Charging Effects, Forces, and Conduction in Molecular Wire Systems

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ABSTRACT: **Recently, experiments have shown that effects arising from charging and conformational changes in a molecular wire due to an applied voltage bias can have a significant influence on the transport characteristics of the system. We introduce a tractable theoretical approach based on Landauer 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 short chain molecules with different electronic and structural properties bonded to metal contacts. We find that the nonlinear conductance characteristics of these systems are remarkably similar and can be understood in terms of a single physical mechanism. We predict that negative differential resistance should occur at high bias in such molecular wires due to the combined effects of charging and conformational changes on their electronic structure.**

KEYWORDS: **molecular wire; charging; conformational change; transport**

I. INTRODUCTION

A molecular wire is a single molecule that forms an electrically conducting bridge between a pair of metallic contacts. During the last few years molecular wires have begun to be 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] Molecular wires have been observed to switch from a conducting to a nonconducting state due to the occurrence of a voltage-induced redox reaction, that is, a change in the charge distribution along the wire.[5] Switching between conducting and nonconducting states due to conformational changes has also been reported.[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[3,7–15] but there has been little work directed at bringing all three of them together within a single theoretical framework.

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In this article we introduce a self-consistent tight-binding theoretical approach that unifies the three phenomena. Charging is incorporated by evaluating the electron density that arises from the filled electron scattering states of the molecular wire. This density is calculated self-consistently. Forces are determined from the variation of the total energy of the system with respect to the atomic coordinates. The minima of this energy surface define conformations where the net forces acting on the atoms that make up the molecule are zero. The Landauer physical picture of transport is used both to establish the boundary conditions deep within the contacts for the self-consistent energy calculations and to evaluate the electric current in the molecular wire. Nonlinear effects are included explicitly in that all quantities can be calculated at finite voltage bias and temperature.

We have applied this theory and performed calculations for the simplest molecular wires, namely, small chain molecules bonded to metal electrodes. At low bias some of these molecular wires are conductors while others are 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 does not increase 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 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.

Section II presents the theoretical methods developed to bring together the effects of charging and forces in the calculation of the transport properties of a molecular wire. In Section III the theory is applied to the study of several simple yet representative molecular wire systems. The conclusions of this work are presented in Section IV. The Appendix summarizes some results for various electrostatic potentials of the two-terminal geometry considered.

II. CALCULATION OF CHARGES, FORCES, AND ELECTRIC CURRENTS IN MOLECULAR WIRE SYSTEMS

The molecular wire system that we consider in this article is a molecule chemically bonded to two metallic electrodes (see FIG. 1). Electrons may be transferred from the electrodes to the molecule, which can lead to a nonuniform charge distribution in the system. Under an applied bias, this charge distribution may change as

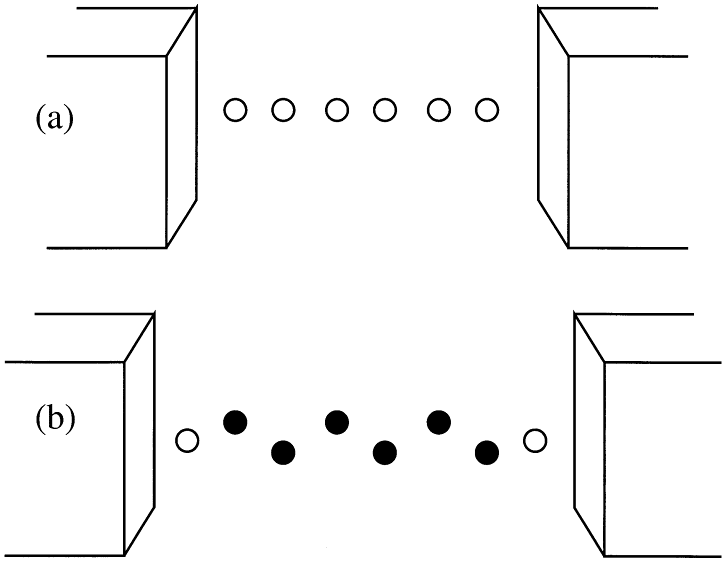

FIGURE 1. Schematic of the geometries considered for **(a)** homogeneous molecular wires and **(b)** inhomogeneous molecular wires.

charge is deposited on or depleted from the molecule. Conformational (or shape) changes of the molecule may also occur, which can in turn affect the charge distribution on the molecule. Both of these affects can be included into transport theory in a rather straightforward manner, as shown below.

Our analysis begins by considering the total electronic energy due to the electron density in the system. We represent the electronic energy $\mathcal{E}$ of the molecular wire as a functional $\mathcal{E}[\{N_i\}]$ of the of the numbers N_i of electrons occupying atomic sites i at positions $\vec{R}_i$:

$$\mathcal{E}[\{N_i\}] = \mathcal{K}[\{N_i\}] - e\sum_i N_i V_{\text{ext}}(\vec{R}_i) + \frac{1}{2}\frac{e}{4\pi\varepsilon_0}\sum_{i \neq j}\frac{N_i N_j}{\left|\vec{R}_i - \vec{R}_j\right|} + \mathcal{F}[\{N_i\}]. \tag{1}$$

This is a tight-binding analog of the Koh–Sham[16] 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 which includes voltage biases applied on the various metallic contacts in the system. 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 approximation[16] we approximate $\mathcal{F}$ in terms of a local function $f_i(N_i)$ that depends on the atomic species at site i as $\mathcal{F}[\{N_i\}] = \Sigma_i f_i(N_i)$. Varying $\mathcal{E}[\{N_i\}]$ with respect to $\{N_i\}$ with the conformation $\{\vec{R}_i\}$ held fixed we obtain the tight-binding analog

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

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, and ϕ_i is the electrostatic energy of an electron on site i interacting with the charge distribution,

$$\phi_i = -eV_{\text{ext}}(\vec{R}_i) + \frac{e^2}{4\pi\varepsilon_0}\sum_{j \neq i} \frac{N_j}{\left|\vec{R}_i - \vec{R}_j\right|} + \frac{\delta f_i(N_i)}{\delta(N_i)} . \tag{3}$$

V_{ext} includes potentials due to the bias applied to the contacts and image charges (details of the evaluation of this potential are given in the Appendix). $\delta f_i(N_i)/\delta N_i$ is the variation of the electronic site energy with the electron occupation N_i of the site. 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 semi-empirical chemistry literature where it is estimated from experiment.[17]

We remark that since our derivation of Eq. (2) follows Kohn–Sham theory which is a ground state formalism, we apply nonequilibrium scattering state solutions of Eq. (2) to the present problem in the same spirit as *ab initio* calculations of transport such as those in Refs. 7–9 employ the nonequilibrium scattering state solutions of the Kohn–Sham equations that are also derived within a ground state formalism, namely, we regard such solutions as practical mean-field approximations to a problem that does not at present admit rigorous solutions.

For a given molecular conformation $\vec{R}_i$ and applied bias we solve for the N_i self-consistently. At each iteration the scattering states ψ are determined for a range of incident electron energies E by solving Eq. (2) using standard techniques.[c] Then N_i is evaluated by integrating over those scattering states which are occupied by incident electrons from either the source (s) or the drain (d). This gives,

$$N_i = \frac{1}{\pi}\sum_{\alpha = s, d}\sum_m \int dE\, D_{\alpha}(E)\left|\psi^{im}\right|^2 F(E, \mu_{\alpha}), \tag{4}$$

where $D_{\alpha}(E)$ is the density of states factor for the asymptotic incident states in contact α, $F(E, \mu)$ is the Fermi function, and $\mu_{s,d} = E_F \pm \text{eV}/2$ are the source and drain electro-chemical potentials with E_F the common Fermi energy.[d] This procedure is iterated until the N_i converge.

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[c] Solving for the scattering states can be accomplished by a variety of techniques. We use the method described in Ref. 18.

[d] Since in the present model the electrons in the ideal leads are considered to be noninteracting, the lead electrochemical potentials do not need to be evaluated through a self-consistent calculation. Instead they are defined as is usual in Landauer theory. For a comprehensive review of Landauer-Büttiker theory, see Ref. 19

The electric current carried by the wire is then given by Landauer-Büttiker theory:

$$I(V) = \frac{2e}{h}\int dE\; T(E, V)[F(E, \mu_s) - F(E, \mu_d)]\,. \tag{5}$$

Equation (5) 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. 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.[19]

In the Landauer picture of transport that gives rise to Eq. (5), 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 are partly reflected. We adopt the same physical picture in calculating 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, that is, it depends only on the applied bias and the temperature and not on the conformation of the wire. Finally, we assume that electron scattering at the wire is elastic and the conformation that the wire takes minimizes the total energy of the system, the filling of the asymptotic incident states with electrons being held fixed.

While this variational principle has considerable intuitive appeal and is known to be valid for the ground state of the system, it cannot be justified rigorously under nonequilibrium conditions. However, with it as a starting point we are able to make specific theoretical predictions regarding the effects that current-induced conformational changes may have on electron transport through molecules, a complex nonequilibrium many-body problem about which very little is known at present. We expect that these predictions will stimulate experimental work that will test the predictions and ultimately the usefulness of this variational principle for this class of problems.

The total energy $E_{\mathrm{tot}}(\{R_i\})$ for any trial conformation $\{R_i\}$ is found from the self-consistent solution of Eq. (2). Its electronic part E_e is equal to $\{\mathcal{E}\}[\{\overline{N}_i\}]$ for the conformation $\{R_i\}$ (and the fixed incident electron population) and is given by

$$\begin{aligned} E_e = {} & \int E[D_s(E)F(E, \mu_s) + D_d(E)F(E, \mu_d)]dE \\ & - \frac{e^2}{8\pi\varepsilon_0}\sum_{i \neq j}\frac{\overline{N}_i\overline{N}_j}{\left|\vec{R}_i - \vec{R}_j\right|} + \sum_i\left[-\overline{N}_i\frac{\delta f_i(\overline{N}_i)}{\delta\overline{N}_i} + f_i(\overline{N}_i)\right], \end{aligned} \tag{6}$$

where $\overline{N}_i$ is the self-consistent value of N_i that corresponds to the solution of Eq. (2). 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 $E_{\text{tot}}(\{R_i\}) = E_e(\{R_i\}) + E_n(\{R_i\})$ wrt $\{R_i\}$ where

$$E_n = -\frac{e^2}{8\pi\varepsilon_0}\sum_{i \neq j}\frac{Z_i Z_j}{\left|\vec{R}_i - \vec{R}_j\right|} + e\sum_i Z_i V_{\text{ext}}(\vec{R}_i) \tag{7}$$

Notice that the energy eigenvalue integral in Eq. (6) is *independent* of the conformation of the wire. This independence is a consequence of working with an open system with a continuous spectrum and of our adoption of the Landauer picture of the contacts discussed earlier.

III. APPLICATION TO CHAINLIKE MOLECULAR WIRES

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.*[20] Each atom of the backbone of the chain has a single orbital with bare energy $\varepsilon_C = -11.4$ 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 Å over a single metal atom of the electrode which has a bare orbital energy $\varepsilon_M = -10$ 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), the unrelaxed geometry is a linear chain with a 2.5 Å spacing. The same bare orbital and charging energies are used for the above 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. 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/Å. We calculate the current–voltage characteristics of 6 and 7 atom inhomogeneous and homogeneous chains, allowing the atoms to relax both in the presence and absence of a bias voltage.

Before showing the results of the calculation that includes both charge transfer and atomic relaxation, we highlight now the differences that arise in transport due to the inclusion of these effects. This is illustrated in FIG. 2. In FIG. 2a, the transmission probability as a function of incident electron energy is shown for the 6 atom inhomogeneous chain at 0 V using just the tight binding Hamiltonian above and without including the self-consistent potential or atomic relaxation. There are six resonances in total, one for each molecular orbital of the wire. With the Fermi energy of the leads at −10 eV, almost four resonances lie completely below it. Each resonance below E_F contributes approximately two electrons, thus we roughly estimate that the molecule should have on the order of 7 to 8 electrons. Thus the simple tight binding model would predict a charge transfer of more than one electron, since the neutral

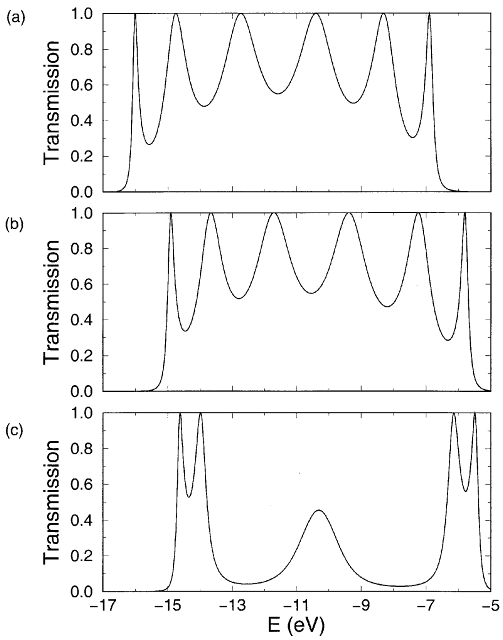

FIGURE 2. Transmission probability calculated for 6 atom inhomogeneous wire for different models. **(a)** Tight-binding calculation with *no* self-consistent potential. **(b)** Tight-binding calculation with self-consistent potential. **(c)** Tight-binding calculation with self-consistent potential and atomic relaxation.

wire only has 6 electrons. FIGURE 2b shows how including the self-consistent potential affects the transmission probability. The six resonances remain, but they are shifted up in energy. This occurs in order to reduce the amount of charge transfer from the leads to the molecule. Now only 3 plus a bit of the fourth resonance lie below the Fermi energy. Thus the inhomogeneous chain is only slightly charged. The last figure, FIG. 2c includes both the self consistent potential and atomic relaxation. There is now a significant difference between the preceding two results. Dimerization has lead to the shifting of the resonances and the creation of a degenerate state near −10.5 eV. These graphs highlight the importance of including self consistency and atomic relaxation into transport calculations.

In FIGURE 3, the calculated site charges $-e(\overline{N}_i - N_i^0)$ are shown for bias voltages of 0, 1, and 2 V. For the homogeneous chains (FIG. 3a,3b) each atom is neutral at 0 V. At higher bias, a charge density wave (CDW)[e] forms in both the 6 and 7 atom chains. The CDW arises from a superposition of standing electron waves[21,22] 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

[e] The role of standing waves in *linear* transport in molecular wires has noted been earlier.

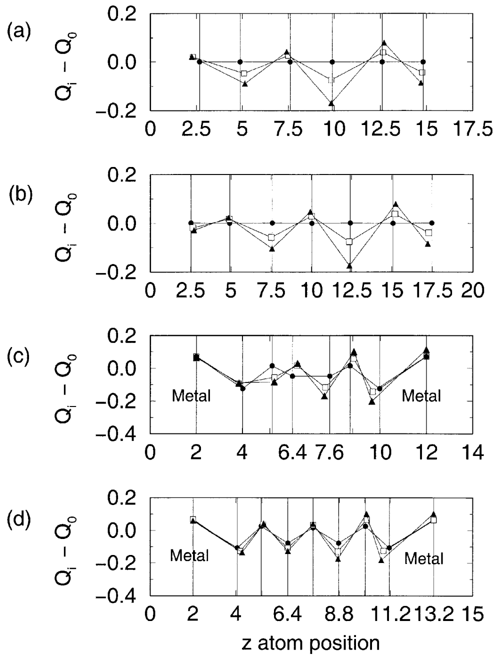

FIGURE 3. Site charges $-e(\overline{N}_i(R_i) - N_i^0)$ in units of e and atomic positions (Å) for different voltages: *circle*, 0 V; *square*, 1 V; *triangle*, 2 V. **(a,b):** 6 and 7 atom homogeneous wire. **(c,d):** 6 and 7 atom inhomogeneous wire.

the ticks on the *z*-axis. At 0 V the 6 atom chain dimerizes while the 7 atom chain has a frustrated dimerization pattern. At higher V, the weakening of some bonds amplifies the standing waves and CDWs. The inhomogeneous chains (FIG. 3c, 3d) show similar features although the CDWs 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 FIG. 2c,2d are metal electrode atoms. These metal atoms are positively charged as charge is transferred from them to the chain. For the 6 atom chain, this charge transfer at the ends of the chain frustrates the CDW, and a charged soliton forms. At 0V 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 transport of electrons through the wires. The voltage-dependent transmission probabilities for 0, 1, and 2 V are shown in FIG. 4. Consider first the case of zero bias and odd atom chains (FIG. 4b,4d). In isolation these chains have an odd number of valence electrons (in this case 7) which occupy molecular orbitals, the highest occupied molecular orbital (HOMO) being half-filled. In an open 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

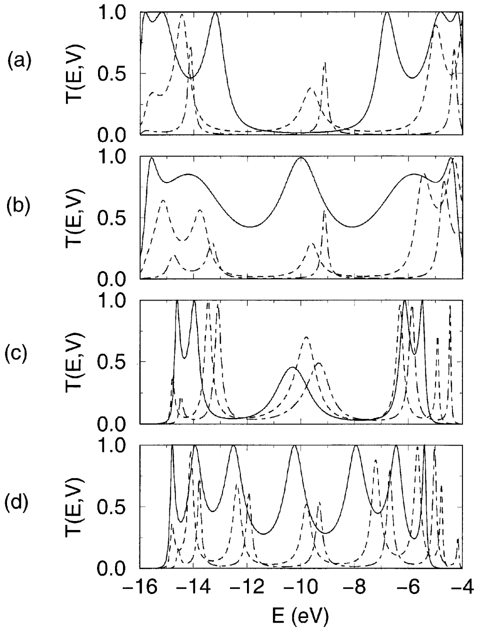

FIGURE 4. Voltage-dependent transmission probability at 0 (*solid line*), 1 (*dashed*), and 2 V (*dash-dotted*). **(a,b):** 6 and 7 atom homogeneous wire. **(c,d):** 6 and 7 atom inhomogeneous wire.

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. 4d is slightly below E_F). The 6 atom inhomogeneous chain also has a resonance near E_F at zero bias (FIG. 4c). 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. 3c. However, the 6 atom homogeneous chain has no resonance at E_F at 0 V (FIG. 4a) 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 6 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 versus voltage characteristics calculated from these transmission probabilities are shown in FIG. 5. Their physical meaning is as follows: At moderate

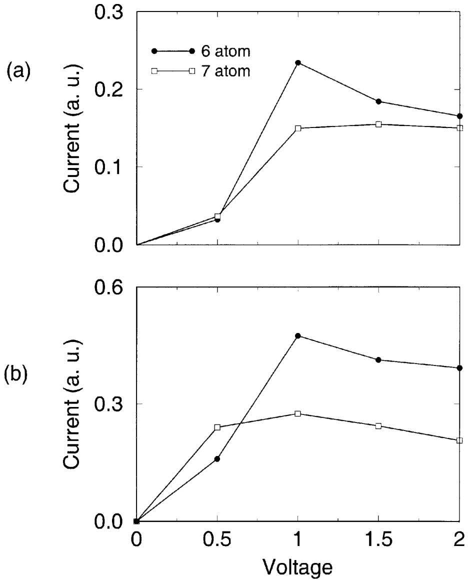

FIGURE 5. Calculated current vs. voltage for **(a)** homogeneous wires and **(b)** inhomogeneous wires at $T = 100$ K.

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. CONCLUSIONS

In summary, we have presented theoretical work that unifies nonlinear transport, charging and conformational change in molecular wires in a tractable model. The model was applied to several representative linear molecular wires. Several interesting phenomena were found that arose due to charging and conformational change. The first was that charging of a linear chain requires a state near the Fermi energy. The second was that the chain will undergo a conformational change so as to generate such a state. Both types of chains studied displayed generic current-vs.-voltage characteristics at high bias, as the current carried by the state near the Fermi energy saturated. Negative differential resistance may arise in these systems if bond weakening is sufficient to reduce the current flowing through this state.

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APPENDIX

The external potential V_{ext} is a sum of the potential due to the applied bias, $\phi(\vec{r}\,,\{V_\gamma\})$ and the potential due to image charges in the contacts $\phi_{\text{image}}(\vec{r}\,,\{q_j\})$. This Appendix evaluates these two potentials for a simple two-terminal set up. The two-terminal system that is considered is that of a left and right metallic lead which are bridged by a molecule. The two metallic leads are assumed to terminate at equipotential surfaces. It will also be assumed that the dimensions of the metallic leads are large compared to the molecule. Thus it will be assumed that the metallic contacts can be modeled as infinite parallel plates. One plate is located at $z = 0$ and the other is at $z = L$. A symmetric voltage V is applied to the two plates, and an electrostatic potential is formed in the region between them. There will also be some charge on the molecule between these two plates.

For this configuration the potential $\phi(z)$ is given by

$$\phi(z) = -V/2 + \frac{V}{L}z\,. \tag{8}$$

The potential due to the presence of charge between the two metal plates can be found by solving Poisson's equation subject to the boundary conditions $\phi_{\text{image}}(0) = 0$ and $\phi_{\text{image}}(L) = 0$. For a charge $q_j = e(N_j - N_j^0)$ at position z_j on the z-axis in between the plates, the potential of a test charge at position z on the z-axis can be found using the method of images. This charge will induce an infinite series of charges along the z-axis. The potential at z is given by (here $k_Q = 1/(4\pi\varepsilon_0)$),

$$(\phi_{\text{image}}(z, z_j))_j =$$

$$k_Q q_j\left[-\frac{1}{z+z_j} + \frac{1}{2L}\left\{\psi\left(1-\frac{a}{2L}\right) + \psi\left(1+\frac{a}{2L}\right) - \psi\left(1-\frac{b}{2L}\right) - \psi\left(1+\frac{b}{2L}\right)\right\}\right] \tag{9}$$

where $a = z + z_j$ and $b = z_j - z$ and $\psi(z)$ is the digamma function.

For a test charge located off the z axis at a position given by $\vec{r} = (\rho, z)$ where ρ is the perpendicular distance from the z-axis the potential is given by Jackson [see Ref. 23, p. 132],

$$(\phi_{\text{image}}(z, \rho, z_j))_j =$$

$$k_Q q_j\left[\frac{-1}{\sqrt{(z-z_j)^2+\rho^2}} + \frac{4}{L}\sum_{n=1}^{\infty}\sin\left(\frac{n\pi z_j}{L}\right)\sin\left(\frac{n\pi z}{L}\right)K_o\left(\frac{n\pi\rho}{L}\right)\right], \tag{10}$$

where $K_o(\rho)$ is a modified Bessel function. (This series converges rapidly and thus only a few terms are needed in a numerical computation.)

The total image potential is found by summing the image potential due to each charge q_j on the molecule.