

Molecular Electronics: Theory and Device Prospects

A.W. Ghosh, P.S. Damle, S. Datta, and A. Nitzan

Abstract

Understanding current flow through molecular conductors involves simulating the contact surface physics, the molecular chemistry, the device electrostatics, and the quantum kinetics of nonequilibrium transport, along with more sophisticated processes such as scattering and many-body effects. We summarize our current theoretical understanding of transport through such nanoscale devices. Our approach is based on self-consistently combining the nonequilibrium Green's function (NEGF) formulation of transport with an electronic structure calculation of the molecule. We identify the essential ingredients that go into such a simulation. While experimental data for many of the inputs required for quantitative simulation are still evolving, the general framework laid down in this treatment should still be applicable. We use these concepts to examine a few prototype molecular devices, such as wires, transistors, and resonant-tunneling diodes.

Keywords: *molecular electronics, nanoscale devices, transport.*

One of the principal driving forces behind the semiconductor microelectronics industry has been miniaturization, motivated by a large device density per chip and high operational speeds. State-of-the-art transistors in industry are currently at the 90 nm node,¹ while transistors with gate lengths of 6 nm,² comprising just a few dozen atoms, have been demonstrated. Although this represents a technological tour de force, it will be progressively difficult to continue downscaling at this rate, as quantum tunneling, interconnect delays, gate oxide reliability, and excessive power dissipation, among other factors, start hampering the performance of such devices.³ While some of these issues can, in principle, be handled by improving device design, packaging, processing, and channel mobilities,⁴ the rapidly increasing cost of fabrication motivates exploration of entirely new paradigms, such as novel architectures and new channel materials. One promising direction involves replacing the "top-down" lithographic approach with a "bottom-up" synthetic chemical approach of assembling nanodevices and circuits directly from their molecular constituents.

Molecules are naturally small, and their abilities of selective recognition and bind-

ing can lead to cheap fabrication using self-assembly. In addition, they offer tunability through synthetic chemistry and control of their transport properties due to their conformational flexibility. Remarkable progress in this field has been made in the last few years, as researchers have developed ways of growing, addressing, imaging, manipulating, and measuring small groups of molecules connecting metal leads. Several prototype devices such as conducting wires, insulating linkages, rectifiers, switches, and transistors have been demonstrated.⁵ In parallel, there has been significant theoretical activity toward developing the description of nonequilibrium transport through molecules.⁶ It is hard to say whether in time such devices could conceivably complement the current silicon-based integrated circuit (IC) industry or generate entirely new areas of applicability. It is clear, however, that in any case we will need to develop models to describe large-bias transport through ultra-small devices, whether based on silicon or molecules.

Theoretical Methodology

Transport through a molecule under bias is essentially a nonequilibrium, quan-

tum kinetic problem. Contacting a molecule with two leads effectively "opens up" the system, replacing the discrete molecular energy levels with a continuous density of states and establishing a common electrochemical potential and a band lineup between the contacts and the molecule. Under bias, the two contact electrochemical potentials split, and the molecule, in its bid to establish equilibrium with both contacts, is driven strongly out of equilibrium.⁶ Current flow thus requires a formal treatment of nonequilibrium transport, through a suitable wave function (scattering theory) or Green's function technique. The Keldysh-Kadanoff-Baym nonequilibrium Green's function (NEGF) formalism gives us a rigorous theoretical basis for describing quantum transport through such a system at an atomistic level.^{7,8}

The central quantity in NEGF is the two-time correlation function, whose equal-time component relates to the density matrix that describes how the device levels are filled by the contacts in a correlated way. Under various approximations, the NEGF equations simplify to generate other widely used transport formalisms. For instance, for bandlike transport and strong incoherent scattering that causes the electrons to lose their phase memory, NEGF has been shown to reduce to the Boltzmann formalism, while in the absence of such dephasing processes, it is equivalent to the Landauer transmission formalism.⁷ Furthermore, for small bias, the Landauer formalism can be mapped onto Marcus electron-transfer theory for a molecular bridge sandwiched between a donor-acceptor species.⁹

The insights and methods of mesoscopic physics from the late 1980s are relevant to the field of molecular electronics. One significant difference, however, is that mesoscopic physics is primarily focused on low-temperature, low-bias (or linear response) conductance, which is determined solely by the transmission characteristics at the Fermi energy. By contrast, many of the interesting issues in molecular electronics involve the shape of the current-voltage characteristics (nonlinear conductance), which is profoundly affected by the profile of the applied potential¹⁰ (see also Reference 11).

A typical simulation procedure consists of self-consistently coupling an electronic structure calculation with a suitable transport solver.¹² Transport involves a nonequilibrium, open-boundary problem. We formally partition this problem into an active device and semi-infinite contacts that add or remove charges from it. The device energy levels and electrostatics are described by a Hamiltonian and a self-consistent potential, respectively, while the semi-infinite

external contacts influence those levels by shifting and broadening them through self-energy matrices with complex eigenvalues. Starting from an initial guess for the device density matrix described in a suitable basis set, we calculate the self-consistent potential, which, added with the device Hamiltonian, generates the device Fock matrix. The Fock matrix, together with the contact self-energies, determines the nonequilibrium Green's function that describes the causal response of the device to a unit excitation. The NEGF formalism gives us exact prescriptions thereafter for recomputing the nonequilibrium density matrix and current density, including the effects of many-body interactions and scattering within the device.^{8,13} The great advantage of this method is its generality: within the same framework, we can describe transport through various materials such as molecules, silicon transistors, nanowires, nanotubes, spintronic devices, and quantum dots (Figure 1).

Scattering can be included in the NEGF by including a self-energy, which shifts and broadens energy levels in response to a perturbation, obtained from a proper microscopic Hamiltonian.⁷ Such self-energies have been widely used to include strong electron-phonon and electron-electron correlations.^{8,15,16} Various simplified treatments of scattering also exist in the literature. Device physicists often use phenomenological Büttiker probes that extract and reinject current from the device,⁷ while simplified rate equations can be derived from the NEGF in the limit of non-interfering, independent transport channels. Within the density matrix formalism in steady state, Redfield theory has been widely employed by chemists to describe scattering.¹⁷ The scattering current has two contributions: a coherent component that decays exponentially with length and an incoherent component that decreases linearly with length.^{17,18} In addition, the electron can exchange energy with other molecular or environmental degrees of freedom, producing inelastic sidebands.¹⁸

Molecular Wires

Figure 2 shows the simulated transport characteristics for two prototype molecular wires: (1) current-voltage (I - V) characteristics for a six-atom gold quantum point contact (QPC) and (2) conductance-voltage (G - V) data for xylyl dithiol (XDT). The QPC shows ohmic I - V behavior with a quantized conductance, in agreement with experiments, indicating perfect transmission over an energy band around the Fermi energy. The QPC I - V characteristic could thus provide a benchmark for the accuracy of the contact self-energy matrices.

XDT shows resonant conduction through broadened levels, with a peak structure in the conductance-voltage curve that agrees with theoretical estimates. The calculated conductance values are consistent with expectations based on Landauer theory, as well as on electron transfer rates calculated from reorganization energies of donor-acceptor species. The magnitude of the conductance estimated by *ab initio* theory

is much larger than in experiments, indicating a poor contact between the molecule and the scanning tunneling microscope (STM) tip. However, the theoretical current levels compare well with break junction measurements on well-contacted molecules.¹⁹ The plots in Figure 2 were obtained at two levels of sophistication: a simple semi-empirical extended Hückel treatment, involving parameters such as

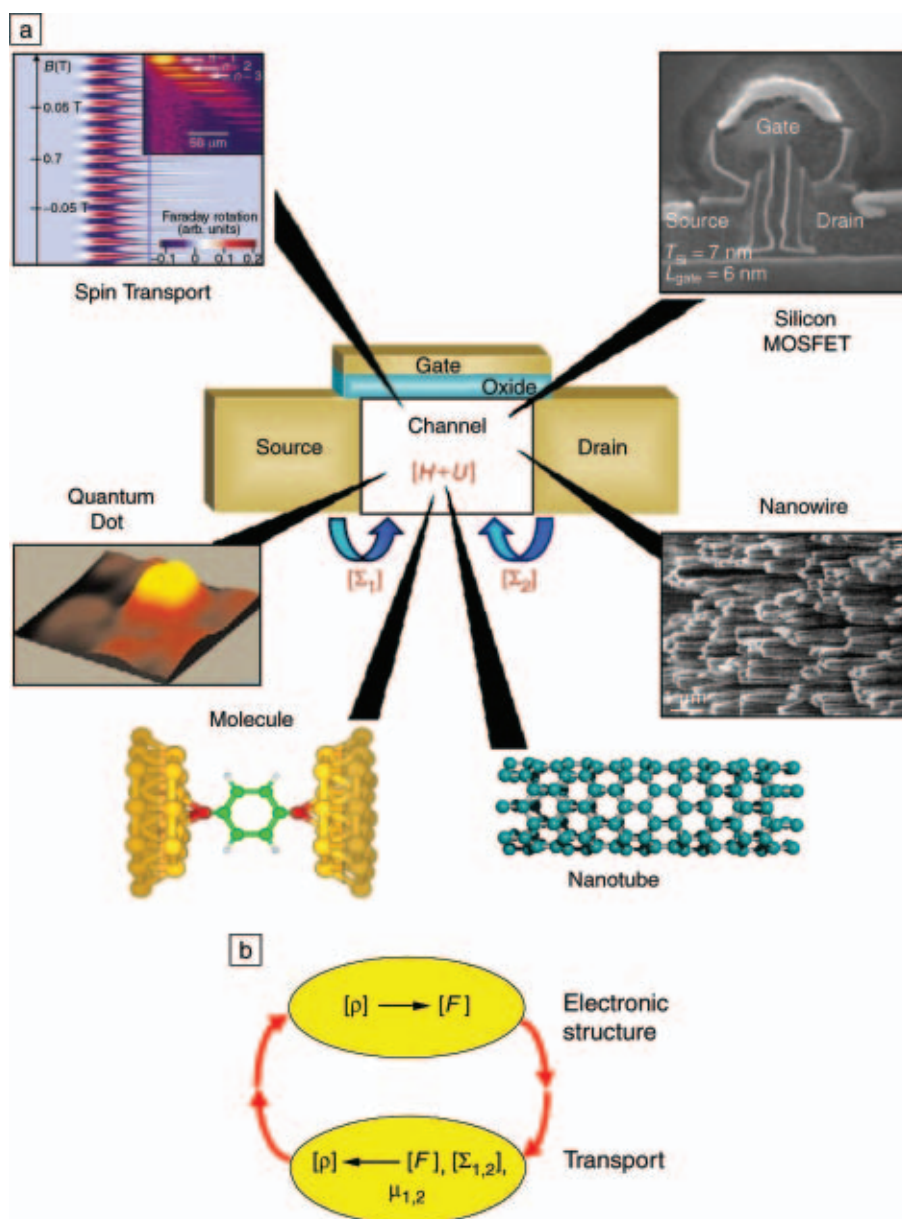


Figure 1. (a) Schematic illustration of a generic, simulated three-terminal structure, described by a device Hamiltonian H and self-consistent potential U , and contact self-energy matrices $\Sigma_{1,2}$ representing contact couplings. The illustration describes the partitioning of the semi-infinite system in various cases into the model Hamiltonian and the self-energies. (b) The simulation consists of a self-consistency procedure combining an electronic structure calculation with a transport calculation and describes transport through various experimentally explored structures.¹⁴ ρ is the electron density matrix and $\mu_{1,2}$ are the contact electrochemical potentials under bias.

the contact Fermi energy, the broadenings, and the voltage division between the contacts,²⁰ and a density functional theory (DFT) calculation that yields I - V information with no adjustable parameters.¹²

Several molecular I - V characteristics have been measured, including off-resonant tunneling conduction through alkanethiols, incoherent transport through DNA, and current rectification through spatially asymmetric molecules. There have been

attempts at controlling individual parts of the molecule, such as increasing the length of nonconjugated molecules, altering the number and orientations of rings of conjugated assemblies, varying the positions and work functions of the electrodes, and altering the surface linker groups.⁵ A good qualitative understanding of molecular conduction is emerging, with many experiments describable in simple physical terms such as band alignment and charge

transfer⁶ and quantitatively modeled using semi-empirical or *ab initio* theories.

Molecular Transistors

Experiments involving three-terminal gated molecules have been few and have largely demonstrated weak gate modulation of the molecular I - V characteristics.²² Electrostatic control in a ballistic transistor requires the gate to lie much closer to the channel than the contacts. Simulations show that the oxide needs to be about 40 times thinner than the channel for a single-gate silicon transistor, and 10 times thinner than the channel for a molecule, in order to get nominal gate control for power gain.²³ For short molecules like XDT, such oxide thicknesses are prohibitive and significantly below the threshold for gate leakage. This is a fundamental restriction imposed by electrostatics, and it cannot be rectified simply with better molecular chemistry. The transistor characteristics are further degraded by metal-induced gap states (MIGS) from gold contacts traditionally employed in these measurements, leading to high OFF currents and poor ON-OFF ratios.²⁴

Electrochemical gating, whereupon the redox potential of a surrounding electrolyte acts as an effective gate potential, has been successfully used in several cases. Alternatively, the conformational flexibility of molecules offers possible ways to offset the poor electrostatic gate control inherent in molecular transistors. It is possible in principle to engineer large dipoles into the molecule along the source-drain field, so that in a dual-gate structure, the dipole moment is more susceptible to rotation by the gate field rather than by the source-drain field. The vector directionality of the dipole could provide an advantage to the gate electrode even if the gate lies farther from the channel than the source and drain contacts.²⁴ Rotating the molecule could lead to a molecular relay (Figure 3), as has been demonstrated with carbon nanotubes.²⁵ Although gate control in such relays seems to be easy to achieve, especially with soft bonds in the molecule, it is important that the dipole moments be large enough to allow the molecule to overcome the effects of thermal fluctuations at room temperature. Alternate gating principles involving bistable potentials can be invoked to isolate the ON and OFF states from thermal mixing; however, such principles may not be compatible with traditional CMOS (complementary metal oxide semiconductor) design.

Hybrid Silicon Molecular Devices

While traditional molecular electronics studies have been done on gold contacts,

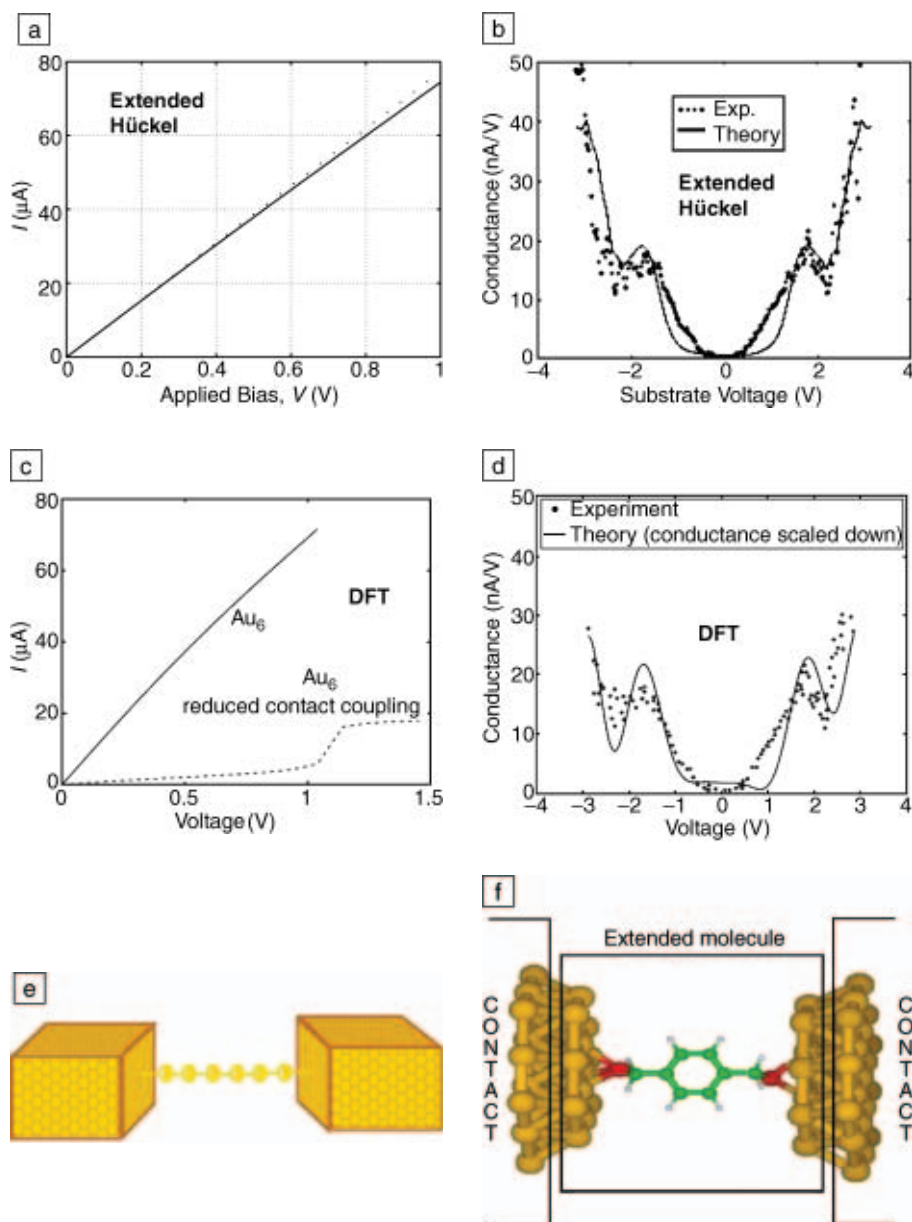


Figure 2. Simulated transport characteristics for two prototype molecules: a six-atom gold quantum point contact (left column) and xylyl dithiol (right column). (a), (c) Calculated current-voltage (I - V) characteristics and (b), (d) conductance-voltage (G - V) characteristics, using semi-empirical extended Hückel theory¹¹ and density functional theory (DFT).^{12,21} The quantum point contact exhibits an ohmic I - V behavior with a quantized conductance, while xylyl dithiol shows resonant conduction through its highest occupied molecular orbital (HOMO) level. (e), (f) Schematic illustrations of the molecules.

mainly prompted by the quality of self-assembly, several researchers have recently managed to grow single molecules and monolayers on silicon²⁶ (see the article by Hersam and Reifengerger in this issue). This has opened the way for a new paradigm involving molecular devices that complement silicon as “add-on” components and use the existing infrastructure of the IC industry. There still are several challenges, such as eliminating the native oxide, depositing a top contact to address molecules individually without damaging them, and preserving the integrity of the molecular device despite the high temperatures attained during chip fabrication. However, the idea of molecules functionalizing silicon and acting as sensors, memory, or optical elements integrated on a silicon substrate is exciting indeed.

One of the principal challenges in simulating transport through molecules on silicon is developing a quantitative atomistic model of silicon that does justice to its bulk band structure, band bending, surface reconstruction, surface states, and the silicon molecular chemistry. While density functional theories have been used to describe the silicon molecular chemistry,²⁷ they tend to do poorly in describing the bulk band structure and surface properties of silicon. Semi-empirical theories, however, do quite a good job of describing the bulk and surface properties of silicon. It is important therefore to develop a hybrid formalism whereby semi-empirical results from bulk silicon can be interfaced with *ab initio* results for the molecule without any spurious interfacial basis-mixing-related artifacts. Such models, currently under development,²⁸ would offer a way to make quantitative predictions about molecular conduction on silicon.

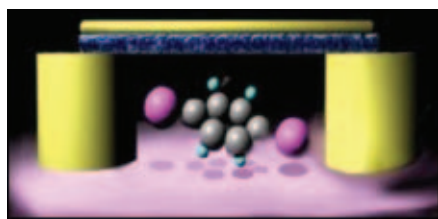


Figure 3. Schematic illustration of a molecular relay consisting of a molecule anchored strongly to one contact and weakly to the other. A gate field acts on a dipole engineered into the molecule through a redox side group, rotating it away from the weak contact and dropping its transmission abruptly. The feasibility of such a device depends on the ability of the gate–dipolar coupling to overcome thermal fluctuations at room temperature.²⁴

The presence of the silicon band edge can lead to new physics, such as a novel molecular resonant tunneling diode (RTD), showing a one-sided negative differential resistance (NDR) in the I – V behavior as probed with an STM.²⁹ In contrast to resonant conduction, where levels create peaks in the conductance, and inelastic tunneling, where peaks appear in the sec-

ond derivative of the current with voltage,³⁰ the silicon band edge acts like a filter, leading to signature peaks in the I – V curve itself that can be useful for molecular spectroscopy. The current drops every time a molecular level is driven into the silicon bandgap by the applied bias (Figure 4). The most important part of the simulation, aside from modeling the silicon surface, is the role of three-dimensional electrostatics, which causes the levels to slip past the bulk silicon band edge. This necessitates solving Poisson’s equation for the given device geometry self-consistently with the NEGF, including the effects of charge depletion and band bending in silicon. Theoretically, we expect an NDR for positive bias on p -doped silicon and for negative bias on n -doped silicon, as recently confirmed by STM experiments on molecules grown on degenerately doped silicon.³¹ In effect, this anticipates a molecular RTD integrated onto silicon, with pos-

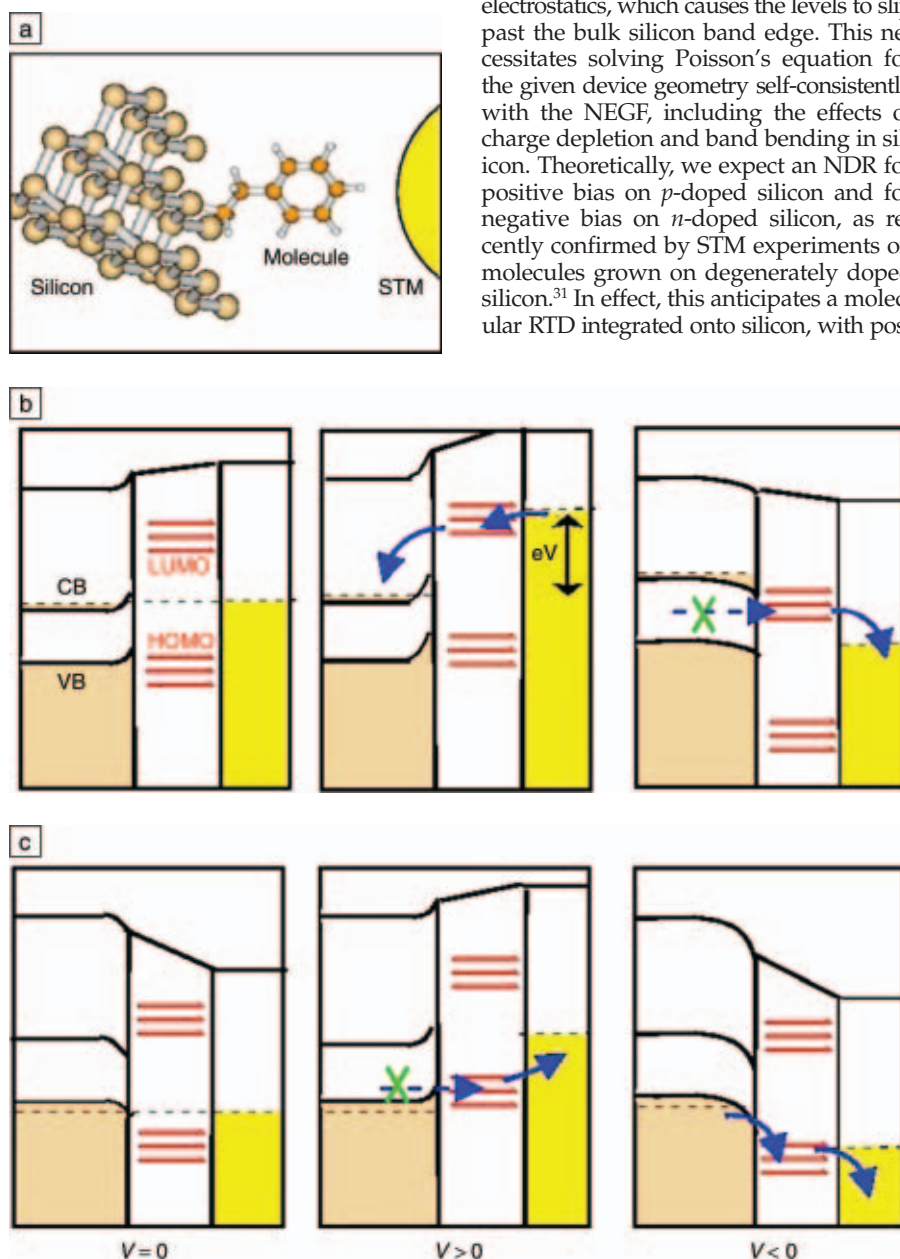


Figure 4. (a) Schematic illustration of a molecule grown on silicon and addressed with a scanning tunneling microscope tip. For molecules like styrene and 2,2',6,6'-tetramethyl-1-piperidinyloxy (TEMPO), theory and experiments demonstrate a negative differential resistance in the I – V curve for (b) negative substrate bias on n -doped silicon and (c) positive bias on p -doped silicon.^{29,30} Such structures in the I – V curve can be understood from the band diagrams, which show molecular levels slipping past the silicon band edge. CB is the conduction band, VB is the valence band.

sible applications in logic and low-power memory.³²

Summary

The last few years have witnessed exciting developments in our theoretical and experimental understanding of electron transport through molecules. A lot of theoretical challenges still remain to be sorted out. We need to refine our existing descriptions of the molecular chemistry, device electrostatics, band structure, and surface physics for novel molecules and contacts, including spin and time-dependent effects. Our transport formalism needs to be generalized or reformulated to incorporate new physics, such as those arising from strong electron–electron and electron–phonon correlations. Molecules are in effect ultrasmall quantum dots with strong Coulomb charging, and on hybridization with metal contacts, they provide an interplay of localized and extended states that creates a perfect laboratory for studying many-body effects.³³ New, reproducible experiments are essential in sorting out many of these open issues, achieving a better theoretical understanding of transport at these length scales, and designing better devices. The real promise of molecular electronics lies in its unique position at the junction of fundamental understanding and device applications.

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MRS Future Meetings

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Nov. 29-Dec. 3
Exhibit: Nov. 30-Dec. 2
Boston, MA

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Exhibit: March 29-31
San Francisco, CA

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