Carbon-Atom Wires: Charge-Transfer Doping, Voltage Drop, and the Effect of Distortions

N. D. Lang and Ph. Avouris
IBM Research Division, Thomas J. Watson Research Center,
Yorktown Heights, New York 10598

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We present first-principles calculations on electrical conduction through carbon atomic wires. The changes in charge distribution induced by a large bias exhibit the primary involvement of the wire's π states. A significant fraction (~40%) of the voltage drops across the atomic wire itself. At zero bias, there is a large transfer of charge from the electrodes to the wire, effectively providing doping without introducing scattering centers. This transfer leads, however, to potential barriers at the wire-electrode junctions. Bending the wire reduces its conductance.

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There is currently strong interest in and intense activity involving the preparation of nanoscale and atomic-scale structures and the elucidation of their electronic properties. Techniques for forming short metal-atom wires have been discovered and this has given great impetus to their detailed study [1]. Another type of nanowire is provided by covalently bonded systems such as carbon-based materials [2]. Carbon nanotubes represent such a covalently bonded wire with exceptional properties [3]. The metal-electrode–atomic-wire interaction, which is important to the electrical properties of these systems, is, however, not well understood. To gain insight into these interactions, we have performed first-principles electronic structure calculations on a covalently bonded atomic wire: a linear carbon-atom chain, also known as a "cumulene." Such chains containing up to 20 atoms connected at the ends to metal atoms have been synthesized [4] and have been advocated as ideal one-dimensional (1D) wires [5].

We start by exploring a unique doping process of the wire by electrons transferred from the electrodes [charge-transfer doping (CTD)]. We compute the conductance of a series of wires, and we show that localized charge at the metal-wire contacts generates Schottky-like barriers. How an applied bias voltage drops across an electrode-molecule-electrode system is an important unanswered question in molecular electronics [6]. Attempts to identify the potential profile have been based on calculating the current-voltage (I-V) characteristics of a molecular wire for different assumed profiles, and comparing with experimental I-V curves [7]. Here we present the first nonempirical calculation of this profile when a sizable bias is applied. Finally, we discuss the effect of structural distortions of the wire on its conductance.

In our calculations, we describe the metal electrodes using a semi-infinite uniform background model [8,9], and the carbon atomic cores using a pseudopotential [10]. The geometrical parameters are the same as those in Ref. [11] (equal spacing of 2.5 a.u. between C atoms and the end atoms of the chain 1.4 a.u. inside the positive background edge of the uniform-background model electrodes), and a self-consistent density functional calculation is performed as described in Ref. [8].

Figure 1A shows the calculated additional conductance G due to the presence of the straight C-atom wire (circles) as a function of the number of carbon atoms in the wire. The conductance is given in units of the quantum of conductance $g_0 = 2e^2/h$. The oscillatory character of G is clearly evident [11]. It is important to note that while the

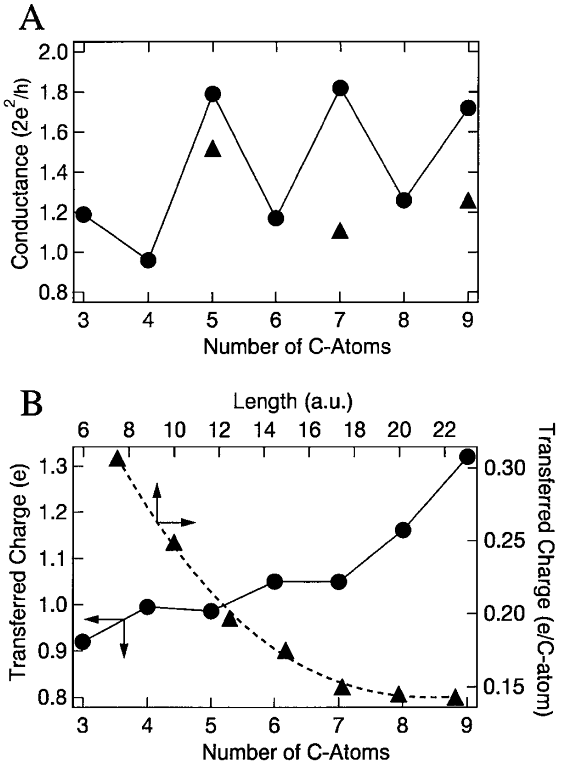

FIG. 1. (A) Circles: conductance of the atomic wires in units of the conductance quantum ($2e^2/h$) as a function of the number of carbon atoms in the wire. Triangles: conductance of wires with a 90° bend at the middle atom. (B) Circles: amount of transferred charge as a function of the number of carbon atoms in the wire. Triangles: amount of transferred charge per carbon atom as a function of the length of the wire in atomic units.

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conductance of a 1D π system with perfect contacts, i.e., contacts with unit transmission ($T = 1$), is expected to be $G = 2g_0$, all wires considered above have $G < 2g_0$.

The bonding (chemisorption) of the end of the carbon wire to the metal electrode is accompanied by a metal-to-wire charge transfer [11]. This process can be considered as a form of doping of the atomic wire since it increases its carrier density. However, unlike the case of conventional doping of semiconductors, CTD does not introduce foreign ionized dopant atoms into the wire. This is of major importance because, in 1D electronic systems, such foreign atoms can lead to electron localization.

We now consider how much charge is transferred upon chemisorption, and how this charge varies with the length of the wire. To address this question, we surround the carbon chain, attached to the electrodes, with a cylinder of radius 1.75 a.u. (with ends 1.75 a.u. from the outermost atoms) [12] and integrate the charge within this cylinder. The difference between this charge and the charge of the free carbon chain within the same cylinder is taken as the transferred charge (TC). Figure 1B shows the results expressed as total charge transferred vs number of atoms in the wire (circles). The transferred charge per C atom is also shown as a function of the wire length (triangles). From the former curve we see that the TC increases with an increasing number of carbon atoms. However, the amount of charge transferred per C atom decreases. It varies from about $0.3e/\mathrm{C}$ atom to about $0.15e/\mathrm{C}$ atom. If we exclude from the count the large charge on the two end atoms (in the two-electrode case), which we find to remain essentially constant as the length of the wire is changed, then the TC to the rest of the wire varies between $\sim 0.02\text{–}0.05e/\mathrm{C}$ atom. This is still a very high introduced carrier density without a corresponding reduction in mobility produced by the introduction of dopant atoms [13].

Next, we explore the factors that control the amount of charge transferred, and the distribution of that charge along the carbon chain, using the 7-atom chain as an example. First, we calculate how the TC is distributed along the wire. We surround each carbon atom in the free chain and in chains connected to either one or two electrodes by a sphere of radius 1.75 a.u., and integrate the charge enclosed [14]. In Fig. 2A (top) we show the difference of the charges on each C atom between the one-metal-electrode/carbon-wire system and the corresponding free carbon chain. Figure 2A (bottom) shows the actual charge-density difference between the attached and free chains. The crosses indicate the positions of the carbon atoms. Figure 2B shows the same quantities when the wire is connected to two electrodes.

Figure 2A (top) shows that a large fraction of the TC is placed on the first C atom (C1) of the chain, the next largest charge is transferred to the end of the chain (C7), while smaller amounts of charge are distributed to the rest of the atoms in an oscillatory manner. By comparing this TC distribution with the distribution of charge in the free wire, we find that the two are anticorrelated. Thus, in the free wire the lowest charge density is at the end atoms C1 and C7, while the highest is at atoms C2 and C6. This anticorrelation suggests that the nonuniform distribution of the TC is one that minimizes intrasite electron-electron repulsion: this repulsion is reduced by not piling charge on sites that already have a high charge density. The large TC on atom 1 is due to the partially ionic character of the metal-C bond, and to the fact that electron repulsion due to the added charge is best screened by the metal at that location. The density difference plot in Fig. 2A (bottom) shows that the TC is placed in π-symmetry levels.

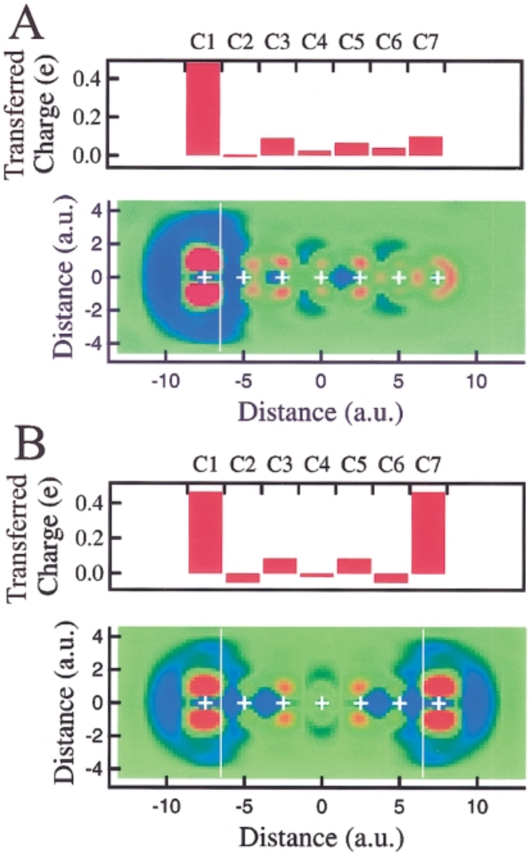

FIG. 2 (color). [(A), top] Distribution of the transferred charge along a 7-atom wire connected to one electrode on the left. [(A), bottom] Difference of the charge densities of the 7-atom wire connected to one electrode on the left and the free wire. (B) As above when the 7-atom wire is connected to two metal electrodes. The white crosses indicate the positions of the carbon atoms and the white vertical lines indicate the edges of the positive backgrounds. The green color indicates an unchanged, red an increased, and blue a decreased electron density.

When the 7-atom carbon chain is connected to two electrodes [Fig. 2B (top)], we observe a charge pileup on C1 and C7 atoms, and secondary maxima on atoms C3 and C5. Similar arguments to the ones presented above can explain this TC distribution. The total TC is not twice the TC with one electrode but only about 30% higher.

We now consider how the TC distribution affects the conductance of the atomic wires. As already discussed, a significant amount of charge ($\sim 0.5e$) is transferred to the C1 and C7 atoms (Fig. 2B). This charge remains essentially constant as the wire length is varied. The presence of this charge leads to the formation of Schottky-like potential barriers at the ends of the wire. Figure 3 shows the electrostatic potential profile obtained by subtracting from the potential of the metal-C_7-metal system the sum of the potentials of the free C_7 chain and of the pair of bare electrodes. The two barriers at the ends of the wire are clearly evident. The presence of the barriers reduces the transmission of the wires, i.e., $T < 1$ [15]. There may be other factors which tend to reduce T in systems involving atomic wires connected to flat metal electrodes, such as the abruptness of the transition from the metal to the wire. However, it is clear from the above that anchoring a wire to electrodes using electronegative attaching groups such as $-S^-$, $-O^-$, or $-CO_2^-$ [16] will reduce the transmission of the contacts.

We now compute how the electronic structure of the wire changes when a significant bias voltage is applied. For comparison, we compute the polarization of the electron distribution of the free wire in an external electric field of 6 V/nm. Figure 4A shows the difference between the charge density of a free 7-atom wire in the field and that of the free wire in zero field. The most significant change for π electrons is an increase in occupation of the π orbital between atoms 1 and 2 and a corresponding decrease between 6 and 7. Smaller, oscillatory changes are observed at the remaining atoms. The σ electrons are oppositely polarized, i.e., there is a decreased occupation between atoms 1 and 2 and a corresponding increase between atoms 6 and 7. In the case of the metal-wire-metal system (Fig. 4B), the changes are significantly different. There is an increased occupation of the antibonding π^* orbital between atoms 1 and 2 and a decrease in the occupation of the π^* orbital between atoms 6 and 7. These changes in the wire are associated with the formation of screening regions of decreased electron density on the left (positive) metal electrode and increased density on the right (negative) electrode. The σ orbitals are also affected; in particular, there is a decrease between atoms 2 and 3 and an increase between atoms 5 and 6. Thus, the effect of the bias is complex and involves changes in the metal-to-wire charge transfer and the polarization of the resulting charge density by the electric field, as well as screening by the electrodes.

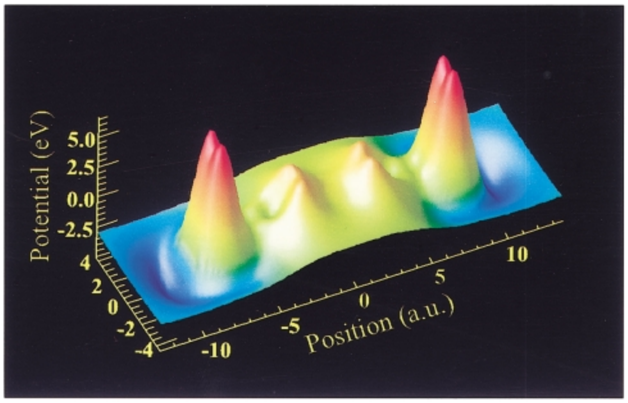

FIG. 3 (color). A 3D plot of the electrostatic potential (minus the superposition of the potentials of the free C_7 chain and the pair of bare electrodes) of a metal-C_7-metal system as a function of position (in atomic units) along and transverse to the wire.

We now explore how the applied bias voltage drops across the metal-wire-metal system. Figure 4C (dashed curve) shows, for the two bare electrodes, the difference in electrostatic potential (energy) of an electron between the cases of having a 3 V bias and having zero bias. The solid curve shows this same difference in the presence of the wire, plotted along the wire axis. The contrast is quite evident. While the 3 V potential difference drops over a distance of about 12 a.u., i.e., roughly between the positive

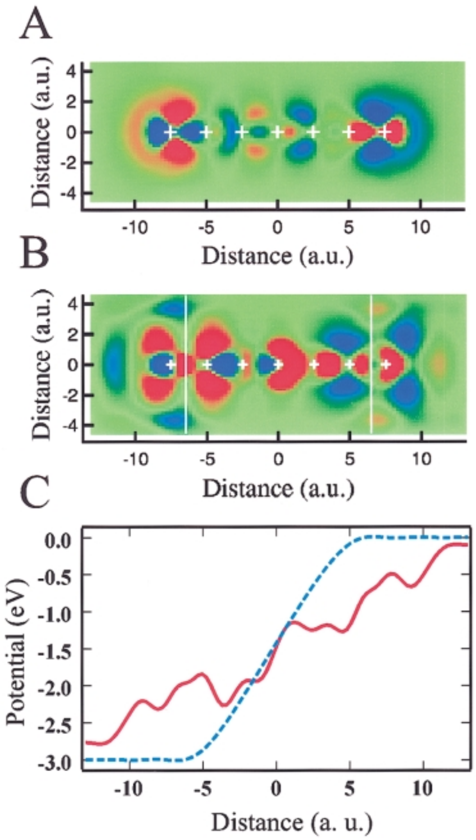

FIG. 4 (color). (A) Difference of the charge densities of the free C_7 wire in a 6 V/nm electric field and that of the free wire in zero field. (B) Difference of the charge densities of the metal-C_7-metal system with an applied bias voltage of 3 V and that of the same system without an applied bias. The green color indicates an unchanged, red an increased, and blue a decreased electron density. (C) Blue dashed line: difference between the electrostatic potential of the bare metal electrodes biased at 3 V and the potential at zero bias. Solid red line: difference between the potential of the metal-C_7-metal system biased at 3 V and the potential of the same system at zero bias voltage, along the wire axis.

background edges of the two metals in the case of the bare electrodes, it drops over about twice that distance in the presence of the carbon-atom wire. A fraction ($\sim$40%) of this potential difference drops across the wire itself [17]. Furthermore, an increase in the potential near the positive (left) electrode and a decrease near the negative electrode are clearly observed. The above observations can be understood on the basis of the charge-transfer processes observed in Fig. 4A, where atoms C1 and C2 were seen to receive charge, while atoms C6 and C7 lose charge, leading to the observed local changes in the electrostatic potential. Most importantly, the distance over which the potential drops now extends to include the screening-charge regions in the two electrodes.

We now briefly address the effect of structural distortions on the electrical properties of these wires. Conductance changes upon bending have been predicted [18,19] and observed [20] in the case of the related 1D system of carbon nanotubes. While distortions lead to an increase in the energy of the system, the conductance can either decrease or increase depending on the effect of the distortion on the density of states (DOS) at the Fermi level DOS (E_F). Here we used a simple distorted geometry involving a 90° bend at the central carbon atom (C_i). The conductance of these wires is given by triangles in Fig. 1A. In all C wires studied, the conductance was found to decrease upon bending. DOS spectra (not shown) indicate that the cause of this decrease is the partially occupied π-HOMO orbitals that are pushed to higher energy, reducing the DOS (E_F). However, not all orbitals of the wires are destabilized. We find that the factor which determines the direction of the shift in these systems is the nature of the interaction between the carbon atoms C_{i-1} and C_{i+1} that are brought in close proximity by bending at the C_i site. Depending on whether, for a particular orbital, this interaction is bonding or antibonding, the orbital is stabilized or destabilized.

In conclusion, we have shown that coupling of the wire to the metal electrodes leads to significant charge-transfer doping of the wire. The extent and spatial distribution of this charge is primarily dictated by the strength of electron-electron interactions. A large bias modifies significantly the electrode-wire interaction and this in turn drastically changes the way the potential drops across the electrode-wire-electrode system. Finally, we have discussed how structural distortions affect the conductance of the wire.

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[14] This radius is larger than half the 2.5 a.u. interatomic bond length, and so there is some double-counting of charge in the bar graph, but a radius of 1.25 a.u., while avoiding this double-counting, would be too small to give a good picture of the charge in the π states.
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