

Chapter 1

The birth of molecular electronics

How does the electrical current flow through a single molecule? Can a molecule mimic the behavior of an ordinary microelectronics component or maybe provide a new electronic functionality? How can a single molecule be addressed and incorporated into an electrical circuit? How to interconnect molecular devices and integrate them into complex architectures? These questions and related ones are by no means new and, as we shall see later in this chapter, they were already posed many decades ago. The difference is that we are now in position to at least address them in the usual scientific manner, i.e. by providing quantitative experimental and theoretical results. The advances in the last two or three decades, both in nanofabrication techniques and in the quantum theory of electronic transport, allow us now to explore and to understand the basic properties of rudimentary electrical circuits in which molecules are used as basic building blocks. It is worth stressing right from the start that we do not yet have definitive answers for the questions posed above. However, a tremendous progress has been made in recent years and some concepts and techniques have already been firmly established. In this sense, one of main goals of this book is to review such progress, but more importantly, this monograph is intended to provide a solid basis for the new generation of researchers that should take the field of molecular electronics to the next level.

Molecular electronics, as used in this book, is defined as the field of science that investigates the electronic and thermal transport properties of circuits in which individual molecules (or an assembly of them) are used as basic building blocks.¹ Obviously, some of the feature dimensions of such

¹Molecular electronics, in the sense used here, should not be confused with organic electronics, the field in which molecular materials are investigated as possible constituents of a variety of macroscopic electronic devices.

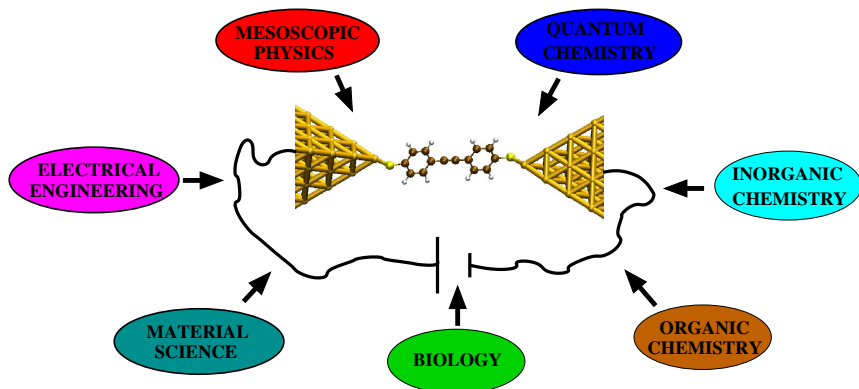


Fig. 1.1 Molecular electronics: An interdisciplinary field.

molecular circuits are of the order of nanometers (or even less) and therefore, molecular electronics should be viewed as a subfield of nanoscience or nanotechnology in which traditional disciplines like physics, chemistry, material science, electrical engineering and biology play a fundamental role (see Fig. 1.1). Molecular electronics, in the sense of a potential technology, is based on the bottom-up approach where the idea is to assemble elementary pieces to form more complex structures, as opposed to the top-down approach where the idea is to shrink macroscopic systems and components. Molecular electronics has emerged from the constant quest for new technologies that could complement the silicon-based electronics, which in the meantime it has become a true nanotechnology. It seems very unlikely that molecular electronics will ever replace the silicon-based electronics, but there are good reasons to believe that it can complement it by providing, for instance, novel functionalities out of the scope of traditional solid state devices. More importantly, molecular electronics has become in recent years a true field of science where many basic questions and quantum phenomena are being investigated. In this sense, the importance of molecular electronics is unquestionable and we are convinced that different traditional disciplines will benefit from advances in this new field.

In the rest of this introductory chapter, we shall first try to answer the questions of why it is worth pursuing molecular electronics research and why it is interesting to work in a field like this. Then, in section 1.2 we shall briefly review the complex history of this field to set the stage for this book. Finally, in section 1.3 we shall clearly define the scope of this

monograph and explain its structure.

1.1 Why molecular electronics?

Every researcher is sooner or later confronted with natural questions like “why do you work in your field?” or “what is your research good for?” Of course, the answers are always personal, but in the case of molecular electronics they also depend on whether one’s interests are closer to fundamental science or to technological applications. From the point of view of basic science, molecular electronics offers, for instance, the possibility to investigate electronic and thermal conduction at the smallest imaginable scale, where the physics is completely dominated by quantum mechanical effects. The small feature dimensions of molecular circuits together with the great variety of electrical, mechanical and optical properties of molecules can give rise to countless new physical phenomena. Molecular junctions are also ideal systems where to investigate and shed new light into the fundamental electron transfer mechanisms that play a key role both in chemistry and biology. These reasons and many others make molecular electronics a very attractive field of basic research. Moreover, we should never forget that the history of science proves that the exploration of new territories and the subsequent discovery of novel phenomena often lead to unexpected technological applications. History also teaches us that there is no technology without basic understanding and thus, the future of molecular electronics as an emerging technology depends on our ability to understand the fundamental mechanisms that govern the electronic conduction at the molecular scale.

From a technological point of view, there are also good reasons to investigate the use of molecules as electronically active elements for a variety of applications. In comparison with the silicon-based technology, which is already a nanotechnology in the sense that the structure sizes are in the range of nanometers,² molecular electronics could in principle offer the following major advantages [2]:

- Size. The reduce size of small molecules (between 1 and 10 nm) could lead to a higher packing density of devices with the subsequent advantages in cost, efficiency, and power dissipation.

²The next generation of transistors for advanced microprocessors will have gate lengths of 22 nm and a SiO₂ gate oxide thickness of less than 1.2 nm [1].

- Speed. Although most molecules are poorly conductive, good molecular wires could reduce the transit time of typical transistors ($\sim 10^{-14}$ s), reducing so the time needed for an operation.
- Assembly and recognition. One can exploit specific intermolecular interactions to form structures by nanoscale self-assembly. Molecular recognition can be used to modify electronic behavior, providing both switching and sensing capabilities on the single-molecule scale.
- New functionalities. Special properties of molecules, like the existence of distinct stable geometric structures or isomers, could lead to new electronic functions that are not possible to implement in conventional solid state devices.
- Synthetic tailorability. By choice of composition and geometry, one can extensively vary a molecule's transport, binding, optical, and structural properties. The tools of molecular synthesis are highly developed.

Molecules have also obvious disadvantages such as instabilities at high temperatures. Moreover, the fabrication of reliable molecular junctions requires sometimes to control matter at an unprecedented level, which can be not only difficult, but also slow and costly. Anyway, the advantages described above are sufficient to motivate the exploration of a molecule-based electronics.

1.2 A brief history of molecular electronics

It is always difficult to trace back the history of an emerging field and to summarize it in a few pages. Anyway, even at the risk of being unfair leaving out some important contributors, we find necessary to say a few words about the history of molecular electronics as a tribute to those visionary scientists that made possible that we are now working in this fascinating field. Our brief account here is partially based on a delightful (non-scientific) article by Choi and Mody [3], which reviews the history of molecular electronics paying special attention to its social aspects.

We start this historical review in 1950's, after the revolution in electronics due to the invention of the transistor and the subsequent introduction of integrated circuits. In that context and in view of the difficulties to radically miniaturize the existent electronic components, Arthur von Hippel,

a German physicist working at the MIT, formulated in 1956 the basis of a bottom-up approach that he called *molecular engineering* [4]. He argued:

Instead of taking prefabricated materials and trying to devise engineering applications consistent with their macroscopic properties, one builds materials from their atoms and molecules for the purpose at hand ...

The concept of molecular engineering introduced by von Hippel [5] led to the first notion of “molecular electronics”, which crystallized in a collaboration between the company Westinghouse and the US Air Force at the end of the 1950’s. Westinghouse had begun a program to implement von Hippel’s ideas and it applied for the financial support of the US Air Force, which at that time was receptive to new ideas and alternatives to the recently introduced integrated circuits. The Air Force organized a conference on “Molecular Electronics” and invited scientists and engineers from military and private research labs. In this conference, colonel C.H. Lewis, director of Electronics at the Air Research and Development Command, expressed the need for a *breakthrough* in electronics in the following way:

Instead of taking known materials which will perform explicit electronic functions, and reducing them in size, we should build materials which due to their inherent molecular structure will exhibit certain electronic property phenomena. We should synthesize, that is, tailor materials with predetermined electronic characteristic. Once we can correlate electronic property phenomena with the chemical, physical, structural, and molecular properties of matter, we should be able to tailor materials with predetermined characteristics. We could design and create materials to perform desired functions. Inherent dependability might eventually result. We call this more exact process of constructing materials with predetermined electrical characteristics MOLECULAR ELECTRONICS.

This is probably the first time that the term molecular electronics was used publicly, although it originally referred to a new strategy for the fabrication of electronic components, and it had yet little to do with the vision of using individual molecules as electronically active elements. Fig. 1.2 summarizes the vision of colonel Lewis, where molecular electronics should constitute be the next breakthrough in electronics, although it was not yet clear what molecular electronics was supposed to mean.

The collaboration between Westinghouse and the US Air Force, which started after the mentioned conference, lasted a few years and certain

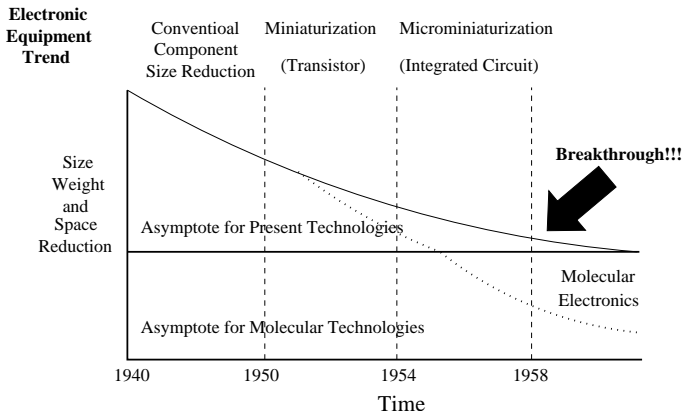


Fig. 1.2 Graph presented by colonel Lewis of the US Air Force in the first conference on molecular electronics held in November 1958. Here, one can see the trend in the miniaturization of the electronic components during the 1940's and 1950's. According to Lewis, molecular electronics should have constituted the next breakthrough in electronics by the end of the 1950's. Adapted from [3].

progress was indeed made in the development of new fabrication strategies. However, these initiatives were not able to compete with the steady miniaturization of the semiconductor-based electronic devices and they were soon abandoned.

From a more scientific point of view, one can consider that molecular electronics, as we understand it today, started at the end of the 1960's and the beginning of 1970's. At that time, different groups started to investigate experimentally the electronic transport through molecular monolayers. For instance, Hans Kuhn, a Swiss chemist working at the University of Göttingen, and his coworkers studied at that time new ways of fabricating the so-called Langmuir-Blodgett films.³ They were able to not only master the fabrication of these molecular films, but also to sandwich them between metal electrodes and to measure the electrical conductivity of the resulting junctions. In Fig. 1.3 we reproduce the experimental results of Ref. [6] for the low-bias conductivity of Al/ $S(n)$ /Hg junctions, where $S(n)$ stands for a monolayer of Cd salt of fatty acid $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOH}$ of different chain lengths. There one can see the exponential decay of the conductivity with the length of the molecules, which is still a very important issue in today's

³A Langmuir-Blodgett film contains one or more monolayers of an organic material, deposited from the surface of a liquid onto a solid by immersing the solid substrate into the liquid. A monolayer is adsorbed homogeneously with each immersion or emersion step, thus films with very accurate thickness can be formed.

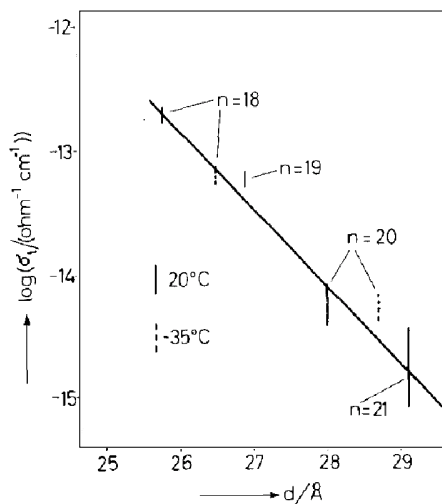


Fig. 1.3 Measurements of the low-bias tunneling conductivity (σ_t) vs. the distance (d) between the electrodes in Al/ $S(n)$ /Hg junctions. Here, $S(n)$ stands for monolayers of Cd salt of fatty acid $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOH}$ with different lengths (n ranges between 18 and 21). The solid line is a linear fit to the experiment data. The measurements were performed at two different temperatures: 20 and -35°C . Reprinted with permission from [6]. Copyright 1971, American Institute of Physics.

molecular electronics (see Chapter 13). This type of experimental results can be considered as the starting point of molecular electronics as a modern field of science.

The idea of molecular electronics reappeared in the States at the beginning of the 1970's at IBM and thanks to the enthusiasm of Ari Aviram, a synthetic chemist. Aviram was working at that time on charge-transfer salts, which had recently been discovered to be reasonably good conductors in their solid form. Although Aviram's task at IBM was to synthesize new types of charge-transfer salts, he started working on the theory of electron transfer through single organic molecules in collaboration with Mark Ratner,⁴ at that time at New York University. In the course of their investigations, Aviram and Ratner saw a clear analogy between charge-transfer salts like TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane), with a functional unit (TTF) rich in electrons and another unit (TCNQ) poor in electrons, and traditional semiconductor diodes. In 1974 they published a now-famous paper on "molecular rectifiers" [8] in which they described

⁴Indeed Ratner was officially Aviram's thesis advisor during that time.

how a modified charge-transfer salt could operate as a traditional diode in an electrical circuit. This is probably the first proposal to use a single molecule as an electronic component, which is something that lies at the heart of the modern molecular electronics. Aviram and Ratner's idea was considered during a long time a theoretical curiosity that could not be tested experimentally and in this sense, it did not have much impact in the scientific community at that time.

In the late 1970's and early 1980's other scientists started to work on ideas similar to Aviram-Ratner's unimolecular concept. Let us mention for instance the name of Forrest Carter, a chemist at the Naval Research Laboratory, who was certainly influenced by Feynman's (1960) famous "Room at the Bottom" speech [9]. Carter introduced concepts such as molecular computing or cellular automata, where the essence was to use individual molecules as the ultimate electronic components or as elementary units where to store bits of information in a hypothetical molecular computer. These ideas were to a large extent purely theoretical and they were not supported by real experiments. However, Carter was able to nucleate a first molecular electronics community around him and, in particular, the organization of a series of conferences on molecular electronics in the 1980's played an important role in the history of this field. People like Robert Metzger, Mark Reed and others, who played later an important role in molecular electronics, attended those conferences and they were inspired by the discussions held there.

As for many other fields in nanoscience, the invention of the scanning tunneling microscope (STM) by Gerd Binnig and Heinrich Rohrer (at IBM Zurich) in 1981 [10, 11] changed the panorama for molecular electronics. The STM was the first tool that provided a practical way to "see", "touch", and manipulate matter at the atomic scale (see Fig. 1.4). Soon after its invention, it became clear to the STM could provide a realistic way to address single molecules and to study their electronic transport properties.

Since the original experiments of Kuhn and coworkers [7], many different groups studied the electrical conductivity through Langmuir-Blodgett (LB) multilayers and even monolayers. For instance, Fujihira and co-workers demonstrated an LB monolayer photodiode already back in 1985 [13], which is probably the first unimolecular electronic device. In the 1990's one of the main goals in this context was to confirm the ideas of Aviram and Ratner about unimolecular rectification. The Aviram-Ratner mechanism, slightly modified, was confirmed by Robert Metzger's group in both macroscopic and nanoscopic conductivity measurements through a monolayer of

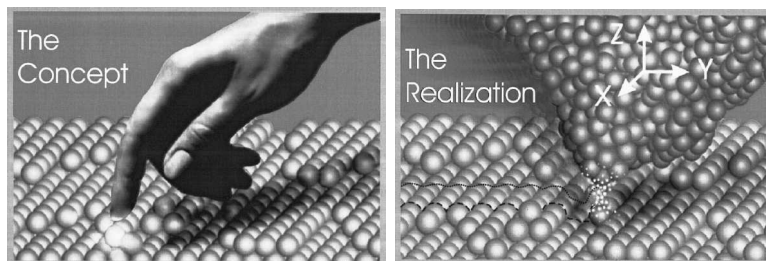


Fig. 1.4 Principle of a local probe like the scanning tunneling microscope: The gentle touch of a nanofinger. If the interaction between tip and sample decays sufficiently rapidly on the atomic scale, only the two atoms that are closest to each other are able to “feel” each other. Reprinted with permission from [12]. Copyright 1999 by the American Physical Society.

γ -hexadecyl-quinolinium tricyanoquinomethanide in 1997 [14].

At the end of the 1980's and the beginning of the 1990's the appearance of the metallic atomic-sized contacts had an important impact in the nanoscience community. Different groups showed that the STM and the recently introduced mechanically controllable break junction (MCBJ) technique⁵ could be used to fabricate metallic wires of atomic dimensions (for a review, see Ref. [15]). Since then these nanowires have become an endless source of new physical phenomena and have played a crucial role in the fields of mesoscopic physics and nanoelectronics. The relevance of these systems for molecular electronics is two-fold. On the one hand, they provide the basis to contact individual molecules with dimensions on the range of a few nanometers, which is out of the scope of conventional lithographies. On the other hand, the atomic contacts (or atomic-size contacts) have allowed establishing the connection between the quantum properties of single atoms and the macroscopic electrical properties of the circuits in which they are embedded, which is an important lesson for molecular electronics.⁶

In 1997 the collaboration between the groups of Mark Reed (a physicist at Yale University) and James Tour (a synthetic chemist at the University of South Carolina) led to the publication of the results of what is often considered as the first transport experiment in single-molecule junctions [16].⁷ These authors used the MCBJ technique to contact benzenedithiol

⁵This technique will be described in the next chapter.

⁶The physics of these metallic nanowires will be described in the third part of this monograph.

⁷Let us clarify that the first transport measurements involving single molecules were indeed performed with the STM, but the experiment of Reed *et al.* is the first one realized

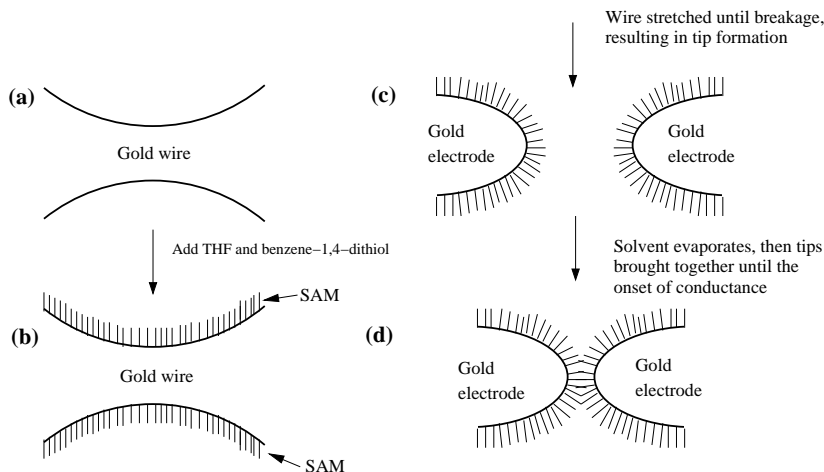


Fig. 1.5 Schematics of the first transport measurements through single-molecule junctions performed with the MCBJ technique [16]. (a) The gold wire of the break-junction before breaking and tip formation. (b) After addition of benzene-1,4-dithiol, self-assembled monolayers (SAMs) form on the gold wire surfaces. (c) Mechanical breakage of the wire in solution produces two opposing gold contacts that are SAM-covered. (d) After the solvent is evaporated, the gold contacts are slowly moved together until the onset of conductance is achieved.

molecules with gold electrodes (the principle of this experiment is schematically illustrated in Fig. 1.5).⁸ The importance of this experiment is that it triggered off the realization of many others in the same spirit. Indeed, our review on single-molecule conduction in the last part of this book will cover the activities from the appearance of this experiment on.

At the end of the 1990's new experimental techniques were introduced and additional results were reported showing that molecules can indeed mimic the behavior of ordinary microelectronics components. Thus for instance, Reed's group adapted the so-called nanopore technique (see Chapter 3) to form metal-self-assembled monolayer-metal heterojunctions. With this technique it was shown that junctions based on certain organic molecules can exhibit, for instance, rectifying behavior [17] or a very pronounced negative differential resistance [18]. On the other hand, James Heath and Fraser Stoddart groups joined efforts to show that junctions based on rotaxanes and catenanes could act as reconfigurable switches [19, 20].

in a symmetric structure that could in principle be integrated in more complex circuits.

⁸This experiment will be described in detail in section 14.1.1.

Techniques like electromigration [21], which were specially designed to contact single molecules, were developed at the turn of the century. These methods made possible to incorporate a gate electrode in single-molecule junctions and thus, to mimic the measurements performed in solid state devices like transistors or in nanostructures like quantum dots. With the use of these techniques it was possible to show that single-molecule junctions can behave as a new kind of single-electron transistors [22] or that they can exhibit basic physical phenomena like Coulomb blockade or the Kondo effect [23, 24], which are well-known in the context of other nanoscopic structures.

These results obtained in academic institutions and research laboratories attracted the attention of global players in information technology like HP, IBM and others that decided to set up small molecular electronics research groups. This gave a new impulse to the field by providing very important missing ingredients like, for instance, strategies to link molecular devices with each other and with external systems. As an example we can mention the nanoscale circuits based on a configurable crossbar architecture introduced by Stanley Williams and coworkers at the HP Laboratories in Palo Alto [25], see Fig. 1.6(a-d). This strategy was used, for instance, to show that molecular crossbar circuits fabricated from a molecular monolayer of [2]rotaxanes can function as an ultra-high-density memory [26], see Fig. 1.6(e-f). The working principle of these molecular memories is supposed to be based on the ability of molecules like rotaxanes to switch between two metastable states upon the application of an external bias voltage. The actual origin of the switching behavior in these molecular junctions has been heavily debated and, in some cases, it has shown that the metal electrodes or the metal-molecule interface are responsible for the switching mechanism rather than the molecules themselves (see e.g. Ref. [27]). The controversy about these results, and also about some of the original experiments mentioned above, led to the extended belief that molecular electronics was going through a midlife crisis [28], although it was no more than a teenager. In the meantime, the situation concerning the molecular memories has been clarified to a large extent and more recently the densest memory circuit ever made (10^{11} bits cm^{-2}) was fabricated using a monolayer of bistable [2]rotaxane molecules as the data storage elements [29]. Although many scientific and engineering challenges, such as device robustness, remain to be addressed before these devices can be practical, these results show clearly the potential of a molecule-based electronics.

On the other hand, the efforts in recent years of numerous research

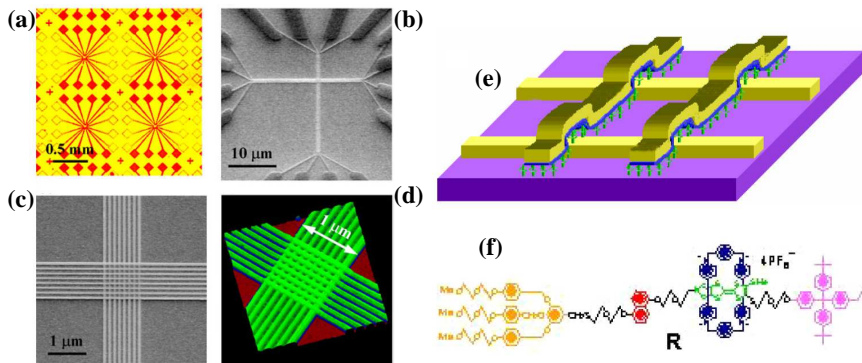


Fig. 1.6 Nanoscale molecular-switch crossbar circuits. (a) An optical microscope image of an array of four test circuits, showing that each has 16 contact pads with micron-scale connections leading to nanoscale circuits in the center. (b) An image taken with a scanning electron microscope (SEM) showing two mutually perpendicular arrays of nanowires connected to their micron-scale connections. (c) A SEM image showing that the two sets of nanowires cross each other in the central area. (d) A 3D image of the crossbar taken with an atomic force microscope. (e) Schematic representation of the crossbar circuit structure in which monolayer of the [2]rotaxane is sandwiched between an array of Pt/Ti nanowires on the bottom and an array of Pt/Ti nanowires on the top. (f) Molecular structure of the bistable [2]rotaxane **R**. Reprinted with permission from [26]. Copyright 2003 IOP Publishing Ltd.

groups world-wide have established molecular electronics as a true field of science, where there is a lot of new physics and chemistry to be learned. Although it is still difficult to fabricate reliable molecular junctions, in particular at the single-molecule level, and there are other basic problems to be solved, many concepts and techniques are by now well established and they are precisely the subject of this book. For us, it is clear that molecular electronics has reappeared this time to stay forever with us. In the next years we shall surely contemplate many basic discoveries in this field and some of them will hopefully lead to new and unforeseen technological applications.

1.3 Scope and structure of the book

By now molecular electronics is a very broad field with many different interesting aspects and special topics. These topics can be divided in a natural way into those related to the development and potential applications of molecular devices and those concerning the novel physical phenomena that

take place in molecular-scale junctions. In this monograph we are interested in the latter type of topics and, in particular, we shall focus our attention on the understanding of the basic mechanisms that dominate the electronic transport at the molecular scale. To be precise, we shall concentrate on the analysis of the properties of single-molecule junctions, although some examples of junctions based on molecular assemblies will also be presented and discussed.

Our main goal in this monograph is two-fold. On the one hand, we want to provide a true textbook on molecular electronic for advanced undergraduate and graduate students both in physics and chemistry. The book has been designed so that, by the end of it, a student with a background in quantum mechanics and some elementary notions of solid state physics⁹ and organic chemistry¹⁰ should be able to start doing research in the field of molecular electronics. On the other hand, we also want to provide a thorough review of the activities on single-molecule conduction over the last ten years, from which both newcomers and researches working in the field can profit.

With this double goal in mind, we have divided this monograph into four parts that can be read independently.¹¹ The first two are meant as textbook material that can be used for a regular course, while the last two ones are closer to a topical review. Part 1 includes, apart from this introductory chapter, a detailed description of the experimental techniques that are currently being used to fabricate both atomic-scale wires and molecular junctions as well as the basic principles of transport measurements. Here, we have tried to explain both the basis of the different techniques as well as their advantages and disadvantages. Moreover, we have included in section 3.2 a brief discussion about the main molecules used in molecular electronics and their basic properties, which can be viewed as an accelerated course in organic chemistry.

Part 2 contains an extensive theoretical background that provides a basic introduction both to the transport mechanisms in nanoscale systems and to the standard theoretical techniques that are used to describe the transport in molecular systems. We want to stress that this theory part is not just meant for theoreticians and theory-inclined students, but for every-

⁹For the students in chemistry we recommend the brief introduction to solid state physics provided in Chapter 4 of Ref. [30] or in Chapter 3 of Ref. [31].

¹⁰For the students in physics we recommend the brief introduction to organic chemistry provided in Chapter 5 of Ref. [31].

¹¹There is indeed a fifth part that contains an appendix about the second quantization formalism of quantum mechanics.

body. All the topics are discussed in a didactic and self-contained manner so that students without a previous knowledge on these topics should be able, after reading this part, to follow the theory papers in this field. To be precise, this part starts in Chapter 4 with an introduction to the scattering (or Landauer) approach, which provides an appealing framework to describe coherent transport in nanostructures. Then, we go on with several chapters devoted to Green's function techniques (Chapters 5-8), which provide powerful tools to compute equilibrium and nonequilibrium properties of atomic-scale junctions beyond the capabilities of the scattering approach. Finally, Chapters 9 and 10 deal with the two most widely used electronic structure methods in molecular electronics, namely the tight-binding approach and density functional theory. These methods in combination with the Green's function techniques provide the starting point for the realistic description of the transport properties of atomic and molecular junctions. Let us emphasize that at the end of every chapter one can find several exercises that have been chosen to illustrate the main concepts.

Part 3 presents a basic description of the physics of atomic-sized contacts. Although this is not the main topic of the book, it is crucial to have a basic knowledge about the transport properties of the metallic wires that are then used as electrodes in molecular junctions. We have divided this part into two chapters where we describe the physics of non-magnetic atomic contacts (Chapter 11) and magnetic ones (Chapter 12).

Finally, Part 4 presents a detailed review on the transport through molecular junctions. We have organized the material according to the physical mechanism which dominates the transport properties. Thus, we start this part with two chapters devoted to the coherent transport in molecular junctions (Chapters 13 and 14). Then, we discuss in Chapter 15 the physics of the so-called molecular transistors, which are nothing but weakly coupled molecular junctions where the transport is dominated by electronic correlations that lead to phenomena like Coulomb blockade or the Kondo effect. We then proceed to discuss in Chapters 16 and 17 the role of molecular vibrations in the electrical current through molecular junctions. Chapter 19 is devoted to other transport properties beyond conductance and we discuss there, in particular, shot noise and thermal transport in molecular conductors. The optical properties of current-carrying molecular junctions are the subject of Chapter 20. Chapter 18 deals with the electronic transport in long molecules where the hopping (or incoherent) transport regime is realized. Finally, we conclude this part in Chapter 21 with a list of topics that have not been addressed in this monograph and we indicate where to

find information about them. It is worth remarking that these chapters have been written so that they can be read almost independently. This way a reader can concentrate on those topics or chapters that are of special interest for him/her.

Parts 3 and 4 are meant for both students and researchers working in the field. We do not only review what has recently been done in the field, but we also introduce the different topics at a elementary level. In this sense, whenever it was possible, we have provided simple arguments and suggested additional exercises. These two parts are intended for both experimentalists and theoreticians and, most of the time, we have intentionally avoided the typical separation between experiment and theory, which we find particularly harmful in this field.

Let us close this chapter with some recommendations about the existent literature. For those who want a quick overview about molecular electronics, we recommend the short reviews of Refs. [2, 32–37]. A nice general overview of the field can be found in Chapter 20 of Ref. [31]. For more extensive introductions, we recommend Ref. [38] for the theory in molecular systems and Refs. [39–41] for a discussion of the experimental techniques used in molecular electronics. There already exist several books that deal with different aspects of molecular electronics, see e.g. Refs. [42–49]. Most of them consist of a collection of articles written by different authors, but they are very useful if one wants a more detailed discussion of certain topics. Concerning the theory of quantum transport or transport in nanoscale systems, which is one of the central subjects of this manuscript, we recommend the monographs of Refs. [50–53].