negligibly small as compared to bulk ones*.

Now, the point is: what does 'large enough' mean? There is no rigorous answer to such a seemingly innocent question. For instance, we could be tempted to provide a simple pragmatic reply: such a condition is reached whenever bulk-like properties become unaffected by surface phenomena. Unfortunately, this apparently reassuring definition is not accurate enough to deal with a number of important issues like, e.g. the proper definition of the work required to extract an electron from a solid[5] or the accurate description of polarisation effects in ionic crystals[6].

The conclusion is that the present introduction to solid state physics, basically focussed on the bulk properties of crystalline materials, is made conceptually clean only by introducing an abstraction, namely by *introducing suitable periodic boundary conditions* that allow for dealing with *ideal surface-free systems*[7]. The procedure is illustrated in figure 1.3 in the case of a one-dimensional crystalline solid[8]: a number N of atoms is considered so that they are arranged with the proper crystalline regularity (that is: atoms are equally spaced by an amount a hereafter referred to as the lattice spacing); next, we join the two terminal ends of the crystalline chain so that the first and last atom actually overlap, their positions coincide, and they are further treated as one particle. The formalisation of this procedure is

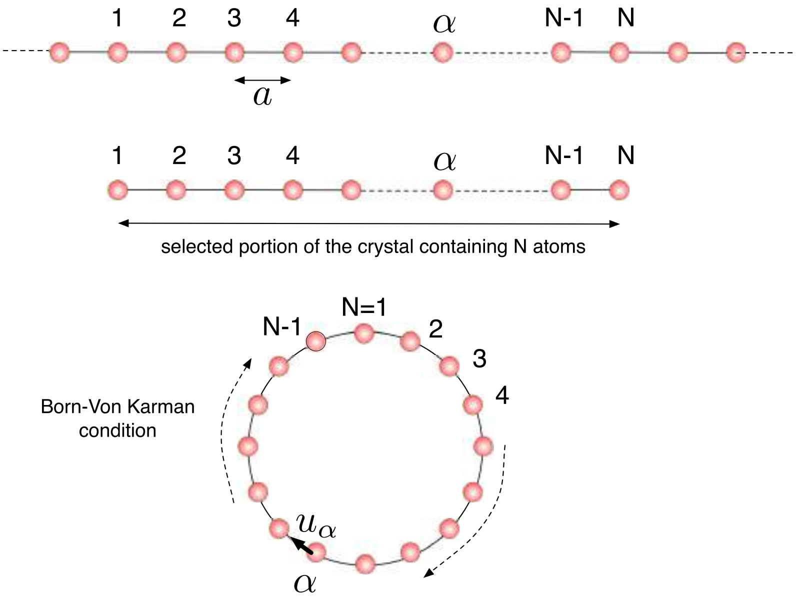
1
2
3
4
α
N-1
N
a
1
2
3
4
α
N-1
N
selected portion of the crystal containing N atoms
N-1
N=1
2
3
4
Born-Von Karman condition
u_α
α

Figure 1.3. Graphical representation of the Born–von Karman periodic boundary condition for a one-dimensional crystalline solid with lattice spacing a.

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[5] Such an energy does depend on some surface-specific features like the distortion of the electronic charge distribution with respect to the inner bulk.

[6] Any arbitrary truncation of a solid of such a kind generates a different charge distribution at the surface which, because of the long-range character of Coulomb interactions, differently affects the physics in the bulk region.

[7] We remark that selecting a solid state condensate with crystal order, among many other possible atomic gatherings, was just a matter of choice. On the other hand, the use of conditions that free us from the existence of something as real as a surface corresponds to *adopting a model*. Accordingly, the physics we will elaborate within its framework will be paradigmatically representative, conceptually relevant, and predictive under many concerns, but unavoidably incomplete.

[8] Of course, the choice of a one-dimensional system is made just for convenience of graphical representation: as a matter of fact, boundary conditions can be applied in one, two, or three dimensions, as needed.

straightforward: let us indicate by $u(R_\alpha)$ the displacement of the αth atom along the chain[9]. Imposing the above periodic boundary conditions is equivalent to placing

$$u(R_\alpha) = u(R_\alpha + (N - 1)a) \qquad \text{and} \qquad \psi(r_i) = \psi(r_i + (N - 1)a), \tag{1.4}$$

where we have completed the picture by specifying as well how such conditions act on the wavefunction $\psi(r_i)$ of the ith crystalline electron[10]. We take this opportunity to specify that throughout this book the positions of the atoms and electrons will be indicated by upper and lower case letters, respectively, and labelled by Greek and Latin indices, respectively. Equation (1.4), known as the *Born–von Karman condition*, completes the reasoning aimed at removing surfaces from our problem. We finally remark that following this construction we effectively reduce the number of atoms of the system from N to $(N - 1)$. However, provided that N is 'large enough' we can set $(N - 1) \sim N$. It is easy to understand that the expression 'large enough' in this case is used in a less dense way of physical consequences than previously discussed: it is just an allowable mathematical convenience.

In conclusion, we have eventually set all terms unequivocally defining what 'a bulk property of a crystalline system' indeed means. After this semantic introduction we are ready to start with the true solid state physics.

1.2 Synopsis of atomic physics

In order to fully exploit the atomistic picture that we are going to use as the constitutive hypothesis to describe solid state materials, we need to recall some basic notion of atomic physics [1, 2, 10], define the notation adopted throughout the present volume, and set the value of some fundamental physical constants.

1.2.1 Atomic structure

We know that an atom is a *bound system* consisting of a *nucleus* with a positive charge $+N_\mathrm{p}e$, where N_p is the *atomic number*, that is the number of *protons*, and a set of Z *electrons*, each carrying a charge $-e$. We recall that $e = 1.602\,19 \times 10^{-19}$ C is the elementary electric charge. If $Z = N_\mathrm{p}$ then the atom is in a neutral configuration, while if $Z \neq N_\mathrm{p}$ then we say that the atom has been ionised (either positively or negatively provided that Z is smaller or larger than N_p, respectively). The nucleus also contains a number N_n of *neutrons*, carrying no electric charge. While all electrons have the same mass $m_\mathrm{e} = 9.109 \times 10^{-31}$ kg, the nucleus of each chemical species has instead a specific mass M determined as: $M = (N_\mathrm{p} + N_\mathrm{n})m_\mathrm{p}$, where $m_\mathrm{p} = 1.672 \times 10^{-27}$ kg is the proton mass[11]. We remark that $A = N_\mathrm{p} + N_\mathrm{n}$ is referred to as the *atomic mass number*. Atoms with the same number of protons, but a different number of neutrons are referred to as *isotopes*.

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[9] The notion that atoms oscillate around their equilibrium position is here assumed on a purely intuitive basis, but it will be extensively discussed in the next chapters.

[10] We have anticipated an important twofold concept, namely that under some suitable approximations we can treat electrons as single particles and we can separate atomic motions from electron dynamics. The next section is devoted to this issue.

[11] For our purposes it is sufficient to set the same mass to both protons and neutrons.

As for nuclei, we will further neglect their inner structure by treating them as point-like, massive, and charged objects[12]. This is indeed a very good approximation for any situation described in this volume and, therefore, protons and neutrons will no longer enter as single objects in our theory. On the other hand, electrons will be individually addressed. Nuclei and electrons are inherently non-classical objects and, therefore, they must be duly described in quantum mechanical terms.

1.2.2 Angular and magnetic momenta

In addition to their charge and mass, electrons are further characterised by their *spin* [2, 10]: an *intrinsic angular momentum* **S**, whose square modulus S^2 and z-component obey the following quantisation rules

$$\begin{aligned} S^2 &= s(s+1)\hbar^2 \\ S_z &= m_s\hbar, \end{aligned} \tag{1.5}$$

with $s = 1/2$ and $m_s = \pm 1/2$ (spin 'up' or 'down') known as the spin quantum numbers and $\hbar = h/2\pi = 1.054\,46 \times 10^{-34}$ J s is the reduced Planck constant. An *intrinsic spin magnetic moment* $\mathbf{M}_S$, similarly quantised, is attributed to each electron according to

$$\mathbf{M}_S = -g_S\,\frac{\mu_B}{\hbar}\mathbf{S}, \tag{1.6}$$

where $\mu_B = e\hbar/2m_\mathrm{e} = 9.273\,2 \times 10^{-24}$ J T^{-1} is the Bohr magneton, and $g_S \sim 2$ is the spin g-factor.

Similarly, each nucleus, in addition to being charged, also carries a *magnetic moment* $\mathbf{M}_N$ [11] which for our purposes is conveniently defined as

$$\mathbf{M}_N = g_N\,\frac{\mu_\mathrm{N}}{\hbar}\mathbf{N}, \tag{1.7}$$

where g_N is the *nuclear g-factor* (a dimensionless constant), μ_N is the *nuclear magneton*

$$\mu_\mathrm{N} = \frac{m_\mathrm{e}}{m_\mathrm{p}}\,\mu_B = 5.050\,82 \times 10^{-27}\ \mathrm{J\ T^{-1}}, \tag{1.8}$$

and **N** is the *nuclear spin* or, equivalently, the total nuclear angular momentum.

Electrons are also characterised by an *orbital magnetic moment*, since their orbital motion around the nucleus corresponds to a current or, equivalently, to a magnetic moment $\mathbf{M}_L$ defined as [1, 2, 10]

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[12] Actually, nuclei are neither really point-like nor is their charge spherically distributed. Because of this, nuclear electric quadrupole moment effects can be observed in high-resolution atomic spectroscopy measurements [10].

$$\mathbf{M}_L = -g_L \frac{\mu_B}{\hbar} \mathbf{L}, \tag{1.9}$$

where g_L is the *orbital g-factor* and $\mathbf{L}$ is the electron *orbital angular momentum* obeying the quantisation rules

$$\begin{aligned} L^2 &= l(l+1)\hbar^2 \\ L_z &= m_l \hbar, \end{aligned} \tag{1.10}$$

cast in terms of the *orbital quantum number* $l = 0, 1, 2, \ldots$ and of the *magnetic quantum number* $m_l = 0, \pm 1, \pm 2, \ldots, \pm l$. The spectroscopic notation is widely adopted to label quantum states differing by l: we will set $l = 0 \rightarrow$ s-states, $l = 1 \rightarrow$ p-states, $l = 2 \rightarrow$ d-states, and so on [2].

1.2.3 Electronic configuration

The central problem of the physics of atoms is to determine their *ground-state configuration*, that is: the distribution of their electrons, among all available quantum states, corresponding to the minimum total energy. For a multi-electron atom this task is accomplished by following a rather complex procedure, qualitatively summarised below. A full account can be found elsewhere [1, 2, 10].

The first step consists in solving the complete Schrödinger equation[13] for the atom: a formidable indeed many-body quantum problem. The full scenario contains *electrostatic interactions* (among electrons and between the nucleus and each electron) as well as *magnetic interactions* (among all existing magnetic dipoles). Coulomb interactions are by far the strongest ones and they determine the main features of the atomic energy spectrum which can be calculated, for instance, within the central field approximation (CFA)[14]. Here each electron is treated as a *single-particle* undergoing an *average central field* due to the nucleus and the remaining electrons. In this way the many-body problem is reduced to Z single-particle ones, each separately solved by ordinary methods of atomic physics. The resulting CFA electron wavefunctions $\psi^{\mathrm{CFA}}_{nlm_l}(\mathbf{r}) = \bar{R}_{nl}(r)\ Y_{lm_l}(\theta, \phi)$ are written in polar coordinates (the central field has by construction a spherical symmetry!) as the product between a radial function $\bar{R}$ and a spherical harmonic function Y. Accordingly, each quantum state is labelled by three quantum numbers, namely: the *principal quantum number* $n = 1, 2, 3, \ldots$ and the l and m_l ones already introduced in section 1.2.2 where their values have been assigned[15]. A twofold picture emerges that (i) the *energy spectrum is discrete* and (ii) *allowed atomic quantum states are organised in*

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[13] For brevity we will hereafter adopt a widely used notation abuse: what in the text has been called the 'Schrödinger equation' should be more rigorously indicated as the eigenvalue equation for the Hamiltonian operator describing the system of our interest. In short: time dependence has been already eliminated from our problem.

[14] Although some important many-body features are overlooked in this theory, it nevertheless contains all the essential features needed for the present discussion.

[15] We remark that the emerging organisation of quantum states is justified straightforwardly within the central field approximation, but it is also fruitfully adopted in more refined quantum approaches like the Hartree, the Hartree–Fock or the configuration-interaction theory.

shells and sub-shells, respectively, corresponding to a given value of the n and of $l = 0, 1, 2, \ldots, (n-1)$.

Once the energy spectrum has been determined by only considering Coulomb couplings, we can add magnetic interactions as twofold perturbations of electronic and nuclear nature. The semi-classical *vector model of the atom* provides a very direct and pedagogical treatment of magnetic interactions among electrons: each electron pair i, j undergoes the following interactions

- *orbit–orbit coupling*, corresponding to an energy $E_{\text{oo}} = \xi_{LL}\, \mathbf{L}_i \cdot \mathbf{L}_j$
- *spin–spin coupling*, corresponding to an energy $E_{\text{ss}} = \xi_{SS}\, \mathbf{S}_i \cdot \mathbf{S}_j$
- *spin–orbit coupling*, corresponding to an energy $E_{\text{so}} = \xi_{LS}\, \mathbf{L}_i \cdot \mathbf{S}_j$

where ξ_{LL}, ξ_{SS} and ξ_{LS} are the *magnetic coupling constants*. A major task of atomic physics is providing their accurate determination. While electrostatic interactions determine the main features of the atomic energy spectrum, magnetic interactions provide its *fine structure*. Next, we eventually consider the nucleus by observing that its dipole moment given in equation (1.7) feels both the magnetic field $\mathbf{B}_{\text{electrons}}$ generated by the orbital motion of the electrons and the dipole–dipole interactions between electron and nuclear spins. Accordingly, a new energy term E_{hp} comes into play

$$E_{\text{hp}} = -\mathbf{M}_{\text{N}} \cdot \mathbf{B}_{\text{electrons}}, \tag{1.11}$$

providing the ultimate *hyperfine structure* of the atomic energy spectrum.

The next step eventually provides the electronic configuration we are interested in. It basically consists in placing electrons on each allowed state, starting from the lowest-energy one, by fulfilling both the *Pauli principle* and the *Hund rules*. According to the Pauli principle, the maximum number of electrons that can be accommodated in a sub-shell with orbital quantum number l is $2(2l+1)$ and, therefore, we can place up to $2n^2$ electrons in a shell with principal quantum number n. A sub-shell is said to be incomplete if the number of electrons there accommodated is smaller than $2(2l+1)$. Following a standard picture, fully exploited in the periodic table of elements, we will refer to electrons belonging to the highest-energy and incomplete sub-shell as *valence electrons*, while electrons belonging to low-energy and complete sub-shells will be named *core electrons*.

1.3 Setting up the atomistic model for a solid state system

Trying to plug the full atomistic picture into condensed matter physics is a hopeless enterprise and an unreasonable choice as well: the resulting mathematical problem would be too complicated to be solved by any analytical or numerical tool and, furthermore, several details specific to the single atomic system are actually marginal when matter is organised in condensates. In order to proceed, *we need approximations*. Far from being a fallback choice, this way of proceeding will allow us to bring out the most salient physical aspects of the solid state, avoiding an excess of detail that, in reality, would not translate into new meaningful knowledge. We are therefore going to develop a *hierarchy of approximations* that will actually constitute the backbone of our *working model* for crystalline solids. In the following chapters these approximations will be critically readdressed whenever some phenomenology questions their validity.

1.3.1 Semi-classical approximation

In general, we will treat electric, charge current, and magnetic effects according to the *classical Maxwell electromagnetism*; on the other hand, ion and electron physics will be described according to *quantum mechanics*. However, there will be some exceptions to this general choice.

First of all, we remark that the process of emission or absorption of electromagnetic energy by any material system will be described through the concept of *photon*. This approach represents the most basic way to include the quantum nature of electromagnetic radiation into our elementary theory. We will not go any further because any improvement of this picture, admittedly simplified, would fall beyond the scope of this tutorial introduction to solid state physics.

Finally, the dynamics of crystal lattices will be firstly treated by classical mechanics in order to easily catch the phenomenology of ionic vibrations. Next, a fully quantum picture will be developed through the concept of *phonon*.

1.3.2 Frozen-core approximation

To a large extent, the chemical properties of an atom are dictated by its valence electrons [2]. In particular, valence electrons rule over the formation mechanism of interatomic bonds, so ultimately affecting most of the physical properties in a condensed matter system. This suggests that *core electrons are expected to play a minor role in determining most of solid state properties*. We can exploit this observation by introducing the *frozen-core approximation* which will greatly simplify the picture. This approximation can be cast in a very simple form according to the scheme

$$\begin{aligned}\text{atom} &= \underbrace{\text{nucleus} + \text{core electrons}}_{\text{ion}} + \text{valence electrons}\\ &= \text{ion} + \text{valence electrons},\end{aligned}$$

which suggests the following: we will implement the atomistic description of a crystalline solid assuming that it consists of a *collection of ions and valence electrons*. The former will be described as point-like objects with a nuclear mass specific to their chemical species[16] and carrying a positive charge. If there are in total $Z = Z_c + Z_v$ electrons (where Z_c and Z_v are the number of core and valence electrons, respectively), then the *ionic charge* Q will be assigned the value $Q = +Z_v$, in units of the elementary charge e.

The main advantage of the frozen-core approximation is a *dramatic reduction of the number of electronic degrees of freedom to deal with*: for instance, the main features of the electronic structure in a silicon crystal will be studied by considering just four valence electrons for each ion, instead of the full 14 electron set found in a silicon atom. In conclusion, hereafter *when referring to 'electrons' we will actually mean 'valence electrons'*, while core ones will never be addressed since they are attached to nuclei forming ions.

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[16] The total mass of the core electrons is definitely negligible with respect to that of the bare nucleus.

1.3.3 Non-magnetic and non-relativistic approximations

A detailed calculation of the three coupling constants ξ_{LL}, ξ_{SS} and ξ_{LS} providing the atomic fine structure leads to important information, namely: *magnetic interactions are comparatively much smaller than electrostatic ones* [10]. This is confirmed experimentally by observing that the splitting of the energy levels caused by the above coupling terms is always some good order-of-magnitude smaller than their separation predicted by only considering Coulomb interactions [2]. Therefore, our choice will be to *completely neglect magnetic interactions* among electrons. This choice is straightforwardly extended to the nucleus, following a simple argument. The hyperfine energy terms given in equation (1.11) depend on $\mathbf{M}_N$, that is, on the nuclear magneton. Now, it turns out that $\mu_N \ll \mu_B$ since the proton mass is much larger than the electron one and, therefore, *hyperfine interactions are also negligibly small if compared to Coulomb ones*. In summary, *no magnetic couplings of whatsoever origin will be in the first instance considered* when developing our solid state theory[17].

It is, however, important to remark the above *non-magnetic approximation does not imply that we are neglecting the true existence of the electron spin*: as a matter of fact, this cannot be done because we would lose the fundamental notion that electrons are fermions and, therefore, they obey (i) the Fermi–Dirac statistics (see section 6.2) and (ii) the Pauli principle. Rather, we reconcile the simplified non-magnetic treatment with the need to take into account the spin by multiplying the space part of the wavefunction by a spin function which is in charge of just characterising the actual spin state of the electron. The resulting total wavefunction will be labelled[18] by a fourfold set of quantum numbers $\{n, l, m_l, s\}$ so that, although no spin-related features are present in this simplified picture, it will not be possible for two electrons to have the same set of four quantum numbers: if they lie on the same energy level, then they must differ at least for their spin orientation.

Since spin is a relativistic feature [10, 12], neglecting any corresponding coupling term is tantamount to developing a theory in the *non-relativistic approximation*. We will take this in the widest meaning and, accordingly, we will overlook not only spin-mediated interactions but also any other relativistic effect[19]. In particular, we will use anywhere the *rest mass* m_e for electrons.

In conclusion, ions and electrons will interact only via Coulomb coupling: indeed a major simplification for our developing theory.

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[17] Their effects are usually treated as a perturbation on the quantum energies predicted by only considering Coulomb interactions. This is, for instance, the case of the spin-splitting of the energy bands.

[18] This is strictly true only within the central field approximation.

[19] They correct the electron kinetic energy and the nuclear Coulomb potential energy [10].

1.3.4 Adiabatic approximation

It is now time to formulate the full quantum mechanical problem describing the physics of a solid; to this aim we are exploiting the set of approximations discussed in the previous sections and using the labelling notation for ions and electrons anticipated in section 1.1. In particular, the full set of electronic and ionic coordinates will be indicated by the shortcuts **r** and **R**, respectively, while the *total crystalline wavefunction* will be written as $\Phi(\mathbf{r}, \mathbf{R})$.

The classical expressions for the Coulomb interactions at work within the crystal (under the frozen-core, non-magnetic, and non-relativistic approximations) are

$$\begin{aligned} V_{\text{ne}}(\mathbf{r}, \mathbf{R}) &= -\frac{e^2}{4\pi\epsilon_0} \sum_{i,\alpha} \frac{Q_\alpha}{\mid \mathbf{r}_i - \mathbf{R}_\alpha \mid} \\ V_{\text{nn}}(\mathbf{r}, \mathbf{R}) &= +\frac{e^2}{4\pi\epsilon_0} \sum_{\alpha>\beta} \frac{Q_\alpha Q_\beta}{\left| \mathbf{R}_\alpha - \mathbf{R}_\beta \right|} \\ V_{\text{ee}}(\mathbf{r}, \mathbf{R}) &= +\frac{e^2}{4\pi\epsilon_0} \sum_{i>j} \frac{1}{\left| \mathbf{r}_i - \mathbf{r}_j \right|}, \end{aligned} \tag{1.12}$$

describing, respectively, the ion–electron, the ion–ion, and the electron–electron interactions. The corresponding Schrödinger equation is written as

$$\left[-\frac{\hbar^2}{2} \sum_\alpha \frac{1}{M_\alpha} \nabla_\alpha^2 - \frac{\hbar^2}{2m_{\text{e}}} \sum_i \nabla_i^2 + \hat{V}_{\text{ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\text{nn}}(\mathbf{R}) + \hat{V}_{\text{ee}}(\mathbf{r}) \right] \Phi(\mathbf{r}, \mathbf{R}) = E_T \Phi(\mathbf{r}, \mathbf{R}), \tag{1.13}$$

where E_T is the *total energy of the crystal* including any electronic or ionic contribution, while the symbols ∇_α^2 and ∇_i^2 imply derivatives with respect to the αth ion and ith electron coordinates, respectively. We remark that quantum operators will always be indicated with the same symbol used for their classical counterpart, but topped with the ^ hat symbol.

The quantum problem given in equation (1.13) is still unsolvable by any analytical or numerical tool, in spite of the many drastic approximations we have worked out to formulate it. This implies that in order to continue we need to further simplify our theory. Good for us, we can take profit from a very basic fact: ions are always much more massive than electrons and, therefore, their dynamics is expected to be much slower. In other words, *at any moment electrons feel ions as if they were stationary in their instantaneous positions*. The opposite view is equally valid: *at any moment electrons will be in their ground-state for the specific ionic configuration occurring at that time*. This conclusion is better understood by taking into account that the maximum ionic oscillation frequency is about 10^{13} s^{-1}, while the collective excitations of the electron system[20] have a typical 10^{16} s^{-1} frequency. Consequently, electrons almost immediately respond to a perturbation due to ionic motion, re-adjusting in their new ground-state. In other words, *electrons instantaneously follow the atomic vibrations*. The separation between vibrational and electronic excitations is reflected in spectroscopic measurements: while emission/absorption of photons caused by the oscillations of the ions around their equilibrium position typically occurs in the infrared region, transitions occurring between electronic states fall in the visible and ultraviolet regions of the electromagnetic spectrum. In short: *the physics of electrons and nuclei unfolds on quite different energy scales.*

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[20] They are called *plasma oscillations* and will be studied in section 7.2.2.

We exploit these phenomenological arguments by formally *decoupling electronic and vibrational degrees of freedom* or, equivalently, by separating the **r**- and the **R**-dependence of the total wavefunction Φ as

$$\Phi(\mathbf{r}, \mathbf{R}) = \Psi_{\mathrm{n}}(\mathbf{R})\ \Psi_{\mathrm{e}}^{(\mathbf{R})}(\mathbf{r}), \tag{1.14}$$

where $\Psi_{\mathrm{n}}(\mathbf{R})$ and $\Psi_{\mathrm{e}}^{(\mathbf{R})}(\mathbf{r})$ are the *total ionic wavefunction* and the *total electronic wavefunction*, respectively. More specifically, we state that $\Psi_{\mathrm{e}}^{(\mathbf{R})}(\mathbf{r})$ describes the crystalline electronic structure corresponding to the clamped-ion configuration **R** and, therefore, it must be understood that Ψ_{e} has an analytical dependence of the **r**-coordinate set, while it has a parametric dependence on the **R**-coordinate set. Equation (1.14) is usually referred to as the *adiabatic approximation* because *it implies that there is no exchange of energy between the system of electrons and the ion lattice*. Although we will also deal with non-adiabatic phenomena in the following chapters, let us for the moment proceed below this approximation.

By inserting equation (1.14) into equation (1.13) we straightforwardly obtain the following *eigenvalue problem for the total electron wavefunction*

$$\left[-\frac{\hbar^2}{2m_{\mathrm{e}}}\sum_i \nabla_i^2 + \hat{V}_{\mathrm{ne}}(\mathbf{r}, \mathbf{R}) + \hat{V}_{\mathrm{ee}}(\mathbf{r})\right]\Psi_{\mathrm{e}}^{(\mathbf{R})}(\mathbf{r}) = E_{\mathrm{e}}^{(\mathbf{R})}\Psi_{\mathrm{e}}^{(\mathbf{R})}(\mathbf{r}), \tag{1.15}$$

where $E_{\mathrm{e}}^{(\mathbf{R})}$ has the meaning of *total electron energy when ions are clamped in the configuration* **R**. This is an important achievement: setting the problem as shown in equation (1.15) implies that we need to separately calculate $E_{\mathrm{e}}^{(\mathbf{R})}$ for each possible ion displacement pattern. By combining equations (1.13) and (1.15), the corresponding *eigenvalue problem for the total ion wavefunction* is immediately obtained as

$$\left[-\frac{\hbar^2}{2}\sum_\alpha \frac{1}{M_\alpha}\nabla_\alpha^2 + \hat{V}_{\mathrm{nn}}(\mathbf{R}) + E_{\mathrm{e}}^{(\mathbf{R})}\right]\Psi_{\mathrm{n}}(\mathbf{R}) = E_T\Psi_{\mathrm{n}}(\mathbf{R}), \tag{1.16}$$

where in this case the difference $E_T - E_{\mathrm{e}}^{(\mathbf{R})} = U(\mathbf{R})$ must be understood as the crystalline ion energy. In practice, the main conceptual consequence of the adiabatic approximation is that *solid state physics is traced back to the separate solution of equations (1.15) and (1.16)*; any non-adiabatic effect will be treated as a perturbation to their solutions.

Although we have based the adiabatic approximation on very robust phenomenological evidence, we still need to rigorously establish its accuracy. This task is accomplished by a non trivial argument that we are developing in a simplified form, just focussing on its main conceptual steps[21]. The $\Psi_{\mathrm{e}}^{(\mathbf{R})}(\mathbf{r})$ solutions of equation (1.15) represent a complete set and, with no loss of generality, we can further assume that they have been properly orthonormalised. Therefore, we can express the total wavefunctions Φ as the following linear combination[22]

$$\Phi(\mathbf{r},\,\mathbf{R}) = \sum_m \Xi_m(\mathbf{R})\ \Psi_{\mathrm{e},\,m}^{(\mathbf{R})}(\mathbf{r}), \tag{1.17}$$

where $\Xi_m(\mathbf{R})$ are the expansion coefficients and in the present context the label m is a shortcut for the full set of quantum numbers describing the states of the electron system, found by solving equation (1.15). By inserting this representation into equation (1.13) and using the orthonormality of the $\Psi_{\mathrm{e}}^{(\mathbf{R})}(\mathbf{r})$ wavefunctions, after some algebra we obtain the eigenvalue equation for the $\Xi_m(\mathbf{R})$'s

$$\left[-\frac{\hbar^2}{2}\sum_\alpha \frac{1}{M_\alpha}\nabla_\alpha^2 + \hat{V}_{\mathrm{nn}}(\mathbf{R}) + E_{\mathrm{e}}^{(\mathbf{R})} + \sum_m (\hat{A}_{mm'} + \hat{B}_{mm'})\right]\Xi_m(\mathbf{R}) = E_T\ \Xi_m(\mathbf{R}), \tag{1.18}$$

where[23]

$$\begin{aligned}
\hat{A}_{mm'} &= -\,\hbar^2 \sum_\alpha \frac{1}{M_\alpha}\left[\int d\mathbf{r}\ \Psi_{\mathrm{e},\,m}^{(\mathbf{R})*}(\mathbf{r})\nabla_\alpha \Psi_{\mathrm{e},\,m'}^{(\mathbf{R})}(\mathbf{r}))\right]\cdot\nabla_\alpha \\
\hat{B}_{mm'} &= -\,\frac{\hbar^2}{2}\sum_\alpha \frac{1}{M_\alpha}\ \int d\mathbf{r}\ \Psi_{\mathrm{e},\,m}^{(\mathbf{R})*}(\mathbf{r})\nabla_\alpha^2 \Psi_{\mathrm{e},\,m'}^{(\mathbf{R})}(\mathbf{r}).
\end{aligned} \tag{1.19}$$

We easily recognise that the adiabatic approximation is formally equivalent to dropping off the terms $\sum_m (\hat{A}_{mm'} + \hat{B}_{mm'})\ \Xi_n(\mathbf{R})$ from equation (1.18): under this condition, the $\Xi_m(\mathbf{R})$ functions are nothing other than the total ion wavefunctions $\Psi_{\mathrm{n}}(\mathbf{R})$ calculated when the electronic contribution to the total energy is provided by the mth state. Now, the point is to assess how really accurate is the choice of neglecting these terms in our theory.

To this aim we write the position of the αth atom in the form $\mathbf{R}_\alpha = \mathbf{R}_\alpha^{(0)} + \kappa\ \mathbf{u}_\alpha$, where $\mathbf{R}_\alpha^{(0)}$ is its equilibrium position, $\mathbf{u}_\alpha$ its displacement, and κ a suitable expansion parameter which allows us to write the total crystalline Hamiltonian appearing in equation (1.13) in the form

$$\begin{aligned}
\hat{H} &= -\frac{\hbar^2}{2}\sum_\alpha \frac{1}{M_\alpha}\nabla_\alpha^2 - \frac{\hbar^2}{2m_{\mathrm{e}}}\sum_i \nabla_i^2 + \hat{V}_{\mathrm{ne}} + \hat{V}_{\mathrm{nn}} + \hat{V}_{\mathrm{ee}} \\
&= -\frac{\hbar^2}{2}\sum_\alpha \frac{1}{M_\alpha}\nabla_\alpha^2 - \frac{\hbar^2}{2m_{\mathrm{e}}}\sum_i \nabla_i^2 + \hat{V}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}}^{(0)} + \hat{V}_{\mathrm{nn}}^{(0)} \\
&\quad + [\kappa\hat{V}_{\mathrm{ne}}^{(1)} + \kappa^2\hat{V}_{\mathrm{ne}}^{(2)} + \kappa^3\hat{V}_{\mathrm{ne}}^{(3)} + \cdots] + [\kappa\hat{V}_{\mathrm{nn}}^{(1)} + \kappa^2\hat{V}_{\mathrm{nn}}^{(2)} + \kappa^3\hat{V}_{\mathrm{nn}}^{(3)} + \cdots],
\end{aligned} \tag{1.20}$$

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[21] The complete formal development is found in [13, 14].

[22] In general, the eigenfunctions of an Hermitean operator represent a complete set and, therefore, they can be used to expand any other wavefunction defined in the same volume of space and obeying the same boundary conditions as a linear combination of them.

[23] The asterisk * indicates the complex conjugate function.

where $\hat{V}_{\mathrm{ne}}^{(0)}$ and $\hat{V}_{\mathrm{nn}}^{(0)}$ are the nucleus–electron and the nucleus–nucleus terms calculated for ions at their equilibrium positions, respectively, while any term written as $\hat{V}^{(\lambda)}$ is λth order in the ionic displacements $\mathbf{U}_\alpha$ (the derivatives appearing in these terms are evaluated with all ions in their equilibrium positions). Equation (1.20) is known as the *Born–Oppenheimer expansion*. In the limiting case of $M_\alpha \to +\infty$ the total Hamiltonian operator reduces to

$$\lim_{M_\alpha \to 0} \hat{H} = -\frac{\hbar^2}{2m_{\mathrm{e}}} \sum_i \nabla_i^2 + \hat{V}_{\mathrm{ee}} + \hat{V}_{\mathrm{ne}}^{(0)} + \hat{V}_{\mathrm{nn}}^{(0)}, \tag{1.21}$$

indicating that $\kappa \to 0$ as well. Since such an expansion parameter is adimensional, this conclusion suggests that we can set $\kappa = (m_{\mathrm{e}}/\langle M \rangle)^\zeta$ where $\langle M \rangle$ is the average ion mass and $\zeta > 0$ a real number[24].

By using the Born–Oppenheimer expansion for the $\hat{V}_{\mathrm{ne}}$ term, it is possible to get a solution of equation (1.15) through a standard perturbative quantum mechanical calculation: this provides the $\Psi_{\mathrm{e}}^{(\mathbf{R})}(\mathbf{r})$ functions. Next, by repeating a similar expansion procedure to equation (1.18), the $\hat{A}_{mm'}$ and $\hat{B}_{mm'}$ operators are, after a non trivial calculation, eventually found to be $\hat{A}_{mm'} \sim \mathcal{O}(\kappa^3)$ and $\hat{B}_{mm'} \sim \mathcal{O}(\kappa^4)$. In conclusion, *non-adiabatic terms appear at high order in the expansion parameter* κ. Since for any possible real crystal we have $m_{\mathrm{e}}/\langle M \rangle \ll 1$, the conclusion is twofold: (i) the Born–Oppenheimer expansion is quickly convergent and (ii) dropping off the terms $\sum_m (\hat{A}_{mm'} + \hat{B}_{mm'})\, \Xi_m(\mathbf{R})$ from equation (1.18) is really a more than acceptable approximation.

It is worth remarking that the formal argument we outlined above is centred on the expansion parameter $\kappa = (m_{\mathrm{e}}/\langle M \rangle)^\zeta$ and, therefore, it is fully consistent with the phenomenological argument used to set the discussion on the adiabatic approximation: *the very large difference in dynamical inertia between electrons and ions supports a theoretical approach where their degrees of freedom are separately taken into account.*

1.4 Mastering many-body features

Equations (1.15) and (1.16) are the *constitutive equations of solid state theory*. Although they have been derived under many (and sometimes strong) approximations, they both are a formidable many-body quantum problem complicated to the extent that the present theoretical and computational knowledge does not allow for their exact solution. In order to overcome this impasse two rather different strategies will be adopted, as presented below.

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[24] Its is proved [13, 14] that by setting $\zeta = 1/4$, the total Hamiltonian expanded up to the second order corresponds to the so-called harmonic approximation. While we will not provide the formal proof of this, we will make an extensive use of this approximation when studying the lattice dynamics, although we will formulate it in a much more phenomenological way.

1.4.1 Managing the electron problem: single-particle approximation

As far as the electronic problem given in equation (1.15) is concerned, we choose to adopt another very drastic approximation, namely: we will handle the electron problem within the *single-particle approximation*.

In principle, by exploiting a key result of atomic physics [2, 10], we could represent the total electron wavefunction $\Psi_e^{(\mathbf{R})}(\mathbf{r})$ as an anti-symmetrised product of one-electron wavefunctions. In this context, each electron is described by a *spin-orbital* function given by the product between a space- and a spin-wavefunction (this latter is added to correct the limitations of the non-relativistic approximation and thus enforcing the Pauli principle). Next, the best set of spin-orbitals is obtained by a quantum mechanical variational procedure, where the total energy of the ground-state of the crystalline system we are interested in is usually minimised. This leads to rather complicated integro-differential equations, known as Hartree–Fock (HF) equations [15], which are typically solved through a self-consistent procedure implemented by a numerical calculation. We remark that the HF ground-state energy is an excess approximation to the true value since it is obtained through a variational principle. Furthermore, we remark that, while the HF method correctly accounts for exchange effects (which are a truly many-body attribute), it is unable to deal with quantum correlation features. The HF method [16] has been widely used since it allows for qualitatively understanding many solid state physics problems. Nevertheless, its deficiencies in fully catching all the many-body features and the fact that a single anti-symmetrised product of spin-orbitals is in general found to be a poor representation of the true $\Psi_e^{(\mathbf{R})}(\mathbf{r})$ many-particle wavefunction have motivated the development of more sophisticated many-body theories which are overviewed in [15, 17] and fully developed in [18, 19].

A more accessible approach consists in adopting the *single-particle approximation*[25]: the full set of electron–ion and electron–electron interactions are represented by *an effective one-electron potential with the same periodicity of the underlying crystal lattice*, hereafter referred to as '*crystal field*'. In other words, we will assume that *each electron independently moves under the action of a local crystal field potential* describing its embedding into a crystalline environment made by all ions and by all the remaining electrons. We will indicate such a crystal field potential (cfp) as $V_{\text{cfp}}(\mathbf{r})$.

The first feature of $V_{\text{cfp}}(\mathbf{r})$ to account for is its periodicity. At this stage we have not yet developed the mathematical background to rigorously treat the geometrical characteristics of a crystal. We can nevertheless justify our assumption of periodic potential by looking at the simple graphical rendering of figure 1.4: by embedding an electron into a crystal, it will experience a net potential closely resembling that of an isolated bare ion when closely approaching it; on the other hand, the net potential will flatten off in the interstitial regions. Next, we remark that the crystal field potential is local: its value only depends on the instantaneous position actually

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[25] This picture is equivalently referred to as *independent electron approximation* or *one-electron approximation*.

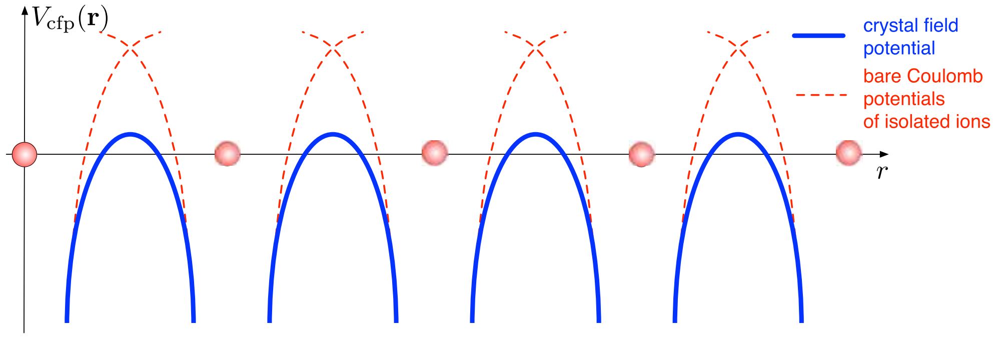

Figure 1.4. Graphical representation of the potential acting on an electron in the case of a one-dimension solid. Full line (blue): actual crystal field potential; dashed line (red): superposition of bare Coulomb potentials due to isolated ions.

occupied by the single electron. This is another very convenient practical advantage offered by the one-electron approximation with respect to many-body theories.

The resulting formalism is clean and conceptually simple: we are reduced to solving the one-electron Schrödinger equation for each ith electron

$$\left[-\frac{\hbar^2}{2m_{\mathrm{e}}}\nabla^2 + \hat{V}_{\mathrm{cfp}}(\mathbf{r}_i)\right]\psi_{m_i}(\mathbf{r}_i) = E_{m_i}^{(\mathbf{R})}\psi_{m_i}(\mathbf{r}_i), \tag{1.22}$$

where $\psi_{m_i}(\mathbf{r}_i)$ and $E_{m_i}^{(\mathbf{R})}$ are its wavefunction and energy, while m_i stands for a suitable set of quantum numbers describing the crystalline quantum state of the ith electron. The adopted labelling once again makes it clear that the equation is solved for ions clamped in the **R** configuration. The total electron energy approximating the eigenvalue of equation (1.15) is calculated as

$$E_{\mathrm{e}}^{(\mathbf{R})} = \sum_i E_{m_i}^{(\mathbf{R})}. \tag{1.23}$$

It is manifest that equation (1.22) greatly simplifies the actual many-body problem describing the electron system. However, we remark that *we are not treating electrons as non-interacting particles*. Rather, we are assuming that a suitable choice of $V_{\mathrm{cfp}}(\mathbf{r})$ will allow us to include in this simplified picture the most relevant features of the electron–electron interactions.

Before even addressing the resulting description of the crystalline electronic structure, we need to clarify, at least conceptually, how $V_{\mathrm{cfp}}(\mathbf{r}_i)$ can be defined. The most effective procedure is implemented by the *self-consistent-field method*, which is nowadays the most widely used approach in modern solid state physics since it naturally translates into efficient computational algorithms allowing for its numerical determination. Let us assume that a clever initial guess for the single-particle wavefunctions $\psi_{m_i}^{(0)}(\mathbf{r}_i)$ is possible. For instance, these functions could be atomic orbitals, superpositions of plane waves, or any other orthogonalised set of suitable wavefunctions. Then, the zero-order approximation of the electron–electron Coulomb potential energy for the ith electron can be written as

$$V_{\mathrm{ee}}^{(0)}(\mathbf{r}_i) = \frac{e^2}{4\pi\epsilon_0}\sum_{j\neq i}\int\left[\psi_{m_j}^{(0)}(\mathbf{r}_j)\right]^*\frac{1}{\mid \mathbf{r}_j - \mathbf{r}_i \mid}\,\psi_{m_j}^{(0)}(\mathbf{r}_j)\;d\mathbf{r}_j, \tag{1.24}$$

so that the classical total potential energy on such a particle is

$$V_{\mathrm{cfp}}^{(0)}(\mathbf{r}_i) = V_{\mathrm{ee}}^{(0)}(\mathbf{r}_i) + V_{\mathrm{ne}}(\mathbf{r}_i, \mathbf{R}). \tag{1.25}$$

By inserting the corresponding operator $\hat{V}_{\mathrm{cfp}}^{(0)}(\mathbf{r}_i)$ into equation (1.22) and solving it, we get a new set of wavefunctions $\psi_{m_i}^{(1)}(\mathbf{r}_i)$: they allow us to refine our initial guess on electron–electron Coulomb potential energy, now calculated as

$$V_{\mathrm{ee}}^{(1)}(\mathbf{r}_i) = \frac{e^2}{4\pi\epsilon_0}\sum_{j\neq i}\int\left[\psi_{m_j}^{(1)}(\mathbf{r}_j)\right]^*\frac{1}{\mid \mathbf{r}_j - \mathbf{r}_i \mid}\,\psi_{m_j}^{(1)}(\mathbf{r}_j)\;d\mathbf{r}_j. \tag{1.26}$$

By repeating the previous calculation, we solve again equation (1.22) for the new estimate of the potential energy term. This will return a set of second-order eigenfunctions $\psi_{m_i}^{(2)}(\mathbf{r}_i)$ which we can further use to generate the second-order approximation to the potential energy, and so on. The procedure is iterated until the $(n - 1)$ th order wavefunctions are found to differ from the nth order ones less than an agreed degree of numerical accuracy. Full convergence is at this stage proclaimed: we have both the 'true' effective crystal field potential and one-electron wavefunctions.

In the next chapters the electronic structure of crystalline solids will be studied under assumption that the one-electron local crystal field potential is known: this will lead to the so-called electronic band theory. A rather different approach will be outlined as well, named *density functional theory* (DFT). In this case, the key quantities of the theory are the density (instead of wavefunctions) and the total energy of the electron system. DFT is nowadays considered the 'standard model' for the ab *initio* prediction of the physical properties of condensed matter systems.

1.4.2 Managing the ion problem: classical approximation

Let us now turn to considering equation (1.16). Even in this case the quantum mechanical problem is inherently many-body and, therefore, quite difficult to solve. However, we can adopt a simplification procedure based on the same arguments put forward in support of the adiabatic approximation: ions are comparatively very massive objects and, accordingly, *we can in first approximation treat them classically*.

In practice, we will at first elaborate some suitable classical model for the force field describing the interactions among ions. Next, we will investigate the ionic displacements by solving their Newton equations of motion. Any relevant quantum feature will be eventually added *ex post*, by a quantisation procedure of the classical displacement field. As we will see, this will replace the classical description based on lattice waves with the notion of quantum lattice vibrational field, whose quanta will be referred to as *phonons*.

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