Towards a theory of single molecule conduction

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Abstract— We discuss recent progress in our theoretical understanding of molecular electronics on three fronts: (a) at a formal level involving quantum transport in presence of strong correlation effects; (b) at a computational level for modeling heterogeneous integrated systems such as molecules on silicon, and (c) at a device level by exploring novel concepts such as conformational transistors and surface modulated transistors.

Keywords - *quantum transport, molecular electronics*

I. INTRODUCTION

Molecular electronics represents an ultimate dream for ‘bottom-up’ technology and for exploring fundamental transport physics. With reports of reproducible, well-characterized experiments, there is a real urge for developing formal and computational tools for basic understanding and exploration of novel device paradigms. In the past quantitative agreement between theory and experiment has been rather limited. Part of the problem was at the theorists’ end - formal theories for quantum transport, especially for weak coupling, are still evolving. There are computational challenges as well, related to the choice and implementation of suitable electronic structure techniques. Part of the problem was also experimental - the lack of reproducibility among different experimental groups in the past, poor knowledge of the contact microstructure, and the frequent occurrence of artifacts like traps or electromigration made it difficult to put theoretical and experimental current-voltage (I-Vs) on the same page.

Over the last few years, the situation has changed rapidly, as experimentalists have concentrated on characterizing simpler systems like alkanethiol molecules using various powerful tools such as inelastic electron tunneling spectroscopy (IETS) [1]. Much effort has also concentrated on molecules on well-characterized substrates like silicon [2], allowing us to put our theoretical understanding on a solid footing and benchmark our quantitative predictions. In addition, the ability to grow and manipulate molecular assemblies on various substrates has opened up opportunities for exciting devices, such as molecular transistors, switches, memories and sensors. Finally, studying molecules allows us to flesh out fundamental transport-related concepts that apply to other nanoscale systems, such as ballistic MOSFETs, nanotubes, quantum dots and spintronic devices.

II. FORMAL CHALLENGES

Formal treatment of conduction requires us to solve for quantum transport with open boundary conditions set by the

statistics of the contact or scattering reservoirs. Current flow through a molecule is at heart a nonequilibrium problem driven by the different electrochemical potentials in the contacts under bias. In addition, the presence of macroscopic contacts makes it necessary to ‘open up’ Schrödinger’s equation by allowing addition and removal of charge in the molecule by the leads, which act as reservoirs externally held in thermal equilibrium.

Conduction through any generic nanoscale quantum system involves partitioning it into a device and a contact, coupled with self-consistent electrostatics [3] and quantum transport [4,5,6]. Within an effective one-electron theory, we employ a non-equilibrium Green’s function formalism (NEGF) for quantum transport coupled with electronic structures for the central device and self-energies for the contacts. The approach is quite general, and has been fairly successful in quantitatively explaining many experimental molecular current-voltage (I-V) characteristics [4]. However in some cases, notably for systems with localized wavefunctions and strong charging, as in unconjugated molecules or molecules with weak coupling with contacts, experiments show a variety of novel features such as ultralow zero-bias conductance, abrupt current onsets, extended quasilinear regimes with multiple closely spaced structures, and gate modulated current levels [7,8]. These features are hard to capture even qualitatively by effective one-electron theories and require an entirely different approach, involving rate equations for transitions between many-body states [8].

A particular phenomenon that emerges from the many-electron interaction is the possibility that the contacts could remove an electron from a molecular ground state and reinject it into an excited state. It is hard to imagine how capturing such a rich spectrum of excitations using a one-electron potential; however, a proper many-electron theory of transport yields many of these features quite naturally. In fact, the resemblance between experimental and theoretical results within such a transport approach is quite compelling (Fig. 1). Given that continued device scaling is progressively making the transistor channel behave more like a quantum dot than a quantum wire, it is becoming crucial to further explore such formal techniques for incorporating electron-electron and electron-vibronic correlations within a transport model. Furthermore, correlation brings novel opportunities for device structures, since semiconducting dots with a rich internal dynamics governed by excitation physics, are believed to be excellent candidates for sensing, single-electron switching, memory and heat sinking.

Our present approaches to transport cover two opposites: (a) for molecules with strong coupling to contacts and adiabatic

charge addition, we employ self-consistent fields (SCF) or one-electron potentials coupled with an NEGF treatment of transport [9]. External perturbations like electron-electron, electron-lead or electron-vibronic coupling are incorporated in formally analogous ways through an effective one-electron self-energy, with a need for self-consistency to capture feedback effects between the system and the perturbing influence. While it is relatively easy to include level-broadening in this approach, the challenge is to systematically include correlation effects, particularly non-perturbative contributions; (b) for molecules with weak coupling and strong single-electron charging, a multielectron rate equation approach must be used to handle the proper many-body Hamiltonian [8]. A particular challenge is to add coherent broadening by the contacts. While the two limits are separately understood, there is a wealth of physics and device prospects that span the intervening regime. A typical example is a molecular component integrated onto a nanowire template, where we may need to devise techniques for coupling a many-body treatment of switching or vibrations in the molecule with an SCF treatment of conduction through the wire.

Figure 1. Left: Excitation diagram that takes a dot from one ground state to another and back to an excited state. Such transitions are responsible for the quasiohmic regions in molecular I-Vs, along with a multitude of other fine structures, seen theoretically (top right) and experimentally (bottom right).

III. COMPUTATIONAL CHALLENGES

While there are obvious computational challenges in the weak coupling regime of handling the many-electron configuration space that increases exponentially with basis size, the SCF regime has its own computational hurdles. Between various systems such as molecules, nanowires, or nanotubes, the main operational differences involve different basis sets (real-space, momentum space, plane wave or atomistic bases), different bandstructures (effective mass, tight-binding, density functional, configuration interaction etc.) and effective one-electron potentials (Coulomb energy from Poisson's equation, possibly augmented by exchange-correlation as in density functional or GW calculations). Although different basis sets or one-electron potentials have been developed by researchers separately for different systems such as molecules or silicon, their inherent similarity at an atomistic level argues in favor of

adapting one set of techniques to another set of systems, such as a chemists' approach to contact bandstructure, for example.

Much of our past achievements have involved molecules on metal substrates, using an NEGF approach coupled with semi-empirical or ab-initio molecular bandstructures. However, metal contacts are harder to characterize or control, leading to artifacts and parasitic effects that have hampered quantitative benchmarking of theory and experiment. In comparison, we have had considerable success in adapting these techniques to silicon, a better understood, well-characterized substrate with covalent bonding chemistry and novel physics due to band-filtering and current triggered desorption. Significantly, the complex bandstructure and complicated electrostatics of silicon requires practical schemes for combining quantum chemistry and surface physics that allows us to describe silicon atomistically while doing justice to its surface chemistry [10], bandstructure, band-bending, reconstruction and surface states.

These techniques have led to a powerful quantitative model for molecular electronics on silicon that allow us to deconstruct the role of contact microstructure on molecular conduction. We demonstrated recently that various scanning tunneling spectra on buckyballs on silicon can be accounted for (Fig. 2) simply by invoking variations in the attachment geometry between the molecule and the surface silicon dimers [11].

Figure 2. Schematic buckyball scanning tunneling spectroscopic setup on a silicon substrate (top left), involving an interdisciplinary mix of issues (bottom left). Combining electronic structures at the interface by partitioning and matching basis functions, we can theoretically reproduce (bottom right) experimental features (top right) for a variety of bonding configurations.

There are real computational challenges to dealing with larger systems (like biomolecules or nanotubes). A particular thrust has been towards develop practical embedding schemes to combine coarse-grained descriptions (e.g. effective mass theories) of parts of a heterostructure with atomistic treatments of others (e.g. the contact-device interface), leading to multiscale techniques that could allow us to handle large realistic systems. A significant progress has been the development of an Extended Huckel approach to parametrize the bandstructure of technologically important materials like carbon nanotubes and silicon. The presence of explicit, non-orthogonal, flexible basis sets has led to robust bandstructure parameters that are transferrable between bulk and surface including large reconstruction effects, and between different

chemical environments such as diamond, graphite and buckyball for carbon, for example [10]. Our approach compares well quantitatively with $sp^3s^*d^5$ tight-binding for bulk silicon and GW calculations for silicon surface bands. It is much more transferable than orthogonal tight-binding while being significantly faster than GW approaches.

IV. DEVICE LEVEL CHALLENGES

Figure 3. Molecular relay created by rotating a dipole with a top gate. One can exploit the vector directionality of the gate-field to selectively eliminate the source-drain torque and get a good effective transfer characteristic.

A proper formal and computational understanding of molecular electronics allows exploration of novel device paradigms and functionalities. We have identified fundamental challenges to molecular transistor action, gated electrostatically or conformationally. Gate control is compromised by the difficulty of bringing it near the channel without causing leakage, leading to non-saturating I-Vs [12,13]. The presence of contact metal-induced gap states further degrades transistor performance by increasing the subthreshold swing and reducing the ON-OFF ratio. Conformational gating can provide ways around these bottlenecks by exploiting the vector directionality of the gate field to selectively couple it to molecular dipoles to create a relay, for example [13] (Fig. 3). The main challenge is to allow adequate gate control by engineering large dipolar coupling to eliminate thermal fluctuations. Proper damping mechanisms need to be explored to stop the molecule at requisite orientations to prevent such thermodynamic averaging. One way to achieve this is by engineering molecular potential barriers. Aside from thermodynamic concerns associated with dissipation in such two-state systems, it remains to be seen whether such a structure can be incorporated into a typical MOSFET architecture.

Single molecule sensors have also been under active investigation. The observable in typical molecular sensing systems is a modulation of the current in a nanowire by attachment of a single molecule [14]. While various experimental demonstrations have probed such possibilities in the past, the operational principles are far from clear. Molecules create a range of possibilities upon attachment, such as influencing the potentials and depletion widths of the wire, the contact Schottky barriers, the conformations of different parts of the heterostructure, or the creation of traps, each bearing a qualitatively different influence on conduction.

An interesting system is a hybrid molecule-silicon device where the molecule adds functionality to a silicon chip. Perhaps a promising architecture involves the molecule sitting ON the channel rather than IN the channel, leading to interesting device possibilities such as trap-assisted switches, spin-controlled memory [15] or conformation mediated heat sinks.

Aside from fabrication advantages associated with only one contact needed to the molecule and the relative ease of incorporating a gate, such a surface modulated transistor might actually be compatible with existing CMOS architectures.

Hybrid molecule-silicon structures can lead to new physics, as in a molecular resonant tunneling diode on silicon [16]. Utilizing the bandgap of silicon as an energy-filter, we predicted a novel doping-dependent negative differential resistance for molecules on degenerately doped silicon at high STM bias voltages. The prediction seems consistent with recent experiments [2] that probe a variety of single or self-assembled molecules on variously oriented silicon substrates, at different temperatures and tip-substrate separations. While this is still far from a functioning device, and while important quantitative details still need to be sorted out, it provides an excellent system to refine our formal, computational and device-level understanding of molecular electronics.

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