

NEGF-DFT: a first principles formalism for modeling molecular electronics

Nikolai Sergueev and Hong Guo ^a

^aCenter for the Physics of Materials and Department of Physics, McGill University, Montreal, PQ, Canada H3A 2T8

By carrying out density functional theory (DFT) analysis within the Keldysh non-equilibrium Green's function (NEGF) framework, we have investigated quantum transport properties of an Au – C₆₀ – Au molecular junction. In this paper we briefly review the NEGF-DFT formalism and present our data.

En procédant à un calcul de théorie de la densité fonctionnelle (DFT) dans le formalisme de Keldysh de la fonction de Green hors d'équilibre (NEGF), nous étudions les propriétés de transport quantique d'une jonction moléculaire Au – C₆₀ – Au. Nous présentons ici une brève revue du formalisme, ainsi que nos résultats.

1 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. 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, despite the advances and wide-spread application of large scale density functional theory (DFT) based *ab initio* modeling over the last two decades.

Recall that most of the previous DFT-based *ab initio* condensed matter simulations[2,3] solve only two kinds of problems: (i) finite systems such as isolated molecules, 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: it typically has open boundaries which are connected to long and different electrodes extending to electron reservoirs far away, where the external bias potentials are applied. In other words, calculations of finite or periodic systems do not have the correct boundary conditions for quantum transport. Therefore, new formalisms for electronic analysis are required to carry out first principles transport modeling for molecular electronics.

In this work, we briefly outline a formalism that combines DFT with the Keldysh non-equilibrium Green's functions (NEGF) so that nonequilibrium quantum transport properties can be predicted from atomistic approach without any phenomenological parameters[4,5]. We then apply our NEGF-DFT approach to investigate a C₆₀ molecular junction connected to Au electrodes. The rest of the paper is organised as follows. In Sec.2 we present the NEGF-DFT formalism. In Sec. 3 we present the transport properties of the Au-C₆₀-Au tunnel junction. Sec. 4 is reserved for a short summary and outlook of future work.

2 NEGF-DFT Formalism

The simplest model of a molecular device is schematically shown in Fig.1 where a C₆₀ 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 that manageable on a computer, *i.e.* one has to solve a open boundary problem. Second, one has to construct charge density when there is a bias voltage across the molecule—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 Fig.1.

To reduce the infinitely large problem to that defined inside the scattering region (see Fig.1), we notice that the effective Kohn-Sham (KS) potential $V_{eff}[\rho(\mathbf{r})]$, where charge distribution is $\rho(\mathbf{r})$, deep inside a solid surface (the lead) is very close to the corresponding bulk KS potential. This fact makes the boundary conditions to be written in the following form[4]

$$V_{eff}(\mathbf{r}) = \begin{cases} V_{l,eff}(\mathbf{r}) = V_{l,bulk}(\mathbf{r}) & Z < Z_l \\ V_{c,eff}(\mathbf{r}) & Z_l < Z < Z_r \\ V_{r,eff}(\mathbf{r}) = V_{r,bulk}(\mathbf{r}) & Z > Z_r \end{cases}, \quad (1)$$

where the planes $Z = Z_{l(r)}$ are the left (right) limits of the scattering region (See Fig.1). In practice, within DFT where 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 in a 3D real space grid. Once $V_H[\rho(\mathbf{r})]$ is matched, we can show that $V_{r,eff}(\mathbf{r})$ will also be matched within DFT. The 3D real space Poisson solver also allows us to deal with any gate potentials as they provide additional boundary conditions for the electrostatics. Furthermore, once $V_{r,eff}(\mathbf{r})$ is matched across the boundaries, the charge density $\rho(\mathbf{r})$ will automatically match at the boundaries. The lower panel of Fig.1 shows the charge density: although the densities in the leads and in the scattering region are calculated by separate calculations, they match perfectly across the boundaries.

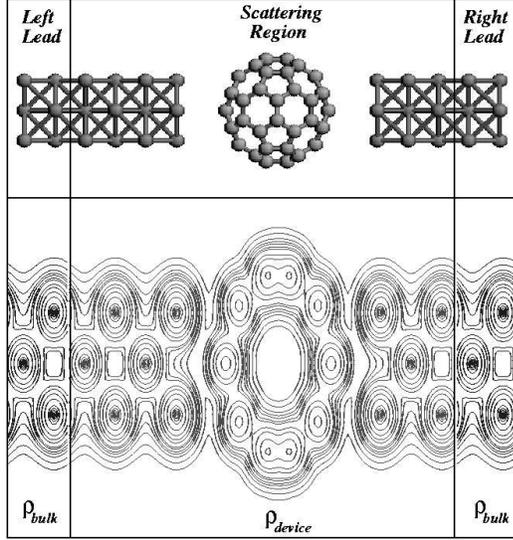


Figure 1. Schematic plot of the Au- C_{60} -Au molecular tunnel junction. The Au electrode consist of repeated unit cells extending to $z = \pm\infty$, and its surface is oriented along the (100) direction. The lower panel shows the calculated charge density at equilibrium where perfect matching is obtained across the boundaries between the leads and the central scattering region.

The above “screening approximation”[4] allows us to reduce the infinitely large problem to 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 will contribute to the scattering region. That contribution is included through the self-energies in the Green’s function of the scattering region.

In order to calculate charge density away from equilibrium (due to bias voltage), we apply NEGF[6]. The density matrix is calculated from NEGF $\mathbf{G}^<(E)$, as

$$\rho = -\frac{i}{2\pi} \int dE \mathbf{G}^<(E), \text{ where} \quad (2)$$

$$\mathbf{G}^< = \mathbf{G}^R \mathbf{\Sigma}^< [f_l, f_r] \mathbf{G}^A, \quad (3)$$

where $\mathbf{G}^{R(A)}$ is the retarded (advanced) Green’s function. $\mathbf{G}^<$ is defined through the Keldysh equation[6]. The lesser self-energy $\mathbf{\Sigma}^< [f_l, f_r]$ within DFT can be evaluated by:

$$\mathbf{\Sigma}^< [f_l, f_r] = -2i \text{Im} [f_l \mathbf{\Sigma}_l^R - f_r \mathbf{\Sigma}_r^R], \quad (4)$$

where $\mathbf{\Sigma}_{l(r)}^R$ is the retarded self-energy of the left (right) electrode and they can be calculated for the semi-infinite leads by an iterative technique[4]. $f_{l(r)}$ are the corresponding Fermi distribution functions. Note that $\mathbf{\Sigma}^< [f_l, f_r]$ is not a Fermi distribution: a fact reflecting the non-equilibrium nature of the problem.

In our numerical procedure, we use a LCAO s,p,d atomic basis set[3] to expand the wavefunction and to define the

Hamiltonian matrix. The atomic core is defined by standard norm conserving nonlocal pseudopotential[7]. We evaluate $\mathbf{G}^{R(A)}$ by direct matrix inversion, and construct $\rho(\mathbf{r})$ by numerical evaluation of Eq.(3) aided by a contour integration trick. Once $\rho(\mathbf{r})$ is obtained, we evaluate the KS potential and iterate the above procedure until numerical convergence.

Because we construct $\rho(\mathbf{r})$ by NEGF which takes care of the non-equilibrium statistics, and we calculate the Hartree potential by directly solving the 3D Poisson equation that includes all external fields as electrostatic boundary conditions, our NEGF-DFT formalism is able to solve charge transport problems in addition to the conventional electronic structure calculations.

3 The Au- C_{60} -Au Molecular Tunnel Junction

In this section we report our analysis on the transport properties of an Au- C_{60} -Au molecular tunnel junction calculated using our NEGF-DFT electronic package as discussed above. The device structure is shown in the upper panel of Fig.1. So far a considerable amount of theoretical and experimental effort has been devoted to investigate transport properties of C_{60} and other fullerene molecules[8–10]. The device we present consists of fullerene molecule C_{60} fixed in between two gold electrodes with an Au- C_{60} distance of 3.3a.u. (1a.u. = 0.529Å.). Each electrode consists of repeated unit cells with nine Au atoms in the (100) direction and extended to infinity. The entire calculation is performed on a Pentium-IV processor with 512 Mb of RAM. A typical solution of KS equation for this device requires a few hours of runtime.

The current-voltage (I-V) characteristics is calculated by

$$I = \frac{2e^2}{h} \int T(E, V_b) [f_l(E) - f_r(E)] dE, \quad (5)$$

where $T(E, V_b)$ is the transmission coefficient at energy E and bias voltage V_b . The Fermi distribution functions $f_{l(r)}(E)$ limit the integration to a small energy range eV_b at the Fermi level of the electrodes. Transmission coefficient $T(E, V_b)$ is calculated using Green’s function[11] which we have already obtained during the NEGF-DFT self-consistent iterations,

$$T(E, V_b) = \text{tr} [\mathbf{\Gamma}_l \mathbf{G}_c^R \mathbf{\Gamma}_l \mathbf{G}_c^A]. \quad (6)$$

The function $\mathbf{\Gamma}_\lambda$ describes the line-width resulting from the coupling of the scattering region to the lead λ and is evaluated in terms of corresponding self-energies $\mathbf{\Sigma}_\lambda$ as

$$\mathbf{\Gamma}_\lambda = i[\mathbf{\Sigma}_\lambda - \mathbf{\Sigma}_\lambda^\dagger], \quad (\lambda = l, r). \quad (7)$$

The retarded Green’s function of the scattering region, \mathbf{G}_c^R , in Eq.(6) is given as

$$\mathbf{G}_c(E) = [E\mathbf{I} - \mathbf{H}_c - \mathbf{\Sigma}]^{-1}, \quad (8)$$

where \mathbf{H}_c is the Hamiltonian of the scattering region and $\mathbf{\Sigma} = \mathbf{\Sigma}_l + \mathbf{\Sigma}_r$ is the total self-energy.

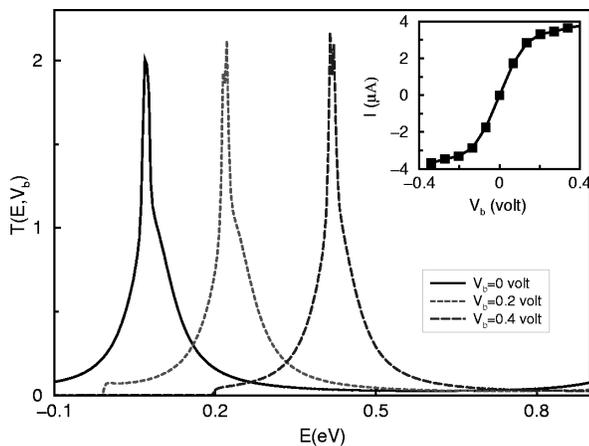


Figure 2. Transmission coefficient $T(E, V_b)$ versus electron energy E for three bias voltages V_b . The sharp transmission peak, which results from a resonance of the fullerene+contacts Hamiltonian, dominates the conductance as well as the current-triggered dynamics. The inset shows the calculated I-V curve from which metallic behavior is evident.

The transmission coefficient obtained from Eq.(6) is presented on Fig.2 as a function of the electron energy E for three different bias voltages at 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 zero bias, this resonance lies just above the Fermi level of the leads (Fermi level is $E_F = 0$ in Fig.2). As a bias voltage is applied, the peak position shifts to higher energies. If the system is absolutely symmetric, we would expect the same voltage drop at the two electrode-molecule junctions. In our system, the atomic structure of C_{60} facing the two electrodes are not the same thereby breaking the left-right symmetry. We therefore observe an asymmetrical voltage drop at the two contacts. Consequently the transmission peak position shifts by about ~ 0.15 eV when V_b is increased by 0.2V, *i.e.*, the voltage drops more on one side than on the other side of the C_{60} . We also calculated the I-V curve from Eq.(5) for this device, shown in the inset of Fig.2. Similar metallic behavior has been reported before[8] for Al contacted C_{60} device. The interesting physics is that despite the large HOMO-LUMO gap of C_{60} (~ 1.8 eV), here we predict a metallic transport characteristics of the Au- C_{60} -Au device. The reason is that when a C_{60} molecule is bonded to metallic leads, there is a strong charge transfer from the leads to the C_{60} cage, thereby partially filling the original empty LUMO. In other words, charge transfer from leads to C_{60} aligns the LUMO to the Fermi energy of the leads, which gives a large conductance and hence a metallic I-V curve.

4 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 $O(N)$: this is because atoms far away from each other do not have overlap and the Hamiltonian matrix is therefore 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 Prof. Jeremy Taylor and Dr. Brian Larade for their contributions throughout the work presented here.

References

1. A. Aviram and M. A. Ratner, *Chem. Phys. Lett.* **29** (1974) 277.
2. M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias and J. D. Joannopoulos, *Rev. Mod. Phys.* **64** (1992) 1045.
3. P. Ordejón, E. Artacho, and J. M. Soler, *Phys. Rev. B* **53** (1996) R104441.
4. J. Taylor, H. Guo and J. Wang, *Phys. Rev. B* **63** (2001) 245407.
5. M. Brandbyge, J.-L. Mozos, P. Ordejón, J. Taylor, and K. Stokbro, *Phys. Rev. B* **65** (2002) 165401.
6. H. Haug and A.-P. Jauho, *Quantum Kinetics in Transport and Optics of Semi-conductors*, Springer-Verlag, New York (1998).
7. G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26** (1982) 4199.
8. J. Taylor, H. Guo, and J. Wang, *Phys. Rev. B* **63** (2001) R121104.
9. H. Park, J. Park, A. K. L. Lim, E. H. Anderson, A. P. Alivisatos, and P. L. McEuen, *Nature* **407** (2000) 57.
10. S. Alavi and T. Seideman, *J. Chem. Phys.* **115** (2001) 1882.
11. S. Datta, *Electronic Transport in Mesoscopic Systems*, Cambridge University Press (1997).