Preface

At present, we observe a long-lasting process of miniaturization of electronic devices. The ultimate limit for the miniaturization of electronic components is set by the atomic scale. However, in the case of conventional "top-down" fabrication methods and usual semiconductor materials, the smallest attainable size of the electronic components is well above this ultimate limit. Many ways for further miniaturization have been and still are suggested, including those using graphene and carbon nanotubes. The idea of using molecules as elements in electronic devices was first suggested in the seminal work by Aviram and Ratner [1], where they did envision a diode made out by assembling several diverse components into a single molecule creating a donor–bridge–acceptor combination. This work had been published in 1974 well before any clear indications within the electronic industry for the need of molecular or any other novel material technologies. However, further development of electronics brought a new interest and greatly increased research activities in this field. These activities in the field of molecular electronics reflect the convergence of two trends in the fabrication of nanodevices, namely, the "top-down" device miniaturization through lithographic methods and "bottom-up" device manufacturing through atom-engineering and self-assembly approach. The principal goal of molecular electronics is to construct electronic circuits in a "bottom-up" fashion, so that specifically designed molecules could take parts of active components as well as interconnects. Presently, molecular electronics is known to be one of the most promising developments of nanoelectronics, and the last two decades have seen an extraordinary progress in this field [2–6]. As discussed in the existing literature, the most important advantages of molecules as elements of nanodevices could be summarized as follows [5]:

- Smallness of molecules provides a faster charge transport through molecular channels and opens up opportunities for greater packing densities and higher functionalities on a chip.
- Lower heat dissipation in molecular mechanical devices which originates from typically low currents and small separation in excitations (as in conformationally mediated transitions). Switching energies of molecular mechanical devices are

expected to take on values several orders of magnitude less than those typical for the start-of-the art transistors.
- Organic chemistry and self-assembly which should be used to fabricate molecular electronic devices are significantly less expensive than the lithographic patterning typically employed in silicon-based microelectronics.
- Using molecules as building blocks of nanodevices gives means to circumvent difficulties occurring due to the necessity of patterning channels for the charge transport out of larger templates. Dealing with molecules, one may bypass these difficulties by exploiting their ability to self-assemble on various substrates.
- Potentially, molecules could be assembled in multilayers using Langmuir–Blodgett techniques. This would allow circuits including the molecules as active elements and/or interconnects to grow in the third dimension, thus creating opportunities to build up devices with complex and reconfigurable architectures.
- Silicon-based electronics has limitations caused by properties of the silicon which is characterized by a certain set of parameters that are hard to significantly change. Naturally, heating, doping, straining, and alloying of silicon offer some variability to characteristics of this material, but this variability is quite small when compared with much greater variability which organic molecules can easily accomplish just by modification of their side groups.

Successful transport experiments on molecules [7–17] confirm their significance as active elements of nanodevices. These include applications as rectifiers (molecular diodes), field effect transistors (molecular triodes) switches, memory elements, and sensors. However, it is necessary to remark that, to a significant extent, the advantages of molecule-based electronics still remain potentialities rather than established facts. In many cases the molecules do not really behave as anticipated, and performance of existing molecular-based devices needs significant improvement to make them suitable for industrial applications. This means that further and deeper understanding of processes determining transport characteristics of molecules is necessary to achieve. This is especially important in view of the fact that in the last two decades this particular research field has been suffering through a state of flux which was ranging from exaggerated optimism to clearly expressed pessimism. Currently, the situation is improving. Recent experiments are reporting higher yields and become reproducible between diverse research groups. Also, better agreement between theory and experiment is being achieved [6, 18]. All these emphasize the above-mentioned importance of thorough analysis of the physics underlying electron transport through molecular junctions. Detailed understanding of the electron transport at the molecular scale is a key step to device designing and controlling. Theory of electron transport through MMMs is being developed in the last two decades, and main transport mechanisms are currently elucidated in general terms. However, progress of experimental capabilities in the field of molecular electronics brings new theoretical challenges causing further development of the theory.

The key element and basing block of molecular electronic devices is a junction including two metal electrodes (leads) linked by a molecule. Usually, the electrodes

are microscopically large but macroscopically small contacts which may be connected to a battery to provide the bias voltage across the junction. Accordingly, most of the theoretical and experimental studies so far have been concentrated on various aspects of electron transport through such systems known as metal–molecule–metal (MMM) junctions. A molecule included into the junction may be treated as a quantum dot coupled to the charge reservoirs. The discrete character of energy spectrum on the dot (molecule) is combined with nearly continuous energy spectra on the reservoirs (leads) occurring due to their comparatively large size, and this combination determines transport properties of the junction. To a considerable extent, transport characteristics of a certain MMM depend on the composition and structure of the molecular linker. It opens opportunities to take advantage of the variability of chemical compounds to design MMMs with the desired properties for use as elements in molecular electronic devices, so the molecular electronic research often requires participation of chemists as well as physicists. Therefore, molecular electronics is a multidisciplinary research field. Also, the coupling between the molecule and the leads significantly affects the transport properties of MMMs. As a part of a MMM, the molecule is turned into a open system electronically hybridized with the contacts, often making it difficult to ascertain where the molecule ends and the leads begin. Significant hybridization may occur even in the case of well-defined molecules put in contact with metal electrodes. As a result, molecular linkers in MMM junctions often behave similar to other open systems such as carbon nanotubes.

In practical molecular junctions the electron transport is always accompanied by nuclear motions in the environment. Accordingly, the MMM conduction is affected by the coupling between electronic and vibrational degrees of freedom. Nuclear motions underlie the interplay between the coherent electron tunneling through the junction and inelastic thermally assisted hopping transport [2]. Also, electron–phonon interactions may result in polaronic conduction [19, 20], and they are directly related to the junction heating [21] and to some specific effects such as alterations in both shape of the molecule and its position with respect to the leads [22, 23]. The effects of electron–phonon interactions may be manifested in the inelastic tunneling spectra (IETS), which present the second derivative of the current in the MMM d^2I/dV^2 versus the applied bias voltage V [24–26]. The inelastic tunneling spectroscopy may be a valuable method for identification of molecular species within the conduction region, especially when employed in combination with scanning microscopy. However, one may remark that the theory suggested so far needs further development to ease its application to practical MMMs.

To a significant extent, the specifics of the interplay between different transport mechanisms depend on the molecule size. Usually, electron transport through small individual molecules is nearly ballistic, and it may be reasonably considered as coherent resonance tunneling. As the size of the relevant molecule increases, the contribution from stochastic nuclear motions to the molecular conduction strengthens, destroying the coherence and removing the interference effects. Exploring electron transport through macromolecules such as proteins and DNA, one must emphasize incoherent scattering and consider thermally assisted intermolecular

hopping as the predominating transport mechanism. Accordingly, there exist a hierarchy of models suitable for analyzing the transport properties of MMM junctions. The hierarchy is built up based on the fact that the increasing degrees of dephasing in the transport require decreasing amounts of quantum mechanics in the corresponding theoretical model. So, as the dephasing strengthens one must move from multielectron rate equations and coherent quantum kinetics to semiclassical Boltzmann approach and then to classical diffusion equations.

As well, transport characteristics of molecular junctions could show effects originating from electron–electron interactions, which give rise to such interesting quantum transport phenomena as Coulomb blockade and Kondo effect. Both suppression of the electron transport through molecular junctions at low values of the bias voltage occurring due to the charging energy in the molecule (Coulomb blockade) and the increase in the electrical conduction of the junction near zero bias voltage (Kondo effect) were observed in experiments on molecular and carbon nanotube junctions [3, 8, 27–33]. Theory of electron transport through MMMs and quantum dots taking into account electron–electron interactions on the dot is being developed (see, e.g., [34–37] and references therein). However, this theory is not completed so far, and it still meets with unresponded challenges.

Presently, significant attention of the research community is being given to studies of transport properties of magnetic molecules and molecular clusters. Electron–electron correlations leading to Coulomb blockade and Kondo physics and ferromagnetic many-body correlations play the predominating part in transport properties of these molecules and molecular complexes. Break-junction experiments and modeling of the electron tunneling through Mn_{12} complexes were reported [38]. The effect of spin blockade when a molecule traps an electron and blocks the current because transitions out of the trapping state are forbidden due to the spin conservation rules is also being studied [39, 40]. Another interesting subject is the electron transport through molecular networks made out of metal nanoparticles linked by molecules [40–42]. These systems reveal significant potentialities for nanoelectronic applications. To properly study electron transport in the networks one may treat them as sets of MMM junctions, each including two metal clusters connected by a molecular linker. An important issue in these studies is the effect of the electron structure of the clusters (nanoelectrodes) which in this case cannot be ignored. Another important aspect is to develop an approach enabling to compute the network conductance taking into account its geometry, which is a nontrivial and currently unresolved task.

The significance of electron spin in semiconductor physics was recognized in 1990s, thus making an opening for a new research field commonly called spin-electronics or spintronics. The electron spin in semiconductors can preserve coherence over long times and distances which offer opportunities to use it as the logic bit in memory and logic devices. The usefulness of electron spin is emphasized by the fact that its orientation may be manipulated by means of electric field. This is based on spin–orbit interaction, which is an intrinsic property of electronic structures. The spin Hall effect utilizing spin–orbit interaction instead of the magnetic field gradient gives a good example of all-electrical spin manipulation

in semiconducting materials. However, the spin–orbit interactions play a double part. Giving the means to manipulate the electron spin direction by the external electric field, these interactions also serve as the main source of spin dephasing, thus destroying spin coherence and shortening spin relaxation times.

The recent progress in molecular electronics gave rise to the prospects of molecular spintronics. These prospects are appealing because the spin–orbit interactions in carbon-based organic molecules are known to be weak, which results in extremely long spin relaxation times. At the same time, the electron spin direction may be manipulated by the external magnetic field and by intrinsic magnetic moments of the ferromagnetic leads or those characterizing the molecular linker (in the case of magnetic molecules used as such). Presently, various aspects of spin transport through MMM junctions are being intensively studied both theoretically and experimentally.

To quantitatively analyze transport properties of metal–molecular junctions, one needs to have detailed knowledge concerning the electron band structure of these systems. Electronic structure plays a crucial part in determining important transport properties of molecules in both ballistic and diffusive transport regimes. When the transport is strongly inelastic (diffusive regime), the molecular conductance is related to the mobilities in the transport channels. In turn, these mobilities are determined by the scattering times and the effective masses of charge carriers in the channel. All these parameters take on values controlled by the specifics of the electron band structure through the electron density of states associated with the channel. In the case of ballistic transport, the current through the molecule is determined by the quantum mechanical electron transmission which explicitly depends on the energies related to molecular orbitals.

The electron structure of the considered system could be analyzed using different ways depending on its specifics. For instance, in studies of junctions where the electrodes are linked with the graphene nanoribbon, one may employ a phenomenological approach to describe the ribbon electronic structure, for within such approach one could successfully capture its most important features stipulated by the edge chemistry and the roughness of the ribbon. However, while considering proper MMM junctions, one needs to employ advanced computational methods to analyze the electronic structure of molecular linkers which includes effects due to exchange-correlation interactions as well as those originating from the interaction with contact atoms.

Being a very interesting research subject by itself, the studies of electron transport through molecules are equally important due to essential similarities between the latter and long-range electron transfer chemical reactions, which are already studied for several decades. These reactions could be developed in donor–bridge–acceptor molecular systems. The donor is some molecule (reductant) or a part of a macromolecule, which donates an electron to the acceptor (oxidant) via the molecular bridge. The long-range electron transfer plays an essential part in biological processes such as signal transduction across membranes, photosynthesis, enzyme catalysis, and some others [43]. Historically, studies of the long-range electron transfer strongly contributed to the “birth” of molecular electronics.

Similarities between the electron transport through MMMs and long-range electron transfer reactions were repeatedly emphasized in theoretical works (see, e.g., [44–52]). Thus the studies of electron transport through molecular junctions may bring new insight into the nature and characteristics of the long-range electron transfer reactions.

Molecular electronics is a diverse and rapidly growing field. Currently there exists a multitude of works reporting the results of both theoretical and experimental studies of transport properties of molecules and MMMs. The purpose of this book is to give an overview of the main physical mechanisms controlling the transport and the main characteristics of the latter. As far as possible we avoid the detailed descriptions of computational formalisms commonly used to theoretically analyze electron transport through molecules as well as experimental techniques. These methods and formalisms are described elsewhere. In the first chapter of this book we introduce basic concepts, which enter into a description of the electron transport through molecular junctions and briefly describe relevant experimental methods. In the next chapter we describe theoretical methods commonly used to analyze the electron transport through molecules. The next three chapters contain a description of various effects manifested in the electron transport through MMMs as well as the basics of density-functional theory and its applications to electronic structure calculations in molecules. Some nanoelectronic applications of molecular junctions and similar systems are discussed in the last chapter. In the Appendix, several MATLAB codes used to solve some problems discussed in the book are presented.

The author is sincerely grateful to all colleagues with whom she collaborated during the years given to studies of various aspects of electron transport through molecules, namely: G. Gumbs, N.J. Pinto, A.T. Johnson, M.R. Pederson, A. Blum, and B. Ratna. Also, the author is pleased to thank S. Datta and M.A. Rather for helpful and elucidating discussions, and G.M. Zimbovskiy for his help with the manuscript preparation.

Humacao, PR Natalya A. Zimbovskaya

http://www.springer.com/978-1-4614-8010-5

Transport Properties of Molecular Junctions

Zimbovskaya, N.A.

2013, XIII, 338 p. 104 illus., 95 illus. in color., Hardcover
ISBN: 978-1-4614-8010-5