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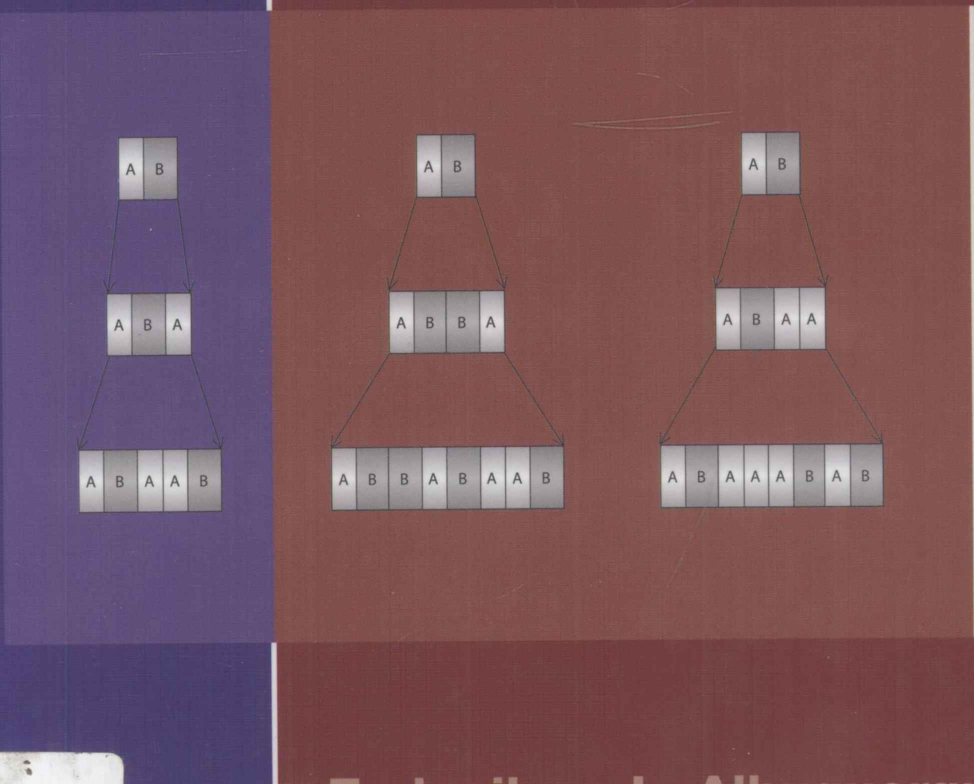
Polaritons in Periodic and Quasiperiodic Structures



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POLARITONS IN PERIODIC

AND

QUASIPERIODIC STRUCTURES

To

Juliana M. L. Albuquerque

In Memoriam

Preface

Artificial (or fabricated) periodic systems have been of considerable interest in physics and materials science since 1970, when Esaki and Tsu proposed a synthesized semiconductor superlattice of a one-dimensional periodic structure of alternating ultrathin layers, with its period less than the electron mean free path and the de Broglie wavelength. They envisioned two types of synthesized superlattices, namely the doping and the compositional ones, where in either case a superlattice potential was introduced by a periodic variation of impurities or composition during their growth. It was shown theoretically that such synthesized structures would possess unusual physical properties, not seen in the constituent semiconductor materials, due to predetermined quantum states that are of a two-dimensional character. Because of the potential device applications of such systems, their achievement and understanding has been a mixture of strong motivation from basic interest and technical applications, and much work has been devoted to understanding their unique physical properties. Further stimulus arose when modern growth techniques, such as molecular-beam epitaxy and metal-organic chemical vapor deposition, made it possible to fabricate these periodic layered materials with sharp, high-quality interfaces. Nowadays the fabrication of material structures with dimensions of the order of micrometers and nanometers is feasible to a high degree of precision.

On the other hand, the subject of quasicrystals first achieved prominence in 1984, when measurements using high-resolution X-ray scattering techniques produced electron diffraction patterns consisting of sharp spots but showing specific symmetries, forbidden by the rules of crystallography for an infinite lattice. Theoretical studies explained these types of symmetry through the aperiodic two- and three-dimensional Penrose tilings and their diffraction patterns (tiling is the geometrical operation that results in filling space with an arrangement of regular polyhedra). One important feature of these quasicrystal structures is that in one dimension they behave like the quasiperiodic structures formed by the incommensurate arrangement of periodic unit cells following a given mathematical sequence (like the well-known Fibonacci one). In turn, such structures can be tailored using the modern layer-growth techniques mentioned earlier. An appealing extra motivation for studying these quasiperiodic structures is that they exhibit a highly fragmented energy spectrum displaying a self-similar pattern. From the mathematical perspective, it has been proved that their spectra are Cantor sets in the thermodynamic limit. Moreover, the localization of electronic states, which is one of the most active fields in condensed-matter physics, could thus occur not only in disordered systems but also in deterministic quasiperiodic systems. Another interesting feature of these structures is that they exhibit collective properties that are not shared by their constituent materials. They are due to the presence of long-range correlations, and are expected to be reflected somehow in their various spectra (light propagation, electronic transmission, density of states, polaritons, etc.), defining a novel description of disorder. One of the main reasons for this is the fact that they represent an accessible and intermediate case between a periodic crystal, with extended Bloch states, and random disordered solids, with exponentially localized states. Furthermore, it obviously opens the way to many theoretical approaches in attempts to understand and foresee their physical properties, without the degeneracy rules of periodic invariance. Theoretical treatments (based, for example, on the transfer-matrix method described later) show that a common factor shared by all these excitations is a complex fractal or multifractal energy spectrum.

The purpose of this book is to present an overall account of the dynamical properties of these periodic and quasiperiodic structures, in terms of the polaritons (bulk and surface modes) that propagate in them. In general, the term polariton refers to a mixed excitation (or wave) made up from a dipole-active elementary excitation (such as a phonon, plasmon, magnon, exciton, etc.) coupled to a photon (a quantum of light). The basic properties of polaritons may be obtained using simple theories that are related to the frequency-dependent dielectric, optical, and magnetic characteristics of the media.

Motivated by the potential device applications of such systems, our intention here is to provide a text, at the graduate level, for students, researchers, and academic staff working in this field who have an interest in understanding the unique physical properties of polaritons in these artificial systems. This includes the methods of generating polaritons in laboratories at frequencies of interest to experimentalists and the physics that may be learned from them. The book addresses the fundamentals of the propagation process for polaritons in such artificial structures, keeping in mind that, since experimental reality is approaching theoretical models and assumptions, detailed analysis and precise predictions are being made possible.

The book is organized so that we start with the basic properties of excitations in solids, highlighting their main concepts that can be found in some solid-state physics textbooks (Chapter 1). Next we define the periodic and quasiperiodic structures of interest (in the sense that they either can be or already have been grown by experimentalists), and we give the mathematical properties of some of them, namely Cantor, Fibonacci, Thue–Morse, and Double-period (Chapter 2). A discussion then follows of bulk and surface polariton modes of various types (mainly plasmon, phonon, magnetic, and exciton), stressing the role played by the dielectric function as well as the magnetic susceptibility (Chapters 3 and 4). This serves as the main introduction to these excitations. From that point on, the book presents the wide-ranging and interesting physical concepts behind the properties of polaritons in periodic and quasiperiodic artificial structures, stressing their spectra, localization and scaling properties, and power laws, which are a guide to their *universality classes*, and defining a novel description of disorder. In particular, important questions are addressed such as the propagation of polariton modes in doped semiconductors, piezoelectric, metamagnetic and rare-earth materials, among others, as well as the behavior of the thermodynamic quantities (particularly the specific heat spectra) in these systems (Chapters 5–10). Experimental techniques to probe these spectra are described in Chapter 11, with emphasis given to the (currently) most powerful spectroscopic method of Raman and Brillouin scattering of light, as well as to the so-called attenuated total reflection spectroscopy. Finally, in Chapter 12, we present some additional topics (in particular, systems with non-linear dielectric properties) and we point to future directions for this research field. A few important theoretical tools are presented in Appendix A to help readers with the theoretical methods employed throughout this book.

Both of us have been engaged heavily for many years in research programs focused on the physical properties of these elementary excitations, with two review articles already published on this subject. We believe that our book devoted to this burgeoning area will be valuable in covering the many new developments that have occurred since the, now classical, books *Polaritons* (edited by E. Burstein and F. de Martini) in 1974 and *Surface Polaritons* (edited by V.M. Agranovich and D.L. Mills) in 1982. Furthermore, as this field is rapidly changing, a good comprehension of the fundamental concepts presented here should be important for readers interested in this subject and for researchers seeking to make further advances.

We are indebted to a large number of friends and collaborators who directly or indirectly have influenced this book and provided ideas. We gratefully acknowledge the award of a fellowship from the Brazilian Research Agency CAPES, and leave granted by the Universidade Federal do Rio Grande do Norte to one of us (E.L.A.) to spend the summer of 2003 at the University of Western Ontario, where the main ideas of this book were established. Last, but not least, we would like to thank our families for their invaluable support and unfailing encouragement in addition to sustaining us through many difficult and challenging moments.

June 2004

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Contents

Chapter 1

Basic Properties of Excitations in Solids

The dynamical properties of a crystalline solid in terms of its constituent particles are of great interest to solid-state physicists and materials scientists. In particular, the concept of excitations in solids, especially in bulk materials, forms a significant part of the standard textbooks (see e.g. Refs. [1–3]). Typically these books cover a wide range of matters related to the dynamical response of the crystal to various kinds of external stimuli (such as temperature, electric field, magnetic field, etc.). All the excitations have at least one feature in common: they are associated with the whole crystal collectively and not just with a particular atom. As such, they depend sensitively on the structure of a solid and the interactions within it.

In general, the topic of excitations in solids is very complex, and it is not our intention to give a detailed account in this chapter, since this is done elsewhere. Instead, it is our aim to present here those fundamentals of the theory at a level sufficient to provide readers with the necessary background to understand better the specific material to be covered in the following chapters related to periodic and quasiperiodic structures.

We start this chapter with general considerations about the periodic arrangements of atoms, leading to the definition and characterization of a crystalline solid. This brings us to symmetry-related restrictions on the excitations themselves (e.g. through the well-known Bloch's theorem). Then we introduce the basic concepts of the main excitations to be considered in this book, namely the phonons, plasmons, magnons, and excitons. Later we shall be considering the properties of these excitations in various artificially structured materials, both individually and especially as "mixed" excitations in which they couple with a photon (or light quantum) to form a *polariton*.

1.1 Symmetry and Crystal Lattices

A crystalline solid is essentially an ordered array of atoms, bound together by electrical forces that may be attractive (as for the Coulomb interaction between electrons and protons) and repulsive (as for the electron–electron and proton–proton Coulomb interactions) to form a very large system. The different strengths and types of bond are determined by the particular electronic structures of the atoms involved and may, in principle, be found from quantum mechanics [4,5].

Magnetic forces have only a weak effect on cohesion and the gravitational forces are negligible. In a typical solid there are as many as 10^{23} nuclei and 10^{24} electrons in a cubic centimeter, which, at first sight, implies that it is almost impossible to study effectively such a large number of interacting particles theoretically. Fortunately, this complication can be overcome due to the high symmetry of a solid.

Indeed, although a bulk crystalline solid may be arbitrarily large, it can be viewed effectively as an infinite three-dimensional (3D) regular repetition of much smaller identical building blocks (or *repeating units*), which can be set up following specific symmetry relationships among its various physical parameters. The arrangements of the repeating units of the crystalline solids specify a set of operations, which is known today as the symmetry group or space group of the *Bravais lattice.* In short, a Bravais lattice can be introduced as a pure geometrical concept, in which an infinite array of the periodic crystal appears to be exactly the same, no matter from which position the array is viewed.

The most obvious operation in the symmetry group of a Bravais lattice is the *translational symmetry.* It is defined in terms of three non-coplanar basis vectors, denoted by $\hat{a}_1$, $\hat{a}_2$, and $\hat{a}_3$. These vectors are called the *primitive vectors* of the lattice, and are responsible for its generation. The parallelepiped defined by the primitive axes is called a *primitive cell*, and it fills all space under the action of a suitable translation operation. It is also the minimum-volume cell in the Bravais lattice and must contain precisely one lattice point. Note that there is no unique way of choosing a primitive cell for a given Bravais lattice.

If a translation is made between any two locations in the crystal, having identical atomic environments, they can be linked through the fundamental translation vector $\vec{R}$ given by

$$\vec{R} = n_1\hat{a}_1 + n_2\hat{a}_2 + n_3\hat{a}_3, \tag{1.1}$$

where n_1, n_2, and n_3 range through all integer values. The main property of the fundamental translation vector $\vec{R}$ is that the atomic arrangement of the lattice looks the same in every respect, whether viewed from any point $\vec{r}$ or from

$$\vec{r'} = \vec{r} + \vec{R} = \vec{r} + n_1\hat{a}_1 + n_2\hat{a}_2 + n_3\hat{a}_3. \tag{1.2}$$

Apart from the translational symmetry (which has the most important influence on the properties of the crystal), the space group associated with a lattice may also present symmetry operations due to the various rotations and reflections (and combinations of them), which leaves the crystal, as well as its primitive cells, unchanged [6,7]. For instance, for a hypothetical two-dimensional (2D) solid there are five different Bravais lattices, as shown in Fig. 1.1. For 3D solids 14 Bravais lattices are possible (see e.g. Ref. [1]). The points in a Bravais lattice that are closest to a given point in the lattice are called its nearest neighbors, and their number is an invariant property of the lattice.

Since a Bravais lattice is not an arrangement of atoms but a geometrical arrangement of points in the space, it is necessary when defining a more complex *crystal structure* to associate to each point of the Bravais lattice a *basis of atoms.*

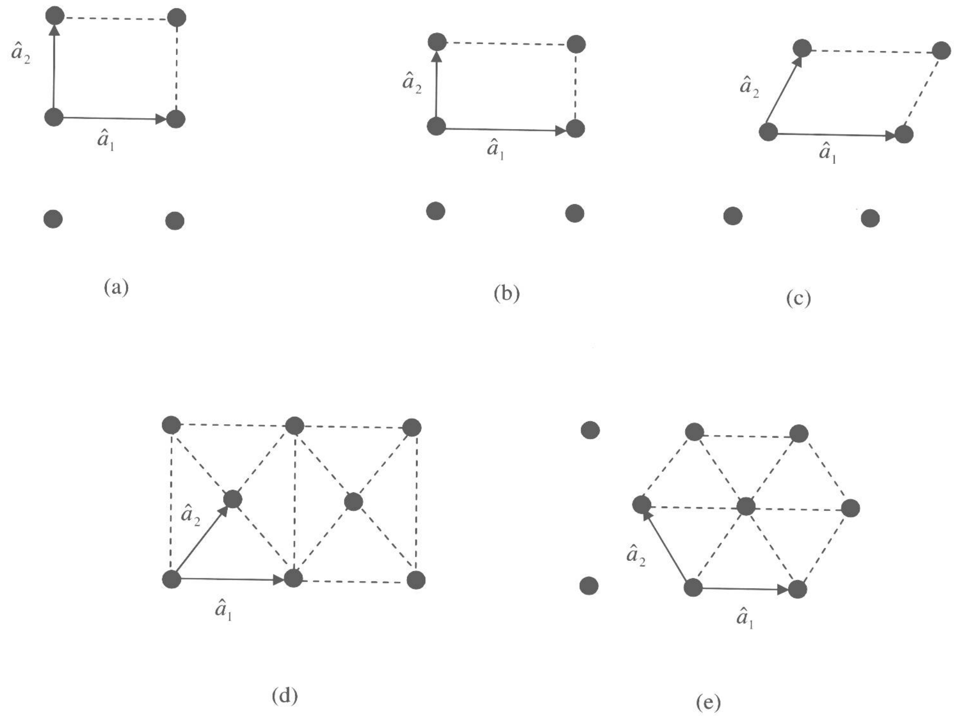


Fig. 1.1. Schematic representation of the five Bravais lattices in 2D: (a) square lattice; (b) rectangular lattice; (c) oblique lattice; (d) centered rectangular lattice; (e) hexagonal lattice.

By a basis of atoms we mean not only the atoms themselves but also their spacing and bond angles, which may form molecules, ions, etc. Of course, the number of atoms in the basis may sometimes simply be unity, as for many metals and the inert gases (He, Ne, Ar, Kr, Xe, and Rn), but it may be larger in general, exceeding 1000 for some inorganic and biochemical structures. Therefore, a crystal structure can be defined as identical copies of the same physical unit, the basis, located at all the points of a Bravais lattice. The geometrical space lattice (defining the Bravais lattice), plus the basis of atoms attached to each lattice point, specifies the full crystal structure [1].

Although the primitive cell is sufficient for characterizing the Bravais lattice, it is sometimes more convenient to work with the so-called *unit cell* of the lattice. The unit cell is the simplest geometrical figure that we can select from a Bravais lattice. Depending on its geometrical arrangement, it may or may not coincide with the primitive cell and therefore it is not always the minimum-volume cell of the Bravais lattice. However, the more straightforward geometrical appearance of the unit cell compensates by far this feature. For example, the body-centered cubic lattice, one of the most studied 3D Bravais lattices, is more easily visualized as a cubic structure with two atoms than its primitive counterpart, which is a much

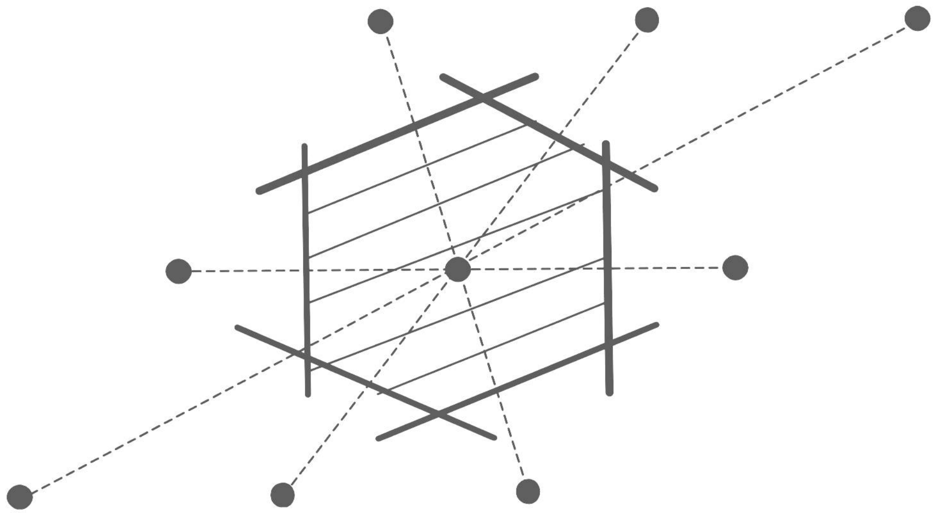


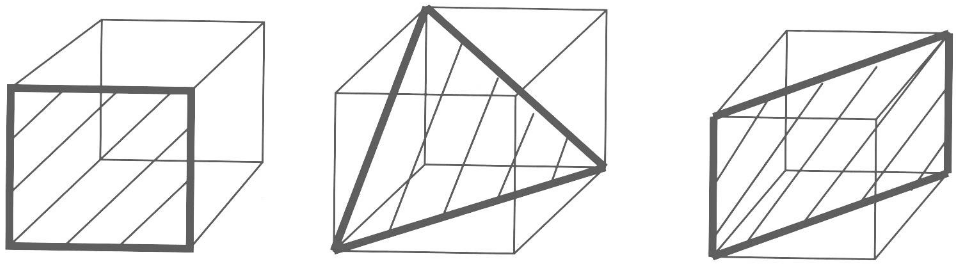
Fig. 1.2. Construction of a primitive Wigner–Seitz cell.

complicated rhombohedron of edge $a\sqrt{3}/2$, with a being the side of the cube, and angle $109^\circ\ 28'$ between adjacent edges.

On the other hand, there is a clever way to construct a primitive cell of any Bravais lattice, the so-called Wigner–Seitz primitive cell [8]. In Fig. 1.2 we show how to draw a Wigner–Seitz cell for a 2D Bravais lattice. The procedure is quite simple: (a) draw lines to connect a given lattice point to all its nearby lattice points; (b) at the midpoint and normal to these lines, draw new lines. The simplest volume enclosed in this way is the Wigner–Seitz primitive cell. It can be shown that in 2D the Wigner–Seitz cell is always a hexagon, with the obvious exceptions of the square and rectangular lattices. As we will see in the next paragraph, the Wigner–Seitz primitive cell plays an important role in the determination of the Brillouin zones.

We often need to describe a particular crystallographic plane or a particular direction within a real 3D crystal. Although a plane can be specified by any three points lying in it, provided the points are not collinear, it is more useful for structural analysis to describe it in terms of its so-called *Miller indices.* For planes the recipe is very simple. First, find the intercepts on the axes $\hat{a}_1$, $\hat{a}_2$, and $\hat{a}_3$, expressed in multiples of the lattice constant. Then, take the reciprocal of these numbers, scaling them (if necessary) to the smallest three integers having the same ratio. The result is displayed in parentheses as (hkl). When a plane cuts an axis (say the $\hat{a}_1$-axis) on the negative side, it is conventional to employ the designation as $(\bar{h}kl)$. Fig. 1.3 shows some examples of planes for cubic lattices, with their Miller notations.

A similar convention is used to specify a particular direction normal to a plane in the real lattice. To avoid confusion with the crystallographic planes, however,



(100) **(111)** **(110)**

Fig. 1.3. Miller indices for three lattice planes in a simple cubic Bravais lattice.

square brackets, i.e. $[hkl]$, are used instead of parentheses. For instance, the body diagonal of a simple cubic lattice lies in the $[111]$ direction.

1.2 Reciprocal Lattices and Brillouin Zones

A consequence of the translational symmetry of a crystal is that some of the physical properties can be described by a multiply periodic function (denoted here by F), which satisfies the condition

$$F(\vec{r}+\vec{R}) = F(\vec{r}) \tag{1.3}$$

for all points $\vec{r}$ in space and for all translation lattice vectors $\vec{R}$. On expanding $F(\vec{r})$ in a Fourier series in 3D, we have

$$F(\vec{r}) = \sum_{\vec{Q}} g(\vec{Q}) \exp(i\vec{Q}\cdot\vec{r}). \tag{1.4}$$

It then follows straightforwardly from Eqs. (1.3) and (1.4) that

$$\exp(i\vec{Q}\cdot\vec{R}) = 1, \tag{1.5}$$

which implies that $\vec{Q}\cdot\vec{R} = 2\pi \times \text{integer}$. The infinite set of all $\vec{Q}$ vectors that satisfy these conditions defines the *reciprocal lattice*. $\vec{Q}$ is a *reciprocal lattice vector*, and it has the dimension of wavevector (inverse length). Thus multiplication of the set of all reciprocal vectors $\vec{Q}$ by $\hbar$ converts reciprocal space into momentum space. Since the crystal (or Bravais) lattice is in real or ordinary space, the reciprocal (or Fourier) lattice is, apart from a multiplicative constant, in momentum space.

Defining the reciprocal lattice as

$$\vec{Q} = h\hat{b}_1 + k\hat{b}_2 + l\hat{b}_3, \tag{1.6}$$