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***Ab initio* I-V characteristics of short C₂₀ chains**Christopher Roland,¹ Brian Larade,² Jeremy Taylor,^{3,2} and Hong Guo²¹*Department of Physics, The North Carolina State University, Raleigh, North Carolina 27695*²*Center for the Physics of Materials & Department of Physics, McGill University, Montreal, Quebec, Canada H3A 2T8*³*Mikroelektronik Centret (MIC), Technical University of Denmark, East DK-2800 Kgs. Lyngby, Denmark*

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We have calculated the *I-V* characteristics of short chains of C₂₀ molecular cages between Al and Au leads with an *ab initio* formalism. The results indicate that a linear chain of such molecules acts primarily as *metallic* nanowires. The transmission, however, depends sensitively both on the orientation and distance between the individual C₂₀ molecules. Transport through the molecular chains is accompanied by a significant amount of charge transfer, which remains localized at the electrode/molecular interface.

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The recent advent of nanometer electro-mechanical systems (NEMS) has attracted considerable attention, both for practical application purposes and as a fundamental area of research.¹⁻⁷ Despite the impressive progress achieved, the physics of many important issues still needs to be resolved before NEMS becomes a viable technology. For example, inherent in the problem of quantum transport through NEMS is the strong coupling between the *atomic* and the *electronic* degrees of freedom. At a truly *molecular* scale, how then does the coupling of the different functional units effect the electron transport? What is the role of the electrode-molecular interaction? Which factors critically influence current flow? All these questions need a thorough investigation in order to gain fundamental understanding of the operation of NEMS devices.

In this paper, we report on an *ab initio* investigation of these issues for a NEMS device consisting of a short chain of C₂₀ cages between atomistic Al and Au leads. This choice is motivated by the recent fabrication of fullerene-based NEMS devices such as the C₆₀-amplifier.¹ Because the C₂₀ cage is the *smallest* fullerene, it represents a useful model for prototypical fullerene-based devices that are at the same time numerically tractable. The C₂₀ cage is the ground-state structure of the C₂₀ clusters, within density-functional theory.^{8,9} It has a relatively small gap of 0.96 eV between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and a chain of them provides insight as to how molecules may, or may not, act as resistors when arranged in series. Our main results are the following. Surprisingly, the chains display current-voltage (*I-V*) characteristics similar to that of metallic nanowires. However, depending on the relative orientation of the C₂₀ molecules with respect to each other, the chains display either a strong or weak dependence on the number of molecules in the chains, which may be understood in terms of the formation of an effective tunneling barrier. Transmission through the chains is also characterized by a considerable amount of charge transfer from the electrodes to the cages, which depends strongly on the type of electrode material and the electrode/molecular distance.

The C₂₀ fullerene (CF) consists of twelve pentagons arranged in a cage structure, as shown in Fig. 1. To construct a C₂₀ chain, many different atomistic arrangements are pos-

sible, but for simplicity we have concentrated on the following.¹⁰ The chains are characterized by two important lengths: the electrode/C₂₀ distance d_1 , and the distance d_2 between each of the C₂₀ molecules. In terms of the molecular orientation, we have focused on the two cases shown in Fig. 1. The molecules are arranged such that the C atoms are either directly opposite (top configuration CF1) as is characteristic of polymerized fullerenes,¹¹ or maximally incommensurate with respect to each other (lower configuration CF2).

To calculate the *I-V* curves, we made use of a recently developed formalism¹² that combines the Keldysh nonequilibrium Green's functions (NEGF)^{13,14} with pseudopotential-based real-space *ab initio* density-functional theory.¹⁵ The main advantages of this approach are (i) a proper treatment of the *open-boundary* conditions for the system as appropriate for quantum transport under an external bias voltage; (ii) an atomistic treatment of the electrodes; and (iii) a self-consistent calculation of the charge density via NEGF thereby incorporating the effects of both the *scattering* and *bound* states present in the system. Details about this methodology can be found in Ref. 12.

Figure 2 shows the *I-V* curves for the short C₂₀ chains, with up to four molecules, coupled to either Au or Al-(100) leads. All of the *I-V* curves have a significant nonzero slope, indicating conduction. Hence, to first order, all the chains act as metallic nanowires. However, there are some differences in the results as obtained via CF1 and CF2. First, given a similar d_1 from the electrodes, the *I-V* characteristics for

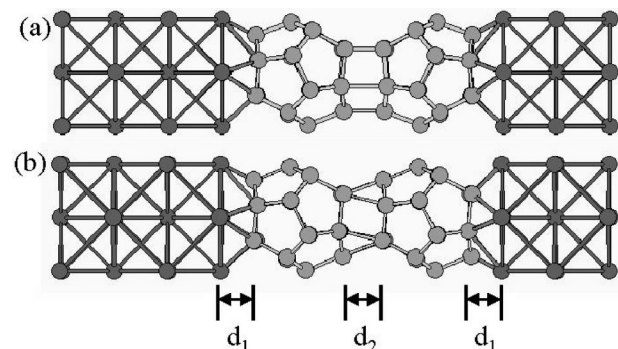


FIG. 1. Atomic configuration of the *central* scattering region of a typical chain of *two* C₂₀ molecules between Al(100) leads: (a) CF1; (b) CF2. The arrow marks the intermolecular distance d_2 .

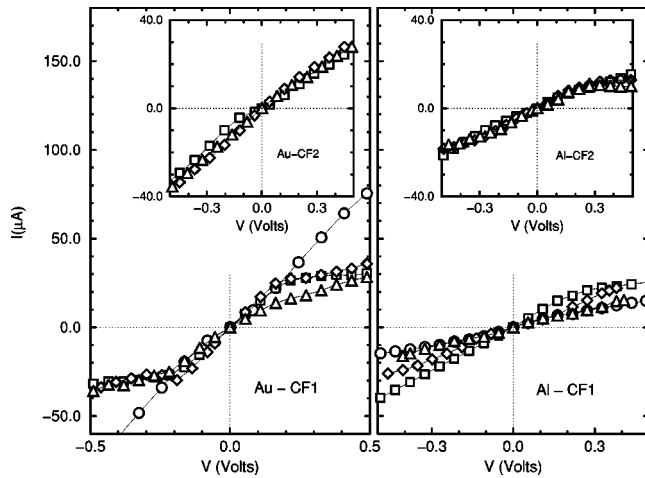


FIG. 2. I - V signatures of short C_{20} chains between Au (left panel) and Al (right panel) with C_{20} 's in CF1. Here circles, squares, diamonds, and triangles indicate one, two, three, and four C_{20} molecules in the chain, respectively. The insets show the corresponding results for chains in CF2.

chains in CF1 have a somewhat larger slope, as compared to those in CF2. This may be understood in terms of a larger overlap, and, therefore, a better coupling between the orbitals on the different C_{20} molecules in CF1. For the most part, for chains with C_{20} 's in CF2, the I - V curves are very similar, lying virtually on top of each other. The exception to this appears to be that of a single C_{20} molecule coupled to Au leads, which has a very much larger slope than all the other curves. This slope is, however, comparable to what is obtained for longer chains in CF1 between Au leads. Similar to the results for the CF2 chains, the I - V curves in this case are virtually identical, although there is a bit of a numerical deviation for the four C_{20} chain under positive bias voltages. Nevertheless, the overall behavior of these curves is quite similar. For Al leads, there is a reduction in the slopes, that manifests itself primarily under larger biases. For the smaller biases, the curves for the *three* and *four* molecules are quite similar and overlap. Hence, in general, there appears to be no dramatic reduction in the I - V slopes as the number of molecules is progressively increased.

This result is somewhat surprising, generally speaking one would expect the formation of an effective barrier through which the electrons need to tunnel. The presence of such barriers would definitely lead to a strong length-dependent resistive behavior. However, there is no clear evidence of such a barrier. These results, therefore, differ, with the exception of Al in CF1, from the previously analyzed cases of linear C chains,^{16,17} which are characterized by significant variations in the I - V slopes as the number of C-atoms is increased, along with even-odd oscillations in the I - V curves.^{16,17}

Quantum transport through the C_{20} cages is accompanied by a significant charge transfer from the electrodes to the molecules, which acts not only to align the Fermi level of the system, but also builds up a Schottky barrierlike structure through the formation of an interface dipole. Such charge doping has previously been noted for the case of chains of C

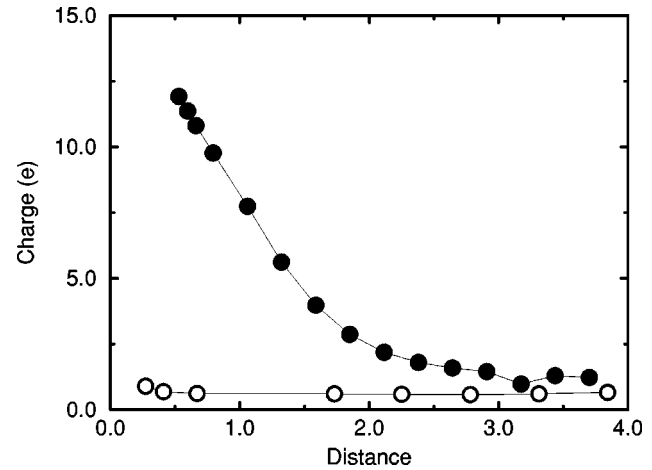


FIG. 3. Charge transferred as a function of distance (in Angstroms). Here the solid circles indicate results for a single C_{20} molecule between Al(100) leads as a function of d_1 . The open circles denote the charge transferred to the *middle* molecule of a three C_{20} chain as a function of the intermolecular distance d_2 .

atoms coupled to Jellium leads.¹⁶ However, our use of *atomic* leads allows us to investigate this process in detail. Analysis shows that for the C_{20} chains, more than 90% of the transmission takes place through the LUMO states, which are partially filled because of the charge transfer. The amount of charge transferred depends both upon the electrode material and the distance d_1 . As shown in Fig. 3 for Al leads, the amount of charge transferred is greatest when the molecules are closest to the lead, where it comprises about 12% of the total charge on a single- C_{20} molecule. This transferred charge decreases rapidly with distance, and ultimately comes to represent only about 2.5% of the total charge. These relatively large variations in the charge transfer with distance manifests itself in the very sensitive behavior of I - V curves: even very small changes in d_1 can lead to significant changes in the slopes of the I - V curves, which essentially interpolate between the results obtain with CF1 and CF2.

Table I summarizes the amount of charge transferred to each of the C_{20} molecules within the different chains. First, it is clear that there are only *small* variations as a function of the bias voltage. Second, the amount of charge transferred is mostly *independent* of the number of molecules in a given chain, and the internal C_{20} conformation CF1 or CF2. This is a reflection of the internal charge distribution within the chains. Almost all of the transferred charge is located on the C atoms closest to each of the electrodes, where they form significant multipoles. As expected, while there is an *increase* in the C-atom charges, there is a corresponding charge *depletion* for electrode atoms closest to the C_{20} molecules that almost exactly cancel each other. At the lowest order, the charge distribution is characterized by its dipole moment, for which typical magnitudes of 20.2, 14.0, and 12.0 D are obtained for Al leads and distances $d_1 = 0.53, 1.85$, and 3.44 Å, respectively. However, it must be emphasized that all of the charge distribution have a significant quadrupole moment as well, whose contributions to the interface potential appears to be significant. Finally, note that only a small amount of the

TABLE I. Excess charge on each C₂₀ molecule for different atomistic leads and bias voltages. The molecules are oriented in CF2, and have parameters $d_1 = 1.31$ (1.10) Å and $d_2 = 2.42$ Å for Al (Au), respectively.

| Voltage (V) | Al leads | | Au leads | |
|-----------------------|----------|--------|----------|--------|
| | -0.408 | +0.408 | -0.408 | +0.408 |
| One C ₂₀ | 6.59 | 6.58 | 7.71 | 7.68 |
| Two C ₂₀ | 3.02 | 3.06 | 4.52 | 4.47 |
| | 3.03 | 3.07 | 4.50 | 4.50 |
| Three C ₂₀ | 3.01 | 3.01 | 4.47 | 4.52 |
| | 0.49 | 0.54 | 0.55 | 0.58 |
| | 3.06 | 3.14 | 4.55 | 4.57 |
| Four C ₂₀ | 3.00 | 2.99 | 4.48 | 4.51 |
| | 0.45 | 0.50 | 0.55 | 0.61 |
| | 0.45 | 0.51 | 0.54 | 0.62 |
| | 3.05 | 3.13 | 4.50 | 4.48 |

transferred charge, $\sim 0.5e$, is associated with all of the *internal* C₂₀ molecules. Since such molecules are relatively far away from the electrodes, this charge is mostly *independent* of the electrode characteristics. It does, however, depend very weakly on d_2 as summarized in Fig. 3.

As may be expected, transport through the chains is quite sensitive to the intermolecular distance d_2 , especially when the molecules are in configuration CF1. Figure 4 shows some typical results for two C₂₀ molecules between Al leads. When the distance between the two molecules is very close, there is relatively little transport through device with a flat *I-V* curve. As the C₂₀'s are moved further apart, the slopes of the *I-V* curves increases and the device displays full metallic behavior that is maximal at a distance of ~ 2.4 Å. Increasing the distance even further leads to a general decrease in the conductance, with the *I-V* curves even displaying some characteristics of negative differential resistance beginning at ~ 3.2 Å. Ultimately, the signal disappears as the overlap between the wave functions vanish. Note also that the decrease from the maximal value is nonmonotonic, when the negative differential resistance behavior begins to manifest itself, i.e., the slope for larger distance of 3.18 Å is actually higher than the preceding one at 2.66 Å, as shown in Fig. 4. A detailed analysis of the transport shows that these variations are due to changes in the transmission eigenvalues as a function of distance. For all the devices, transmission takes place predominantly through the LUMO states whose cou-

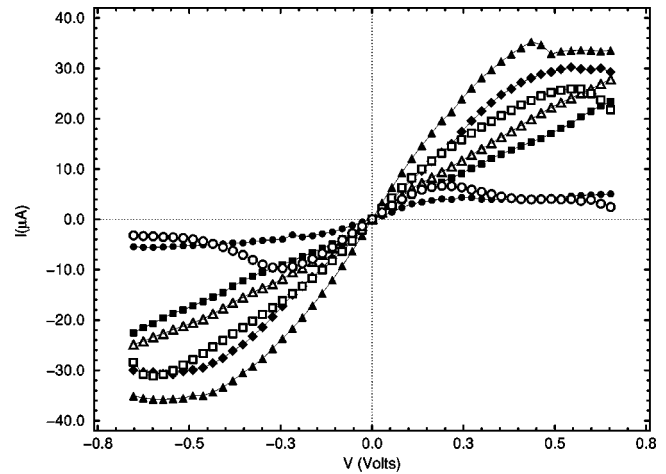


FIG. 4. *I-V* characteristics of a two C₂₀ chain in CF1 as a function of intermolecular distance d_2 . The values of d_2 are as follows: filled circles, 1.62 Å; filled squares, 1.88 Å; filled diamonds, 2.14 Å; filled triangles, 2.4 Å; open triangles, 2.66 Å; open squares, 3.18 Å; open circles, 3.7 Å. Parameter $d_1 = 1.32$ Å is fixed.

pling to the scattering states of the system first increases, and then decreases with distance as reflected in the *I-V* curves. Finally, we note that negative differential resistance in molecular devices have been observed experimentally in a number of systems,^{2,18,19} and we refer interested readers to them and to Ref. 17 that reports a theoretical analysis of it for carbon atomic wires.

In summary, we have investigated quantum transport through paradigmatic NEMS devices consisting of chains of C₂₀ cages with *ab initio* simulations. Our results indicate that these molecules act largely as quantum nanowires, whose *I-V* characteristics depend only weakly on the number of molecules in the chains. While there are some changes for a differing number of molecules in CF1, no such changes are observed when they are in CF2. Transport through the chains is also accompanied by a significant transfer of charge from the metal to the molecules themselves, with most of the charge being localized at the electrode-C₂₀ interface. We expect that the features explored here will be generic to other NEMS systems, particularly ones consisting of other fullerenes and nanoclusters.

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