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APERIODIC STRUCTURES IN CONDENSED MATTER

FUNDAMENTALS AND APPLICATIONS

Enrique Maciá Barber

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Aperiodic Structures in Condensed Matter

Fundamentals and Applications

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Preface

The universe is nicely ordered. There is order in the sequence of events determining the pace of evolution and the rhythms of life alike. Order can be found in all the structures unfolding around us at different scales. There is order in the arrangements of matter, in energy flow patterns, in every work of Nature interweaving space and time. This book is devoted to the study of a special kind of order referred to as aperiodic order.

Etymologically aperiodic order means order without periodicity. Accordingly, aperiodic order has nothing to do with disorder in any of its possible multiple forms. Aperiodic ordered matter exhibits long-range order in space, just as periodic orderings do. This property clearly distinguishes aperiodic structures from amorphous matter, the latter being able to display short-range correlations only. Aperiodic systems can be classified according to different criteria. For instance, certain aperiodic arrays of atoms are able to give rise to high quality x-ray or electron diffraction patterns composed of a collection of discrete Bragg spots, as periodic arrays of atoms also do. This phase of matter is referred to as quasiperiodic crystals (quasicrystals, for short) and they represent a natural extension of the periodic crystal notion. The diffraction patterns of quasicrystals are quite bizarre, unveiling the existence of unexpected symmetries which endow them with an impressive esthetical appeal. They also exhibit unusual physical properties, closely related to the fractal nature of their energy spectra. Physically this feature means that some specific fragments of the spectra appear once and again at different scales. Accordingly, we do not have periodicity but scalability. Indeed, fractal structures, characterized by their invariance under inflation/deflation operation symmetries, provide another representative example of aperiodically ordered systems.

But, in my opinion, the most important feature of aperiodic systems is their ability to encode relevant information in a way periodic order is completely unable to do. It suffices to compare a periodically arranged string of letters, namely *abcabcabcabc...*, with the preceding paragraph to immediately grasp the main point: in a periodic arrangement the information stored is limited to the basic period defining its structure (the unit cell in the case of a periodic crystal, for instance), whereas the amount of information stored in an aperiodic structure progressively increases as the system size is increased. The stacking of Watson-Crick complementary bases determining the genetic code in DNA is perhaps the most paramount example one can find in Nature. In fact, in DNA two kinds of order coexist in the same sample at just the same space scale. On the one hand, one has the aperiodic stacking of bases determining its biological information. On the other hand, one has the periodic arrangement of sugar-phosphate groups conforming the double-helix structure which preserves the physical integrity of the macromolecule at physiological conditions.

Such a blending of ordering principles can provide an inspiring guide for technological applications. For instance, one can grow layered structures consisting of a large number of films aperiodically stacked. The simplest example of such nanostructured materials is a two-component aperiodic heterostructure, where layers of two different materials (metallic, semiconductor, superconductor, dielectric, ferroelectric, ceramics) are arranged according to certain aperiodic sequence. In this way, two kinds of order are introduced in the same sample at different length scales. At the atomic level we have the usual crystalline order determined by the periodic arrangement of atoms in each layer, whereas at longer scales we have the aperiodic order determined by the sequential deposition of the different layers. This long-range aperiodic order is artificially imposed during the growth process and can be precisely controlled. Since different physical phenomena have their own relevant physical scales, by properly matching the characteristic length scales we can efficiently exploit the aperiodic order we have introduced in the system, hence opening new avenues for technological innovation. Recent works in optoelectronics and signal communication have fruitfully considered aperiodic designs in order to obtain improved devices and the very possibility of intentionally combining periodic and aperiodic materials in hybrid order composed structures has been recently explored in some detail.

Several topics on the role of aperiodic order in different domains of physical sciences and technology will be covered in this book. The first chapters address some basic notions and present the most characteristic features of different kinds of aperiodic systems in a descriptive way. In Chapter 1 we introduce different orderings of matter and describe the progressive transition from periodic to aperiodic thinking in physical sciences. In Chapter 2 the very notion of aperiodic crystal is introduced, fully describing its historical roots as well as the paramount discovery of quasicrystalline alloys and their beautiful forbidden symmetries. The study of the unusual physical properties of quasicrystalline alloys is then presented in more detail in Chapter 3, paying special attention to their intriguing electronic structure and the possible nature of chemical bonding in hierarchically arranged cluster-based solids. In Chapter 4 we introduce the basic structural properties of man-made materials consisting of aperiodic sequences of layers such as Fibonacci semiconductor-based superlattices or Cantor-like dielectric multilayers. The main mathematical features of the substitution sequences defining their growth rule are also reviewed along with the possible signatures of quasiperiodicity in their physical properties.

The two following chapters focus on some theoretical aspects and useful mathematical approaches introduced to properly study the physical systems introduced in previous chapters. Accordingly, Chapter 5 is devoted to introducing some simple models describing the fundamental physics of several aperiodic systems in one dimension. Remarkable properties of their energy and frequency spectra, such as a highly fragmented, self-similar arrangement of progressively narrower bands or the critical nature of the eigenstates, are discussed in detail by considering suitable models for different systems of interest. The impact of the peculiar energy spectra on their related transport properties is also addressed. In Chapter 6 we turn our attention to the aperiodic crystal of life, by considering some basic features of DNA molecules from the perspective of condensed matter physics. Some fundamentals on the diffraction theory by helices are first introduced. Then we discuss the electronic structure of nucleic acids and summarize what experiments say about the possible charge transfer processes in DNA. Different effective Hamiltonians aimed at describing the basic physics of these processes are subsequently introduced. On the basis of these results, the role of long-range correlations is critically analyzed from the biophysicist viewpoint.

Afterwards we shift towards more applied issues. Chapter 7 discusses how to exploit aperiodic order in different technological devices based on multilayered optical systems, photonic and phononic quasicrystals, complex metallic alloys or DNA-based nanocells. The appealing possibility of introducing novel designs based on the aperiodic order notion to achieve some specific applications is further discussed in Chapter 8 by considering not only one-dimensional systems, but also arrangements of matter in two and three dimensions. Finally, in Chapter 9 we present some useful mathematical tools which are of common use in the study of aperiodic systems.

The book is specially intended for both condensed matter physicists and materials science researchers coming into the field of aperiodic systems from other areas of research. It can also serve as a useful text for graduate students.

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Enrique Maciá Barber Madrid, June 2008

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Orderings of matter

1.1 Periodic thinking in physical sciences

The notion of periodicity allows one to easily grasp the basic order underlying certain patterns and rhythms in Nature. The essence of periodicity relies on a basic motif which is indefinitely repeated, along with a set of basic rules prescribing the way such a repetition process takes place. Periodicity can occur in time, space, or simultaneously in both of them. Periodicity in time guarantees that what is known to occur now will also occur later, and can be asserted to have already occurred before, provided that a certain relationship between those different instants is fulfilled. Let t be a real number measuring the passage of time. Then, a function satisfying the condition $f(t \pm T) = f(t)$ is periodic in time with a period T, since its value is preserved (i.e., it is invariant) under transformations describing the set of translations generated back and forth by the arrow of time by the real number T.

The existence of cyclic processes in Nature accurately obeying such a periodicity condition is the basis for the possible adoption of physical clocks (characterized by their T value). In fact, from the galactic scale down to atomic and subatomic scales, the natural world has plenty of physical systems exhibiting nearly exact periodicity in time. Most of these systems can be described, at least as a first approximation, in terms of dynamic equations of the form

$$\frac{d^2 f}{dt^2} + \omega^2 f = 0, \tag{1.1}$$

which is usually referred to as the harmonic oscillator equation, where f is some physical magnitude (e.g., a position coordinate, the intensity of an electric or magnetic field, or the chemical concentration of a substance) and ω, the so-called natural frequency, is a quantity which depends on characteristic physical parameters of the system. For instance, in the case of a (low amplitude) swinging pendulum we have $\omega^2 = g/l$, where l is the pendulum's length, and g measures the local intensity of the Earth's gravitational field.

Eq.(1.1) is a second order differential equation. To solve it one must find a mathematical function $f(t)$ whose second derivative coincides with (minus) itself, once properly scaled by a factor ω^2. The theory of differential equations tells us that these requirements are met by solutions of the form

$$f(t) = a\cos\omega t + b\sin\omega t, \tag{1.2}$$

where the value of the constants a and b is determined from the knowledge of a suitable set of initial conditions, and $\omega \equiv 2\pi/T$. In the particular case $a = b \equiv R$ the function given by Eq.(1.2) simply describes a uniform circular motion of radius R with angular frequency ω. Since trigonometric functions satisfy (by definition) the relations $\sin[\omega(t \pm T)] = \sin\omega t$, and $\cos[\omega(t \pm T)] = \cos\omega t$, we see that the periodicity condition $f(t \pm T) = f(t)$ is properly satisfied by Eq.(1.2). Therefore, the periodicity in time exhibited by the solutions of Eq.(1.1) naturally emerges from its basic mathematical structure. Quite remarkably, harmonic equation describes a broad collection of cyclic motions in nature, ranging from atomic vibrations in solids to population dynamics in ecosystems. The profuse appearance of this basic equation in the study of such diverse dynamical systems certainly accounts for the important role played by periodic thinking in theoretical physics, probably starting with the pioneering quest for the isochronous pendulum by Galileo Galilei (1564-1642) and Cristiaan Huygens (1629-1695) in the 17th century.[1]

Periodicity in space guarantees that what is located here must also occur over there, provided that certain geometrical relationships between "here" and "there" are fulfilled. Thus, a vector function satisfying the condition $\mathbf{f}(\mathbf{r}+\mathbf{R}_0) = \mathbf{f}(\mathbf{r})$ is periodic in space, since it is invariant under transformations describing the set of space translations generated by the vector $\mathbf{R}_0$ in the vectorial space to which the variable $\mathbf{r}$ also belongs. Periodicity in Euclidean space can involve rotations as well as translations, and can be expressed in the general form $\mathbf{Mr} + \mathbf{R}_0 = \mathbf{r}$, where

$$\mathbf{M} = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{1.3}$$

is an orthogonal matrix describing rotations by an angle φ. Let us consider the vectors describing a lattice of points, which have the general form $\mathbf{r} = n_1\mathbf{e}_1 + n_2\mathbf{e}_2 + n_3\mathbf{e}_3$, where $\{\mathbf{e}_i\}$ is a suitable vector basis and $n_i \in \mathbb{Z}$. The periodicity condition then implies that the trace of matrix $\mathbf{M}$ must take on integer values.[2] This leads to the so-called crystallographical restriction

$$1 + 2\cos\varphi = n \in \mathbb{Z}, \tag{1.4}$$

which has played a significant role in the development of classical crystallography. The main consequence of the relationship given by Eq.(1.4) is that only a few number of rotations are compatible with the periodicity condition. Thus, only two-fold, three-fold, four-fold, and six-fold symmetry axes are allowed in periodic lattices, as it can be straightforwardly deduced from Eq.(1.4). To this end, we express the crystallographic restriction in the form

$\cos\varphi = (n-1)/2$. The condition $|\cos\varphi| \leq 1$ implies $n = \{-1, 0, 1, 2, 3\}$. By plugging these values into the former expression we obtain the solutions listed in Table 1.1.

TABLE 1.1
Allowed symmetry axes in periodic crystals.

n	φ	AXIS
-1	π	2-fold
0	$2\pi/3$	3-fold
1	$\pi/2$	4-fold
2	$\pi/6$	6-fold
3	0	identity

The simplest illustration of processes which are simultaneously periodic in space and time can be found in wave phenomena. For instance, sinusoidal waves of the form $\Psi(\mathbf{r}, t) = \Psi_0 \sin(\mathbf{k}.\mathbf{r} - \omega t)$, where $k = 2\pi/\lambda$ is the wave number and λ measures the wavelength, often occur in waves propagating in gases, liquids or solids as well as in electromagnetic waves propagating in vacuum. Their characteristic wave function describes a periodic pattern in space if we fix the time variable (i.e., $t \equiv t_0$). Alternatively, if we fix the space variable (i.e., $\mathbf{r} \equiv \mathbf{r}_0$), it describes a harmonic motion in time at every point of space, where the quantity $\mathbf{k}.\mathbf{r}_0$ measures the relative dephasing between the oscillations of two points separated by a distance $\mathbf{r}_0$. The double periodicity (in space and time) of wave motion can be traced back to the very structure of the corresponding wave equation, which reads

$$\nabla^2\Psi + \frac{1}{c^2}\frac{\partial^2\Psi}{\partial t^2} = 0, \tag{1.5}$$

where $c = \omega/k$ is the phase velocity of the wave. The first (second) term in Eq.(1.5) describes the periodicity in space (time) of the propagating wave, while its phase velocity couples its spatial pattern to its propagation rhythm.

A key feature of sinusoidal waves, significantly contributing to pervade periodic thinking in scientific thought, is that any non-sinusoidal, periodic wave can be represented as a collection of sinusoidal ones (with different frequencies) blended together in a weighted sum of the form [cf. Eq.(1.2)]

$$f(t) = \frac{a_0}{2} + \sum_{m=1}^{\infty} \left[a_m \cos(\omega_m t) + b_m \sin(\omega_m t)\right], \tag{1.6}$$

where $\omega_m = 2\pi m/T$, and

$$a_m = \frac{2}{T}\int f(t)\cos(\omega_m t)dt, \quad b_m = \frac{2}{T}\int f(t)\sin(\omega_m t)dt, \tag{1.7}$$

are the so-called Fourier coefficients, after the French mathematician Joseph Fourier (1788-1830) who introduced this procedure in 1822. Closely related to this series expansion, one can consider the so-called Fourier transform, which decomposes a function into a continuous spectrum of its frequency components according to the expression

$$F(\omega) = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt. \tag{1.8}$$

Note that completely analogous expressions hold for periodic functions in space by simply replacing the corresponding variable in Eqs.(1.6)-(1.8). In this way, a Fourier transform can be envisioned as a linear transformation relating two different mathematical domains: that corresponding to usual time or space variables (which come closer to our everyday experience), and that corresponding to the related frequency or reciprocal space spectrum, which encloses a more abstract view of the underlying order in the considered phenomenon. Remarkably enough, there exist processes in Nature able to Fourier-transform material structures in a natural way, namely, diffraction of electromagnetic (x-ray) or matter quantum waves (electrons, neutrons) by atomic scatters in condensed phases. The resulting diffraction spectra exhibit regular arrangements of bright spots (the so-called Bragg peaks) disclosing the abstract information encoded within Fourier space to our eyes. In this way, the workings of Nature translate wave motion into geometrical patterns engraved in reciprocal space through the orchestrated interaction of matter and energy in condensed matter.

Diffraction spectra contain a lot of information about structural details which must be carefully analyzed, generally requiring a formidable task in the case of relatively complex structures. But a key, basic feature follows from the very mathematical definition of the Fourier transform: close spots in diffraction patterns correspond to scattering centers which are far apart in physical space. Accordingly, Fourier space description of crystal structures takes place in the so-called reciprocal space. In Fig.1.1 a celebrated example of diffraction pattern, ultimately leading to the elucidation of the double-helix structure of DNA, is shown for the sake of illustration. The cross-shaped arrangement of Bragg spots in reciprocal space is a characteristic telltale of the helicoidal distribution of sugar-phosphate groups in physical space. The two broad dark features located up and down the image correspond to the stacked nucleotides along the helix axis. We will study the physical implications of this impressive picture in more detail in Chapter 6.