

MODELING OF ELECTRONIC TRANSPORT IN MOLECULAR DEVICES

V. K. Lamba*, D. Engles**, S.S. Malik***, M.Verma*

*HCTM Kaithal, India, Deptt of ECE, lamba_vj@hotmail.com

**GNDU Amritsar, India, Deptt of ECE

***GNDU Amritsar, India, Deptt of Physics

ABSTRACT

In this paper a novel approach for simulating electronic transport in nanoscale structures is introduced. We consider an open quantum system (the electrons of structure) accelerated by an external electromotive force and dissipating energy through inelastic scattering with a heat bath (phonons) acting on the electrons. We use periodic boundary conditions and employ Density Functional Theory to recast the many-particle problem in an effective single-particle mean-field problem. By explicitly treating the dissipation in the electrodes, the behavior of the potential is an outcome of our method, at variance with the scattering approaches based on the Landauer formalism. We study the self-consistent steady-state solution, analyzing the out-of-equilibrium electron distribution, the electrical characteristics, and the behavior of the self-consistent potential and the density of states of the system. We apply the method to the study of electronic transport in several molecular devices, consisting of small organic molecules or atomic wires sandwiched between gold surfaces. Here we also studied the effect of doping in molecular devices.

Keywords: DFT, Scattering, Molecular Electronics, Organic Electronics

I. INTRODUCTION

From vacuum tube to modern CMOS transistor devices which control the flow of electrical current by modulating an electron energy barrier are ubiquitous in electronics. In case of nano-electronics we try to control the electron flow using quantum interference. Here we studied a conductance in a molecule/group of molecules interconnected with conductor atom (called as molecular bridge[1]). The functionality of electronic devices will rely on conducting properties of nanoscopic region composed of no of atoms that can range typical from several thousand to single one. The main idea behind the molecular electronics is the possibility that functional unit can be built out of very stable and well characterized molecules. The simplest molecular devices is the molecule/group of molecules sandwiched between two metals electrodes, and if the arrangement is of type molecular bridge then the contacts/metallic nano contacts help us to learn about the electronic transport at atomic scale. Here we used periodic boundary conditions and employ Density Functional Theory[2] to recast the many-particle problem in an effective single-particle mean-field problem. By explicitly treating the dissipation in the electrodes, the behavior of the potential is

an outcome of our method, at variance with the scattering approaches based on the Landauer formalism.

II. SIMULATION & MODELING [3,5,6,8]

As a general model of a quantum conductor we consider a central region (C) (Shown in table 1) connected to left (L) and right (R) leads. The leads are kept at chemical potentials μ_L and μ_R , respectively. We construct the matrix $H_{ij} = \langle \phi_i | H_s | \phi_j \rangle$ (1) where $H_s = H_{mol} + H_l + H_{tun} + H_c$ is the KS Hamiltonian of the combined L-C-R system in equilibrium, and $\{\phi_i\}$ is a corresponding set of maximally localized, partly occupied WFs [4]. The calculation is performed using DFT approximations. As Hamiltonian of the system is written as the sum of the four terms:

$$H = H_{mol} + H_l + H_{tun} + H_c \quad (2)$$

The first is the π electron molecular Hamiltonian

$$H_{mol} = \sum_{n\sigma} \epsilon_n d_{n\sigma}^\dagger d_{n\sigma} - \sum_{(nm)\sigma} (t_{nm} d_{n\sigma}^\dagger d_{m\sigma} + H.c.) + \sum_{nm} \frac{U_{nm}}{2} Q_n Q_m \quad (3)$$

where $d_{n\sigma}^\dagger$ creates an electron of spin σ in the π -orbital of the n^{th} atom constituting the molecule, ϵ_n is the orbital energies, while $\langle \rangle$ indicates a sum over nearest neighbors. The values we used for tight binding hopping matrix element (t_{nm}) are 2.2 & 2.4 eV for single & aromatic ring respectively.

As each metal lead possesses a continuum of states, there for H_l is defined as[6,8]

$$H_l = \sum_{\alpha} \sum_{k \in \alpha} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} \quad (4)$$

where ϵ_k represents energies of the single particle levels in the leads, and $c_{k\sigma}^\dagger$ is an electron creation operator.

Tunneling Hamiltonian is defined as

$$H_{tun} = \sum_{(n\alpha)} \sum_{k \in \alpha} (V_{nk} c_{k\sigma}^\dagger c_{n\sigma} + H.c.) \quad (5)$$

Since we have taken bridge arrangement so nano contacts induces another term called contact Hamiltonian defined as $H_c = \sum_{\gamma} \sum_{k \in \gamma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma}$, γ possesses a continuum of states at nano contacts.

Using standard methods [13] we evaluate the coupling self-energies, $\Sigma_{\alpha}(w) = h_{c\alpha} g_{\alpha}(w) h_{\alpha c}$ where $g_{\alpha}(w)$ is the GF of the uncoupled lead $\alpha = L, R$. The interactions inside the central region are described by

$$V_{int} = \frac{1}{2} \sum_{ijkl \in C} V_{ij,kl} c_{i\sigma}^\dagger c_{j\sigma}^\dagger c_{l\sigma} c_{k\sigma} \quad (6)$$

with the Coulomb matrix elements[7]

$$V_{ij,kl} = \iint dr dr' \phi_i(r)^* \phi_j(r')^* \phi_k(r) \phi_l(r') / |r - r'| \quad (7)$$

In practice we use an effective interaction which only involves a subset of the Coulomb matrix elements.

The retarded Green's function of isolated molecular system $G_{\text{mol}}(E) = (E - H_{\text{mol}} + i0^+)^{-1}$, Dyson equation is

$$G_M = [G_{\text{mol}}^{-1}(E) - \Sigma(E)]^{-1}. \quad (8)$$

The retarded self-energy of the left-hand (right-hand) side, is calculated from SGF, and the coupling matrices S_{Mi} and F_{Mi} are extracted from the DFT calculation for the extended molecule (molecule with three Au atoms on each side). In our calculation, the lead is considered as a truly three dimensional one with the semi-infinite periodic bulk lattice. In our calculations we did not included lead-lead correlation. We calculate the retarded and lesser Green's functions of the central region from [6-8]

$$G^r = [\omega + i\eta - h_{CC} + (v_{xc})_{CC} - \Delta v_h - \Sigma_{\text{tot}}^r]^{-1} \quad (9)$$

$$G^< = G^r \Sigma_{\text{tot}}^< G^< + 2\eta i f_c G^r G^< \quad (10)$$

where η is a positive infinitesimal and $\Sigma_{\text{tot}} = \Sigma_L + \Sigma_R + \Sigma$ is the sum of the coupling self-energies and the exchange correlation part of the interaction self-energy. As the effective hopping and orbital energies in H_{mol} depends on the equal time correlation functions, which are found to be

$$\langle d_{n\sigma}^\dagger d_{m\sigma} \rangle = \sum_{\alpha\alpha} \frac{\Gamma_\alpha}{2\pi} \int_{-\infty}^{\infty} dE G_{n\sigma,\alpha\sigma}(E) G_{m\sigma,\alpha\sigma}^*(E) f_\alpha(E) \quad (11)$$

Where $f_\alpha(E)$ is the Fermi function for the lead α . The current in lead is given by the multi-terminal current formula

$$I_\alpha = \frac{2e}{h} \sum_\beta \int_{-\infty}^{\infty} dE T_{\beta\alpha}(E) [f_\beta(E) - f_\alpha(E)] \quad (12)$$

where $T_{\beta\alpha}(E) = \Gamma_\beta \Gamma_\alpha |G_{ba}(E)|^2$ is the transmission probability from lead α to lead β and $a(b)$ is the orbital coupled to lead $\alpha(\beta)$.

III RESULTS & CALCULATIONS

Calculations that illustrate the methodology described above had been carried for DTB (Di-thiol Benzene) molecule sandwiched between Au electrodes of 2 X 2 or 3 X 3 (111) type, and with nano contacts, with varying Inter-atomic bulk distance have been taken for the whole system, although one should keep in mind that an analysis of the structural stability of the nano contact model is an important issue when one is interested in the interpretation of simulated data. We have calculated the average on site energies of the 5d6s6p orbital's for all the atoms at nano-contacts at zero and 3.5eV bias. The magnitude reflects the local self consistent electrostatic potentials on each atom. One can see how an electrostatic potential drops between electrodes, without having imposed an external field just an electrochemical potential difference. The major drops as shown in figure 2 occur at bridge. In case of zero bias the results are symmetric with respect to the geometric center of symmetry as expected. Instead similar symmetry is absent for 3.5 eV bias. The transmission T for zero and 3.5eV is shown in figure 3 & 4, for sample 3. T oscillates around the Fermi energy with an upper limit value of one for both cases. This limit is well documented theoretically for Au Contacts since there is only one s like channel around the Fermi energy for Au chains. The oscillations are due to scattering at the electrode –molecule or molecule-bridge-molecule contacts. This explains why conductance histograms exhibit the lowest peak slightly below G. It is

worth nothing that although the total current calculated by integrating $T(E, V = 0)$ does not differ much from that obtained with the full non-equilibrium approach, the differential conductance is significantly different. As shown in table 3 & 4.

IV REFERENCES

1. S. Selberherr, Analysis and Simulation of Semiconductor Devices, Vienna and New York: Springer, 1984
2. C. Gardner, "The classical and quantum hydrodynamic models," in: Proc. Intern. Workshop Computational Electronics, Univ. of Leeds (1993), pp. 25–36
3. S. Ramaswamy and T.-W. Tang, "Comparison of semiconductor transport models using a Monte Carlo consistency check," IEEE Trans. Electron Dev. **41**, 76 (1994).
4. Abramo, L. Baudri, R. Brunetti, et al., "A comparison of numerical solutions of the Boltzmann transport equation for high-energy electron transport silicon," IEEE Trans. Electron Dev. **41**, 1646 (1994).
5. Troisi and M. A. Ratner: Molecular Nanoelectronics, eds. M. A. Reed and T. Lee (American Scientific Publishers, Los Angeles, 2003) p. 1, and references therein
6. S. Datta: Electronic Transport in Mesoscopic Systems (Cambridge University Press, Cambridge, 1995).
7. M. J. Frisch et al.: Gaussian 98 (Gaussian, Inc., Pittsburg, PA, 1998) revision A.11.1.
8. Lamba, V.K., Engles, D., Malik, S.S., Gupta, A., "Quantum Transport in Nano MOSFETs", (Molecular Simulation, Selected **Id no .GMOS 351389**)(2008).

Table 1: No of molecules in central region

Sample no	Distance b/w Electrodes	No of Molecules	Bridges
1	9.73	1	0
2	18.02	2	0
3	21.87	2	1
4	26.9	3	0
5	31.87	3	2
6	40.5	3	1

Table 2: Conductance and current calculated for samples

Sample no	Current (μA)	Conductance (μS)
1	66.6974	2.1274
2	36.6974	1.0567
3	23.4790	0.9735
4	16.3702	0.6936
5	5.07199	0.1369
6	8.9046	0.2485

Table 3: Peak value of transmission at energy.

Sample no	Energy, eV	Transmission
1	0.7	2.25
2	1.3	1.78
3	1.3	1.79
4	0.6	1.17
5	0.6	1.6
6	0.6	1.7

Table 4: DOS at different energy.

S. No.	Energy, eV	DOS
1	-0.7	1820
2	-0.5	1820
3	-0.6	830
4	-0.4	5900
5	-0.6	58000
6	-0.6	58000

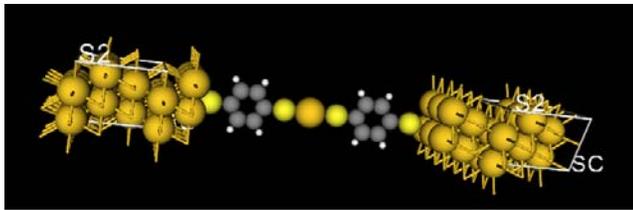


Figure 1: sample no 3

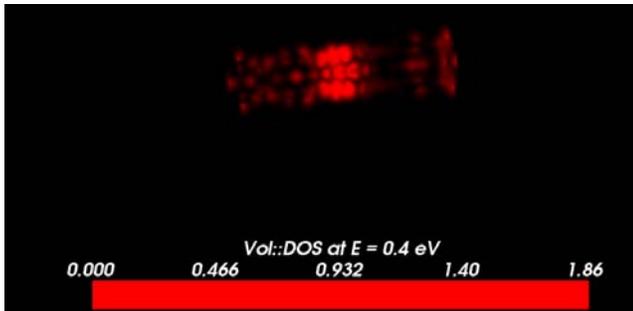


Figure 2: Density of state for sample no 3 at E = 0.4eV.

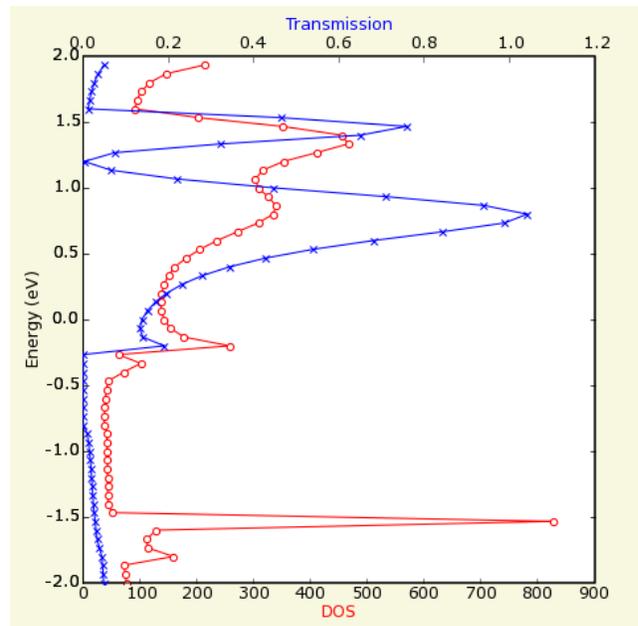


Figure 3: Transmission T for zero bias

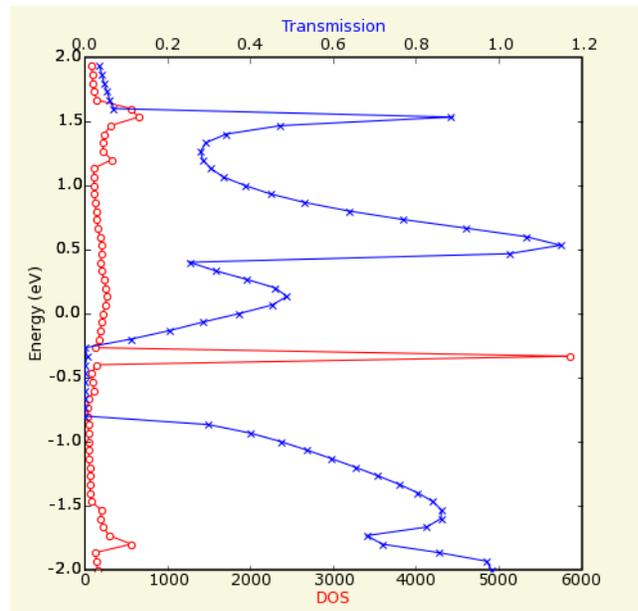


Figure 4: Transmission T for 3.5eV