

A brief history of molecular electronics

Mark Ratner

The field of molecular electronics has been around for more than 40 years, but only recently have some fundamental problems been overcome. It is now time for researchers to move beyond simple descriptions of charge transport and explore the numerous intrinsic features of molecules.

The concept of electrons moving through single molecules comes in two different guises. The first is electron transfer, which involves a charge moving from one end of the molecule to the other¹. The second, which is closely related but quite distinct, is molecular charge transport and involves current passing through a single molecule that is strung between electrodes^{2,3}. The two are related because they both attempt to answer the same fundamental question: how do electrons move through molecules^{4,5}?

Understanding the movement of electrons to and through a single molecule is central to the field of molecular electronics, but presents a significant experimental and theoretical challenge. The principal problem concerns the statistical fluctuations present in single-molecule spectroscopy data⁶. In general, the fluctuations expected from n observations scale as $1/\sqrt{n}$. For bulk measurements, n is very large and the fluctuations are generally unimportant. However, for single molecules, they can be of the same order as the property being measured, and become comparable to the charge transport signal itself (Fig. 1). Despite these difficulties, molecular electronics has made considerable progress in recent years and a variety of important mechanistic insights have been obtained, which could have implications for the development of devices.

The early days

The field of molecular electronics can be traced back to studies conducted by Hans Kuhn and colleagues in the 1970s. In particular, Kuhn and Bernhard Mann reported, in 1971, conductivity measurements through monolayers of cadmium salts of fatty acids⁷. These measurements showed that the

conductivity decreased exponentially with layer thickness, therefore revealing electron tunnelling through the organic monolayer.

In 1974, Arieh Aviram and I published the first theoretical discussion of transport through a single molecule⁸. On reflection now, there are some striking features about this work. First, we suggested a very *ad hoc* scheme for the actual calculation. (This was in fact the beginning of many slightly flawed theoretical approaches, which were finally successfully united through the development of the non-equilibrium Green's function approach in the early twenty-first century^{2,5,9}.) Second, we suggested that a single molecule could act as a device — here a molecular rectifier — and that a single-molecule circuit with two electrodes could actually be made and measured. At the time, this was probably somewhere between science fiction and state-of-the-art, but the most important problem was how to attach electrodes to a molecule.

Later in the 1970s, several conferences in Washington DC were devoted to molecular transport, and some interesting ideas and observations were presented, including unusual transport behaviours and possible mechanisms for new devices. These meetings were also important for raising wider interest in the topic.

It was in the 1980s, however, that perhaps the most important advances in molecular electronics occurred: the development of the scanning tunnelling microscope (STM) and later the atomic force microscope (AFM), both largely products of IBM laboratories in Zurich. It quickly became clear that these tools could be used to measure the conductance of single molecules, but at first, observations of the ability of pure σ -bonded systems to permit transport were puzzling. I recall, for example, being asked at a Gordon Research

Conference by one of the inventors of the STM how to account for the fact that charge could actually move through fatty acids containing long, saturated hydrocarbon chains.

The first significant work attempting to measure single-molecule transport came from Mark Reed's group at Yale University, working in collaboration with James Tour's group, then at the University of South Carolina¹⁰. Their papers in the late 1990s and early 2000s advanced our understanding of how such measurements could be made, and provided insights about the transport properties of different molecules. The dominance of large fluctuations in the experimental data, and therefore the need to treat molecular transport in a similar way to single-molecule spectroscopy, remained unrecognized. The success of these early measurements ignited broad interest worldwide, and significant review articles appeared in 2000¹¹ and in 2001⁵. This was the true beginning of molecular electronics.

Some major issues along the way

Single-molecule electronics requires the combined effort of synthetic chemists, experimental physicists and physical chemists, and theoreticians, all of whom have faced and are facing several challenges. The synthetic problem has been reasonably straightforward to address: once the core of a molecule is completed, it is possible to attach a structural component at either end that will bond effectively to the electrodes. The preferred material for electrodes is gold or platinum, to avoid oxidation and degradation. For gold electrodes, sulphur, amine or a number of lone-pair species are typically used to attach the molecule; for platinum electrodes, lone-pair species are those most often used.

The biggest problems faced by experimentalists involve conductance measurements of single molecules, which almost inevitably result in very large fluctuations in experimental data. The dominant schemes for making good transport measurements are based on either the electrochemical break junction^{12–14} or the mechanical break junction¹⁵. Both techniques produce extensive data sets, because measurements can be made rapidly, and therefore statistical theoretical analysis on the basis of the information in histograms and the distributions of data can be carried out, which allows mechanistic insight to be obtained. Break junctions can also be gated, either electrochemically or by an external third electrode, but these experiments, although important because they provide knowledge of energy levels, are not required for a fundamental understanding of charge transport.

For theory, the question ‘how does current move through molecules?’ is now answered using non-equilibrium Green’s function techniques, a modification of the original approaches to mesoscopic transport in solids developed amongst others, by Rolf Landauer, Markus Büttiker, Yigal Meir and Ned Wingreen^{2,3,9}. The adaptation of non-equilibrium Green’s function techniques to molecular transport problems has been undertaken by a number of laboratories, and the agreement between the calculation and experiment is now strikingly good.

Beyond simple charge transport

Simple arguments and qualitative predictions are one way in which theoretical models contribute to molecular electronics. Straightforward ideas of barrier tunnelling, and of the dependence of the tunnelling process on the shapes and sizes of the barrier, often invoke the Simmons model from the early 1960s¹⁶, as well as some empirical rules of thumb. The latter includes predictions such as ‘ π systems will conduct better than σ systems’ or ‘current decays exponentially with the length of the molecule’ or ‘frontier molecular orbitals and their structures will determine molecular conductance’. These rules are true in many cases, and have been invoked to explain transport in a wide variety of molecular constructs.

However, it is important to move beyond simple transport models and beyond these simple rules of thumb. Indeed, contemporary research in molecular electronics is already moving in this direction. Examples include: work on molecular spintronics, which

involves both closed-shell and odd-spin molecular species; work on vibronic effects involving interaction between electronic and vibrational degrees of freedom; work on excitation of the molecular junction using polarized light¹⁷; work on quantum interference and decoherence; work on molecular chirality¹⁷; work on molecular stretching and distortion; and work on the thermoelectric response in molecular junctions^{18,19}. Related fundamental work has focused on noise in molecular junctions and statistical analysis including full counting statistics²⁰.

Recent studies on vibronic effects using inelastic electron tunnelling spectroscopy (IETS), for example, have shown striking aspects of the electronic–vibrational coupling during charge transfer in single-molecule junctions²¹. Depending on the magnitude of the conductance through the relevant channels, IETS data can result in different plots of current versus voltage that can be described by the interaction of vibrational excitations with the electronic motion corresponding to conductance. This can be used in various ways, such as deducing pathways for transport through intensities of IETS spectra, or studying magnetic effects in electronic–vibronic coupling.

Another important aspect of charge transport is linked to time-evolution of the process. Standard circuit analysis suggests that measurements in molecular junctions cannot resolve features that occur much faster than microseconds, because of limitations due to resistor–capacitor time constants and other

experimental aspects. This is in contrast to intramolecular charge transfer, where femtosecond timescale measurements are common, and the attosecond scale is being investigated. As the two phenomena are closely related, surprises may yet occur in understanding the time dependence experimentally. Theoretically, the time dependence can be investigated using several approximate schemes, ranging from Ehrenfest dynamics to more sophisticated propagation techniques⁴. Using a density matrix approach (as is usual in magnetic resonance) is quite common for model investigations²², and by using density functional methods, closure of the quantum Liouville equation for the molecular density matrix can be attained — recent work in this area is particularly promising because of the interpretive advantages of density matrix methodology²³.

Some quantum coherence effects

Some elegant and striking measurements have been completed on a number of designed organic molecular systems. Generally, the observations of the structure–function relationship between the individual molecules and their conductances have been based on the empirical rules of thumb just discussed. Indeed, the Simmons analysis and the HOMO/LUMO structures are standard for explaining molecular transport even for quite sophisticated measurements.

Interference structures were noted in early measurements on extended molecular π systems²⁴, and the understanding and analysis of interference effects is now one

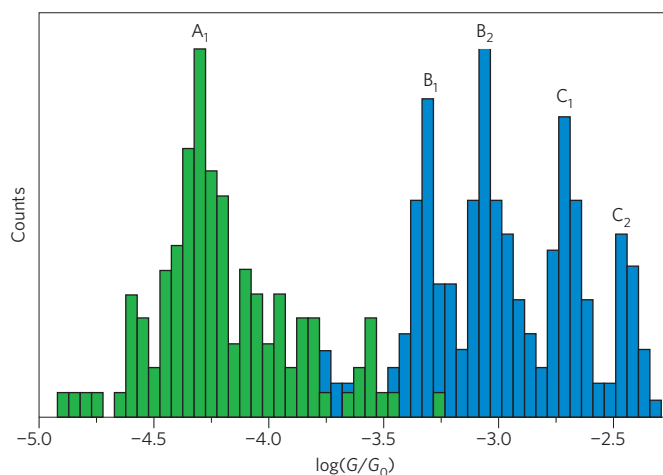
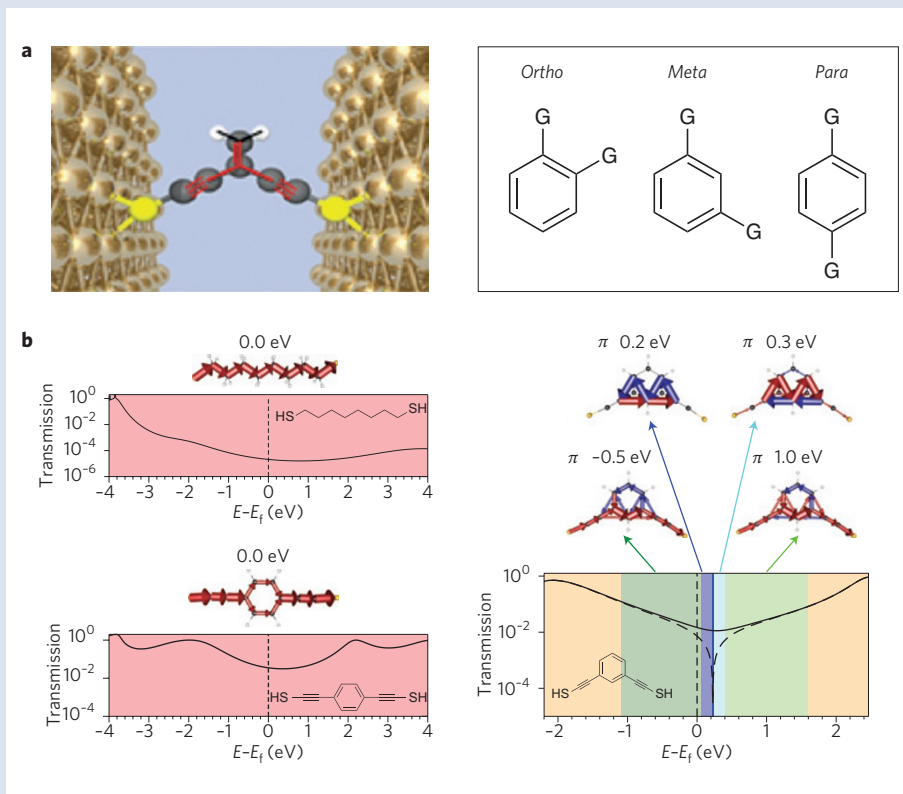


Figure 1 | Measured conductance histogram of a pentanediol species using two different methods of analysis (green, blue). The characteristic fluctuations that are found in many single-molecule phenomena are clear. G and G_0 are the conductance and the quantum of conductance, respectively. The peaks labelled by B and C correspond to stable geometries. Figure reproduced with permission from ref. 28, © 2010 RSC.

Box 1 | When rules of thumb fail.

One situation in which the simple rules of thumb can fail badly involves intramolecular interferences arising from different chemical pathways. Two very simple examples are shown in **a** — the molecular structures of both the stub resonator (left) and transport junctions through the *ortho*, *meta* and *para* pathways of a benzene molecule (right) can be explained in terms of the concept of cross-coupling or, more generally, in terms of interference between possible molecular charge transport pathways. The rules of interference (which occurs when several possible pathways exist, as sketched in red in **a**) depend on simple quantum mechanics: If two possible pathways exist through a molecule, the probability of transport through that molecule is not simply the sum of the transport by one path and the transport by the other path, but rather it is necessary to add the wave functions together before squaring to find the total probabilities. This accounts for the standard interference structures, depending on the relative phases of the pathways and their amplitudes.

Based essentially on the idea that the net current through planes perpendicular to the interelectrode line must be the same for all planes at steady state, Solomon and co-workers²⁹ developed a visualization scheme, based on computation, for how electron pathways can occur for simple molecular structures — two examples are shown in **b**. Note that in the two examples on the left (linear alkane and *para*-disubstituted benzene) the red arrows flow continuously (top), and current is



transmitted at any bias voltage, as shown in the transmission spectrum (bottom). In the *meta*-substituted benzene (**b**, right), substantial backflow (blue arrows) can be seen in the current plots, and a deep π -type interference feature (dashed line) is seen in the transmission plot. The transmission plot obtained without taking into consideration the quantum interference effect is shown as a solid

line. More recently, Chen and Ratner (unpublished observations) have used a time-dependent approach to transport to compute molecular currents. Combining **a** and **b** shows clearly the differences when interference can occur, and simple analysis such as Simmons barriers or the rules of thumb mentioned in the previous paragraphs fail dramatically. Part **b** reproduced from ref. 29, © 2010 NPG.

of the most actively investigated areas in molecular electronics. It involves the understanding of pathways, of coherence and decoherence, and of how molecular design can provide both different pathways and different decoherence mechanisms^{25,26}. Its understanding, on a quantitative level, follows directly from the usual non-equilibrium Green's function methodologies, and its qualitative understanding can be deduced from mappings of two different sorts (Box 1).

As these behaviours arise from electronic coherence in molecular transport, they can be removed by decoherence effects. This is an active area of theory/computation in molecular electronics, and comparisons with other situations of coherence in molecular science, including important biological

systems and polymeric models, are being actively pursued.

Towards devices and applications

The emerging areas of molecular spintronics and interference directly relate to possible device applications. Recall that even before scanning probe techniques were introduced in the 1980s, possible applications of molecular transport to devices were discussed⁸. The original suggestion of molecular rectification has, for example, been extensively investigated, and new molecules have recently yielded preliminary measurements involving very high rectification ratios (approaching a factor of one hundred). By definition, molecules define space and energy in ways that depend uniquely on their structure,

and this can vary considerably among similar species (see, for instance, the transport through benzene-based wires in *meta* and *para* structures discussed in Box 1). For this reason, molecular devices may work quite differently from traditional solid-state ones. One example is thermoelectrics, for which the first measurements and computations have been carried out, and hint to the fact that the usual figures of merit for bulk thermoelectrics (the so-called ZT product) may be irrelevant in understanding thermoelectric transport in molecules. In the future, the design of pathways in molecular systems could lead to a strikingly strong thermoelectric response.

Perhaps the newest work involves memristors — two-terminal non-volatile

memory devices based on resistance switching²⁷. Hewlett-Packard laboratories have worked extensively on such devices, beginning with molecular electronics and eventually moving to oxide-based materials, and this work has led to the use of memristors in some of their latest commercial instruments. Memristor structures based on the molecule ferritin have also been reported, and this may represent an important new direction for molecule-based devices.

As there are so many possible molecular structures (estimated to be roughly 10^{60} for organic compounds with 15 atoms or fewer), our understanding of the nature of molecular transport is clearly in its infancy. The field of molecular electronics can be traced back to 1971, but molecular electronics is a vibrant and dynamic area of science and technology, and numerous challenges and opportunities lie ahead. □

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Wiring molecules into circuits

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Inexpensive, functional and atomically precise molecules could be the basis of future electronic devices, but integrating them into circuits will require the development of new ways to control the interface between molecules and electrodes.

In the early 1970s, a visionary concept for exploiting the intrinsic functionality of molecules for electronics was sketched out by Arieh Aviram and Mark Ratner¹, and experiments on single layers of molecules were conducted by Hans Kuhn and Dietmar Möbius². At that time, the gate length of a transistor was around 10 μm (ref. 3), but over the past 40 years, transistors have shrunk dramatically and have now reached dimensions of less than 5 nm in research devices. During that same time, the potential of single molecules for electronic applications has, in contrast, not been capitalized on. However, owing to recent work on understanding electron transport at the molecular scale, the chances that a powerful nanoelectronics technology based on single molecules could emerge in the coming years have significantly improved.

A vision facing a complex reality

In their pioneering theoretical work,

Aviram and Ratner¹ suggested that a single molecule could function as a rectifier. The molecule would mimic a semiconductor-like band structure by taking advantage of electron-rich and electron-poor moieties to achieve one-way conduction through differently aligned molecular orbitals with respect to the Fermi energy of the electrodes. In this approach, the possibilities for designing electronic functionality are determined by bottom-up synthetic methods with atomically identical basic building blocks. This is a revolutionary concept even today when considering the increasing device variability of complementary metal–oxide–semiconductor (CMOS) technology and the struggle to control the position and distance of smaller and smaller numbers of atoms in the active regions of devices made using top-down methods. However, already in the earliest experiments, the vision of molecular electronics encountered tremendous difficulties.

First, and in contrast to silicon where research was facilitated by the availability of large crystals, the size of an individual molecule cannot be easily scaled up, which means that atomic-sized electrodes are needed to contact an individual molecule. By pulling and then breaking ductile metal wires, suitable electrodes⁴ can be fabricated, and over the past 15 years a variety of innovative approaches have been developed to experimentally conduct charge-transport studies at the few-molecule level.

Second, when the number of active molecules in the junction was reduced down to a single molecule, the variability of the ‘devices’ increased because the molecular junction became sensitive to every microscopic detail of its atomistic configuration (Fig. 1a). Until now, only a few experiments have gained control over the crucial atoms in the junction⁵, but such atomic control is essential for the development of molecular electronic applications.