

A Green's Function approach to the study of the conduction properties of electron transport through CNT/*trans*-PA/CNT system

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Abstract: - Using a tight-binding model and methods based on Green's function theory and Löwdin's partitioning technique, we numerically investigate the effects of the coupling strength CNT/molecule, the length of the molecule and the properties of metallic single-walled carbon nanotube(CNT) on the electronic transmission through a CNT/molecule/CNT system, as a full carbon transistor model. We rely on *Landauer* formalism as the basis for studying the conductance properties of this system. The dependence of the conductance on the above basic parameters of the system, are investigated. Our calculations show that the conductance is sensitive to the CNT/molecule coupling and exponentially decreases with the increase of the length of the molecule, and the parameters of CNT also play an important role in overall conductance of the system.

Key Words: - molecular wire, carbon nanotube, electronic transmission, *Landauer* formalism, Green's function

1 Introduction

The incessant development of single molecule techniques is forcing a paradigm shift in the many neighboring branches of nano-sciences. This process does not exclude the modeling and design of electronic devices. Novel fabrication methods that create metallic contacts to a small number of conjugated organic molecules allow the study of the basic transport mechanism of these systems and will provide direction for the potential development of molecular scale electronic systems[1].

Important applications of molecular wires are also suggested in molecular electronics,[2-3] where long conjugated molecules are used to electrically connect two electronic components.

In a typical experimental setup however, a molecular bridge connects two electrodes acting as electron donor and acceptor reservoirs. Despite this conceptual separation of molecular device into its constituents, what is measured is the conductance across the whole system. This implies that besides the intrinsic molecular ability to convey charge, the coupling of the molecular bridge to the electrodes is significant. The molecular orbitals of the molecule when it couples to the electrodes provide

favorable pathways for electrons. Small conjugated polymers, as the molecular bridges, can be easily processed to afford functional electronics, such as field effect transistors (FETs)[4-6].

Among these, *trans*-PA is the most studied molecule. This is due to the fact that while, being the simplest π -conjugated polymers, *trans*-PA has considerable potential applications as an alternative conductor. The possibility of the semiconductor-to-metal transition and the capability of becoming a very conductive material have been the reason for the experimental and theoretical investigations on the physical properties of *trans*-PA in comparison with the other conducting polymers[7]. Several studies on the structural, electronic and conduction properties of *trans*-PA have been published [8-12], in which the molecule is usually bridge between to simple metallic leads. However, other bridge systems with more complex metallic leads could also be of interest and the factors that influence the conductance of such molecular wires needs to be studied. This has been our motive for the work presented in this paper. Here we numerically investigate the effects of some of the basic features of the CNT/*trans*-PA/CNT structure (figure 1) on

the electronic transport through this system.

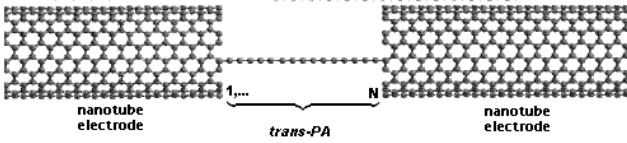


Fig.1 a schematic representation of the CNT/trans-PA/CNT structure as described in the text.

It is shown that SWNTs can be used as quasi one-dimensional (1D) electrodes to construct organic FETs[4].

The significantly improved switching characteristics of the short organic FETs with metallic SWNT electrodes over those with metal electrodes are attributed to the excellent electrostatics attainable with the nanotube electrode geometry. It has been shown theoretically that for transistors involving Schottky barriers(SB) at the contacts (which is the case for organic devices), sharp quasi-1D geometry for the source(S) and drain(D) electrodes can facilitate the optimum gate control[13-16].

The procedures we have numerically applied in this work is based on Green's function theory, density functional algorithms and *Landauer* formalism.

The organization of the article is as follows. In Sec. 2, we review the scattering formulation of electronic conduction across a molecular wire. In Sec. 3, the results and discussion are presented. Some concluding remarks and a summary are given in Sec. 4.

2 Methodology

The most commonly used computational schemes for calculating the (coherent) conductance g are the *Landauer* theory [17] and the Green's function formalism [18-28].

The conductance g at zero temperature is simply proportional to the total transmittance,

$T(E_F)$, for injected electrons at the Fermi energy E_F ,

$$g = g_0 T(E_F), \quad g_0 = \frac{2e^2}{h} \quad (1)$$

the factor two accounts for spin degeneracy. The transmission function can be calculated from the knowledge of the molecular energy levels, the nature and the geometry of the contacts.

Making use of the Fisher-Lee relation [29], the conductance can be expressed as

$$g = \frac{2}{\pi} \Delta^L(E) \Delta^R(E) |G_{1N}^+(E)|^2, \quad (2)$$

(in units of e^2/h), where $G_{1N}^+(E)$ is the molecular

electronic Green's function element between the first and last site state of the molecule containing all the molecular information, and Δ^k , $k = L$ and R , are the CNT spectral densities which minus the imaginary part of the CNT self-energies (per spin).

To simplify the analysis, we have assumed that the electrodes are identical, so $\Delta^L = \Delta^R = \Delta$.

We note that Eq. (2) is only valid if through-space coupling is negligible compared with through-bond. We expect this approximation to be a good one, provided the wire is long enough.

The spectral density of the left (right) lead is related to the semi-infinite lead Green function matrix $g^{L(R)}$.

$$\Sigma^\alpha = \Lambda^\alpha - i \Delta^\alpha = \sum_{m_\alpha, m'_\alpha} \Gamma_{m_\alpha} \Gamma_{m'_\alpha}^* g_{m_\alpha, m'_\alpha}^\alpha \quad \alpha = L(R) \quad (3)$$

$m_{L(R)}$ and $m'_{L(R)}$ run over interfacial end-atoms of the CNTs. Γ is the coupling strength molecule/CNT. Owing to the causality of self-energy, its real part Λ can be entirely derived from the knowledge of Δ via a Hilbert transform.

In general, there are M atomic positions, defining the perimeter of the tube ends that the leads could join to the molecule. For an armchair (ℓ, ℓ) SWNT topology is imposed the number of carbon sites at the interface is $M = 2\ell$. It is the same approach as Ref. [25], the single-particle Green function can be written in the following,

$$g_{n_y, n'_y}(E) = \frac{1}{2\ell} \sum_{j=1}^{2\ell} \varphi_j(n_y) \tilde{G}^j(E) \varphi_j^*(n'_y), \quad (4)$$

where $\varphi_j(n_y) = \exp(ik_y^j n_y a)$, with $k_y^j a = \pi j / \ell$,

$1 \leq j \leq 2\ell$ and a is the lattice space. We assume the x direction to be parallel to the tube (and to the transport direction) and y to be the finite transverse coordinate.

$\tilde{G}(E)$ is the surface Green function given by[25],

$$\tilde{G}^j(E) = \frac{1}{2\gamma} \frac{E - \varepsilon}{2\gamma} \left[1 + i \frac{\sin\left(\frac{q_\beta^j a}{2}\right)}{\sqrt{\left(\frac{E - \varepsilon}{2\gamma}\right)^2 - \sin^2\left(\frac{\pi j}{\ell}\right)}} \right] \quad (5)$$

$\beta^* = \text{sign}(E - \varepsilon)$

and

$$\cos\left(\frac{q_\beta^j a}{2}\right) = \frac{-1}{2} \cos\left(\frac{\pi j}{\ell}\right) - \frac{\beta}{2} \sqrt{\left(\frac{E - \varepsilon}{2\gamma}\right)^2 - \sin^2\left(\frac{\pi j}{\ell}\right)} \quad (6)$$

in which ε and γ are the lattice on-site energy and the hopping term between nearest-neighbors,

respectively.

The molecular electronic Green's function is introduced as self-energy corrections into the bare 'molecule' Green function,

$$G^{-1} = G^{M-1} + \Sigma^L + \Sigma^R, \quad (7)$$

where G^{M-1} and $\Sigma^{L(R)}$ are the bare 'molecule' Green's function and the left(right) CNT self-energy. The bare 'molecule' Green's function operator is given by,

$$G^M = (1z - H_{SSH})^{-1} \quad (8)$$

in which H_{SSH} represents the well-known SSH(Su-Schrieffer-Heeger) Hamiltonian of the bare molecule, 1 stands for identity matrix and z is the complex variable with real part equal to E .

The molecule is *trans*-PA that one of the well-known frameworks for studying of electronic and structural properties of *trans*-PA is the Su-Schrieffer-Heeger (SSH) model [30].

It has already been shown that the main contribution to the electronic properties comes from the π -electrons [31-33], such that one may only consider the electronic part of well-known SSH Hamiltonian.

The electronic part of H_{SSH} is given as follows [7],

$$H_{SSH} = -\sum_n t_{n+1,n} (c_{n+1}^\dagger c_n + c_n^\dagger c_{n+1}), \quad (9)$$

in which $t_{n+1,n}$ is the nearest-neighbor transfer integral and is given as,

$$t_{n+1,n} = t_0 + \alpha(u_n - u_{n+1}), \quad (10)$$

where t_0 is the hopping integral of an undimerized chain, α the electron-phonon coupling constant and u_n the displacement of the n th carbon atom from its equilibrium position. The reference energy is chosen such that the carbon atom on-site energy is zero. For perfectly dimerized of *trans*-PA, u_n and bandgap are given as $u_n = (-1)^n u_0$ and $2\Delta_0 = 8\alpha u_0$, respectively. Throughout this study for $2\Delta_0 = 1.4 eV$, we shall use the parameters of Ref. [30], so $\alpha = 4.1 eV/\text{\AA}$ and $t_0 = 2.5 eV$. These correspond to an equilibrium dimerization amplitude $u_0 \approx 0.04 \text{\AA}$.

Using partitioning techniques [24], $G_{1N}^+(0)$ can be rewritten as the $[1,N]$ Green's function element associated with the effective molecule Hamiltonian,

3 Results and discussion

Considering the remarks in Sec. (2) and calculating the eigenvalues, one may write the following

expression for the electronic density of states (DOS) of the former structures [24],

$$\rho(E) = \frac{-1}{\pi} \text{Im}(G_{1N}^+) \quad (11)$$

Setting the coupling strength CNT/molecule, $\Gamma = 0.3 eV$ and hopping integrals between π -electrons in carbon nanotubes, $t_{CNT} = 3 eV$. The best reported values for t_{CNT} in agreement with experiments are 2.9eV and 3eV [34,35,36]. Figures 2(d)-(f) illustrate the electronic DOS for the CNT/*trans*-PA/CNT structures for the *trans*-PA molecules with 22, 32 and 42 atoms, respectively. Figures 2(a)-(c) show the corresponding conductance in units of G_0 with the same parameters as in figure 2. From figure 2 we see that when the length of the molecule increases, the conductance decreases. We find that the decrease of the conductance follows an exponential law as shown by Magoga and Joachim [37].

To illustrate the exponential behavior, we have shown in figure 3 the variations of the conductance as a function of the length of the molecules, with 22, 32, 42, 52 and 62 atoms. In this figure the same parameters in figure 2 have been used for the calculations of the conductance at the given energy, i.e. the Fermi energy. Another feature of the conductance spectra in figure 2 is the presence of resonance peaks which arise when the energy E coincides with an eigenenergy of the *trans*-PA molecule. The results show that the density of resonances scales with the molecule size. We have also repeated the calculations for different values of the coupling strength CNT/molecule, Γ . Increasing Γ leads to the significant increase of the conductance (figures 4, 5) and our results suggest that for the large coupling, i.e. $\Gamma \geq 2 eV$, the interaction between the electrodes and *trans*-PA molecule are so strong that the molecule loses its identity such that the conductance through the molecule can no longer be considered as a tunneling process. Another setup calculations were performed CNTs with different chiralities which are shown in figure 6. The results show that increasing CNT's chirality leads to the considerable increase of the conductance.

4 References:

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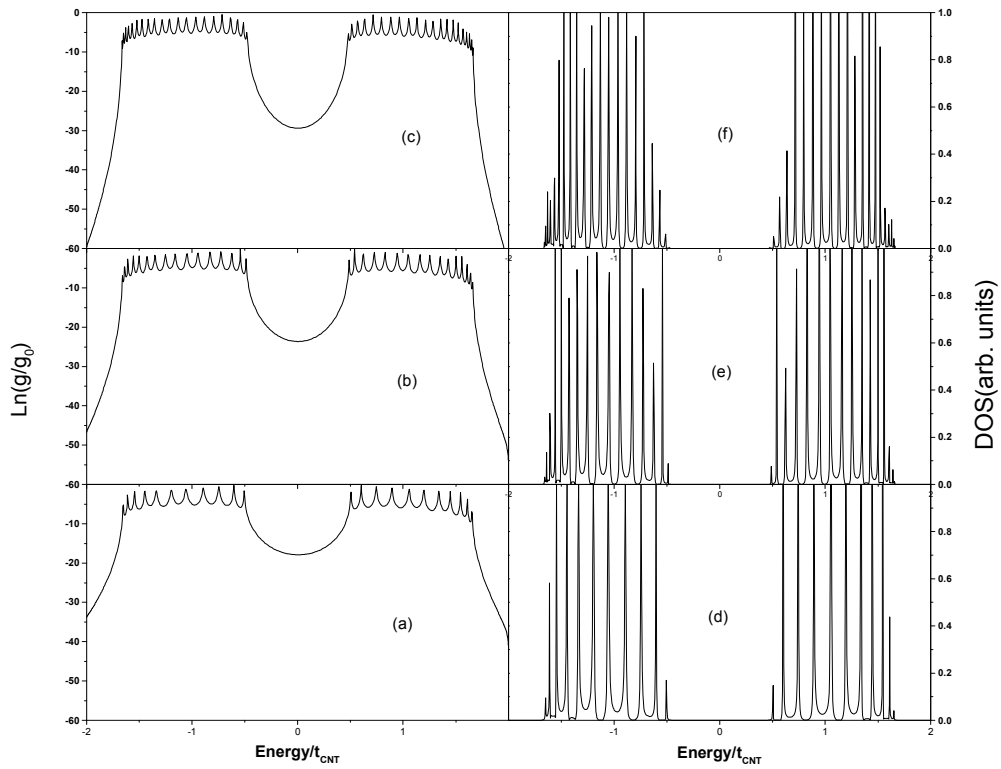


Fig. 2 (a)-(c) show logarithm of conductance (in units of g_0) vs. the dimensionless parameter $Energy/t_{CNT}$ for the CNT/*trans*-PA/CNT system with $t_{CNT} = 3 eV$ and $\Gamma = 0.3 eV$ for the values of the molecular length 22, 32 and 42 atoms and (5,5) armchair CNT, respectively. Figures (d)-(f) show the plot of the electronic DOS vs. the dimensionless parameter $Energy/t_{CNT}$ corresponding to the figures (a)-(c), respectively.

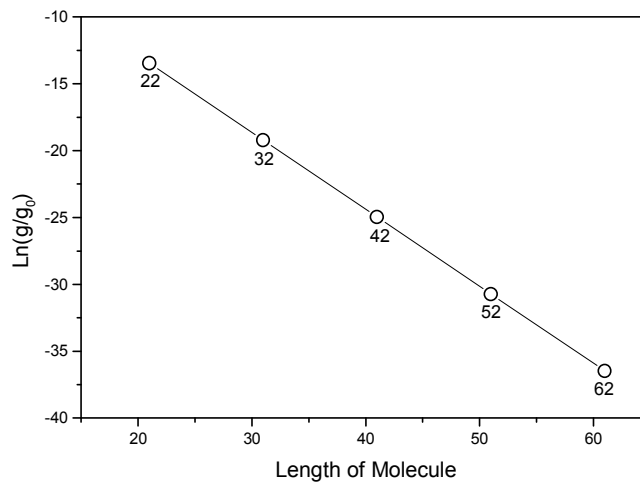


Fig.3 The logarithm of conductance (in units of g_0) as a function of length of the molecule *trans*-PA for $\Gamma = 0.3 eV$, $t_{CNT} = 3 eV$ and the molecules with 22, 32, 42, 52 and 62 atoms with (5,5) armchair CNT.

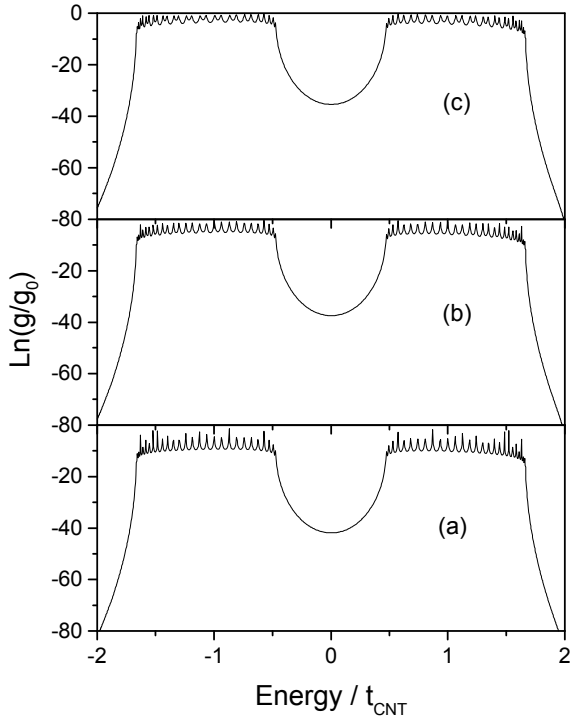


Fig.4 (a)-(c) plots show The logarithm of conductance (in units of g_0) vs. the dimensionless parameter $\text{Energy}/t_{\text{CNT}}$ for the CNT/*trans*-PA/CNT system with $t_{\text{CNT}} = 3\text{eV}$, $\Gamma = 0.1, 0.3, 0.5\text{eV}$ for the value of the molecular length 56 atoms and (5,5) armchair CNT, respectively.

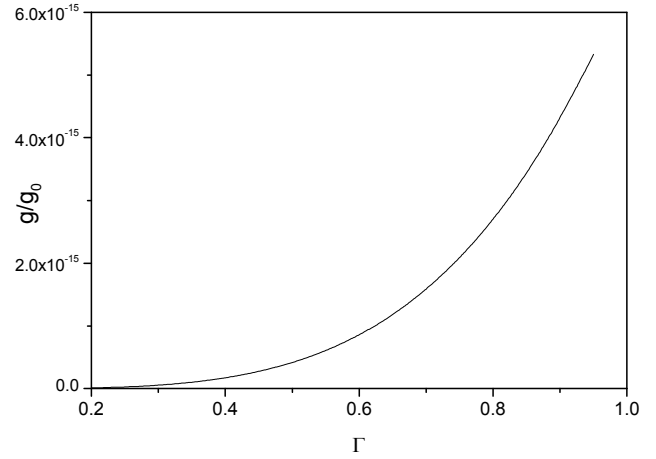


Fig. 5 The logarithm of conductance (in units of g_0) vs. the coupling strength CNT/molecule, Γ for the CNT/*trans*-PA/CNT system with $t_{\text{CNT}} = 3\text{eV}$, and the value of the molecular length 56 atoms and (5,5) armchair CNT.

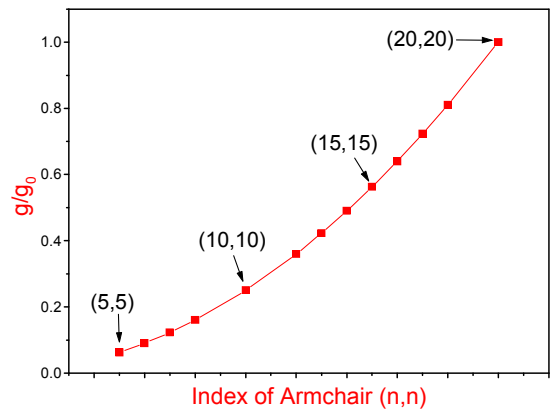


Fig. 6 conductance (in units of g_0) vs. index of armchair CNTs (n,n) for the CNT/*trans*-PA/CNT system with $t_{\text{CNT}} = 3\text{eV}$, $\Gamma = 0.3\text{eV}$ and the value of the molecular length 56 atoms.