Ab initio calculation of transport properties of metal-C$_{60}$-metal junctions

Nikolai Sergueev, Dan Roubtsov, and Hong Guo

Center for the Physics of Materials and Department of Physics, McGill University, Montreal, P.Q., Canada H3A 2T8

By carrying out density functional theory (DFT) analysis within the Keldysh non-equilibrium Green’s function (NEGF) framework, we investigate the quantum transport properties of Au-C$_{60}$-Au molecular junctions from the first principles. We briefly review the NEGF-DFT formalism and present some of our data. We found that at small electrode separations ($\approx 10^{-13}$ Å), the Au-C$_{60}$-Au junctions show metallic behaviour with $G \approx (2e^2/h)$ and $I \approx 1-3$ µA in the linear regime ($|V_{bias}| < 0.3$ V). The physical mechanism is the resonance tunnelling through partially occupied states originated from the lowest unoccupied molecular orbital (LUMO) of the free C$_{60}$. We also found that the charge transfer from the Au electrodes to the C$_{60}$ molecule can be controlled by gate potential.

I. INTRODUCTION

Using molecules as functional units for electronic device application [1] is an interesting perspective and a possible goal of nano-electronics. Work in this field has clearly demonstrated that many of the important molecular device characteristics relate specifically to a strong coupling between the atomic and the electronic degrees of freedom, for a popular introduction see reference [2]. However, from a theoretical point of view, the accurate prediction of the properties of atomic and molecular scale devices – including the true I-V curves with as few adjustable parameters as possible – still represents a formidable challenge [3–5] despite the advances and wide-spread application of large scale ab initio modeling based on the density functional theory (DFT) over the last two decades.

Recall that most of the previous DFT-based ab initio simulations [6,7] solve only two kinds of problems: (i) finite systems such as isolated molecules and clusters, as in quantum chemistry; (ii) periodic systems consisting of supercells, as in solid state physics. However, a molecular electronic device is neither finite nor periodic. Typically, it has open boundaries which are connected to long and different electrodes extending to electron reservoirs far away, and the external bias potentials are applied to these reservoirs. In other words, calculations of finite or periodic systems do not include the correct boundary conditions for a nano-scale device in the quantum transport regime. Therefore, a new formalism for electronic analysis is required to carry out the first principle transport modeling for molecular electronics.

In this article, we briefly outline a formalism that combines the density functional theory with the Keldysh non-equilibrium Green’s functions (NEGF) so that non-equilibrium properties of the quantum transport regime can be predicted from atomistic approach without any phenomenological parameters [8,9]. To show how it works, we apply our NEGF-DFT approach to investigate a C$_{60}$ molecule connected to two Au electrodes. The rest of the article is organized as follows: in section II, we present the NEGF-DFT formalism and, in section III, we present the transport properties of the Au-C$_{60}$-Au tunnel junctions and compare them with the properties of the Al-C$_{60}$-Al ones. Section IV is reserved for a short summary.
### II. NEGF-DFT FORMALISM

The simplest model of a molecular device is schematically shown in figure 1 where a C\textsubscript{60} molecule is contacted by two semi-infinite Au electrodes which extend to \( z = \pm \infty \) where bias voltage is applied. To calculate the electronic states of such a device, two problems should be solved. First, the infinitely large problem (due to the electrodes) must be reduced to something manageable on a computer, i.e., one has to solve an open boundary problem. Second, one has to find the charge density \( \rho (\mathbf{r}) \) of the molecule and electrodes provided there is a bias voltage across the device, and this is a non-equilibrium problem. From the computational point of view, it is convenient to divide our system into three parts: a scattering region with some portion of electrodes and two metal electrodes extending to \( z = \pm \infty \), as shown by the vertical lines in figure 1.

To reduce the infinitely large problem to that defined inside the scattering region (see figure 1), we notice that the effective Kohn-Sham (KS) potential \( V_{\text{eff}}[\rho (\mathbf{r})] \) deep inside the left or right lead is very close to the corresponding bulk KS potential. This fact makes the boundary conditions to be written in the following form \[8\]:

\[
V_{\text{eff}}(\mathbf{r}) = \begin{cases} 
V_{l,\text{eff}}(\mathbf{r}), & z < z_l, \\
V_{c,\text{eff}}(\mathbf{r}), & z_l < z < z_r, \\
V_{r,\text{eff}}(\mathbf{r}) = V_{r,\text{bulk}}(\mathbf{r}), & z > z_r,
\end{cases}
\]

(1)

where the planes \( z = z_{l(r)} \) are the left (right) limits of the scattering region (see figure 1), and \( V_{l,\text{bulk}}(\mathbf{r}) \) and \( V_{r,\text{bulk}}(\mathbf{r}) \) are known. In practice, within the DFT, we only need to match the Hartree potential \( V_{H}[\rho (\mathbf{r})] \) at the boundaries. This can be accomplished by solving the Poisson equation on \( U_{H}(\mathbf{r}) \) by use of a 3D real space grid and boundary conditions at \( z = z_{l(r)} \), and \( V_{H}(\mathbf{r}) \) is matched, and by use of the DFT we can show that \( V_{\text{eff}}(\mathbf{r}) \) is also matched. Thus, equation (1) is valid.

In addition, the 3D real space Poisson solver allows us to deal with any gate potentials, \( V_{g} \). In our model, they provide just additional boundary conditions for the electrostatics, so they change \( U_{H}(\mathbf{r}) \). Furthermore, once \( V_{\text{eff}}(\mathbf{r}) \) is matched across the boundaries, the charge density \( \rho (\mathbf{r}) \) is automatically matched at the boundaries. The lower panel of figure 1 shows the charge density: although the densities in the leads and in the scattering region are calculated separately, they match perfectly across the boundaries.
The above “screening approximation” [8] allows us to reduce the infinitely large Hamiltonian of the system to the effective finite one defined inside the scattering region. In this approximation, we neglected any influence the scattering region may give to the leads, but if the portion of the leads included inside the scattering region is long enough, such an approximation is well controlled. On the other hand, the semi-infinite leads do contribute to the scattering region, and this contribution is included through the self-energies $\Sigma_l(r)(E)$ in the Green’s function $G(E)$ of the scattering region, for example,

$$G^R(E) = (E - H_0 - V_{ps} - V_{H} - V_{xc} - \Sigma^R_l - \Sigma^R_r)^{-1}, \quad (2)$$

$$V_H = eU_H, \quad \Delta U_H(r) = -4\pi \rho(r). \quad (3)$$

Here, $H_0$ is the kinetic energy of a valent electron, and the atomic cores of the scattering region are fixed in space and described by pseudo-potentials, so we have $V_{ps}$, and $V_{eff}[\rho] = V_{H}[\rho] + V_{xc}[\rho]$ is the effective KS potential obtained within the DFT. For example, the exchange correlation potential $V_{xc}$ is taken in a simple local form following the polynomial formula suggested in reference [10], and the (retarded) self-energies due to the semi-infinite left and right electrodes are calculated following an iterative technique described in references [8,11].

However, to calculate the charge density $\rho(r)$ away from equilibrium due to the bias voltage $V_b$, we have to apply the NEGF method [12]. The density matrix of the scattering region is calculated from the so-called lesser Green’s function $G^<(E)$ of the scattering region as follows:

$$\hat{\rho} = \frac{1}{2\pi i} \int dE G^<(E), \quad \text{where} \quad G^<(E) = G^R(E) \Sigma^<(E) G^A(E). \quad (4)$$

Here, $G^R(A)(E)$ is the retarded (advanced) Green’s function of the scattering region. Note that $G^<(E)$ is defined through the Keldysh equation [12]. The lesser self-energy $\Sigma^<(f_l, f_r)$ can be evaluated within the mean field theory as follows:

$$\Sigma^<(E) = i f_l(E, \mu_l) \Gamma_l(E) + i f_r(E, \mu_r) \Gamma_r(E), \quad (5)$$

where $\Gamma_l(r) = i (\Sigma^R_l(r) - \Sigma^A_l(r))$ and $\Sigma^R(A)_{l(r)}$ is the retarded (advanced) self-energy of the left (right) electrode, and $f_l(r)(E)$ are the corresponding Fermi distribution functions. Note that $\Sigma^<(f_l, f_r)$ is more than a simple Fermi distribution: a fact reflecting the non-equilibrium nature of the problem, $\mu_l \neq \mu_r$.

In our numerical procedure, we use a LCAO minimal $s, p, d$ atomic basis set (a real space fireball linear combination of atomic orbitals [7]) to expand the electron wavefunction and define the effective Hamiltonian matrix $F$:

$$H_0 + V_{ps} + V_{H} + V_{xc} \rightarrow F_{jk}[\rho(r)]$$

Here, to calculate $V_{ps, jk}$, the atomic cores are described by standard norm conserving nonlocal pseudo-potentials [13]. We evaluate $G^R$ by direct matrix inversion, $G^A(E) = G^R(E)\Gamma$, and we construct $\rho(r)$ from numerical evaluation of the integral in equation (4) using a suitable contour in the complex plane $E$ [8]. Once $\rho(r)$ is obtained, we evaluate the KS potential and iterate the above procedure, equations (2), (3), and (4), until numerical convergence is reached.

Thus, we construct the self-consistent $\rho(r)$ by the NEGF technique (it takes care of the non-equilibrium statistics) and we calculate the Hartree potential by solving the 3D Poisson equation directly (equation (3) includes all the external fields as the electrostatic boundary conditions). As a result, our NEGF-DFT formalism is able to solve charge transport problems in addition to the conventional electronic structure calculations: we know both the density of states $\text{DOS}(E)$ and the density matrix $G^<(r, r', E)/2\pi i$ of the scattering region. Moreover, we can easily calculate the electron charge on the molecule at no zero $V_b$ and $V_g$. Of course, the density matrix $\hat{\rho}$ is normalized to the total number of valent electrons in the scattering region,

$$\text{Tr}(\hat{\rho}S) = N_e = \text{const},$$

where $S$ is the overlap matrix of the atomic orbitals we use. Then, one can introduce the (average) number of electrons in the molecule by calculating this trace over the molecular orbitals belonging to the molecule only:

$$\text{Tr}_{\text{mol}}(\hat{\rho}S) = N_{e, \text{mol}}(V_b, V_g).$$

The difference between the calculated $N_{e, \text{mol}}(V_b, V_g)$ and $N_{e, \text{mol}}^{(0)}$ of a free molecule can called an (average) excess charge on the molecule in the units of $e$,

$$Q = N_{e, \text{mol}}(V_b, V_g) - N_{e, \text{mol}}^{(0)}.$$
In this section we report our analysis on the transport properties of an Au-C\textsubscript{60}-Au molecular tunnel junction calculated by use of our NEGF-DFT electronic package as discussed above. The device structure is shown in the upper panel of figure 1. So far a considerable amount of theoretical and experimental effort has been devoted to investigate transport properties of C\textsubscript{60} and other fullerene molecules [14–16]. The device we present consists of the fullerene molecule C\textsubscript{60} fixed in the middle of two gold electrodes. Here, we consider two distances between the electrodes, 11.7 Å and 13.7 Å. This corresponds to the minimum distance between an Au atom and C atom of 2.3 Å and 3.3 Å, respectively. Each electrode consists of repeated unit cells with nine Au atoms in the (100) direction and extended to infinity. Note that we do not expect that the C\textsubscript{60} molecule can be found in the Coulomb blockade regime in such junctions if the electrode separation is small, say 9−13 Å. The number of electrons in the molecule is not a good quantum number if the interaction with electrodes is strong.

The current-voltage (I-V) characteristics is calculated as follows:

$$I = \frac{2e^2}{h} \int T(E, V_b) [f_l(E) - f_r(E)] dE,$$

(6)

where $T(E, V_b)$ is the transmission coefficient at the energy $E$ and bias voltage $V_b$. The Fermi distribution functions $f_l(r)(E)$ limit the integration in equation (6) to the small energy range $eV_b$ at the Fermi level of the electrodes (in the zero temperature limit). Transmission coefficient $T(E, V_b)$ is calculated by use of the Green’s functions [17] which we have already obtained as a result of the NEGF-DFT self-consistent iterations, so we write

$$T(E, V_b) = \text{Tr} \left[ \Gamma_l(E) G^R(E) \Gamma_r(E) G^R \dagger (E) \right].$$

(7)

Here, the matrix $\Gamma_{l(r)}(E)$ is related to the line-widths resulting from the coupling of the scattering region to the left (right) lead. It is evaluated in terms of the corresponding self-energy matrices $\Sigma_{l(r)}$ as follows:

$$\Gamma_{l(r)}(E) = i \left( \Sigma^R_{l(r)}(E) - \Sigma^R_{l(r)}(E) \right).$$

(8)

The retarded Green’s function of the scattering region $G^R(E)$ is given as the following matrix:

$$G^R(E) = \left( ES - F[\rho] - \Sigma^R(E) \right)^{-1},$$

(9)

where $F[\rho]$ is the effective Hamiltonian of the scattering region and $\Sigma^R = \Sigma^R_l + \Sigma^R_r$ is the total self-energy matrix. The density of state function is calculated from the density of state matrix $A(E) = i \left( G^R(E) - G^R \dagger (E) \right)$ as follows:

$$\text{DOS}(E) = \text{Tr} \left( A(E) S \right)/2\pi.$$

For the Au-C\textsubscript{60}-Au junctions at $V_b = 0$, the density of states near the Fermi energy is presented on figures 2 and 3 (the Fermi level is set to $E_F = 0$ in this article). Note that at positive gate voltages, $V_g \geq 0$, the energy levels originated from the LUMO of C\textsubscript{60} are partially occupied so they lie near $E = 0$ and $Q > 0$ (in the units of $e$). At negative gate voltages, $V_g < V_g^* < 0$, the energy levels originated from the highest occupied molecular orbital (HOMO) of C\textsubscript{60} begin to be depopulated, so the energy levels originated from the LUMO of C\textsubscript{60} are shifted far to the right from $E = 0$ and $Q < 0$ (in the units of $e$).
FIG. 2. Density of states of the Au-C\textsubscript{60}-Au junction and excess charge of the C\textsubscript{60} molecule are presented for the electrode separation of 11.7 Å and \(V_b = 0\). At the zero gate, the excess charge is \(\approx 0.7e\). Note that the C\textsubscript{60} molecule is not in the Coulomb blockade regime (the broadening is large).

FIG. 3. Density of states of the Au-C\textsubscript{60}-Au junction and excess charge of the C\textsubscript{60} molecule are presented for the electrode separation of 13.7 Å and \(V_b = 0\). At the zero gate, the excess charge is \(\approx 0.5e\). Note that the C\textsubscript{60} molecule is not in the Coulomb blockade regime yet.
FIG. 4. Transmission coefficient $T(E, V_b)$ versus electron energy $E$ is presented for the electrode separations of 11.7 Å and three bias voltages $V_b$, $V_g = 0$. The sharp transmission peak, which results from a resonances of the fullerene + contacts Hamiltonian, dominates the conductance as well as the current-triggered dynamics. Positions of the Renormalized Molecular Levels (RML) [15] of C$_{60}$ are depicted over the peaks of $T(E, V_b)$, and these levels are the LUMO-derived states. The inset shows the calculated I-V curve from which the metallic behaviour of the junction is evident.

The transmission coefficient obtained from equation (7) is presented on figure 4 as a function of the electron energy $E$ for three different bias voltages and the zero gate potential. The sharp peak in $T(E, V_b)$ is the result of a resonance transmission through the LUMO of the C$_{60}$. At $V_b = 0$, this resonance lies just above the Fermi level of the leads, see figures 2 and 3. As the bias voltage is applied, the peak position shifts toward higher energies. If the system is absolutely symmetric and $V_b \neq 0$, we would expect the same voltage drop at the two electrode-molecule junctions. In our system, the atomic structures of C$_{60}$ facing the left and right electrodes are not the same, and this breaks the left-right symmetry. We therefore observe an asymmetric voltage drop at the two contacts. Consequently, the transmission peak position shifts by about $\sim 0.15$ eV when $V_b$ is increased by 0.2 V, i.e., the applied voltage drops more on one side than on the other side of the C$_{60}$. We also calculated the I-V curve for this device by use of equation (6); it is shown in the inset of figure 4.

FIG. 5. Equilibrium conductance $G$ is plotted as a function of the gate voltage $V_g$ for the electrode separations of 11.7 Å. Note that $G \approx G_0$ at $V_g = 0$. 

6
FIG. 6. Equilibrium conductance $G$ is plotted as a function of the gate voltage $V_g$ for the electrode separations of 13.7 Å. Note that $G \approx 0.25 G_0$ at $V_g = 0$.

We can easily calculate the equilibrium conductance $G$ of the junction, $G = dI/dV$. In the linear regime, $-0.25 V < V_b < 0.25 V$, see figure 4, we can use the following formula:

$$G = G_0 T(E = E_F, V_b = 0)$$

(valid in the zero temperature limit). Here, $G_0 = 2e^2/h$ is the quantum of conductance. As the positive gate potential changes the occupancy of the LUMO-derived energy levels, we can expect the strong dependence of $G(V_g)$ for different separations of the leads. These results are presented in figures 5 and 6.

Similar metallic behaviour has been reported before [14] for Al-C$_{60}$-Al junctions at the electrode separation of 9.3 Å (it corresponds to the minimum distance between an Al atom and C atom of $\approx 1.1$ Å). Note that the work function of Al is $\approx 4.19$ eV whereas the work function of Au is $\approx 5.3$ eV. At $V_b = V_g = 0$, we have $Q \approx 3e$, $G \approx 2.2G_0$ for the Al-C$_{60}$-Al junction [14] and $Q \approx 0.7e$, $G \approx G_0$ for the Au-C$_{60}$-Au one (the electrode separation of 11.7 Å). In addition, for the Au-C$_{60}$-Au device, the current in the linear (metallic) regime is (roughly) one order of value smaller than the current calculated for the Al-C$_{60}$-Al one.

Here, the interesting physics is that despite the large HOMO-LUMO gap of a free C$_{60}$ ($\approx 1.8$ eV [19]), we predict metallic transport characteristics for the Au-C$_{60}$-Au devices, and they are qualitatively the same as the properties of the Al-C$_{60}$-Al devices. We found that if the C$_{60}$ molecule is relatively well bonded to metallic leads, there is a strong charge transfer from the leads to the C$_{60}$ cage and it partially fills the (empty) LUMO of C$_{60}$. In other words, charge transfer from the electrodes to C$_{60}$ aligns the LUMO to the Fermi energy of the leads. As a result, we obtain a large resonance conductance and the metallic I-V curve.

IV. SUMMARY

We have shown that the NEGF-DFT formalism is a powerful technique for modeling charge transport properties of molecular electronic devices. The novelty of this technique is in constructing electron charge density via nonequilibrium Green’s functions and the very effective screening approximation. Since the entire algorithm is based on evaluating Green’s function, the technique is intrinsically $O(N)$ [20]: this is because atoms far away from each other do not overlap so that the Hamiltonian matrix is block-diagonal. This has tremendous computational advantage which we demonstrated by calculating the nonlinear I-V curve of the Au-C$_{60}$-Au molecular tunnel junction.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support from Natural Science and Engineering Research Council of Canada, le Fonds pour la Formation de Chercheurs et l’Aide à la Recherche de la Province du Québec, and NanoQuebec. We gratefully acknowledge Jeremy Taylor and Brian Larade for their contributions throughout the work presented here.
[1] Aviram A and Ratner M A 1974 Chem. Phys. Lett. 29 277
[2] Heath J R and M. Ratner M 2003 Physics Today 56 May 43
[3] Damle P S, Ghosh A W and Datta S 2001 Phys. Rev. B 64 R201403
[4] Di Ventra M, Pantelides S T and Lang N D 2000 Phys. Rev. Lett. 84 979
[5] Palacios J J, Pérez-Jiménez A J, Louis E and Vergés J A 2001 Phys. Rev. B 64 115411
[6] Payne M C, Teter M P, Allan D C, Arias T A and Joannopoulos J D 1992 Rev. Mod. Phys. 64 1045
[7] Ordejón P, Artacho E and Soler J M 1996 Phys. Rev. B 53 R104441
[8] Taylor J, Guo H and Wang J 2001 Phys. Rev. B 63 245407
[9] Brandbyge M, Mozos J-L, Ordejón P, Taylor J and Stokbro K 2002 Phys. Rev. B 65 165401
[10] Goedecker S, Teter M and Hutter J. 1996 Phys. Rev B 54 1703
[11] Sanvito S, Lambert C J, Jefferson H and Bratkovsky A M 1999 Phys. Rev. B 59 11936
[12] Haug H and Jauho A-P 1998 Quantum Kinetics in Transport and Optics of Semiconductors (Springer-Verlag, New York)
[13] Bachelet G B, Hamann D R and Schlüter M 1982 Phys. Rev. B 26 4199
[14] Taylor J, Guo H and Wang J 2001 Phys. Rev. B 63 R121104
[15] Park H, Park J, Lim A K L, Anderson E H, Alivisatos A P and McEuen P L 2000 Nature 407 57
[16] Alavi S and Seideman T 2001 J. Chem. Phys. 115 1882
[17] Datta S 1997 Electronic Transport in Mesoscopic Systems (Cambridge University Press)
[18] Larade B, Taylor J , Zheng Q R, Mehrez H, Pomorski P and Guo H 2001 Phys. Rev. B 64 195402
[19] Science of Fullerenes and Carbon Nanotubes 1996 edited by Dresselhaus M S, Dresselhaus G and Eklund P C (Academic Press, New York)
[20] Goedecker S 1999 Rev. Mod. Phys. 71 1085