

Molecular Electronics and Resistance of Molecule-Metal Interfaces

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Abstract

Molecular electronics is an emerging field that aims at controlling physical systems on the level of individual molecules. While initial applications are thought to be in digital memory and logic, potential benefits include manipulation of light on the sub-wavelength level. In this presentation, I will describe the basic ideas and current status of the field. The recent demonstrations of the single-molecule conduction, rectification, amplification, and switching, will be briefly reviewed. I will specifically address the problems of conformational switching and the resistance of a metal – self-assembled molecular film interface. A class of recently designed bistable stator-rotor molecules, whose shape can be changed by external electric field, will be described. Also, the resistance of the metal – molecular monolayer contact will be shown to be strongly dependent on the orientation of the molecules' main axis relative to the metal surface. The sensitivity originates from the angular anisotropy of the conductive molecular orbitals that are usually built from very directional atomic wave functions. This effect should be taken into account in designing low resistance interfaces.

Molecular Electronics

The exponential growth of the computer speed and memory capacity poses the question of the ultimate limit of miniaturization of electronic elements. The workforce of the contemporary integrated circuit technology is the metal-oxide-semiconductor field effect transistor. Its operation is based on the very robust principle of gating that is scaleable below 10 nanometers (nm). However, recent simulations have shown that fluctuations in the device performance increase dramatically at deep nanoscale, with key parameters becoming sensible to the presence or absence just one additional atomic layer.¹ The necessary stability of the transistor performance will require fabricating the entire macroscopic device with atomic precision. Even though this is conceivable in principle, the enormous fabrication costs will likely make such a "top-down" approach impractical. It is imperative to begin looking for alternative ways to fabricate complex electronic structures, which would complement silicon technology in the future.

Molecular electronics is one attractive possibility that takes advantage of the great uniformity between the shapes of individual molecules with the same chemical structure. Besides, molecules are synthesized in bulk quantities, which makes this part of the fabrication process really inexpensive. The challenge therefore shifts to the ways to organize the molecules in regular structures and integrate them with other parts of the circuit. Another clear advantage of molecules is their very small size. Typical molecules range from 1 to 10 nm. Arranging such small objects even in two-dimensional geometry would lead to element densities of 10^{12} - 10^{14} cm⁻². Arranging molecules in *three*-dimensional structures would lead to astronomical densities of elements. One kilo-mole contains so many molecules (6×10^{26}) that it could store 6 billion 30 year-long continuous videos, provided one molecule can represent one memory bit.

It is important to stress that the small sizes of the molecules are already being matched by the small sizes of wires. Regular arrays of 8 nm-wide platinum wires and 20 nm-wide silicon wires were recently fabricated by Melosh et al.,² using the superlattice technique.³ Another possibility is to use carbon nanotubes as electrical wires. Unfortunately, no reliable method to arrange nanotubes in regular structures is known at present. Also, no technique to arrange molecules in three-dimensional structures has been proposed.

The key assumption of molecular electronics is that molecules can perform non-trivial and useful electronic functions. This idea was pioneered by Aviram and Ratner in 1973,⁴ who proposed a design for the single-molecule current rectifier (diode). Since molecules can be made very complex, there exist no fundamental reasons why just one molecule cannot be a transistor, a switch, a memory bit, or an even more complex circuit. Since the Aviram-Ratner paper, several designs for single-molecular devices have been proposed theoretically, including rectifiers,^{5,6} switches,⁷⁻¹² and transistors.¹³ Experimentally, electrical properties of molecules have been studied by mechanically-controlled break junctions,¹⁴⁻¹⁶ electro-migration break junctions,^{17,18} scanning tunneling microscopy (STM),¹⁹⁻²¹ and by other methods.²²⁻²⁴

In the rest of this paper, we present some of the recent ideas about molecular rectification, molecular switching, and the importance of the molecule-electrode interface.

Other important issues such as performing logical operations with molecules, demultiplexing, and tolerance to defects are beyond the scope of this paper.

Principles of Molecular Conduction and Rectification

Similarly to conventional electronics, molecular electronics possesses a standard toolkit of elements.⁵ In general, moieties with small optical gaps are relatively good conductors (or rather semiconductors). Usually, these groups have multiple double or triple π -bonds, such as the benzene ring or conjugated oligomers. Moieties with single σ -bonds have large optical gaps and constitute a wide class of molecular insulators. Another interesting element is the molecular capacitor. Those are molecules that can exist in different charge states for sufficiently long times. For instance, triple porphyrins can accept up to 6 elementary charges.²⁵ Molecular capacitors may prove much more efficient than silicon capacitors. This fact is being utilized in developing hybrid silicon-molecular dynamic random access memory.²⁶

From the elementary building blocks one can assemble more complex elements. For example, the Aviram-Ratner rectifier consists of three parts: one conjugated unit with low ionization potential (*donor*), another conjugated unit with high electron affinity (*acceptor*), and an insulating group between the two (σ -*bridge*). A related type of molecular rectifier was proposed by Ellenbogen and Love.⁵

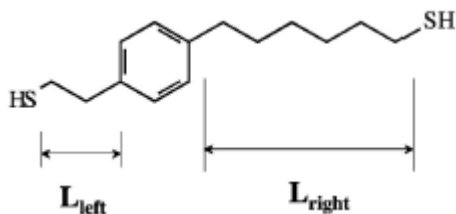


Figure 1. This simple molecule becomes a current rectifier if sandwiched between two gold electrodes. The necessary condition is the asymmetric position of the conducting orbitals of the central benzene unit with respect to the Fermi energy of gold.

A simpler rectification principle was recently proposed by Kornilovitch et al.,⁶ see figure 1. It requires only one conductive molecular orbital in the vicinity of the electrode Fermi level. However, the conducting group has to be positioned asymmetrically with respect to the two electrodes. This is achieved by attaching to the conductive group two insulating “legs” of different lengths $L_{\text{left}} \ll L_{\text{right}}$. When a voltage is applied between the electrodes, most of the potential drops on the longer leg. As a result, the Fermi level of the right electrode shifts with respect to the molecular orbital much “faster” than the left Fermi level. At some positive voltage, the right Fermi level aligns with the molecular level, satisfying the conditions for resonant tunneling, and the current through the junction picks up. Under the opposite polarity, the right Fermi level shifts

away from the orbital, which results in no appreciable current. Eventually, the left Fermi level aligns with the orbital, and current picks up in the negative direction as well, but this occurs at a much higher bias. As a result, the current-voltage characteristic of the device is strongly asymmetric. Tight-binding calculations on the family of molecular rectifiers $\text{SH}-(\text{CH}_2)_n-\text{C}_6\text{H}_6-(\text{CH}_2)_m-\text{SH}$ revealed current rectification ratios as high as several hundred.⁶ A more sophisticated Density Functional calculation on a similar molecular family²⁷ resulted in smaller but still significant rectification ratios ~ 35 .

Experimentally, current rectification in Langmuir-Blodgett films of asymmetric molecules was observed by Ashwell et al.,²⁸ Metzger et al.,²⁹ and more recently by Lenfant et al.³⁰ However, in those studies the insulating legs of the molecules were very long resulting in extremely large resistances. It would be very interesting to study shorter molecules, especially by methods allowing probing of single molecules, such as STM or mechanical break junctions.

One should add that the molecular rectifiers described here could be fine-tuned to very low threshold voltages. As such, they could find interesting applications outside the molecular electronics paradigm.

Molecular Switches

The molecular switch is a highly non-trivial element of molecular electronics. Indeed, switching implies bistability (or even multiple stability) of the molecule. The latter can be realized via bistability of electronic structure, for example as two different charge states. Alternatively, switching can be achieved via bistability in the molecular *shape*. The shape bistability is harder to realize but it has several potential advantages over the charge bistability, for example the non-destructive readout of information and greater stability against temperature and quantum fluctuations. One type of conformational molecular switch was developed by Stoddard and co-workers.^{31,32} It is suggested that in those *pseudo-rotaxane* and *catenane* molecular complexes, one part of the molecule, a ring, slides up and down another part, “dumbbell”, moving between two equilibrium positions when a sufficient voltage is applied between the electrodes. Although single-bit³³ and multiple-bit³⁴ memories have already been demonstrated with those molecules, conclusive evidence of ring movement is still lacking. Another disadvantage of the rotaxane switches is slow switching speed, which is about 10 milliseconds.

The stator-rotor conformational switches were proposed recently by Kornilovitch et al.⁹ These molecules also consist of two main components. The stationary component is connected to the electrodes, and facilitates transfer of electrons between them. It has to be a relatively good molecular conductor. The rotary component is attached to the stator as a side group. Importantly, the rotor needs to have a large electrical dipole moment. The key design feature is the instability of symmetrical rotor position, when it is oriented perpendicular to the stator. The

feature can be engineered by introducing hydrogen bonding between the stator and the rotor. One example is shown in figure 2. The rotor is represented by the amide with a dipole moment of 4.2 Debye. The oxygen and nitrogen atoms form hydrogen bonds to hydrogen atoms of the stator. As a result, the rotor tilts away from the perpendicular orientation. Since the stator is symmetric, the two tilt directions are equivalent, which leads to bistability. The total energy of the molecule has the double-well shape, as shown in figure 3.

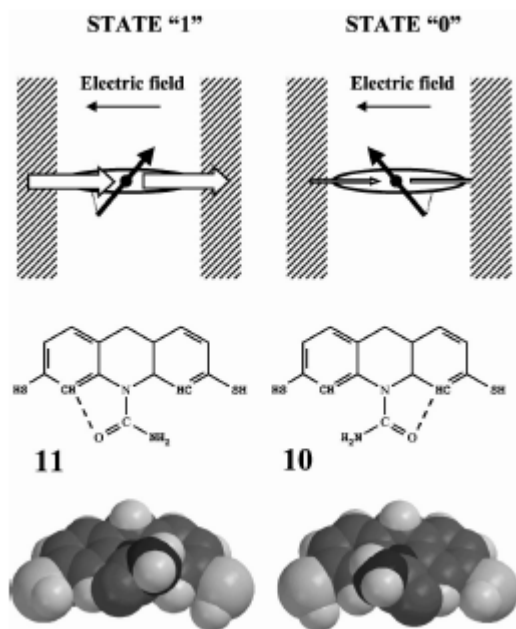


Figure 2. Top: basic principle of the stator-rotor molecular switch. Middle: a specific example. The rotor is represented by the amide group $-\text{CONH}_2$. The dashed lines indicate hydrogen bonding. Bottom: the space-filling model of the same molecule.

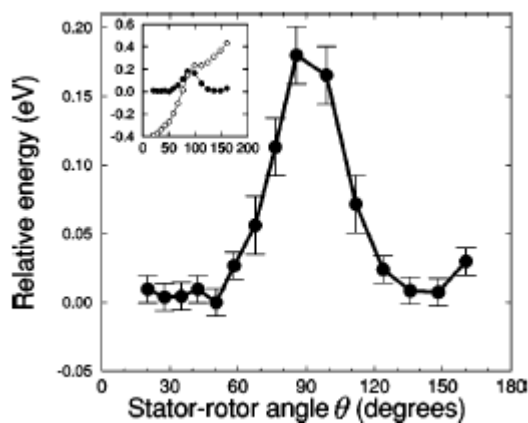


Figure 3. Total energy of the molecule shown in figure 2 as a function of the stator-rotor angle. Inset: the same data (solid circles) compared with the energy in external field of 0.5 volt/angstrom (open circles). The field corresponds to a switching voltage of 7 volts.

It is essential that the dipole moment of the rotor performs two more important functions. First, it makes the two states distinguishable electrically. Indeed, neither of the two tilted states is symmetric, leading to two *asymmetric* current-voltage characteristics that are inverse images of each other. Tight-binding quantum mechanical calculations have shown that the two states are distinguishable in the applied voltage interval between 3 and 4 volts.⁹ Distinguishability of the two states greatly improves if the stator is asymmetric. Second, a large dipole moment makes it possible to flip the rotor between the two stable states by applying a strong enough electric field along the main axis of the molecule. Thus both switching and interrogation of the switch can be done in the two-terminal geometry. Density-functional modeling has shown that the switching voltage for the molecule depicted in figure 2 is ≈ 7 volts, see inset in figure 3.

Experimental observation of single molecule conformational switching would be a significant accomplishment. Apart from potential applications in nano-electronics, it would demonstrate that the structure of molecular systems could be controlled on the level of the shape of individual molecules. This would open entirely new ways of manipulating electrical and optical properties of matter.

The Critical Role of Contacts

As was mentioned above, an appealing feature of molecular electronics is the nature-ensured uniformity among individual building blocks. However, the measurable resistance is the property of the entire junction comprised from the molecule, electrodes, and, very critically, molecule-electrode contacts. The current flowing through the junction is proportional to the square of the two matrix elements that couple the conducting molecular orbitals with the wave functions on both electrodes. The matrix elements themselves exponentially depend on the distance between the molecule and the electrode surface. Removal or displacement of just one surface atom could lead to significant, orders of magnitude, change in the junction resistance.

It was realized recently that the situation is even more complicated.³⁵ Majority of the conducting molecular π -orbitals are built from elongated p -atomic wave functions. The overlap of such wave functions with the wave functions of surface atoms depends not only on the distance but also on the *orientation* of the main molecular axis with respect to the local surface normal. Tilt, rotation of the molecule, local rearrangement of surface atoms, or any other change of mutual orientation results in a substantial change in resistance of up to two orders of magnitude, see figure 4. This result is of practical importance. For instance, in STM experiments the apparent resistance of the molecule would be different depending on the *direction* along which the tip approaches the molecule. Also, surface re-orientation requires much less energy than complete breaking of chemical bonds. Therefore it can occur simply as a result of temperature fluctuations. Such temperature fluctuations of

the contact properties have recently been observed in STM experiments on single molecules.³⁶

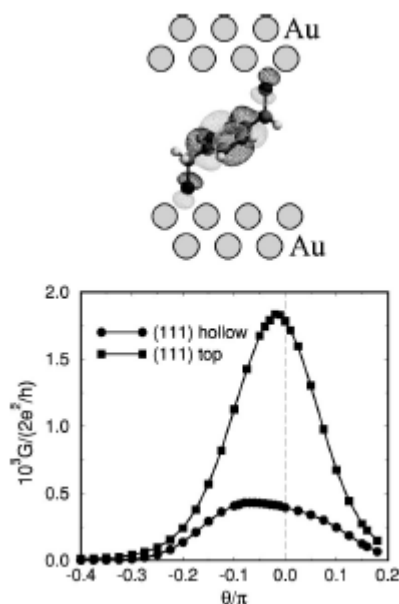


Figure 4. Electrical conductance G of the gold-xylyl-dithiol-gold molecular junction as a function of angle θ between the sulfur-carbon bond and the normal to the gold surface. Top panel illustrates the “hollow” binding scheme. The “top” case refers to sulfur atom being position directly above a gold atom.

The temperature stability of the molecule-electrode contact, as well as the reproducibility between different contacts is currently one of the most pressing practical problems of molecular electronics. One potential solution involves the use of more robust molecule-electrode binding schemes. For example, molecular self-assembly on silicon (100) surface can be realized with the double carbon-carbon bond present on the molecule.³⁷ In this self-assembly scheme, not one but *two* molecular atoms attach to the surface simultaneously. The volatility of the contact is therefore greatly reduced.

Conclusions

Molecular electronics began as a potential alternative to silicon technology. It is becoming clear, however, that it is going to supplement silicon technology rather than replace it. The Langmuir-Blodgett and self-assembly deposition techniques could greatly simplify some fabrication steps of the complex electronic circuits. Molecular capacitors have already led to the development of hybrid molecular-semiconductor devices. Molecular rectifiers, switches, and transistors will also find their applications in the hybrid technology, if their electrical characteristics prove sufficiently reproducible.

As always the case with a non-trivial idea, further development of molecular electronics may yield cardinally novel applications. Being essentially organic material, the molecules could greatly facilitate the development of efficient semiconductor-biological interfaces. The small size and rich functionality of molecules may be exploited to build adaptable neural networks.³⁸ Control on the shape of individual molecules opens new methods to manipulate physical properties of matter. These exciting prospects call for further research in molecular electronics.

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Biography

Dr. Pavel Kornilovitch received his PhD in Theoretical Physics at King's College London, UK in 1997. After that he held post-doctoral positions at Max-Planck Institute in Dresden, Germany, and at Imperial College London, working in condensed matter physics. In 1999, he joined Hewlett-Packard Labs in Palo Alto, CA, to work on modeling electrical properties of organic molecules. Since 2002, he is a member of the Applied Molecular Systems group at HP research division in Corvallis, OR.