

# Electronic transport properties of molecular devices

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## Abstract

Density functional theory calculations combined with non-equilibrium Green's function technique have been used to compute electronic transport in organic molecules. In our approach the system Hamiltonian is obtained by means of a self-consistent density-functional tight-binding (DFTB) method. This approach allows a first-principle treatment of systems comprising a large number of atoms. The implementation of the non-equilibrium Green's function technique on the DFTB code allows us to perform computations of the electronic transport properties of organic and inorganic molecular-scale devices. The non-equilibrium Green's functions are used to compute the electronic density self-consistently with the open-boundary conditions naturally encountered in transport problems and the boundary conditions imposed by the potentials at the contacts. The Hartree potential of the density-functional Hamiltonian is obtained by solving the three-dimensional Poisson's equation involving the non-equilibrium charge density. The method has been applied to study the transport properties of a variety of molecular systems. It also allows for self-consistent computations of the atomic forces and to perform molecular dynamics simulations which are used to investigate the role of thermal fluctuations in coherent transport through organic molecules. © 2003 Elsevier B.V. All rights reserved.

PACS: 70.10–d; 85.65.+h

Keywords: Molecular electronics; Non-equilibrium transport; Green's functions

## 1. Introduction

The information technology is moving towards an increasing level of miniaturization from sub-micrometer conventional inorganic devices to the extreme scale where the active component can involve just a single molecule. Molecular electronics is attracting more and more the attention of theoreticians and computational physicists both for its potential applications and for the interesting fundamental physics involved.

Electronic conduction through a variety of different molecules has been studied experimentally by many research groups [1–5] and novel design architectures for memories and logic circuits have been explored [6].

However, the exact nature of the transport mechanisms in many of such systems remains still open to scientific debate. The role of phonon scattering, coherent tunneling versus multiple incoherent hopping transport and redox-like processes are issues of investigation. In many cases there is experimental evidence that transport is coherent. In carbon nanotubes (CNTs) electronic transport can propagate coherently over surprisingly long distance of about a micrometer.

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Certainly molecular devices require new simulation approaches, since the inherent quantum-mechanical physics involved must be treated properly. In particular, the contact and the device should be treated on an equal footing, since the detailed knowledge of the interactions between molecules and contacts that determines the energy levels of the system and their alignment with respect to the Fermi energy is crucial for transport properties.

In order to tackle these problems we have developed a new code for transport computations [7] based on the well-known density functional tight-binding (DFTB) method, [8] which allows a first-principle treatment of systems comprising a large number of atoms. The code has been recently extended to the non-equilibrium Green's function approach (NEGF) [9,10] for the computation of the charge density and electronic transport. This technique enables the computation of the tunneling current flowing between two contacts in a manner consistent with the open boundaries and non-equilibrium conditions that naturally arise in coherent transport problems.

We give a brief description of our methodology and show applications to molecular *devices* with fully self-consistent computation of the non-equilibrium wind forces acting on the atoms, which enables us to explore the potentiality of molecular systems as electronic switches and bistable rectifiers. Our methodology also allows time-resolved current calculations along the steps of classical molecular dynamics simulations, which enables us to explore the role of dynamics and coherent phonon scattering.

## 2. The self-consistent density-functional tight-binding

The standard DFTB formalism has been explained in detail in a number of Refs. [11–14]. The key ingredient of the method is the two-center approximation [15,16] for the Hamiltonian matrix elements. These can be computed separately, by first principle computations, for each atomic pair and stored in look-up tables that can be used during the actual simulation. The method has proved as capable of giving accurate and transferable potentials and the numerical efficiency of the method allows the computation of the

electronic properties of large super cells, containing several hundreds of atoms.

This methodology is particularly suitable to study large mesoscopic systems, particularly organic molecules such as a CNTs, DNA strands or adsorbates on surfaces. The method has also been applied to study semiconducting heterostructures.

The DFTB method has been extended to self-consistent charge-density computations. The key ingredient is the expansion of the electronic charge density as  $n(r) = n^0(r) + \delta n(r)$ , where  $n(r) = n^0(r)$  is a reference density that can be given by the neutral atoms, and  $\delta n(r)$  is a density fluctuation. The first-order density corrections vanish from the Kohn energy functional [11] which can be written, up to second order in the density fluctuations, as

$$E_{\text{tot}}[n] = \sum_i n_i \langle \Psi_i | H^0 | \Psi_i \rangle + E_{\text{rep}}[n^0] + E^{(2)}, \quad (1)$$

where the first and the second term are the zeroth-order contributions, described in Ref. [11], and the last term is the second-order correction to the Hartree and the exchange-correlation potential

$$E^{(2)}[\delta n] = \frac{1}{2} \int \int \left[ \frac{1}{|r - r'|} + \frac{\delta^2 E_{\text{xc}}}{\delta n(r) \delta n(r')} \right] \times \delta n(r) \delta n(r') dr dr'. \quad (2)$$

Applying the variational principle to the energy functional of Eq. (1), it is possible to obtain a modified Hamiltonian for the Kohn–Sham equations

$$H_{\mu\nu} = H_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_k (\gamma_{ik} + \gamma_{jk}) \Delta q_k, \quad \forall \mu \in i, \nu \in j, \quad (3)$$

where  $\Delta q_k$  is the net excess charge on atom  $k$ , evaluated with the Mulliken charge analysis, and the matrix elements  $\gamma_{ik}$  contain the evaluation of Eq. (2) with the normalized charge densities of atoms  $i$  and  $k$ . Since the atomic charges depend on the one-particle wave functions, a self-consistent procedure is required. The improvement of the self-consistent over the non-self-consistent procedure is considerable in structural and energetic properties of molecular systems [11].

### 3. The Green's function technique for non-equilibrium transport

In order to compute the current, open-boundary conditions for the Kohn–Sham equations must be employed. Open boundary conditions are necessary in order for the eigenstates to carry a current.

The problem of quantum transport through a mesoscopic device linked to two contacting leads can be set by starting from the scattering states which propagate from one lead to the other. Deep in the leads the propagating states are Bloch's waves. The waves scatter at the contact–molecule interface and are partially reflected and partially transmitted across the molecule. Consider the retarded and the advanced Green's functions related to the Hamiltonian of the  $\alpha$  contact,  $H_\alpha$ :

$$g_\alpha^{r,a} = [ES_\alpha - H_\alpha \pm i\delta]^{-1}. \quad (4)$$

Here the overlap matrix,  $S$ , arises because the operators are represented on a local basis set, which is generally not orthogonal. We keep the non-orthogonal basis throughout the computation, since, in this scheme, we need to clearly identify the *device* part from the contacts and this is naturally possible in the local description. Consider now the case of two contacts and a molecular region. Under the assumption that there is no direct interaction between the contacts, the Hamiltonian of the whole system can be written in a block matrix of the form

$$H = \begin{bmatrix} H_D & V_{D1} & V_{D2} \\ V_{D1}^\dagger & H_1 & 0 \\ V_{D2}^\dagger & 0 & H_2 \end{bmatrix}, \quad (5)$$

where  $V$  is the contact–molecule coupling Hamiltonian. A similar structure holds for the overlap matrix,  $S$  [17]. The complete Green's function of the system can be expressed as

$$G_D^r = (ES_D - H_D - \Sigma^r)^{-1}, \quad (6)$$

where  $\Sigma^r$  is the total self-energy of the two contacts,

$$\Sigma_\alpha^{r,a} = (ES_{D\alpha} - V_{D\alpha})g_\alpha^{r,a}(ES_{D\alpha} - V_{D\alpha})^\dagger, \quad (7)$$

which plays the role of an embedding potential. The self-energy can be calculated easily using, for

example, the Decimation technique [18], which is a powerful recursive algorithm suitable to TB matrix representations.

The Green's function expressed in Eq. (6) is defined in the *device* region only, which is desirable for practical computations. The infinite contact leads are mapped into complex self-energies, whose imaginary parts play the role of injecting and extracting wave function probability at the *device* region boundaries, hence, describe a current flow.

Since the *device* region is not in equilibrium, it is not possible to define a common electrochemical potential. What is needed is an expression that accounts for the correct occupation of the states under non-equilibrium conditions. For simplicity, we will refer to a system with two contacts that we will call *left* and *right*. The key assumption is that the states propagating from *left* to *right* originate deep in the *left* contact where there is an equilibrium condition with chemical potential  $\mu_L$ . Similarly, the states propagating from *right* to *left* originate deep in the *right*-contact where there is an equilibrium condition with chemical potential  $\mu_R$ . Hence, the total density of these propagating states is

$$\rho = \int_{-\infty}^{+\infty} dE [d_L f(E - \mu_L) + d_R f(E - \mu_R)], \quad (8)$$

where  $d_L$  and  $d_R$  are the partial densities of states propagating from *left* to *right* and vice versa. Expression (8) can be used to calculate the electronic density needed for the density-functional Hamiltonian. It can be proved that Eq. (8) is linked to the non-equilibrium Green's function (known also as Keldysh GF) [9]. Evaluation of the integration in Eq. (8) requires some particular techniques, discussed, for example, in Ref. [19].

The current flowing in the system can be computed starting from the standard scattering theory. In the simplest case of two contacts and in the absence of incoherent scattering, the final expression for the current is

$$i_{\text{coh}} = \frac{e}{h} \int_{-\infty}^{+\infty} \text{Tr}[\Gamma_L G^r \Gamma_R G^a] \times [f_L(E) - f_R(E)] dE. \quad (9)$$

In this limit the usual expression of the Landauer theory is recovered. An additional factor of 2 usually

must be added because of spin degeneracy. One of the advantages in using the Green's function approach, besides its numerical stability, is that incoherent scattering and relaxations can be included with appropriate self-energies [10,20].

#### 4. The self-consistent solution to the non-equilibrium problem

The implementation of the NEGF into the DFTB code is done at the level of the SCC loop of the DFTB Hamiltonian of Eq. (3). The difference is that in the standard DFTB approach the density matrix is constructed from the direct computation of the eigenstates of the system; within the non-equilibrium Green's functions the density matrix is obtained by Eq. (8). From the density matrix it is possible to compute the Mulliken charges:

$$q_i = \sum_{\mu \in i} \sum_{\nu} \text{Re}[\rho_{\mu\nu} S_{\mu\nu}]. \quad (10)$$

Quite like in standard DFTB, the Mulliken charges are then used to evaluate the atomic excess charge density. The second-order correction to the Hartree potential is obtained by solving the Poisson's equation for the excess charge density:

$$\nabla^2 V^{(2)} = -4\pi \sum_i \Delta q_i n_i(r) \quad (11)$$

with the boundary conditions imposed by the contact potentials. These conditions arise from the natural requirement that deep inside the contacts the effective potential for the Kohn–Sham equations must correspond to the bulk potentials. Therefore, at the boundaries between the *device* region and the contacts, the potential must match the intrinsic effective bulk potential (which originates from any equilibrium excess charge density) shifted by the applied bias. At the device–contacts interfaces,  $C_\alpha/D_\alpha$ , the potential must satisfy

$$V_{D_\alpha}^{(2)}(r)|_{C_\alpha/D_\alpha} = V_{C_{\alpha,\text{bulk}}}^{(2)}(r)|_{C_\alpha/D_\alpha} + \Delta V_\alpha, \quad (12)$$

where  $\Delta V_\alpha$  is the applied external potential in the  $\alpha$ -contact. Note that with the usual boundary condition

of potential vanishing at infinity the solution of the Poisson's equation will give back the result of Eq. (2). The Poisson's equation is solved using a 3D multi-grid technique. This approach allows an easier generalization to more complex device geometries, for example, such a realistic FET configuration.

Application of the Hellman–Feynman's theorem implies that the atomic forces acting on the atoms can be computed as a gradient of the total energy of the system, expressed by functional (1). The atomic forces can be obtained in terms of the density matrix and the Coulomb potential and therefore be fully consistent with the non-equilibrium conditions. This allows the computation of current-induced wind forces and may be used to evaluate the molecular switching and the bistable properties with the applied bias.

#### 5. Results

We have computed tunneling currents in alkeno-thiolate molecules bridging two Au contacts. In Fig. 1 we have compared the current flowing in 2 different molecules:

- (a) Au-S(CH<sub>2</sub>)<sub>12</sub>S-Au
- (b) AuS(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>-Au

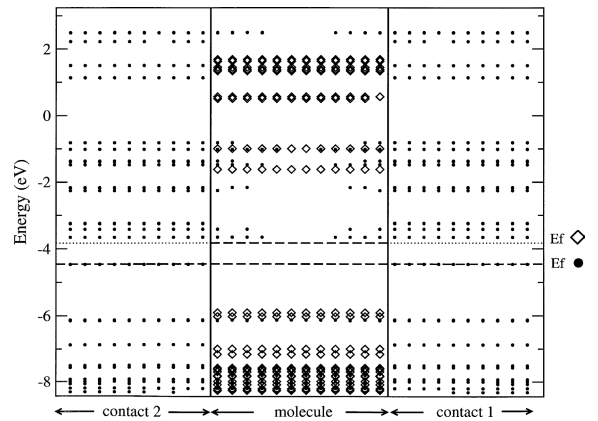


Fig. 1. Energy levels of the simulated system. The dots refer to the alkeno-thiolate molecule bonded to both Au contacts by sulfur atoms, while squares refer to the simple molecule ended with thiolic groups. The middle section refers to the 12 C-atoms of molecular backbone. The degree of localisation is shown by marking a dot only when the wavefunction projections on the corresponding atom is greater than a small cutoff.

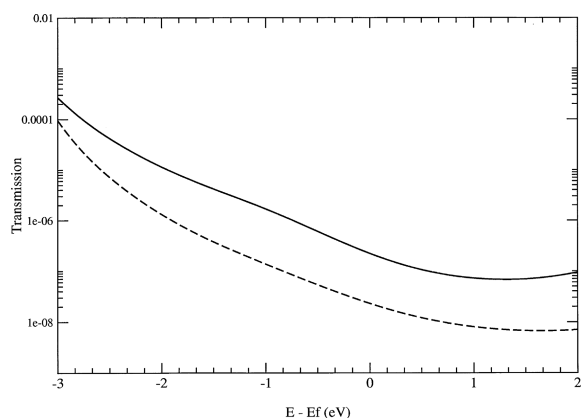


Fig. 2. Tunneling coefficient as a function of energy for alkeno-thiolate molecules, for the case of two (solid curve) and only one (dashed curve) terminating sulfur atoms.

In the case of the molecule, (a), bonded at both ends to the Au surface with a S-atom the current is about 20 pA at 1 V, which agrees with experimental measurements [4].

In the case of the molecule (b), which form a S-Au bond on one end only, the current is about one order of magnitude smaller.

Since there is no chemical bond formation between the Au and the alkane end, we have set the Au-H distance to 2.50 Angstrom, which is consistent to other theoretical computations [12].

In order to show the effects of the Au contacts on the transport in alkeno-thiolate molecules, we compare, in Fig. 1, the energy levels of the single molecule ended with two thiolic groups (represented with diamonds) with those of the molecule bonded to both Au contacts by sulfur atoms (dots).

The dots in Fig. 2 correspond to an atomic position of the contact-molecule-contact structure. The left and right sections of the graph correspond to the two contact regions, whilst, in the central section, is represented the chain of the 12 carbon atoms constituting the molecular backbone. The dots which define the energy levels are marked only when the projection of the wavefunction on the corresponding atom is larger than a given cutoff ( $> 10^{-3}$ ), therefore representing the degree of localisation of the wavefunctions themselves.

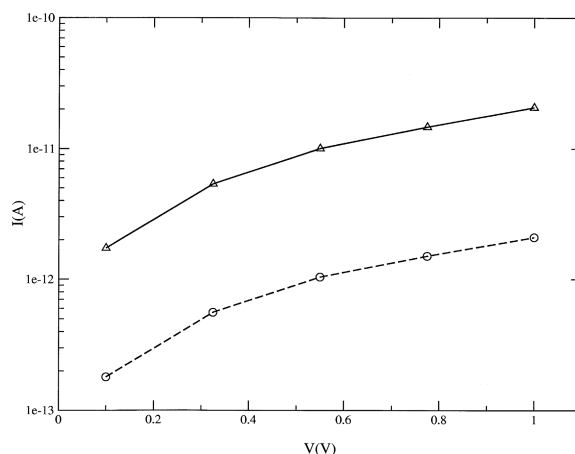


Fig. 3.  $I$ - $V$  characteristics for alkeno-thiolate molecules between Au contacts. The solid curve refers to a molecule bonded to both contacts by a sulfur atom; results for the same molecule with one of the two sulfur atoms substituted by an hydrogen (molecule physisorbed on one contact) are shown by the dashed curve.

We can see from the graph that the interaction with Au contacts is mainly responsible for the lowering of the LUMO levels of the molecule, while the HOMO levels are left essentially unchanged, therefore reducing the energy gap. On the other side, the coupling with the Au orbitals causes a localization of the molecular orbitals near the interface with the contacts themselves, preventing the corresponding energy levels from conducting. This is the reason for the very small current that flows through the molecule in the voltage range we have inspected.

A similar picture holds for the molecule (b), although in this case the localisation is concentrated on the molecular side where the S-Au bond is formed.

Fig. 2 shows the transmission coefficient computed at 0 bias over a broad range of voltages. The Fermi energy is located at 0 eV. The graph exhibits that the HOMO level in the case (a) is closer to the Fermi level with respect to the case (b), and therefore the tunneling current is larger. The small coupling between the Au contact and the molecular terminal  $\text{CH}_3$ -group is also responsible for the smaller tunneling current with respect to the molecule (a) the potential drops almost linearly in both cases (Fig. 3).

## 6. Conclusions

Nanometer scale devices require new simulation tools which treats properly the quantum-mechanical aspects of the electronic and transport properties. Density functional methods have become the standard for solid-state computations. We have implemented the non-equilibrium Green's function technique for transport computations into the density-functional-based code DFTB. We have modified the self-consistent density functional method developed for tight-binding computations by Elstner et al. in order to be completely consistent with the open-boundary conditions needed for transport computations.

To obtain this, we use the non-equilibrium Green's function formalism for the computation of the density matrix. The electronic density determines the Hartree potential of the density-functional Hamiltonian. We show how to compute the Hartree potential by solving the Poisson's equation for the density fluctuations with boundary conditions that can satisfy a precise device geometry.

The new code can compute the coherent tunneling current flowing in a molecular device self-consistently with the boundary conditions imposed on the Hamiltonian of the system. Atomic forces can also be computed at the same time. The code enables molecular dynamic simulations that can be coupled to real-time current computations.

The code was then used to simulate the tunneling current in two types of alkeno-thiolate molecules.

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