Electron transport in carbon nanotube-metal systems: contact effects

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Carbon nanotubes (CNT) have a very large application potential in the rapid developing field of molecular electronics. Infinite single-wall metallic CNTs have theoretically a conductance of $4e^2/h$ because of the two electronic bands crossing the Fermi level. For finite size CNTs experiments have shown that other values are also possible, indicating a very strong influence of the contacts. We study electron transport in single- and double-wall CNTs contacted to metallic electrodes within the Landauer formalism combined with Green function techniques. We show that the symmetry of the contact region may lead to blocking of a transport channel. In the case of double-wall CNTs with both inner and outer shells being metallic, non-diagonal self energy contributions from the electrodes may induce channel mixing, precluding a simple addition of the individual shell conductances.

I. INTRODUCTION

Carbon nanotubes belong to one of the most promising candidates in the era of modern nanoelectronics. They can be generated by wrapping a graphene sheet along different directions as given by the so called chiral vector[1]. Interestingly, depending on the chiral vector, the tubes show markedly different electronic properties ranging from metallic to semiconducting. A considerable amount of theoretical and experimental research has been done to explore their varied interesting properties, which range from very hard inert materials through good conductors to storage devices[2]. Concerning the electronic transport properties of metallic single-wall carbon nanotubes (SWCNT) experiments[2] have nicely demonstrated ballistic transport and conductance quantization with conductance values equal to $2\times G_0$, $G_0 = 2e^2/h$ being the conductance quantum and the factor 2 in the first expression arising from two spin degenerated bands at the Fermi level. Similar quantization effects have been recently observed in multi-wall nanotubes (MWCNTs)[3,4]. However, in contrast to the theoretical expected values conductance steps as low as $0.5G_0$ or $1\times G_0$ were found[3]. Even under the usual assumption that only the outermost shell is the one contributing to transport, such small conductance values suggest that transport channels may be partially or completely closed. Blocking of conductance channels in MWCNTs has been recently addressed in other theoretical works[5]. We will investigate in this paper conductance quantization in finite size CNTs contacted with metallic electrodes. We will show an example of channel blocking and demonstrate that the total conductance of muti-wall CNTs cannot be simply obtained by just adding the individual shell conductances.

II. THEORETICAL MODEL

We investigate electronic transport in a simple model system consisting of carbon nanotubes which are attached to semi-infinite electrodes having an fcc(111) geometry. A typical configuration is shown in Figure 1.
To describe the electronic structure of both subsystems we use a single-orbital nearest-neighbours tight-binding approach. It includes the π-orbitals of the carbon atoms on the tube and s-like orbitals in the electrodes. The metal-CNT coupling terms are set constant for all neighbours of a given carbon atom. The Hamiltonian is

$$\begin{aligned} H &= H_{\mathcal{M}} + H_{\text{leads}} + V_{\text{leads},\mathcal{M}} \\ H_{\mathcal{M}} &= -t_{pp}\sum_{l,j} c_l^\dagger c_j - \beta \sum_{l,\,j} \cos\theta_{lj}\, e^{\frac{a-d_{lj}}{\delta}} c_j^\dagger c_l \\ H_{\text{leads}} &= \sum_k \sum_{\alpha\in \text{L,R}} \epsilon_k^\alpha d_{k\alpha}^\dagger d_{k\alpha} \\ V_{\text{leads},\mathcal{M}} &= \sum_{i,k}\sum_{\alpha\in\text{L,R}} V_{i,\alpha} c_i^\dagger d_{k\alpha} + \text{H.c.} \end{aligned}$$

$H_{\mathcal{M}}$ is the CNT Hamiltonian. Its first term describes the intra-shell interaction with a hopping integral t_{pp} which is set at the constant value of 2.66 eV. The second summand is the inter-shell interaction in the case of MWCNTs

($\beta = t_{pp}/k, k > 1$). $\delta = 0.45\mathring{A}$ is a normalizing factor , a is the difference between the shell radii and θ_{ij} is the angle between the two p_z orbitals on different shells. Finally, $H_{\rm leads}$ is the Hamiltonian of the electrodes and $V_{\rm leads,\mathcal{M}}$ is the mutual interaction.
The linear conductance $G(E)$ can be related to the electronic transmission probability $T(E)$ according to the Landauer formula (at zero temperature): $G = G_0 T(E_{\rm F})$. $T(E)$ can be calculated using Green function techniques[6] via

$$T = {\rm Tr}_{\mathcal{M}}[G^{\dagger}_{\mathcal{M}} \Gamma_R G_{\mathcal{M}} \Gamma_L]$$

$G_{\mathcal{M}}$ is the Green function of the scattering region (in our case the CNT plus two surface layers) which can be calculated by means of the Dyson equation

$$[E 1_{\mathcal{M}} - H_{\mathcal{M}} - \Sigma_L - \Sigma_R] G_{\mathcal{M}} = 1$$

The self-energies $\Sigma_\alpha = V^{\dagger}_\alpha g^\alpha V_\alpha, \alpha = {\rm L, R}$ contain information on the electronic structure of the leads (via the surface Green function g^α) as well as on the electrode-scattering region coupling (via V_α). Finally the spectral functions Γ_α are related to the self-energies by ${\rm i}\Gamma_\alpha = (\Sigma_\alpha - \Sigma^{\dagger}_\alpha)$. We do not consider charge transfer effects between the tubes and the metallic electrodes.The use of a single-orbital picture to describe the electrodes allows to write an analytic expression for the electrodes surface Green function in **k**-space (assuming L=R)[7].

$$\begin{aligned} g(\mathbf{k}, E) &= \frac{E - \epsilon(\mathbf{k}) \pm \sqrt{(E - \epsilon(\mathbf{k}))^2 - 4|V_{01}(\mathbf{k})|^2}}{2|V_{01}(\mathbf{k})|^2} \\ \epsilon(\mathbf{k}) &= 2t_0(\cos k_x a + 2\cos\frac{k_x a}{2}\cos\frac{\sqrt{3}k_y a}{2}) \\ V_{01}(\mathbf{k}) &= -t_0(2\cos(\frac{k_x a}{2})e^{\frac{ik_y a}{2\sqrt{3}}} + e^{-\frac{ik_y a}{\sqrt{3}}}) \end{aligned}$$

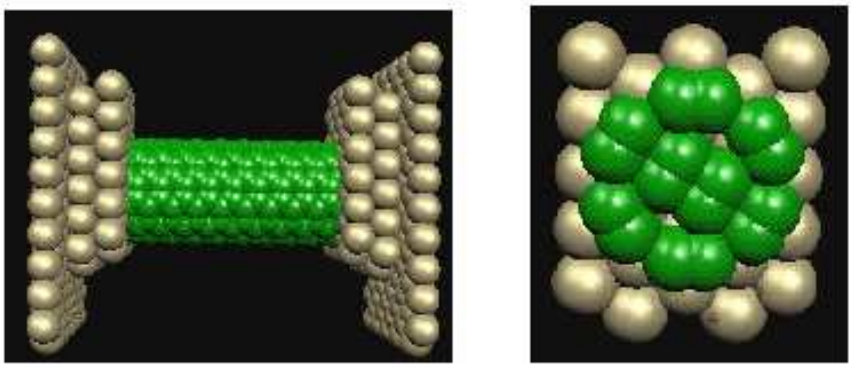

FIG. 1: View of a (2,2)@(6,6) double walled carbon nanotube sandwiched between two fcc(111) leads (upper panel) and details of the contact region (lower panel). The first two layers of the electrodes belong to the scattering region while the third layer extends to infinity and is part of the contact.

A. Electronic Transport in single- and double-wall nanotubes

We first consider the diameter dependence of the conductance for SWCNTs. In Fig. 2 we show the transmission as a function of the energy for (2,2) and (6,6) finite size tubes (10 unit cells). As a reference we also plot the transmission of an infinite tube. For the latter clear quantization steps are obtained and the conductance around the Fermi level is $2\times G_0$. The finite size tubes show however a more irregular, spiky behaviour which can be related to finite size effects and to the lifting of some degeneracies as a result of the coupling to the electrodes. More importantly, while the (2,2) CNT shows conductance oscillations peaking at $2\times G_0$, the (6,6) tube reaches only on average one quantum of conductance, i.e. a transport channel is apparently closed.
We can roughly understand what happens by representing the electronic selfenergy into the eigenstate basis $|\Phi_\sigma\rangle$ of an isolated CNT, with $|\Phi_\sigma\rangle = \sum_{n\in CNT} c_{n,\sigma} |p_{z,n}\rangle$. After some manipulations [8] and assuming a constant coupling of each carbon atom to its nearest neighbours metal atoms [9,10], we arrive at the following expression:

$$\Sigma_{\sigma\sigma'}(E) = |V|^2 \sum_{\mathbf{k}_{||}} g_{0,\mathbf{k}_{||}}(E)\Lambda^{\dagger}_{\sigma}(\mathbf{k}_{||})\Lambda_{\sigma'}(\mathbf{k}_{||}) \quad (1)$$

$$\Lambda_{\sigma}(\mathbf{k}_{||}) = \sum \sum c_{n,\sigma} e^{i\mathbf{k}_{||}\mathbf{m}_{||}}$$

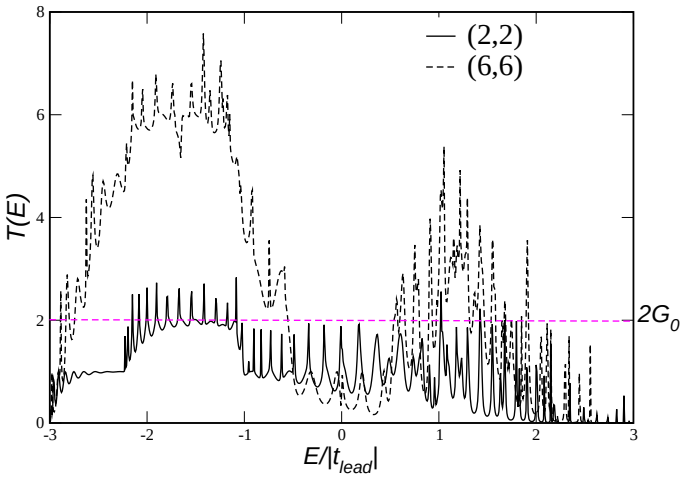

FIG. 2: Electronic transmission of (2,2) and (6,6) SWCNTs (10 unit cells). The strong oscillations are related to finite size effects. For (2,2) two transport channels at the Fermi level are open, while for the (6,6) CNT only one channel does contribute.

Notice that the index n runs now over the CNT atomic slice in *direct* contact with the metal surface and the index $\mathbf{m}_{||}[n]$ denotes the nearest neighbours on the electrode surface of a given carbon atom n. The function $\Lambda_{\sigma}(\mathbf{k}_{||})$ contains information on the symmetries of the CNT wave functions via $c_{n,\sigma}$, and on the electrode surface topology, via the $e^{i\mathbf{k}_{||}\mathbf{m}_{||}}$ factor. We only need to look at the behaviour of $\Lambda_{\sigma}(\mathbf{k}_{||})$ for $\sigma = \pi, \pi^*$, since these are the two eigenstates crossing the Fermi point in metallic CNTs. Remembering that the expansion coefficients $c_{n,\sigma}$ of the π and π^* orbitals along the nanotube circumference comprising $2m$ atoms are proportional to $(+1)^n$ and $(-1)^n$, $\quad n = 1, \cdots, 2m$, respectively, the sums in $\Lambda_{\sigma}(\mathbf{k}_{||})$ can be performed. As a result we find that $\Lambda_{\pi^*}(\mathbf{k}_{||})$ identically vanishes for the (6,6) CNT while it is nonzero for the (2,2) tube. Hence the antibonding π^* orbital does not couple to the electrodes for the (6,6) CNT and it thus gives no contribution to the conductance.

The next issue we have considered is if the conductance of a DWCNT consisting of two armchair SWCNTs can be simply obtained by adding the corresponding conductances of the individual shells. If this holds then, accordning to our previous result, the conductance of a finite size (2,2)@(6,6) DWCNT should yield $3\times G_0$. Two factors can however modify this simple picture. One is the inter-shell coupling, the other is the CNT-electrode interface. We have just seen, that the latter can even induce channel blocking.

Figure 3 shows the transmission function for different values of the inter-shell coupling parameter β. The main influence of β is to introduce mixing of the transport channels which is rather strong at energies far away from the Fermi level E_{F} and leads for some energies to a drastic reduction of the conductance when comparing with infinite tubes. The effect near the Fermi level is however less strong. Thus, for $\beta \neq 0$ the conductances can not simply be added since inter-shell interference effects must be considered. More interesting however is the behaviour for *zero* inter-shell interaction. Even in this case the total conductance near the Fermi level is not simply $3\times G_0$ although it is larger than in the former case ($\beta \neq 0$). The imperfect addition of conductances is now related to interference effects caused by non-diagonal contributions of the electrodes self-energies, $\Sigma_{\sigma\neq\sigma'}(E)$. As a result the transport channels are mixed in a similar way as for non-zero inter-shell coupling. Although there may be some special cases where conductances can be added, we can conclude that in general quantum interference effects induced by finite size effects (the existence of the metal-CNT interface) or by the coupling between the nanotube shells will preclude this simple view.

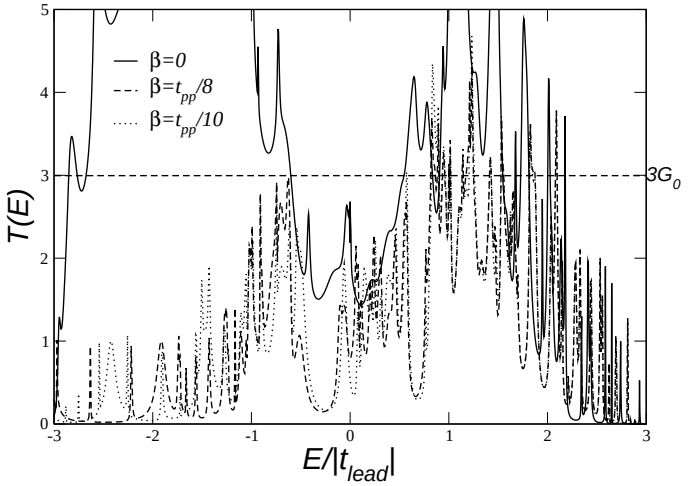

FIG. 3: Energy dependent transmission of a (2,2)@(6,6) DWCNT (10 unit cells) for different values of the inter-shell coupling β. The intra-shell hopping $t_{pp} = 2.66eV$.

III. CONCLUSIONS

In this paper we have investigated quantum transport in finite size armchair single- and double-wall carbon nanotubes contacted by metallic electrodes. We have shown that symmetries of the CNT-electrode coupling, hidden in the electronic self-energies may lead to suppression of transport channels, thus reducing the conductance around the Fermi level when comparing with the theoretical ideal case of infinite nanotubes. Moreover, for DWCNTs the simple approach of adding the single-shell conductances has been shown to be incorrect, even in the case of no inter-shell interactions. This can be traced back to interference effects induced by non-diagonal components of the self-energy. These results accentuate the important role played by the interface in determining electronic transport on nanoscale systems.

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[8] , Using $|\Phi_\sigma\rangle$ and the electrode wave functions $|\mathbf{k}\rangle = \sum_{\ell_{||}} e^{i\mathbf{k}_{||}\ell_{||}} f(\mathbf{k}_\perp) \left|\chi_{\ell_{||}}\right\rangle$ we get: $\Sigma_{\sigma\sigma'}(E) = \sum_{\mathbf{k}} \langle\Phi_\sigma|V^\dagger|\mathbf{k}\rangle\, g(\mathbf{k},E)\, \langle\mathbf{k}|V|\Phi_{\sigma'}\rangle$, which can be put in the form of Eq. (1) by defining $G_{\mathbf{k}_{||}}(E) = \sum_{\mathbf{k}_\perp} |f(\mathbf{k}_\perp)|^2 g(\mathbf{k}_{||},\mathbf{k}_\perp,E)$. $f(\mathbf{k}_\perp)$ is a function of the wave vector perpendicular to the metal surface, only, and the 2d vector $\ell_{||}$ runs over the surface layer .

[9] , This approximation can be justified because of the almost perfect fitting of the (2,2) and (6,6) CNTs lattice constants to the interatomic distances at the electrode surface [10]. Thus, each C atom interacts with just 3 atoms on the metal surface .

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