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***Ab initio* I-V characteristics of short C<sub>20</sub> chains**Christopher Roland,<sup>1</sup> Brian Larade,<sup>2</sup> Jeremy Taylor,<sup>3,2</sup> and Hong Guo<sup>2</sup><sup>1</sup>*Department of Physics, The North Carolina State University, Raleigh, North Carolina 27695*<sup>2</sup>*Center for the Physics of Materials & Department of Physics, McGill University, Montreal, Quebec, Canada H3A 2T8*<sup>3</sup>*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 C<sub>20</sub> 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 C<sub>20</sub> 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.<sup>1-7</sup> 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 C<sub>20</sub> cages between atomistic Al and Au leads. This choice is motivated by the recent fabrication of fullerene-based NEMS devices such as the C<sub>60</sub>-amplifier.<sup>1</sup> Because the C<sub>20</sub> cage is the *smallest* fullerene, it represents a useful model for prototypical fullerene-based devices that are at the same time numerically tractable. The C<sub>20</sub> cage is the ground-state structure of the C<sub>20</sub> clusters, within density-functional theory.<sup>8,9</sup> 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 C<sub>20</sub> 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 C<sub>20</sub> fullerene (CF) consists of twelve pentagons arranged in a cage structure, as shown in Fig. 1. To construct a C<sub>20</sub> chain, many different atomistic arrangements are pos-

sible, but for simplicity we have concentrated on the following.<sup>10</sup> The chains are characterized by two important lengths: the electrode/C<sub>20</sub> distance  $d_1$ , and the distance  $d_2$  between each of the C<sub>20</sub> 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,<sup>11</sup> or maximally incommensurate with respect to each other (lower configuration CF2).

To calculate the *I-V* curves, we made use of a recently developed formalism<sup>12</sup> that combines the Keldysh nonequilibrium Green's functions (NEGF)<sup>13,14</sup> with pseudopotential-based real-space *ab initio* density-functional theory.<sup>15</sup> 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 C<sub>20</sub> 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

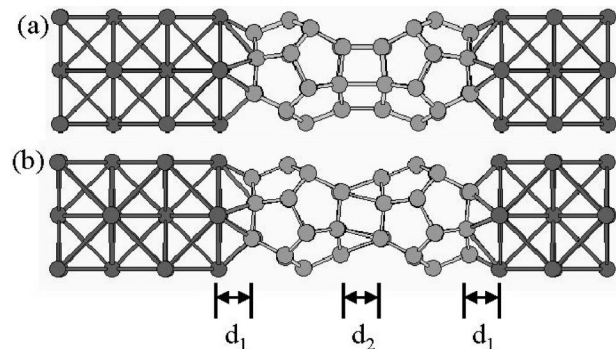


FIG. 1. Atomic configuration of the *central* scattering region of a typical chain of *two* C<sub>20</sub> molecules between Al(100) leads: (a) CF1; (b) CF2. The arrow marks the intermolecular distance  $d_2$ .

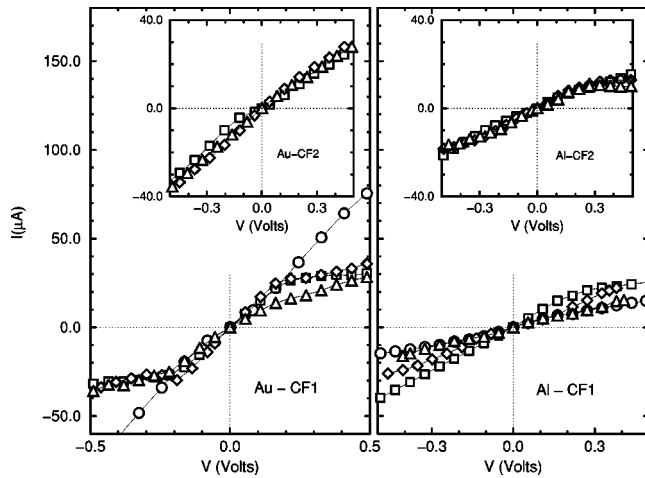


FIG. 2.  $I$ - $V$  signatures of short  $C_{20}$  chains between Au (left panel) and Al (right panel) with  $C_{20}$ 's in CF1. Here circles, squares, diamonds, and triangles indicate one, two, three, and four  $C_{20}$  molecules in the chain, respectively. The insets show the corresponding results 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,<sup>16,17</sup> 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.<sup>16,17</sup>

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

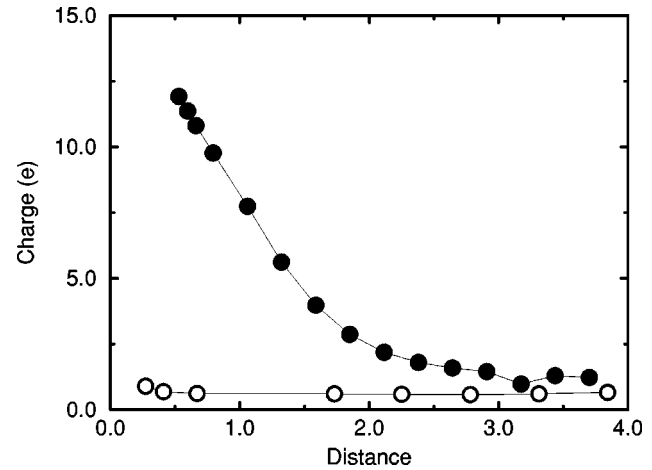


FIG. 3. Charge transferred as a function of distance (in Angstroms). Here the solid circles indicate results for a single  $C_{20}$  molecule between Al(100) leads as a function of  $d_1$ . The open circles denote the charge transferred to the *middle* molecule of a three  $C_{20}$  chain as a function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

atoms coupled to Jellium leads.<sup>16</sup> 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 C<sub>20</sub> 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 <sub>20</sub>	6.59	6.58	7.71	7.68
Two C <sub>20</sub>	3.02	3.06	4.52	4.47
	3.03	3.07	4.50	4.50
Three C <sub>20</sub>	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 <sub>20</sub>	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* C<sub>20</sub> 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 C<sub>20</sub> 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 C<sub>20</sub>'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  $\sim 2.4$  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  $\sim 3.2$  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-

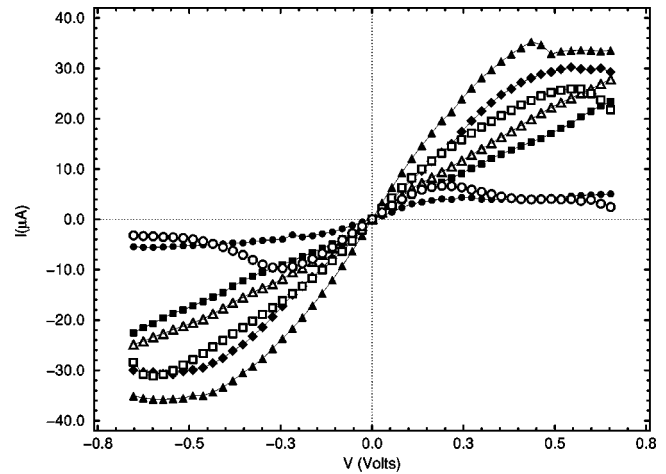


FIG. 4. *I-V* characteristics of a two C<sub>20</sub> chain in CF1 as a function of intermolecular distance  $d_2$ . The values of  $d_2$  are as follows: filled circles, 1.62 Å; filled squares, 1.88 Å; filled diamonds, 2.14 Å; filled triangles, 2.4 Å; open triangles, 2.66 Å; open squares, 3.18 Å; open 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,<sup>2,18,19</sup> 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 C<sub>20</sub> 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-C<sub>20</sub> 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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