

Current-driven conformational changes, charging, and negative differential resistance in molecular wires

Eldon G. Emberly¹ and George Kirczenow²¹*NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08536*²*Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*

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We introduce a theoretical approach based on scattering theory and total energy methods that treats transport nonlinearities, conformational changes, and charging effects in molecular wires in a unified way. We apply this approach to molecular wires consisting of chain molecules with different electronic and structural properties bonded to metal contacts. We show that nonlinear transport in all of these systems can be understood in terms of a *single* physical mechanism, and predict that negative differential resistance at high bias should be a generic property of such molecular wires.

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I. INTRODUCTION

A molecular wire in its simplest definition is a single molecule that forms an electrically conducting bridge between a pair of metallic contacts. During the last few years molecular wires have been realized in the laboratory and the electric current that flows through an individual molecule in response to a potential bias applied between the contacts has been measured.¹⁻⁴ The current-voltage characteristics of molecular wires are sensitive to the electronic structure of the molecule and contacts, which depends on the spatial arrangement (conformation) of the atoms that make up the wire and the distribution of electronic charge along the wire: Molecular wires have been observed to switch between conducting and nonconducting states due to a voltage-induced redox reaction, i.e., a change of the charge distribution in the wire,⁵ and also in response to bias-driven conformational changes.⁶ These experiments indicate that transport nonlinearities, conformational changes, and charging in molecular wires are mutually interdependent phenomena, each of which can strongly influence the others, and that they should therefore be treated theoretically in a unified way. Theoretical work to date has studied some of these phenomena independently^{3,7-13} but there has been little work directed at bringing all three of them together within a single theoretical framework.

In this article we introduce a tractable theoretical approach that unifies the three phenomena and present the results of self-consistent calculations for the simplest molecular wires, namely, small chain molecules bonded to metal electrodes. At low bias these molecular wires are conductors or insulators depending on which atoms make up the chain molecule and electrodes and on the number of atoms in the chain. Remarkably, we find that the nonlinear transport characteristics of these apparently dissimilar systems are strikingly similar and can be understood in terms of a single physical picture: We find that in the nonlinear transport regime the molecular wire acquires excess electronic charge. This charge resides in a molecular orbital which, being partly occupied, lies at the Fermi level and therefore controls electron transport through the molecule. (If there is no molecular

orbital near the Fermi level at zero bias, we find that the conformation of the molecule changes at finite bias in such a way that a suitable orbital appears there.) As the bias increases, the partly occupied orbital acquires more charge and the electrostatic contribution to its energy rises, together with the electrochemical potential of the source electrode. When this orbital rises well above the electrochemical potential of the drain electrode, the electron flux that it transmits from drain to source approaches zero and ceases to decline with increasing bias, while the flux that it transmits from source to drain cannot increase further significantly. Thus the net current through the molecular wire saturates. At the same time a charge density wave grows along the wire and atomic displacements occur, lengthening and thus weakening certain molecular bonds. We find the bond weakening to be sufficient that after saturating the current carried by the wire decreases as the bias increases further. We predict this negative differential resistance phenomenon to be a generic property of molecular wires that involve chain molecules.

Section II presents the theoretical formulation of the model that includes charge transfer and conformational change in the nonlinear transport regime. The transport characteristics of two simple linear-chain-like molecules (homogeneous and inhomogeneous) are presented in Sec. III based on calculations using the model of Sec. II. Finally, Sec. IV summarizes the results of this work.

II. THEORY

Recent theories of electronic transport in molecular wires have been based on semiempirical tight-binding models (such as the extended Hückel model) and on *ab initio* computations that are founded on density functional theory. For standard values of the tight-binding model parameters adopted from the quantum chemistry literature, the tight binding models have yielded results that are similar to (and often in semiquantitative agreement with) those obtained from the *ab initio* computations. For example, tight binding calculations¹¹ have yielded current-voltage characteristics for the benzene dithiolate molecule bonded between gold nanocontacts that are similar to those that have been found in *ab initio* calculations.⁷ These studies^{7,11} have made it evident

that the differences between the results of the tight-binding and *ab initio* calculations for this system are less significant than the uncertainties that are due to the present limited understanding of the conformational aspects of bonding between the molecule and metal contacts. Tight-binding calculations of electronic transport through molecular wires consisting of chains of carbon atoms connecting metal contacts have also yielded results¹⁴ that agree remarkably well with those found in *ab initio* calculations for the same systems.¹⁵ The *ab initio* calculations have the advantage of not relying on the use of empirical parameters. However, they are much more computationally intensive than tight-binding calculations. Therefore they are limited in their application to smaller molecular systems and rely on the use of the jellium approximation to treat the metallic contacts. For the same reason it is difficult to study conformational changes using the *ab initio* techniques and the molecules were assumed to be rigid in the above *ab initio* studies.^{7,15} Since the *ab initio* calculations are based on density functional theory, which is known to be rigorously valid only for ground state properties, their validity for transport calculations far from equilibrium is uncertain *a priori*. Furthermore, even in calculations of ground state properties they rely in practice on the use of the local density approximation. However, it is reasonable to expect them to be more reliable than calculations based on simpler mean field theories such as the Hartree-Fock approximation. While the Keldysh technique can in principle provide a more rigorous approach to the problem of transport far from equilibrium, its practical application to real molecular wires still presents major challenges at this time.

A shortcoming of the tight-binding approach to molecular wire transport has been that it has not provided a way to calculate the conformational changes that occur in a molecular wire when an electric current is driven through it, or to treat the influence of these conformational changes and of charging of the molecule on the current in a consistent way, within the same theoretical framework. The formalism that we present below accomplishes this; however, it should be emphasized that it, like the *ab initio* calculations mentioned above, is based on density functional theory and should therefore also be regarded as a practical mean field approach to the difficult many-body problem of transport in molecular wires far from equilibrium, and not as a rigorous treatment of this problem.

In our tight-binding formalism we represent the electronic energy \mathcal{E} of the molecular wire as a functional $\mathcal{E}[\{N_i\}]$ of the numbers N_i of electrons occupying atomic sites i at positions \vec{R}_i :

$$\begin{aligned} \mathcal{E}[\{N_i\}] = & \mathcal{K}[\{N_i\}] - e \sum_i N_i V_{ext}(\vec{R}_i) \\ & + \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \sum_{i \neq j} \frac{N_i N_j}{|\vec{R}_i - \vec{R}_j|} + \mathcal{F}[\{N_i\}]. \end{aligned} \quad (1)$$

This is a tight-binding analog of the Kohn-Sham¹⁶ density functional: $\mathcal{K}[\{N_i\}]$ is the tight-binding energy of a noninteracting electron system with the same electron distribution

$\{N_i\}$ as the interacting system and V_{ext} is the corresponding external potential. The next term is the electrostatic interaction energy between electrons on different sites. \mathcal{F} represents the exchange-correlation energy and on-site interactions. In the spirit of the Kohn-Sham local density approximation¹⁶ we approximate \mathcal{F} in terms of a local function $f_i(N_i)$ that depends on the atomic species at site i as $\mathcal{F}[\{N_i\}] = \sum_i f_i(N_i)$. Varying $\mathcal{E}[\{N_i\}]$ with respect to $\{N_i\}$ with the conformation $\{\vec{R}_i\}$ held fixed we obtain the tight-binding analog

$$\sum_{jn} t_{ij}^{mn} \psi_{jn}^\lambda + (\epsilon_{im} + \phi_i) \psi_{im}^\lambda = E^\lambda \psi_{im}^\lambda \quad (2)$$

of the Kohn-Sham equations for the effective one-electron eigenstates $\Psi^\lambda = \psi_{im}^\lambda |i, m\rangle$ and energy eigenvalues E^λ . t_{ij}^{mn} is the hopping matrix element between orbitals m and n on atoms i and j , ϵ_{im} is the bare orbital energy,

$$\phi_i = -e V_{ext}(\vec{R}_i) + \frac{e^2}{4\pi\epsilon_0} \sum_{j \neq i} \frac{N_j}{|\vec{R}_i - \vec{R}_j|} + \frac{\delta f_i(N_i)}{\delta N_i}, \quad (3)$$

and V_{ext} includes potentials due to the bias applied to the contacts and image charges. $\delta f_i(N_i)/\delta N_i$ is the variation of the electronic site energy with the electron occupation N_i of the site. In the numerical work reported below we approximate it by $\delta f_i(N_i)/\delta N_i = (N_i - N_i^0) U_i$ where N_i^0 is the electron occupation of the neutral atom and U_i is the on-site interaction energy, whose value we take from the semiempirical chemistry literature where it is estimated from experiment.¹⁷ It is possible to also include corrections to this term that are of higher order in $(N_i - N_i^0)$ since the relevant empirical coefficients are available;¹⁷ we did not do so in our numerical work because they are small for the species that we considered.

For a given molecular conformation $\{\vec{R}_i\}$ and applied bias we solve Eq. (2) self-consistently with N_i in Eq. (3) obtained by integrating $\sum_n |\psi_{in}^\lambda|^2$ over the occupied eigenstates of Eq. (2). The electric current carried by the wire is then given by Landauer-Büttiker theory:

$$I(V) = \frac{2e}{h} \int dE T(E, V) [F(E, \mu_s) - F(E, \mu_d)]. \quad (4)$$

Equation (4) relates the current I at finite bias voltage V to the transmission probability $T(E, V)$ for an electron to scatter from the source metallic contact through the molecule and into the drain at an energy E . $F(E, \mu)$ is the Fermi function, and $\mu_{s,d} = E_F \pm eV/2$ are the source and drain electrochemical potentials with E_F the common Fermi energy of the contacts. We obtain $T(E, V)$ from the eigensolutions Ψ^λ of Eq. (2) and the velocities of electron Bloch states in the contacts in the standard way.¹⁸

In the Landauer picture of transport that gives rise to Eq. (4), the electrons populate scattering states that flow from deep in the contacts toward the wire according to the Fermi functions $F(E, \mu_\alpha)$ of the contacts. These states are partly transmitted through the wire, giving rise to the current I , and partly reflected. We adopt the same physical picture in cal-

culating the actual conformation that the molecular wire takes in the presence of the applied bias and transmitted current: We assume that the asymptotic regions of the contacts constitute ideal leads where the electrons may be treated as noninteracting. We also assume that the filling of electron states that are incident on the wire from each contact is described completely by the Fermi function of that contact, i.e., it depends only on the applied bias and the temperature and not on the conformation of the wire. [In the present work the single-particle states of Landauer theory are replaced by the Kohn-Sham-like effective single-particle states that are the self-consistent solutions of Eq. (2).] Then, if electron scattering at the wire is elastic, the conformation that the wire takes is that which minimizes the total energy of the system, the filling of the asymptotic incident states with electrons being held fixed. The total energy $E_{tot}(\{R_i\})$ for any trial conformation $\{R_i\}$ is found from the self-consistent solution of Eq. (2). Its electronic part E_e is equal to $\mathcal{E}[\{\bar{N}_i\}]$ for the conformation $\{R_i\}$ (and the fixed incident electron population) and is given by

$$E_e = \int E [D_s(E)F(E, \mu_s) + D_d(E)F(E, \mu_d)] dE + - \frac{e^2}{8\pi\epsilon_0} \sum_{i \neq j} \frac{\bar{N}_i \bar{N}_j}{|\vec{R}_i - \vec{R}_j|} + \sum_i \left[-\bar{N}_i \frac{\delta f_i(\bar{N}_i)}{\delta \bar{N}_i} + f_i(\bar{N}_i) \right] \quad (5)$$

where \bar{N}_i is the self-consistent value of N_i that corresponds to the solution of Eq. (2) and $D_{s,d}$ are density of states factors for the asymptotic incident states in the contacts. Equation (5) is the nonequilibrium tight-binding analog of Eq. (2.10) of Ref. 16: The integrand in Eq. (5) corresponds to the sum of the energy eigenvalues of the occupied Kohn-Sham effective single-particle states. These single-particle states correspond to electrons that arrive at the molecular wire from the source and drain leads and are populated according to the Fermi distributions of the source and drain leads, respectively. The first summation corrects for the double counting of the Coulomb energy due to interactions between electrons that is implicit in the integral that precedes it. The second summation corrects the contribution of the on-site energy to the total electronic energy.

E_e includes implicitly the interaction energy between the nuclei and the electrons of the wire but omits the electrostatic energy of the nuclei of charge eZ_i interacting with each other and with the potential V_{ext} due to the applied bias and image charges in the contacts. Thus to find the actual conformation of the wire we minimize $E_{tot}(\{R_i\}) = E_e(\{R_i\}) + E_n(\{R_i\})$ with respect to $\{R_i\}$ where

$$E_n = \frac{e^2}{8\pi\epsilon_0} \sum_{i \neq j} \frac{Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + e \sum_i Z_i V_{ext}(\vec{R}_i). \quad (6)$$

Notice that the energy eigenvalue integral in Eq. (5) is independent of the conformation of the wire. This independence is a consequence of working with an open system with a

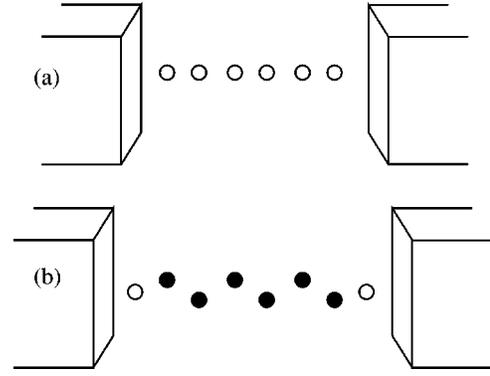


FIG. 1. Schematic of atomic wires bonded to ideal metallic leads. (a) Atomic configuration of homogeneous wire. (b) Atomic configuration of inhomogeneous wire (note the inclusion of metal atoms on the ends to model charge transfer between the metallic contacts and the atomic wire).

continuous spectrum and of our adoption of the Landauer picture of the contacts discussed above.

III. PREDICTIONS FOR SOME SIMPLE MOLECULAR WIRE SYSTEMS

We have applied this methodology to two classes of simple molecular wires consisting of chain molecules bonded to metal contacts (see Fig. 1). The contacts are modeled as single-channel ideal leads with Fermi energy $E_F = -10$ eV and the energy band ranging from -17 eV to -3 eV. They are assumed to form planar equipotential surfaces. For one class (inhomogeneous wires) the molecules are representative of finite polyacetylene chains; we use the model parameters of Su *et al.*¹⁹ Each atom of the backbone of the chain has a single orbital with bare energy $\epsilon_C = -11.4$ eV, nearest-neighbor hopping $t_C^0 = -2.5$ eV for the undimerized case, and charging energy $U_C = -11.5$ eV. Each end of the chain is bonded at a perpendicular distance of 2 \AA over a single metal atom of a gold electrode which has a bare orbital energy $\epsilon_M = -10$ eV, a charging energy $U_M = 8.5$ eV, and is coupled to the end of the chain with a hopping energy $t_{C,M}^0 = -2$ eV. For the other class (homogeneous wires), which is representative of metal atomic chains bonded to metal electrodes, the unrelaxed geometry is a linear chain with a 2.5 \AA spacing. The same bare orbital and charging energies are used as for the above gold metal electrode atom, with a hopping energy $t_M^0 = -3$ eV. As the atomic positions relax in the course of minimizing the energy, the hopping parameters t change. Following Su *et al.*¹⁹ we assume $t = t^0 + \alpha \delta X$ where δX is the change in bond length. For C-C, M-C, and M-M bonds, $\alpha_{C,C} = 4.125$, $\alpha_{C,M} = 2.5$, and $\alpha_{M,M} = 3.0$ eV/ \AA . We calculate the current-voltage characteristics of six- and seven-atom inhomogeneous and homogeneous chains, allowing the atoms to relax in both the presence and absence of a bias voltage.

In Fig. 2, the calculated site charges $-e(\bar{N}_i - N_i^0)$ are shown for bias voltages of 0, 1, and 2 V. For the homogeneous chains [Figs. 2(a),(b)] each atom is neutral at 0 V. At higher bias, a charge density wave (CDW) forms in both the

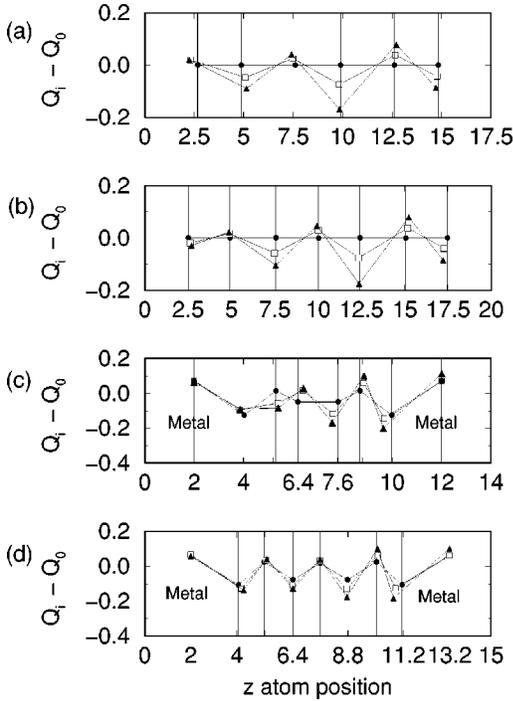


FIG. 2. Site charges $-e[\bar{N}_i(R_i) - N_i^0]$ in units of e and atomic positions (Å) for different voltages. Circle=0 V, square=1 V, triangle=2V. (a),(b) six- and seven-atom homogeneous wire. (c),(d) six- and seven-atom inhomogeneous wire.

six- and seven-atom chains. The CDW arises from a superposition of standing electron waves^{20,21} in the wire. The relaxed atomic positions are the lateral positions of the symbols in each graph. The vertical lines show the relaxed positions at 0 V; the unrelaxed positions match the ticks on the z axis. At 0 V the six-atom chain dimerizes while the seven-atom chain has a frustrated dimerization pattern. At higher V , the weakening of some bonds amplifies the standing waves and CDW's. The inhomogeneous chains [Figs. 2(c),(d)] show similar features although the CDW's are present even at 0 V and there is a net transfer of charge from the metal contacts to these wires. The atoms at the ends of the chains in Figs. 2(c),(d) are metal electrode atoms. These metal atoms are positively charged as charge is transferred from them to the chain. For the six-atom chain, this charge transfer at the ends of the chain frustrates the CDW, and a charged soliton forms. At 0 V the soliton is at the center of the chain. It moves away from the more negatively charged end of the chain at larger bias. The soliton is associated with a stretched bond. For both inhomogeneous chains, there is considerable weakening of the bond between the chain and drain at higher bias. This will be seen to have an important effect on the current flowing through the wire.

These charging and conformational changes are intimately linked to the transport of electrons through the wires. The voltage-dependent transmission probabilities for 0, 1 and 2 V are shown in Fig. 3. Consider first the case of zero bias and odd atom chains [Figs. 3(b),(d)]. In isolation these chains have an odd number of valence electrons (in this case seven) which occupy molecular orbitals, the highest occupied molecular orbital (HOMO) being half filled. In an open

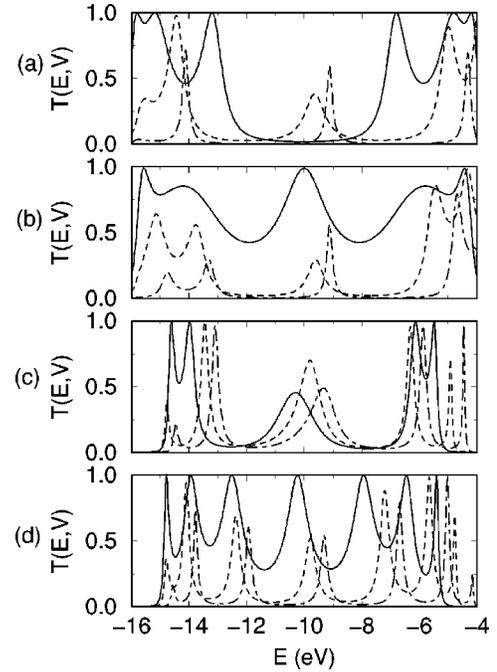


FIG. 3. Voltage-dependent transmission probability at 0 (solid line), 1 (dashed), and 2 V (dash-dotted). (a),(b): six- and seven-atom homogeneous wire. (c),(d): six- and seven-atom inhomogeneous wire.

system if this orbital were well below E_F it would have to be completely filled and if it were well above the E_F it would be completely empty. Both situations lead to unfavorable charging of the wire. Thus the HOMO must be at E_F and transmission resonances due to the HOMO can be seen at $E_F = -10$ eV in the two graphs. [The HOMO of the inhomogeneous wire is more than half full due to charge transfer from the contacts. Thus the center of the 0 V HOMO resonance in Fig. 3(d) is slightly below E_F .] The six-atom inhomogeneous chain also has a resonance near E_F at zero bias [Fig. 3(c)]. This can be explained similarly because there is charge transfer which must go to a partly filled state near E_F . This partly filled state leads to the charged soliton in Fig. 2(c). However, the six-atom homogeneous chain has no resonance at E_F at 0 V [Fig. 3(a)] since there is no unpaired electron and no charge transfer at zero bias. Indeed, it is energetically favorable for this chain to dimerize at 0 V, pushing its HOMO lower in energy and widening the gap around E_F . This explains why there are resonances at E_F at zero bias for some of the systems but not for others. Charge transfer also explains why there are resonances at E_F for all of the chains at nonzero bias: All of the wires become partly charged at nonzero bias. Thus all of them must have a partly filled level at nonzero bias and this level must be near E_F . For the six-atom homogeneous chain, a significant rearrangement of its atomic positions is required to generate this state near E_F . (The appearance of fewer resonances than atoms in the chain in some plots is due to degeneracy of some of the transmitting states.)

The current vs voltage characteristics calculated from these transmission probabilities are shown in Fig. 4. Their

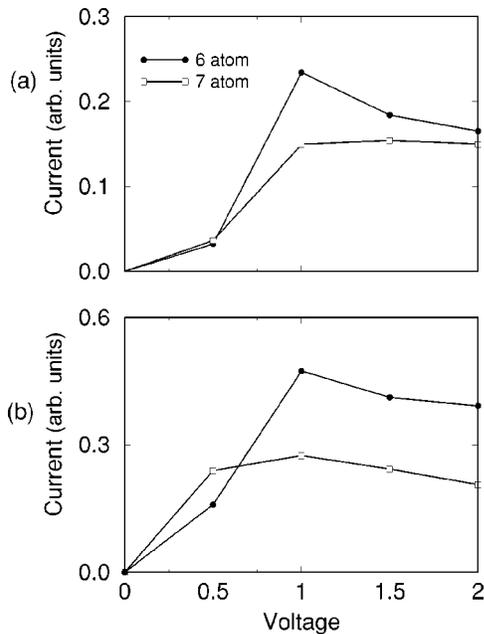


FIG. 4. Calculated current vs voltage for (a) homogeneous wires and (b) inhomogeneous wires at $T=100$ K.

physical meaning is as follows: At moderate and high bias the resonance near E_F carries the net current through the wire. As the bias increases the wire becomes charged and the Coulomb potential due to that charge raises the energy of the resonant state until the bottom edge of the resonance is above the electrochemical potential of the drain. Before this occurs the resonance transmits electrons coming from both

the source and drain. As the bias increases there are fewer electrons from the drain and more from the source going through the resonance, so the current is growing. Eventually there are no electrons from the drain going through the resonance and the current saturates. It then declines and negative differential resistance sets in because the stretching and weakening of bonds inhibits electron transmission through the wire.

IV. SUMMARY

In summary, we have presented theoretical work that unifies nonlinear transport, charging, and conformational change in molecular wires. We have shown that the effects of charging and conformational change can be understood *together* in terms of a remarkably robust physical mechanism of nonlinear transport, and predict negative differential resistance at high bias. One class of molecular wires that we have modeled (the homogeneous wires) is representative of chains of metal atoms connecting metallic contacts such as have recently been realized in the laboratory for the case of gold.^{22,23} Experiments carried out to determine whether these systems exhibit negative differential resistance at high bias would be of interest.

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