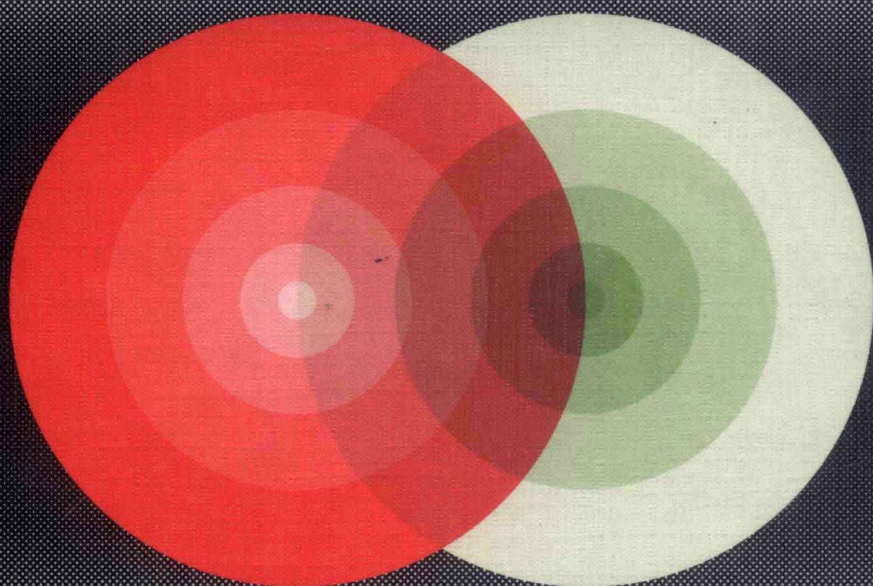


Quantum Theory of the Solid State: An Introduction

by
Lev Kantorovich

Kluwer Academic Publishers



Fundamental Theories of Physics

Quantum Theory of the Solid State: An Introduction

by

Lev Kantorovich

*Department of Physics,
King's College London,
London, United Kingdom*



KLUWER ACADEMIC PUBLISHERS

DORDRECHT / BOSTON / LONDON

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 1-4020-1821-5

ISBN 1-4020-2154-2 (e-book)

Published by Kluwer Academic Publishers,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Sold and distributed in North, Central and South America
by Kluwer Academic Publishers,
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Kluwer Academic Publishers,
P.O. Box 322, 3300 AH Dordrecht, The Netherlands.

Printed on acid-free paper

All Rights Reserved

© 2004 Kluwer Academic Publishers

No part of this work may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission from the Publisher, with the exception of any material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work.

Printed in the Netherlands.

Quantum Theory of the Solid State: An Introduction

Fundamental Theories of Physics

*An International Book Series on The Fundamental Theories of Physics:
Their Clarification, Development and Application*

Editor:

ALWYN VAN DER MERWE, *University of Denver, U.S.A.*

Editorial Advisory Board:

JAMES T. CUSHING, *University of Notre Dame, U.S.A.*

GIANCARLO GHIRARDI, *University of Trieste, Italy*

LAWRENCE P. HORWITZ, *Tel-Aviv University, Israel*

BRIAN D. JOSEPHSON, *University of Cambridge, U.K.*

CLIVE KILMISTER, *University of London, U.K.*

PEKKA J. LAHTI, *University of Turku, Finland*

ASHER PERES, *Israel Institute of Technology, Israel*

EDUARD PRUGOVECKI, *University of Toronto, Canada*

TONY SUDBURY, *University of York, U.K.*

HANS-JÜRGEN TREDER, *Zentralinstitut für Astrophysik der Akademie der
Wissenschaften, Germany*

Acknowledgement

Many people have helped me to accomplish this project by giving their advice and criticism. I am particularly grateful to A. S. Alexandrov, O. Danyliv, I. Ford, A. Sokol, S. Sarkar and T. Trevethan. O. Danyliv also helped with some of the pictures. One picture was also done by my daughter Veronika. The whole manuscript was read by my former student C. Bird whose criticism helped to make the presentation in many places much better; I would also like to thank him for improving the English language considerably. The book has been typed using LyX (see www.lyx.org) and I would like to thank the LyX team for this wonderful code without which this book would have been absolutely unimaginable. My special thanks also go to D. Chana who allowed me to use his Latex macros for brackets.

Finally, this book would not have been possible were it not for the constant communication and discussion with many of my colleagues and friends from whom I have learned so much. I am especially indebted to I. V. Abarenkov, E. Arola, A. Fisher, J. Gavartin, M. Gillan, R. Dovesi, R. A. Evarestov, P. W. Jacobs, V. Kempter, E. Kotomin, C. Pisani, A. Shluger, A. Livshits, A. Sokol, K. Song, M. Stoneham, P. Sushko, M. Tsukada, I. Tupitsin and B. Zapol.

Foreword

“Quantum Physics of the Solid State: an Introduction”

Draft foreword: 26/09/03

If only this book had been available when I was starting out in science! It would have saved me countless hours of struggle in trying to apply the general ideas of the standard solid-state text-books to solve real problems. The fact is that most of the texts stop at the point where the real difficulties begin. The great merit of this book is that it describes in an honest and detailed way what one really has to do in order to understand the multifarious properties of solids in terms of the fundamental physical theory of quantum mechanics.

University students of the physical sciences are taught about the fundamental theories, and know that quantum mechanics, together with relativity, is our basis for understanding the physical world. But the practical difficulties of using quantum mechanics to do anything useful are usually not very well explained. The truth is that the application of quantum theory to achieve our present detailed understanding of solids has required the development of a large array of mathematical techniques. This is closely analogous to the challenge faced long ago by theoretical astronomers in trying to apply Newton's equations of motion to the heavens - they too had to develop a battery of theoretical and computational techniques to do calculations that could be compared with observation. These are often the kind of issues that have to be faced by students when they pass from undergraduate to postgraduate studies, and this is why I believe that many students will find the present book so useful.

The treatment of lattice vibrations is a good example of how the book goes beyond most other texts. The conventional approach is to explain the basics by considering the harmonic chain of beads and springs in one dimension, first with all beads the same, and then with beads of two different masses. There is then an enormous jump to the vibrations of real crystals, and the student is left to guess what might be involved here. The present book fills in all the gaps, so that the student can understand the whole story. The treatment starts in the usual way, but then systematically develops the theory for real-world three-dimensional crystals, explaining how vibrational densities of states come to have the form that they do. In addition, the connections with elasticity theory are developed so that the student gains an understanding of long-wavelength crystal vibrations, in other words sound waves. This approach of telling the whole story from beginning to end is repeated for the other major areas of solid-state theory, including crystal structure, diffraction theory, bonding mechanisms, electronic structure, magnetism, superconductivity, and dielectric properties.

In the final chapter, an up-to-date survey is given of how the theoretical ideas can be turned into practical numerical calculations of solid-state properties. This exciting area, which has seen revolutionary advances in the last 20 years, is barely touched on in most text-books, but I believe is now essential for an appreciation of

modern solid-state theory. For most of the 20th century, computational techniques were simply not up to the challenge of using quantum mechanics to make detailed predictions of things like lattice-vibration frequencies or frequency-dependent dielectric functions, let alone properties such as melting curves of surface structures. All this has now completely changed, and the new spirit in solid-state theory is that anything measurable should also be calculable. There are very few solid-state text-books that attempt to explain these important new ideas.

There is so much in this book, that it will be useful to a very broad readership. It will certainly be a valuable vade mecum for advanced undergraduates and for research students. But it should also be on the bookshelves of lecturers and researchers who find themselves saying “I never really understood how...”. How did we manage without this book before?

Mike Gillan
Professor of physics
University College London

Introduction

This book started from the lecture notes I prepared for evening students at University College London whom I taught the subject of the Solid State Physics in 2001. At that time the size of the notes was only about 200 pages long and did not cover a number of important areas of the subject. Therefore, while preparing this book I decided to include a substantial amount of additional material which I thought necessary for a modern solid state physicist or chemist to be aware of. As a result of these changes, the book size increased by more than two-fold. The direction of the book has also changed. The initial idea was to write a rather simple textbook on quantum theory of the solid state containing very detailed mathematical derivations (which are usually left for a reader in other texts) and discussion of all essential and difficult concepts and ideas so that it would be accessible to any student. However, as more and more advanced concepts and ideas started to appear in the manuscript, it has soon become clear that this initial underlying idea of the book had to be modified.

Now I believe the book serves a number of purposes. First of all, it could still be a useful textbook for an average undergraduate student in physics and solid state chemistry. This is because difficult sections and Chapters in the book which require more effort and may be skipped without harm during the first reading are clearly marked with an asterisk. Secondly, more persistent and energetic students interested in theory of the solid state will also find a lot of more advanced material based on complex ideas and mathematical apparatus which require some persistence and patience to follow. Nevertheless, I tried to be as detailed as possible, both in maths and difficult conceptual points, even in these parts of the book, and the reader will find very detailed derivations and explanations which should certainly help in going through the most difficult places. This should allow the advanced material be accessible for a wider studentship as well. Thirdly, the last Chapter in the book is a little bit special and serves yet another purpose. This is an introductory Chapter for those who would like to pursue a career in theoretical solid state physics or theoretical quantum chemistry, especially in the areas of *ab initio* modelling and simulations, as it reviews modern electronic structure methods. This may also be useful to some of the young researchers who would like to understand better the foundations of modern computational techniques. In addition to very detailed discussions of the main ideas of various methods, the reader will also find many references to other books, review articles and original papers which should allow him/her to continue reading in their chosen direction. Of course, the list of references is mostly based on the author's own preferences and usefulness for this particular project and thus is incomplete, and I

should apologise for not being able to include more.

Another advantage of the book is that it is cross-linked: many phenomena are studied using several different theories of increased complexity; however, the theories are illustrated on the same examples. In addition, a reader will find the same theories applied to different phenomena studied in different Chapters (e.g. the Landau theory of phase transitions). This should allow the reader to see theory of the solid state in a broader context and as a unified theory rather than as a set of ideas not related to each other.

What is needed for a reader to know in order to read the book efficiently, to make it useful? Because of its rather broad appeal, standard undergraduate courses on quantum mechanics, statistical physics and math should suffice. The book does not require any special knowledge which goes beyond those courses usually taught at Universities during the first and second years. Moreover, many concepts which students are supposed to know, both from math and physics, are briefly introduced in the book when needed for the first time, to help the reader. From this point of view, the book can be considered as self-contained.

Because of a rather wide coverage from various areas of solid state physics, the book will be a useful pool of ideas for lectures as well. As difficult sections of the book are indicated by an asterisk, the lecturers should find it easy to select the material for their courses taking into account their own experience, students abilities, etc. Therefore, in my view both introductory and a number of advanced courses, both undergraduate and postgraduate, can be based on this book without difficulty.

Quite broadly, Solid State Physics studies electronic properties of solids. Solids consist of two types of particles: **atomic nuclei** and **electrons**. In solids atoms on average occupy certain positions in space around which they oscillate (vibrate). These vibrations affect the potential in the solid in which electrons are moving, i.e. electronic structure is also affected. Thus, in order to study solids, we have to learn:

- their **atomistic structure**: how atoms are arranged in space;
- **vibrations of atoms**, i.e. so-called phonon structure; this largely determines thermal properties, in fact, most of the temperature dependence of lattice and electronic properties;
- **electronic structure** which is necessary to understand electronic properties of solids (band structure, transport properties);
- **interaction** of electrons with phonons, i.e. how atomic vibrations affect the electronic properties;
- **interaction** with other particles (neutrons, electrons, light, X-rays, etc.).

There is a wide variety of possibilities which result in a rich collection of different materials with variable properties: magnetic and non-magnetic materials, conducting and non-conducting, low temperature and high temperature superconductors, insulators, etc.

Depending on the atomistic structure, we distinguish:

- **ideal (perfect) crystals**, in which atoms form periodic arrays in three dimensions,
- **defective crystals**, in which 3D periodicity is occasionally broken by various kinds of point and extended defects;
- **glasses and amorphous solids**, in which atoms have a random structure as the result of a certain process by which the material is derived; for example, glasses can be obtained by cooling a liquid: the system is undergoing a process of attaining thermal equilibrium (which is a crystal), but it takes a very long time;
- **crystalline alloys**, in which several species occupy regular lattice sites at random; this is an example of a disordered crystal;
- **quasicrystals**, in which structure is highly symmetric but there is no long-range translational periodicity in the system.

Solid State Physics is concerned with all these materials and properties and is a part of a larger discipline which is called Condensed Matter Physics that also includes liquids and dense gases.

As follows from the above, we should first consider the spatial arrangement of atoms in solids. Therefore, the first Chapter of the book contains a very broad introduction to the geometrical structure of solids. It contains elements of group theory, both point and space groups are discussed and explained in detail. To save space, the theory of group representations is not considered here. The only excuse is that there are very good books available on this subject which we refer to in the Chapter. The reader will also find useful explanations of the International Tables for Crystallography and a long list of examples of different crystal structures. The Chapter ends with a review of nonperiodic solids including defects in crystals. The concepts of the reciprocal lattice, Brillouin zones and Miller's indices are thoroughly discussed in Chapter 2. As an example of the application of these ideas, the theory of X-ray diffraction for periodic and nonperiodic solids is considered. The latter is based on the concept of the density-density correlation function.

Chapter 3 starts by explaining in great detail the ideas of the adiabatic approximation which allows separate consideration of electrons and nuclei. Nonadiabaticity is briefly introduced there as well. Then all known types of binding in molecules and solids are considered. Covalent bonding is explained in detail by taking H_2^+ and H_2 systems as examples. This section may also serve as an introduction to main ideas of modern quantum chemistry. We also consider covalent systems with sp^n types of atomic shells and the physics of the van der Waals interaction. When considering binding in crystals, special attention is devoted to ionic systems where long-range electrostatic interactions play a very important role. Therefore, the Ewald method is discussed in great detail.

Chapter 4 is about atomic vibrations in crystals, i.e. phonons. After explaining Lagrangian and Hamiltonian formalisms of classical mechanics, we consider vibrations of a monoatomic chain with one and two atoms in the basis; all the main concepts of the theory of phonons will be introduced there including long acoustic and optical

waves, boundary conditions, normal coordinates (phonons) and density of states. Then all these ideas are generalised for a three dimensional crystal where the classical theory of lattice dynamics in the harmonic approximation is presented with both rigour and detail. Quantum consideration of lattice vibrations comes next. There we introduce creation and annihilation operators for a single oscillator and then for a crystal. Then a wide range of thermal properties following from lattice vibrations are considered including: phonon statistics, displacement-displacement correlation functions, internal energy and specific heat, equation of states in the quasiharmonic approximation, melting and the Debye-Waller factor. Main ideas and difficulties of going beyond the harmonic approximation are also presented. The Chapter ends with a thorough discussion of the elasticity theory of solids based on the Lagrangian strain tensor. It includes elements of the classical macroscopic theory of elasticity and then covers thermodynamics, elastic constants, stability, elastic waves and the method of homogeneous deformation.

Electronic structure of crystals based on the band theory is the subject of Chapter 5. As was the case with Chapter 4 when atomic vibrations were considered, we start here from a very simple model of the free electron gas (applicable only to good metals) for which all essential concepts are introduced such as: plane waves, \mathbf{k} vectors, boundary conditions, quantum statistics, temperature dependence of the chemical potential and heat capacity and, finally, elementary theory of electron transport properties is discussed. In the following section electronic energy bands are discussed from a broader point of view. We start off by proving the Bloch theorem. Then main ideas of modern computational methods based on plane waves and density functional theory (DFT) are briefly discussed (a more detailed account of this and other methods is postponed until Chapter 9). Then the origin of energy bands in solids is illustrated on a number of analytically solvable models such as the approximation of a nearly free electron gas, tight binding approximation and the Kronig-Penney model which are worked out in great detail. The following sections contain discussion of electronic density of states and results of calculations of the electronic structure of some real materials. A more advanced transport theory based on the concept of quasiparticles and the Boltzmann kinetic equation is considered in section 5.3 as a generalisation of the simple transport theory considered at the beginning of the Chapter. This section is finished with an introduction to modern theory of transport properties based on nonequilibrium statistical mechanics and Kubo's linear response theory. As an example of the application of all these theories, the same model of a free electron gas is considered which should provide the reader with a better understanding of the theories. The final section 5.4 of this Chapter is concerned with some aspects of the electron-electron interaction. In particular, "plasma" oscillations are considered both from the classical and quantum points of view, as well as screening in the electron gas. This section is finished with a comprehensive account of the microscopic theory of the dielectric function of solids based on the averaging of the macroscopic dielectric function and the linear response theory. Several important results such as the general expression for the dielectric susceptibility via the density-density correlation function, Kubo-Greenwood and Lindhard formulae, "plasma" oscillations and electron screening are all considered there.

Magnetic properties of solids are studied in Chapter 6 by considering first classical

and then quantum definitions of the magnetic moment. In particular, we consider in some detail derivation of Maxwell equations for materials and the physical nature of the electron spin. The latter is done by a rather brief though detailed excursion into relativistic theory of an electron based on the Dirac equation. This was done, at least partially, to keep the book self-contained; on the other hand, not all students may have had a course of relativistic quantum mechanics and they will find this concise explanation of the nature of the electron spin useful. Then, we consider classical and quantum theories of para- and diamagnetic properties of solids. We first start with studying those properties which arise from localised electrons. Then magnetic properties of the electron gas are studied including Pauli paramagnetism, Landau diamagnetism and the de Haas-van Alphen effect based on the free energy of the electron gas in a magnetic field. Pauli paramagnetism is considered from a very simple model as well. Magnetic ordering is considered in section 6.6. Using the Weiss molecular field theory, we consider ferro-, antiferro- and ferrimagnetism, hysteresis and domain structure. Then, two elementary microscopic theories of magnetic ordering are studied, namely the one based on the exchange interaction and the Stoner model. This Chapter is finished with the theory of ferromagnetic phase transitions based on the ideas of symmetry breaking and general Landau theory of phase transitions. As an illustration of the phenomenological Landau theory, microscopic Bragg-Williams mean-field theory of the phase transition is considered in great detail.

Superconductivity is studied in Chapter 7. First of all, the main experimental results are presented together with the phenomenological Londons theory. Then the concepts of Cooper pairs and electron-electron interaction mediated by the lattice, which are the basic stones of the microscopic theory of superconductivity, are presented. The second quantisation for fermions is introduced here for the first time on an intuitive level which should be easily accessible to an average student (rigorous derivations are left for Chapter 9). Then all the main ideas of the BCS (Bardeen-Cooper-Schrieffer) theory of homogeneous type I superconductors are discussed including the ground and excited states, energy gap, supercurrent, existence of the critical magnetic field, the Meissner-Ochsenfeld effect and the quantisation of the magnetic flux. The phenomenological Ginzburg-Landau theory of superconductivity which is applicable to nonhomogeneous samples as well is introduced next from the general point of view of the Landau theory of phase transitions and symmetry breaking. Finally, the Chapter is finalised with a rather brief overview of type II and high T_c superconductors.

In Chapter 8 we consider dielectric materials and related issues. The Chapter is started by the modern definition of microscopic polarisation of solids. Then we study the phonon contribution to the dielectric function. This is done in several stages: first, the concept of the local field is introduced and a simple Huang theory of binary ionic crystals is discussed. Then, the theory is generalised for arbitrary crystal lattices using at the beginning a classical consideration which is then followed by the entirely quantum approach based on the linear response theory. Next, the thermodynamics of dielectric materials is presented including piezoelectricity and the effect of crystal symmetry. Statics and dynamics (elastic waves in particular) of piezoelectric materials are also discussed. Finally in section 8.4 we discuss ferroelectric phase transitions. First, we start by introducing ferroelectric materials. Then, following the same pattern

as in the previous two Chapters, we study ferroelectric phase transitions from the point of view of symmetry breaking and the Landau theory of phase transitions. A microscopic Luttinger-Wigner theory presented at the end of the Chapter illustrates some points of the phenomenological Landau theory.

Finally, modern theories of electronic structure calculations are considered in the last Chapter 9. It is started by studying many-electron wavefunctions, Slater determinants, second quantisation and reduced density matrices (generalised densities). Then we consider the main ideas of quantum chemistry methods, specifically the Hartree-Fock and Configuration Interaction (CI) methods, which are at the heart of all techniques presently used by most theoretical chemists. Even if you are a devoted density functional user, it is still immensely important to be familiar with these techniques as they are the only rigorous route towards electronic correlation and excited states available to us today. This message has started to penetrate the theoretical physicist community, so that more and more people are currently using quantum chemistry computer codes to study various physical problems. On the other hand, the density functional method (DFT) has made a great impact on the theory of the solid state; most of the numerical results available up to date have been obtained using DFT. Therefore, a large part of Chapter 9 is concerned with detailed discussion of the DFT, including foundations of the method and a rather brief account of its possible extensions such as spin-polarisation, treatment of excited states, time-dependent DFT (TDDFT) and nonzero temperatures. Then some technical details of the DFT and quantum chemistry methods are mentioned such as the choice of the basis set, periodic boundary conditions and the \mathbf{k} -point sampling, the order- N methods and the methods of pseudopotentials; the latter include all existing flavours such as “hard”, “soft” and “exact” (i.e. the Projector Augmented-Wave (PAW) method) implementations.

Finally in section 9.5 we consider the main ideas of *ab initio* simulations. After the Hellmann-Feynman and Pulay forces are discussed in great detail, oxygen adsorption on the MgO (001) surface is considered as an example. Then the concepts of *ab initio* molecular dynamics (MD) simulations are discussed which are followed by two examples: hydrolysis at a stepped MgO surface and the calculation of the melting curve of Al using the thermodynamic integration method. Then we present the so-called direct method of calculating the dynamical matrix of crystals which is based on numerical calculation of atomic forces, and a more powerful method of density functional perturbation theory (DFPT) which allows exact calculation of energy derivatives of arbitrary order with respect to external parameters such as atomic coordinates. Finally, all important equations of the modern theory of quantum polarisation are derived at the end of this section. Note, that the Berry phase is not used there as it is merely a mathematical object and the whole theory can be explained without it.

Contents

Acknowledgement	v
Foreword	vii
Introduction	ix
1 Structures	1
1.1 Crystals: periodic arrays of atoms	1
1.2 Mathematical description of crystal structures	4
1.2.1 Definition of a group	4
1.2.2 Translation groups	5
1.2.2.1 Operators of translation	5
1.2.2.2 Construction of subgroups	6
1.2.3 Point groups	7
1.2.3.1 Elementary point groups	8
1.2.3.2 Symmetry groups of a tetrahedron and a cube	10
1.2.4 Space groups	12
1.2.4.1 Symmetry operations	12
1.2.4.2 Types of Bravais lattices	14
1.2.4.3 Crystallographic (conventional) unit cell	19
1.2.4.4 Crystal classes	20
1.2.4.5 Symmorphic and nonsymmorphic crystal lattices	22
1.2.4.6 Close packing structures	22
1.2.4.7 2D (planar) groups	23
1.2.5 *Matrix and operator representations of a group	23
1.2.5.1 Operator representation of a group	23
1.2.5.2 Matrix representation of a group	24
1.2.6 Indexing of planes and directions: definitions	25
1.3 *International Tables for X-Ray Crystallography	26
1.4 Examples of crystal structures	30
1.4.1 Cubic face-centred structures	31
1.4.1.1 Space group O_h^5 ($Fm\bar{3}m$, No. 225)	31
1.4.1.2 Space group O_h^7 ($Fd\bar{3}m$, No. 227)	32
1.4.1.3 Space group T_d^2 ($F\bar{4}3m$, No. 216)	32
1.4.2 Cubic body-centred structures	32
1.4.2.1 Space group O_h^9 ($Im\bar{3}m$, No. 229)	32

1.4.2.2	Space group T_h^7 ($Ia3$, No. 206)	33
1.4.3	Structures with simple cubic lattice	33
1.4.3.1	Space group O_h^1 ($Pm\bar{3}m$, No. 221)	33
1.4.3.2	Space group T_h^6 ($Pa3$, No. 205)	34
1.4.4	Tetragonal lattice	34
1.4.4.1	Space group D_{4h}^{14} ($P4_2/mnm$, No. 136)	34
1.4.5	Structures with trigonal lattice	35
1.4.5.1	Space group D_{3d}^6 ($R\bar{3}c$, No. 167)	35
1.4.6	Structures with hexagonal lattice	36
1.4.6.1	Space group D_{6h}^4 ($P6_3/mmc$, No. 194)	36
1.4.6.2	Space group C_{6v}^4 ($P6_3mc$, No. 186)	36
1.4.6.3	Space group D_3^4 ($P3_121$, No. 152)	37
1.5	Nonperiodic solids	37
1.5.1	Definition of order and quasicrystals	38
1.5.2	A road to disorder	40
1.5.2.1	Point defects	40
1.5.2.2	Cellular disorder	40
1.5.2.3	Topological disorder	43
2	The reciprocal lattice and X-ray diffraction	45
2.1	The reciprocal lattice	45
2.2	*Once again about crystal planes and Miller indices	47
2.3	Brillouin zones	50
2.4	Periodic functions: Fourier analysis	51
2.5	Introduction to X-ray diffraction	55
2.5.1	Diffraction intensity	55
2.5.2	Bragg law	59
2.5.3	Structure factor	60
2.5.4	Interpretation of diffraction experiments	63
2.5.5	*X-ray diffraction of nonperiodic solids	63
2.5.5.1	Density-density correlation function	64
2.5.5.2	Periodic systems revisited	65
2.5.5.3	Application to a binary alloy	66
2.5.5.4	Glass	68
3	Binding in Crystals	69
3.1	Adiabatic approximation	69
3.2	Molecules: types of chemical bonding	75
3.2.1	Simple example: a molecule with two atoms	75
3.2.2	Ionic bond	77
3.2.3	Covalent bond	77
3.2.3.1	Hydrogen molecular ion H_2^+	77
3.2.3.2	Hydrogen molecule: MO method	78
3.2.3.3	Hydrogen molecule: VB method	82
3.2.3.4	Covalent bonds for elements having the $(np)^3$ shells	83
3.2.3.5	Covalent bonds for elements having the $(ns)^2(np)^2$ shells	83

3.2.3.6	Some other examples of hybrid orbitals	84
3.2.4	Ion-Covalent bond	85
3.2.5	Van der Waals interaction	85
3.2.6	Hydrogen bond	88
3.3	Binding in crystals	88
3.3.1	Cohesive and lattice energies	88
3.3.2	Electrostatic energy	89
3.3.2.1	Conditional convergence	89
3.3.2.2	*Ewald method: electrostatic potential	90
3.3.2.3	*Ewald constant	92
3.3.2.4	*Ewald method: electrostatic energy	93
3.3.2.5	The Madelung energy of a finite large crystal sample	94
3.3.3	Van der Waals crystals	94
3.3.4	Ionic crystals	95
3.3.5	Covalent crystals	97
3.3.6	Hydrogen bond systems	98
3.3.7	Metals	98
3.3.8	Real crystals	99
4	Atomic vibrations	101
4.1	Lagrangian and Hamiltonian method	101
4.2	One dimensional lattice	103
4.2.1	Monoatomic basis	103
4.2.1.1	Lagrangian and equation of motion	104
4.2.1.2	General solution	105
4.2.1.3	First Brillouin zone	106
4.2.1.4	Elastic Waves	106
4.2.1.5	Long wavelength limit	107
4.2.2	Two atoms in the basis	107
4.2.2.1	Lagrangian and equations of motion	108
4.2.2.2	Analysing the solution	109
4.2.2.3	Limiting case of identical atoms	110
4.2.2.4	Why optical and acoustic?	112
4.2.3	Boundary conditions	112
4.2.4	*Normal coordinates	114
4.2.4.1	Discrete Fourier transform	115
4.2.4.2	Matrix form for the eigenvalue problem and the dynamical matrix of the chain	116
4.2.4.3	Diagonal representation for the kinetic and potential energies of the chain	118
4.2.4.4	Normal coordinates of the chain	120
4.2.5	Density of states for the 1D chain	121
4.3	Three dimensional lattice: classical	122
4.3.1	Harmonic approximation	123
4.3.2	Phonons in a 3D crystal	125
4.3.2.1	Hamiltonian and equations of motion	125