

TranSIESTA: A SPICE for Molecular Electronics

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ABSTRACT

With our newly developed method, TranSIESTA[1], it is possible to model nanoscale electronic devices under operation conditions. In this paper we briefly describe the basic principles behind the method and present simulations of recent experiments of atomic wires and molecular devices.

The TranSIESTA method is based on density functional theory, and calculates the selfconsistent electronic structure of a nanostructure coupled to 3-dimensional electrodes with different electrochemical potentials. It uses a full atomistic ab initio description of both the electrodes and the nanoscale device. The calculations reveal information about the scattering states, transmission coefficients, electron current and non-equilibrium forces in the systems.

Keywords: Molecular electronics, first principles simulations, density functional theory, electron transport

1 Introduction

Part of the success of silicon technology is related to the development of reliable tools for device modelling. If nanoelectronics shall mature into replacing silicon it is necessary to develop new techniques that reliably model the transport in the devices. The dimensions of nanoelectronic components are such that it is important to take into account the atomic structure of the device. Since the devices operate under non-equilibrium conditions, methods must be developed that both describe the electronic structure with atomic detail and take into account the change in the electronic structure when a current is flowing through the device. In this paper we present a new method, TranSIESTA, for first principles quantum chemical modeling of nanoelectronic devices under non-equilibrium conditions[1]. The method is based on the non-equilibrium Greens function technique which has been interfaced with the SIESTA electronic structure package[2] in such a way that the density matrix of the system is calculated selfconsistently when the system is subject to an external bias. In this paper we will give a brief overview of the method and present results for electron transport through atomic wires and molecular devices.

First principles Atomic-scale Modeling

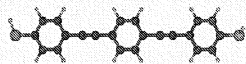

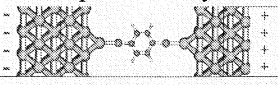
SYSTEM	Industrial applications
Molecules 	New Chemicals New Pharmaceuticals
Periodic systems 	New Materials
Non-equilibrium systems 	Nano Electronics Gate Oxides Biological systems

Figure 1: Quantum chemical methods are very reliable for describing the structure of molecules and periodic systems, and play an important role in developing new chemicals, pharmaceuticals and materials. With TranSIESTA it is possible to model systems driven out of equilibrium by an external bias.

2 The TranSIESTA method

Figure 2 shows a typical non-equilibrium system: Two electrodes with different chemical potentials, left and right, are coupled via a contact region. The system can be separated into three parts, *Left (L)*, *Contact (C)* and *Right (R)*. The part of the Left and Right electrode that has matrix elements with the region C we call I_L , I_R , respectively. The coupling of I_L and I_R with the remaining part of the infinite electrodes is taken into account using selfenergies, Σ_L and Σ_R , in the Hamiltonian, thus we only need to include the atoms in region I_L , C , and I_R . In the direction parallel to the interface we impose periodic boundary conditions. From the Hamiltonian, H , we can obtain the retarded Greens function, G , using matrix inversion

$$G(E) = [E - H - \Sigma(E)]^{-1}. \quad (1)$$

The non-equilibrium density matrix, D , is related to the retarded Greens function through the equation

$$D = \frac{1}{\pi} \int_{-\infty}^{+\infty} dE$$

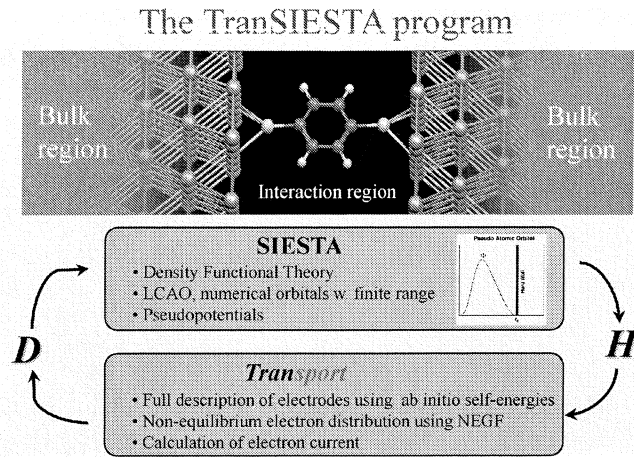


Figure 2: A molecule sandwiched between two semi-infinite gold crystals. Only a finite region of the system needs to be modelled, since the effect of atoms in bulk environments can be described by a self energy. The TranSIESTA packages use the SIESTA program in order to obtain a Hamiltonian in a localized basis set. The *Trans* part of the TranSIESTA package calculates a non-equilibrium density matrix from the Hamiltonian, which is feed back into a selfconsistent cycle.

$$[G(E) \text{Im}\Sigma_L(E) G^\dagger(E) n_f(E - \mu_L) + G(E) \text{Im}\Sigma_R(E) G^\dagger(E) n_f(E - \mu_R).] \quad (2)$$

We use density functional theory to obtain the Hamiltonian,

$$H_{i,j} = \langle i | -\frac{\hbar^2}{2m} \nabla^2 + V^{eff}(\rho) | j \rangle, \quad (3)$$

where $|i\rangle, |j\rangle$ are the localized basis functions used by SIESTA. The SIESTA basis sets[2] are solutions to the Schrödinger equation of the atom with the boundary condition that they should be zero at a specific radius. The implementation includes the possibility of multiple Zetas and Polarization terms, and the accuracy is similar to calculations with Gaussian orbitals. The atom cores are described by Troullier-Martins Pseudopotentials.

In practice, the equilibrium part of the energy integral in Eq. (2) is done over a complex contour and only few energy points are needed for this part. The non-equilibrium part of the density matrix is obtained by a real axis integral, and a dense set of points is necessary for good numerical accuracy. Latest versions of TranSIESTA use sparse matrix inversion techniques, and electron scattering states to describe the non-equilibrium part of the density matrix. With these new developments the computer time for calculating the density matrix becomes comparable to the time for performing normal SIESTA calculations, i.e. the time it takes to diagonalize the Hamiltonian.

The selfconsistent density matrix of the system is obtained by solving the above equations iteratively using

a Pulay mixing scheme[?]. From the the selfconsistent density matrix we can obtain the total energy and forces. The conductance can be found from the retarded Greens function and the left and right selfenergies[1].

3 Test System: Atomic wires

The conductance of single atom contacts is a benchmark in atomic scale conduction. Since the first experiments[4]–[6] numerous detailed studies of their conductance have been carried out through the 1990s until now (see e.g. Ref. [7] for a review). More recently the non-linear conductance[8]–[11] has been investigated and the atomic structure[12], [13] of these systems has been elucidated. There is general consensus of the experimental behaviour of atomic contacts, and they therefore constitute a good test system for theoretical methods.

The I - V characteristics of the single atom Au contacts are very linear with the zero bias conductance close to one conductance quantum (G_0). The behavior of single atom Pt contacts is much more sensitive to the atomic geometry with a zero bias conductance in the range $1.7G_0$ - $2.3G_0$ [14]. Pt contacts display typically a nonlinear I - V characteristic. In Fig. 3 we show the typical I - V behavior of Au and Pt single atom contacts[14].

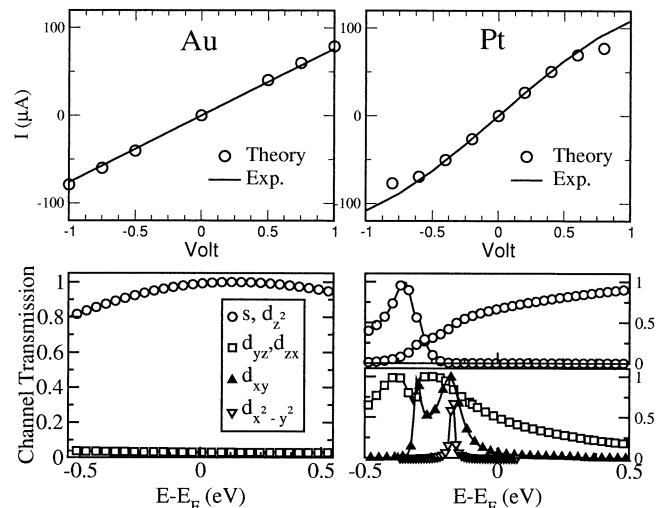


Figure 3: The I - V characteristics can be fitted well to $GV + G'''V^3$. The solid lines represent typical experimental curves for Au and Pt contacts using the average coefficient G''' , for $G = 1.0G_0$ (Au) and $G = 1.7G_0$ (Pt). The calculated I - V characteristics is shown with circles and correspond to $(G, G''') = (1.05G_0, -0.03G_0/V^2)$ for Au and $(G, G''') = (1.73G_0, -0.82G_0/V^2)$ for Pt. Bottom: Total transmission decomposed into transmission eigenchannels.

We have modelled these systems theoretically by plac-

ing a single metal atom between two (111) electrodes. Our calculations show that the zero bias conductance of the Au contacts are relative insensitive to the atom-electrode distance ($G(2.65\text{\AA})=1.1G_0$, $G(3.5\text{\AA})=1.0G_0$), and the system displays linear I - V characteristics. The Pt contact, on the other hand, displays a nonlinear I - V characteristics and the zero bias conductance depends more strongly on the geometry ($G(2.65\text{\AA})=2.1G_0$ and $G(3.5\text{\AA})=1.1G_0$), in accord with the different experimental behaviour of Au and Pt. The calculated curves in Fig. 3 is for an atom-electrode distance of 2.9 Å.

The different I - V spectra of Au and Pt can be understood by decomposing the total transmission into eigenchannels[15] (T_n).

$$T_{\text{Tot}}(E) = \sum_n T_n(E). \quad (4)$$

In the case of Au the transmission at 0V is dominated by a single, broad channel of mainly s character which is a result of the strong coupling of s orbitals. Due to the slow variation of channel transmissions with energy the I - V characteristics is quite linear.

This is in contrast to Pt. Here we find 4 channels with significant contributions and a much stronger variation with energy for 0V. The strong variation with energy and the rich structure is the origin of the nonlinear I - V . The significant participation of the d electrons in the transport gives rise to a decreasing conductance with bias: The d electrons are more easily scattered by the voltage induced potential which in this case is of the same order of magnitude as the strength of the coupling to the electrodes. The same argument goes for the variation with atom-electrode distance. Here it is essentially the d contributions which decrease as the distance increase.

4 Simulation of a molecular device

Reed and co-workers [16]–[19] have shown that a set of phenyl-ethynylene oligomers (known as *Tour wires* (TW)[20]) functionalized with different side groups, can show negative differential resistance (NDR)[16], [17]. This opens the possibility for molecular scale logical operations as previously demonstrated in the context of NDR in semiconductor heterostructures [21]. Despite much interest in these experiments, a fundamental understanding of the microscopic mechanisms governing the NDR is still lacking.

Based on theoretical studies of isolated molecules, Seminario et. al. [22], [23] have proposed that charging of the molecule and the subsequent localization/delocalization of the molecular orbitals might lead to this type of behaviour. Having verified the ability of the TRANSIESTA method to model nanoelectronics devices, we will now test this proposal by calculating the electronic

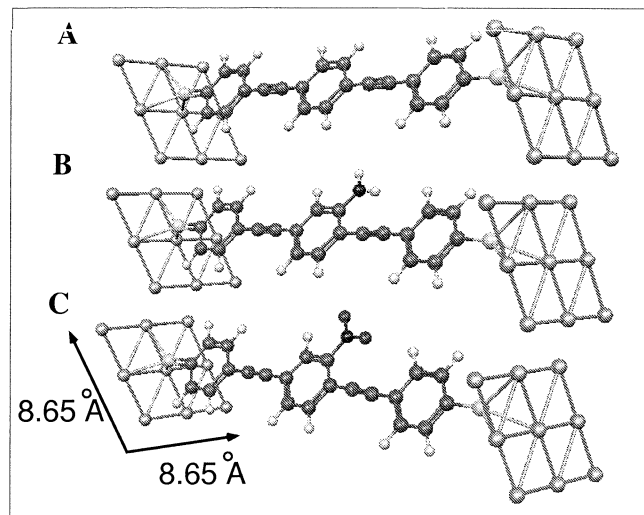


Figure 4: A) A phenylene-ethynylene oligomer connected to two Au (111) surfaces. B) same as A with an amino group attached to the middle phenyl ring. C) A nitro group is attached to the middle phenyl ring.

structure of the Tourwire when it is under nonequilibrium conditions.

The experiments have been carried out in a nanopore structure, formed by evaporating the molecules onto a small Au surface inside a SiO₂ structure, and then evaporating another Au electrode onto the molecular monolayer[16]. Thus, no detailed information is available about the structure of the monolayer. Our approach will be to form an idealized model of the electrode/monolayer/electrode structure and compare the results for the different molecules. We use an Au(111) surface in a 3x3 unit cell for the electrodes and assume that the hydrogen dissociates from the S atoms at the end of the molecules so that Tour wires are chemisorbed to the surfaces through strong thiol bonds. The molecules are placed between the Au(111) surfaces and the molecular coordinates allowed to relax in order to minimize the energy. The three different metal-molecule-metal structures are illustrated in figure 4. Monolayer A consists of a bare TW with thiol end groups, chemisorbed to Au(111) in a 3x3 unit cell. Monolayer B consists of the same TW, functionalized with an NH₂ side group on the middle ring, while TW's in Monolayer C are functionalized with NO₂ side groups.

In figure 5a we show the calculated I - V characteristics of monolayer A, B, and C. We obtain almost identical I - V characteristics of the three systems, and none of the systems display NDR behaviour. At low biases the systems display ohmic behaviour with conductance 2.0 S, 2.3 S, 1.9 S for A, B, and C, respectively. Around 1.8 V the current increases abruptly, in agreement with measured I - V characteristics[16], [17].

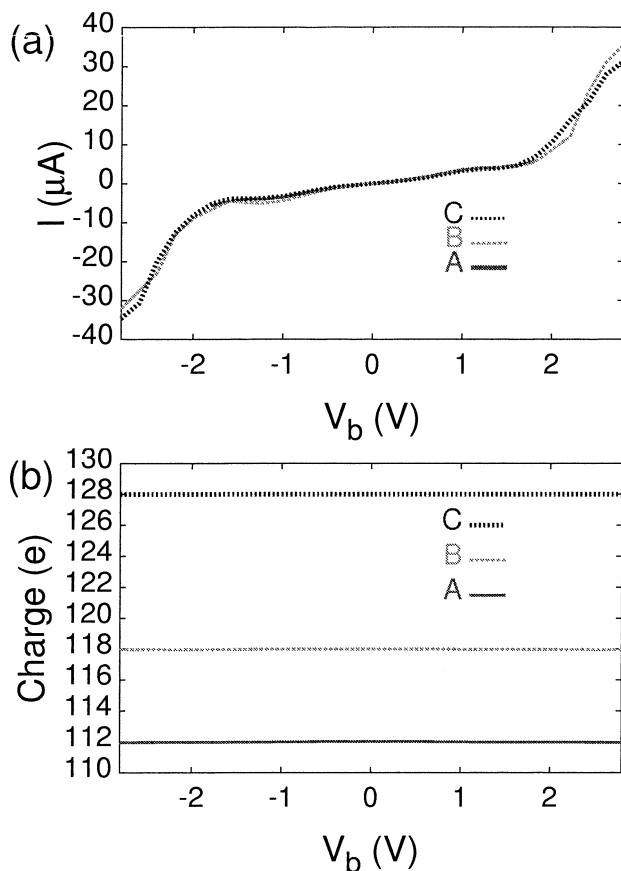


Figure 5: a) I - V characteristics of molecule A, B, and C. b) Total Mulliken charge on molecule A, B, and C as function of the applied bias.

In the work of Seminario *et al.* it was suggested that the molecules would change their charge state as a function of the bias. In our approach with an open metal/molecule/metal system, the charge on the molecule is not fixed but adjusts itself to minimize the free energy as the left/right electrochemical potentials are changed. The charge on the molecule as determined by a Mulliken population analysis, is shown as function of the bias voltage in figure 5b. We notice that at most 0.05 electron enters or leave the molecule as the voltage is varied between -3 and +3 V, thus our calculations suggest that charging effects are not important for these systems and the experimentally observed NDR behavior is of a different origin.

5 Conclusion

We have illustrated that quantum chemical methods can be used to describe the electrical properties of nanoscale systems. With our method, TranSIESTA, we have devised an efficient way of describing such systems, and the computational cost of such calculations

are approaching conventional quantum chemical methods. We have used the TranSIESTA package to simulate the electron transport in atomic point contacts and molecular devices, and shown that new insight can be obtained from such simulations. We acknowledge support from NSERC(JT), STVF(KS,JT), SNF (MBR), and EU SANEME (JT,KS).

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