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An Overview On Birth of Molecular Electronics

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Abstract

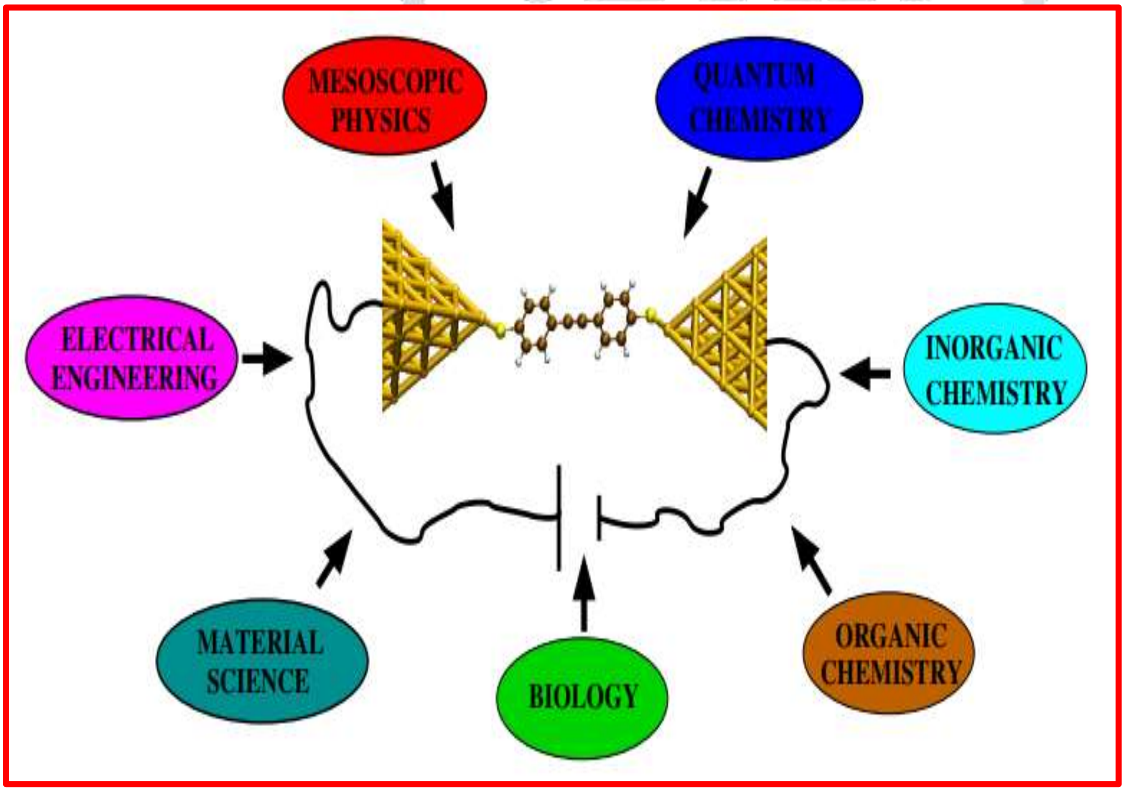
How does the electrical current flow through a single molecule? Can a molecule mimic the behaviour of an ordinary microelectronics component or maybe provide a new electronic functionality? How can a single molecule be addressed and incorporated into an electrical circuit? How to interconnect molecular 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 paper, 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 paper 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 paper, is defined as the field of science that investigates the electronic and thermal transport properties of circuits in which individual molecules (or assemblies of them) are used as basic building blocks. Obviously, some of the feature dimensions of such molecular circuits are of the order of Nano meters (or even less) and therefore, molecular electronics should be viewed as a subfield of Nano science or nanotechnology in which traditional disciplines like physics, chemistry, material science, electrical engineering and biology play a fundamental role. 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 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 it is fair to say that different traditional disciplines are benefiting from advances in this field.

Keywords: electronic transport, molecular electronics, silicon-based electronics.

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 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 unforeseen 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 Nano meters, molecular electronics could in principle offer the following major advantages.



Molecular electronics: An interdisciplinary field.

•**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

•Speed. Although most molecules are poorly conductive, good molecular wires could reduce the transit time of typical transistors (~ 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 behaviour, 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 tailor ability. 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.

A brief history of molecular electronics

It is always difficult to trace back the history of an 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. 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. 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 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

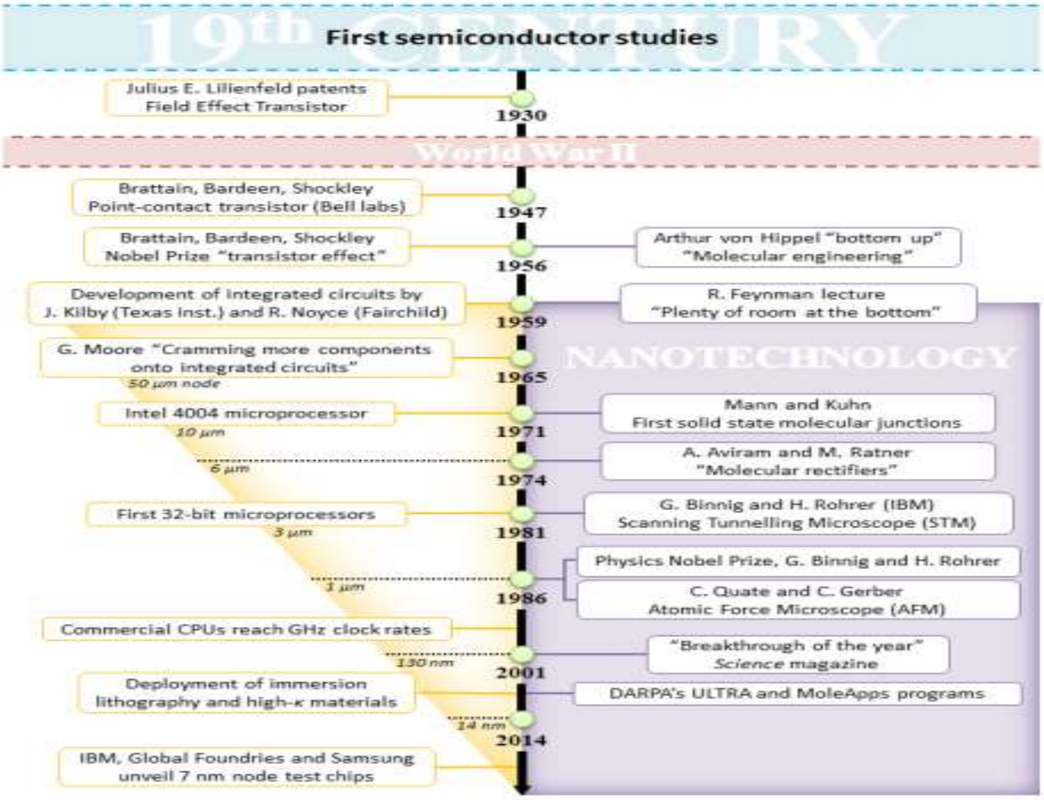
MOLECULAR ELECTRONICS

Molecular electronics is an interdisciplinary field that involves the use of molecules as fundamental electronic components such as wires, transistors, memory cells, and logic elements. The field, sometimes called "moletronics", [1] is currently attracting attention from a broad cross-section of the scientific community in response to both fascination with the fundamental scientific challenges associated with the measurement of the electrical properties of molecules, and manipulation of electronic phenomena via molecular processes, [2] and growing concerns over the technological challenges and ultimate limits facing solid state semiconductor technology. [3] Before entering discussion, a distinction needs to be made between molecular materials for electronics and single molecule electronics. The use of organic materials for electronic applications in which the bulk electronic or optoelectronic response arises from ensembles of several millions of molecules, and for which properties are measured or observed on the macroscopic level, is at a mature stage of development and application. The most obvious examples of molecular materials readily available in the electronics mass market are the use of liquid crystals and organic light emitting diodes (OLEDs) in flat video displays [4] This sector of the electronics industry continues its steady development driven by the promises of transparent, flexible, non-toxic, printable electronics, with improved consumer appeal and reduced fabrication costs. However, the field of single molecule electronics, which is the subject of this review, can be summarised as the use of individual molecules to mimic functional elements in electronic devices. The use of molecules as building blocks to give rise to a more complex system is typically referred to as a the "bottom-up" approach, as opposed to the conventional "top-down" lithographic techniques that are employed to etch small features into single-crystal silicon wafers. Despite, or perhaps because of, the great challenges the field of single molecule electronics presents, the enormous benefits of a molecule-based "bottom-up" approach motivates the scientific community to keep moving the field forward. For example, a typical computer microchip nowadays contains of the order of

10^9 transistors in areas of about 3 cm 2 with all its components working in perfect harmony and capable of changing state in response to an input signal at an astonishing rate and for an almost unimaginable number of cycles. The enormous challenge for single molecule electronics lies in the development of molecular systems that perform in some way better than, or perhaps provide an alternative function to, these extraordinary solid-state devices.

Molecular and semi-conductor electronics

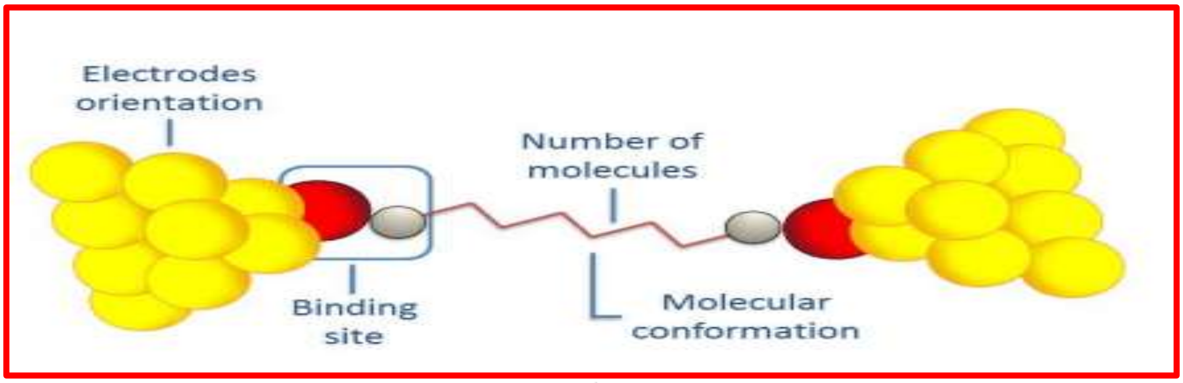
a brief account of an interwoven history to comprehend the incentives that drive the development of molecular electronics (Fig1,right), it is necessary to first appreciate the evolution of the silicon microelectronics industry (Fig1,left). [5] The first experiments concerning the electrical properties of semiconductor materials began early in the 19th century. The surprising properties of these materials, such as their increased conductance when heated or exposed to light, captured the attention of scientists and engineers of the time. Amongst the most renowned contributors of the time are Michael Faraday, who first reported the conductance increase with temperature in silver sulfide (1833), Alexandre Edmond Bequerel, father of the photovoltaic effect (1839), and Alexander Graham Bell who in 1880 took advantage of photo-sensitivity of selenium to transmit sound over a beam of light, inadvertently heralding the fiber-optic communications revolution of the 21st Century, with a remarkable invention that he named the “photophone” (US235199A). In spite of the potential of these early experiments, it is the development of the solid-state transistor that might best be considered to mark the beginning of the semiconductor revolution. Shortly after the end of World War II (1947) Walter Brattain, John Bardeen and William Shockley of Bell laboratories discovered that by applying a small bias to the surface of a germanium block, the current flow through a second circuit connected to that piece of germanium could be modulated, thereby providing the first demonstration of a solid-state transistor.



Fig(1) Silicon industry and molecular electronics roadmap, from the genesis of the first solid-state transistor to our days.

Molecular junctions

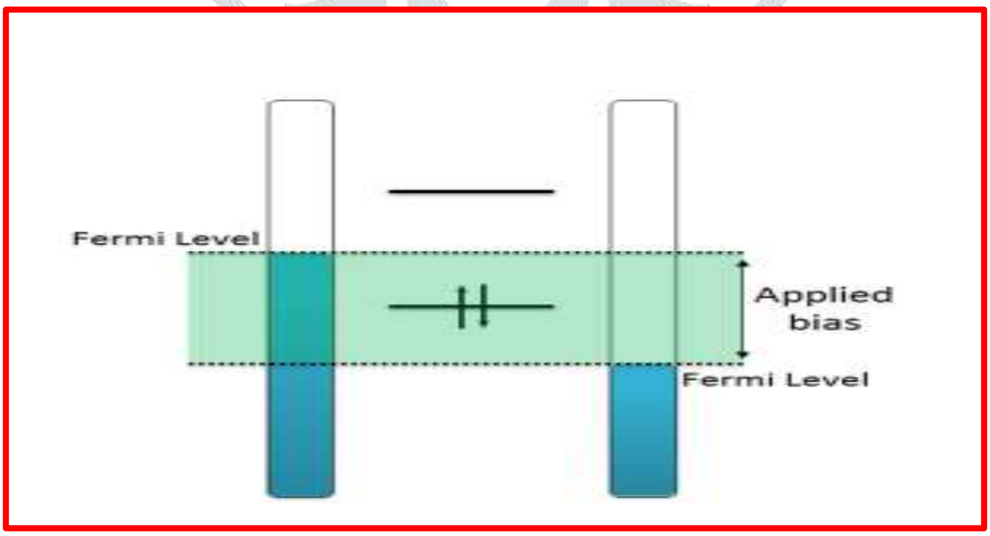
A molecular junction consists of a molecule suspended or sandwiched between two (usually metallic) electrodes. When a molecule is brought in contact with a metallic electrode, the molecular orbitals and the electrode states overlap to a certain extent to form a new hybrid electronic wave function. The degree of coupling may vary from conjugated states extending over the whole molecular junction, to the generation of orbital nodes along the junction acting as barriers to electronic transport between the electrodes. Despite the great progress made in this field, and the apparent simplicity of the sandwich style molecular junction (Figure 2), a full theoretical description of metal |molecule |metal junctions and a detailed understanding of structure-property relationships, remain as challenges.



Fig(2). Schematic representation of a fully characterized molecular junction where: binding sites; electrodes orientation; molecular conformation and number of molecules are accurately characterized.

On the basis of the plethora of studies on molecular junctions that have been reported over the past decade, it has been noted that the conductance of a molecular junction can be affected by several factors such as: the structure and degree of conjugation of the molecular bridge;[26] the nature of the linker group and its geometry;[27] the junction geometry (tilt angles and gap size);[28] and the electronic character of substituents on the molecular backbone.[29].

A simplified electronic description of a molecular junction involving two electrodes bridged by a molecule can be seen in Fig(3). Both electrodes are described as a continuum of energy levels filled up to a given energy level (Fermi level), the energy symmetry between both electrodes is broken by the applied bias. On the other hand, the bridging molecule is characterized by discrete energy levels filled up to the HOMO. Importantly, the orbital alignment relative to the electrode Fermi level is directly characteristic of each molecular junction and dependant on several factors such as: the nature of the molecular bridge; the nature of the metal-molecule interaction;[27e] the electronic and conformational changes induced by the charge transfer; environmental effects[25b] and redox state.



Fig(3). Simplified description of the electronic diagram in a molecular junction.

Charge transport in molecules contacted by macroscopic electrodes is best described by the Landauer formalism. In this description electrons are treated as waves that can be reflected or transmitted through the molecular bridge. According to the Landauer formalism the conductance G of a molecular junction can be calculated (Equation 1)

$$G = \frac{2e^2}{h} \sum n \, T_n$$

where e is the electron charge, h is Planck's and T_n are the transmission coefficients of the individual transport channels. According to this expression, the conductance of a system G, is the summation of all possible individual transmission channels. Perhaps the most relevant implication of this equation is that conductance at the molecular level is quantized. For a perfect coupling i.e. ballistic conductors ($T_n = 1$), the conductance can only increase or decrease in units of the quantum of conductance $G_0 = 2e^2/h \sim 77481$ nS. It is important to clarify that the Landauer formalism does not imply that the conductance of any system must be an integer of G_0 however it defines the maximum

Conclusion and future prospects in molecular electronics

Since its inception some 60 years ago the field of molecular electronics has surged, ebbed, and surged with conceptual, technical and scientific advances. The great advances in our understanding of the unique and complex nature of charge transport at the molecular level, together with a growing and increasingly recognised industrial need, may, perhaps finally, see the potential of molecular electronics realised. Through the wider access to the experimental tools that allow single molecule measurements, many new charge transport phenomena beyond the simple ballistic electron transport have been identified. Amongst those phenomena, molecular rectifying (redox, thermal or mechanic), quantum-interference, spintronics and optoelectronics are now being actively pursued, and open avenues for exploration of both organic compounds and metal complexes. In addition, theoretical models and computational methods based on the non-linear Green's function (NLGF) are providing the theoretical base required to fully understand the transport process at the nano-scale. A full description of the theoretical rules that drive the molecular conduction is of great importance as it would lead to molecular behaviour prediction and therefore to a rational design of the molecules. Molecular electronics seems predestined to converge with the highly developed semiconductor industry, in a curious reunification of ideas shared a common heritage and conceptual beginning. The great effort now being devoted to increase the compatibility of molecular electronics with the fabrication methods employed by the semiconductor industry heralds a new initiative in realising a true molecular electronics technology [23].
Computing with molecules as circuit building blocks is an exciting concept with several desirable advantages over conventional circuit elements. Because of their small size, very dense circuits could be built, and bottom-up self-assembly of molecules in complex structures could be applied to augment top-down lithography fabrication techniques. As all molecules of one type are identical, molecular switches should have identical characteristics, thus reducing the problem of variability of components. However, the success of molecular electronics depends on our understanding of the phenomena accompanying molecular switching, where currently many questions remain The obstacles to this goal should be seen as challenges for the scientific community, acting as motivation and defining the long-term goals of the field. In the words of Heath and Ratner, on the molecular electronics horizon should be placed a very robust, energy-efficient, connected to the outside world, computational platform based on molecular electronics with a bit density of 10^{12} cm^{-2} . The great advances needed to accomplish that goal, would make it hard to believe that an electronic device will be the most significant result of such an effort.

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