Fullerene-based molecular nanobridges: A first-principles study

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Building upon traditional quantum chemistry calculations, we have implemented an *ab-initio* method to study the electrical transport in nanocontacts. We illustrate our technique calculating the conductance of C\textsubscript{60} molecules connected in various ways to Al electrodes characterized at the atomic level. Central to a correct estimate of the electrical current is a precise knowledge of the local charge transfer between molecule and metal which, in turn, guarantees the correct positioning of the Fermi level with respect to the molecular orbitals. Contrary to our expectations, ballistic transport seems to occur in this system.

At the forefront of the carbon-based molecules that are expected to play a key role in nanoelectronic devices one can situate carbon nanotubes and fullerenes. From Coulomb blockade to Kondo-like phenomena through ballistic transport, multiple transport regimes have been observed in nanotubes (even for the same chirality of the nanotube) depending on the way the contact with the electrodes is made \[1\]. Very little is known, however, about the true role played by this contact as well as of the effect of the substrate on which the carbon nanotube has been layed. This is somewhat connected with the difficulties experienced in the interpretation of electronic transport experiments through C\textsubscript{60} molecules. Experiments using a scanning tunneling microscope (STM) \[2\] have shown the possibility of “looking” at individual C\textsubscript{60} molecules when they are adsorbed on a conducting substrate. There is still, however, a lot of controversy in the interpretation of the images obtained by different groups \[3\]. Alternative to STM set-ups, nanoscopic break junctions also revealed themselves as powerful tools to study transport through individual molecules \[4\]. Recently, for instance, in between the two electrodes of a gold break junction, evaporated C\textsubscript{60} molecules unexpectedly created “mechanical” bridges for electrical transport between electrodes \[5\].

Archetypal STM and break-junction set-ups above mentioned can be cataloged under the term molecular nanobridge, i.e., metallic electrode + molecule + metallic electrode. The conductance, \(G\), is essentially determined by the electronic structure of the isolated molecule since the number of available channels for conduction deep in the electrodes is always much larger than those provided by the molecule. However, as already mentioned, this conductance is strongly influenced by the chemistry of the electrode-molecule contacts. Behind this contact lies a key problem: Charge transfers between electrode and molecule when they come in close proximity. The necessity of aligning the Fermi level of the metallic electrodes with the “Fermi level” of the molecule forces a certain amount of charge to be transferred one way or the other. The way this alignment is achieved and how much charge is transferred constitutes a difficult problem which turns out to be essential to understand the electrical transport in molecular nanobridges and, more generally, in nanocontacts or nanoconstrictions. Curiously enough, the prevailing theoretical descriptions in the great body of work done on various types of metal-molecule-metal systems \[6\] as well as on atomic chains and constrictions \[7\] are still based on parametrized tight-binding or semi-empirical models. The theoretical framework to calculate the current is well established \[8\], but, within these models, Fermi level alignment has to be either entirely ignored or imposed with some additional criteria. While local charge neutrality is a sensible criterion for atomic chains and constrictions made of the same material as the electrodes \[9\], there is not the like for metal-molecule-metal systems. This is, in part, the motivation for developing *ab-initio* methods which can provide qualitative and quantitative answers in all possible scenarios. Some groups have already blazed the trail in this direction \[10,11\], although in their methods the problem of the atomic structure of the electrodes is usually put aside. This is not satisfactory when one is trying to describe STM experiments where the detailed atomic structure of the tip determines, to a large extent, whether or not the STM images can resolve the topography or molecular structure of the adsorbate.

What we present here is an *ab-initio* alternative to parametrized tight-binding or semi-empirical models in order to address electrical transport through generic nanocontacts. Our method automatically accounts for Fermi level alignment and charge transfer whenever the latter is expected to occur. This is the case in the system we study here: Al\textsubscript{∞}-C\textsubscript{60}-Al\textsubscript{∞}. Isolated C\textsubscript{60} molecules present a large gap (\(\approx\) 2 eV.) and behave like intrinsic semiconductors. At low temperatures, metal-
Fullerene, metal-fullerene-metal systems do not conduct when the semiconductor is intrinsic regardless of the sign and the amount of charge transferred at the interfaces. In the metal-fullerene-metal system, however, a tunnel current can always be expected due to the nanoscopic size of the fullerene. What is more surprising is the fact that C60 molecules can conduct ballistically (G > e2/h) [15]. Some of the lowest unoccupied molecular orbitals (LUMO’s) of the isolated fullerene still retain its extended character when contact is made to the electrodes and they become partially or fully occupied. In solid-state language: The Fermi level lies above the bottom of the conduction band all across the (nanoscopic) semiconductor. Notice that bigger molecules exhibiting a gap like some families of undoped nanotubes are not expected to conduct at zero bias [1]. Whether or not this occurs depends on the size of the molecule and the details of the charge transfer process which, in turn, relies heavily on the relaxation of the atomic structure of the fullerene when in contact with the metal.

}\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Schematic view of the two-step process for calculating the Green’s function used in the calculation of the conductance: (a) A density functional calculation of a C60 molecule contacted by two electrodes (here in the form of pyramids) is performed. (b) Atoms that are irrelevant for electrical transport are removed and substituted by an effective selfenergy “attached” to the contact left and right atoms remaining in the electrodes (see text).}
\end{figure}

Standard \textit{ab-initio} or quantum chemistry calculations [15,16] are only possible for finite or periodic systems, whereas the transport problem one typically wants to address requires infinitely large leads with no symmetry at all. Drawing on Refs. [12,13], the main idea here consists of performing a density functional (DF) calculation of the molecule including part of the leads with the desired geometry [see Fig. 1(a)]. This can be efficiently done using the Gaussian-98 code [13]. For a sufficiently large number of atoms describing the metallic electrodes the energy of the highest occupied molecular orbital (HOMO) of the whole structure sets the Fermi level. In addition, the correct charge transfer (to or from the molecule) is guaranteed. Next, we perform a Löwdin orthogonalization of the original non-orthogonal gaussian basis set into an orthogonal one which, having basis elements more extended than the original one, still preserves the symmetry of the orbitals and the atomic character. The hamiltonian of the electrode+molecule+electrode system,  $\hat{H}$, as it stands, is finite and, according to the usual theoretical transport schemes [9], its Green’s functions are unsuitable for any current determination since they simply have poles. The following (and crucial) step in our procedure is to transform this finite system into an effectively infinite one. In order to do this we first remove from the hamiltonian all but the N atoms forming the relevant atomic structure of each electrode close to the molecule [see Fig. 1(b)]. The retarded Green’s function associated with this reduced hamiltonian $\hat{H}_r$ is now transformed into the retarded Green’s function of an infinite system:

\begin{equation}
G_r(\epsilon) = (\epsilon \hat{I} - \hat{H}_r + i\delta)^{-1} \to [\epsilon \hat{I} - \hat{H}_r - \hat{\Sigma}(\epsilon)]^{-1}.
\end{equation}

In this expression $\hat{\Sigma} = \hat{\Sigma}_R + \hat{\Sigma}_L$ where $\hat{\Sigma}_R(\hat{\Sigma}_L)$ denotes a self-energy matrix that accounts for the right(left) infinite electrode, part of which has been included in the DF calculation [see Fig. 1(a)]. The added self-energy can only be explicitly calculated in ideal situations, which, in principle, might seem to limit the desired applicability of the above step. However, as pointed out by Landauer in his scattering description of electrical transport [9], the bulk details of a metallic electrode are not necessarily relevant for the electrical transport properties of the region with the smallest number of channels, i.e., the contacted molecule. With this crucial observation in mind we choose to describe the bulk electrode with a Bethe lattice tight-binding model [15] with the appropriate coordination and appropriate parameters. More specifically: We require our Bethe lattice model to reproduce the electrode bulk density of states and to have the same Fermi energy as that of the system on which the DF calculation was initially performed [15]. The advantage of choosing a Bethe lattice resides in that $\hat{\Sigma}$ can be easily calculated through a well-known iteration procedure [17] which we do not detail here. It suffices to say that, for each atom in the reduced electrode that has been stripped from, at least, one nearest-neighbor atom, a contribution from an infinite Bethe lattice calculated in the direction of the removed atom is added to $\hat{\Sigma}$. Assuming that the initial system was large enough and that the reduced system still contains the relevant atomic details of the electrode close to the contact with the molecule, to replace a piece of the electrode by our effective self-energy should introduce no spurious effects, and \textit{it makes the system effectively infinite}. The conductance can now be simply calculated through the expression [9]...
where $\text{Tr}$ denotes the trace over all the orbitals of the reduced hamiltonian and the matrices $\Gamma_R$ and $\Gamma_L$ are given by $i(\Sigma_R - \Sigma_R^\dagger)$ and $i(\Sigma_L - \Sigma_L^\dagger)$, respectively. As in the self-energy matrices, the matrix elements of $\Gamma_R$ and $\Gamma_L$ are only different from zero for the atoms in the reduced electrodes that have been stripped from at least one near-neighbor atom.

\begin{equation}
G = \frac{2e^2}{\hbar} \text{Tr}[\Gamma_L G^\dagger \Gamma_R G^\alpha],
\end{equation}

FIG. 2. (a) Conductance around the Fermi energy (here set to zero) of a C$_{60}$ molecule contacted by two opposite Al electrodes in the form of pyramids composed of 30 atoms each (see inset). We present three different cases: $N=1$ (dotted line), $N=5$ (dashed line), and $N=14$ contact atoms (solid line), corresponding to an increasingly detailed electrode structure in the reduced system (see text). (b) Same as in (a), but with the fullerene in between Al(001) parallel surfaces, each one composed by two atomic planes with a total of 33 atoms (see inset). We present results for $N=1$ (dotted line), $N=5$ (dashed line), and $N=9$ contact atoms (solid line), corresponding to an increasing surface plane.

We apply here the technique just described to the system Al$_\infty$-C$_{60}$-Al$_\infty$ with different geometries. Although they are not commonly used in experiments, we have considered Al electrodes for two independent reasons: (i) The number of electrons per atom is small enough to avoid pseudo-potentials in the DF calculations and, (ii) in contrast to noble metals, Al presents a strong, essentially covalent chemical bond with carbon molecules which, in principle, makes it ideal for the future fabrication of stable nanostructures. For the DF calculation we have used the Becke’s three-parameter hybrid functional using the Lee, Yang and Parr correlation functional with a minimal basis set [19]. The orientation of the fullerene and the separation and atomic structure of the electrodes considered in Fig. 2 (see insets) are reasonable, but arbitrary [20]. In Fig. 4(a) we plot the conductance around the Fermi energy (here set to zero) of the fullerene contacted by two opposite electrodes in the form of pyramids [see inset or Fig. 4(a)]. These are composed of 30 atoms each and their apex atoms are separated by 10.1 Å. We have oriented the fullerene so that two opposite C atoms are as close as possible to the apex atoms of the pyramids (i.e., 1.4 Å between the C atom of the fullerene and the Al apex atom). In order to illustrate the reliability of the method, we present the results for three different approximation degrees: $N=1$ (dotted line), $N=5$ (dashed line), and $N=14$ (solid line), corresponding to an increasingly detailed contact structure. Notice how, as expected, all the curves are very similar since the relevant atomic structure close to the molecule is simply represented by the atom at the pyramid apex. Logically, the results using 5 atoms (two atomic planes) are almost identical to those using 14 atoms (three atomic planes). The gap of the isolated fullerene reflects itself in a vanishing $G$ below the Fermi energy and the LUMO’s of the isolated molecule are now partially occupied. Note that they retain their extended character since the conductance around the Fermi level goes up to $2e^2/h$ at certain energies. Nonetheless, the three-fold degeneracy of the $f_{1u}$ and $f_{1g}$ LUMO’s has been entirely removed by the interaction with the electrodes (this interaction is also responsible for the broadening of the peaks). In this situation Coulomb blockade physics must dominate and spin-splitting will occur in the fullerene [21].

In Fig. 5(b) we present the conductance of the fullerene oriented as in the previous case, but where the two pyramids have been replaced by Al(001) parallel surfaces (see inset). The different types of lines correspond to an increasing definition of the surface plane (1, 5, and 9 surface atoms). Now one atom is not enough to define the contact since there is an important coupling between several Al surface atoms and the fullerene. Not even 5 atoms suffice to define the metallic contact region quite precisely. Now the value of the conductance rises up to $\approx 2.5e^2/h$ right at the Fermi energy. This was somehow expected since, in this situation, the hybridization with the surface is stronger and there are more channels for the electron to travel between electrodes while the LUMO’s appear to be also extended. The gap still reflects itself in $G$, but has been partially closed by the strong hybridization. The excess charge in the fullerene is $\approx 2.6$ which agrees fairly well with a related and recent calculation [13].
We have chosen to study a system of recent interest: A fullerene contacted by Al electrodes. Our main goal was to describe correctly the contact charge transfer so that realistic predictions on the electrical conduction properties of these molecules can be made.

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