

Electronic transport in biphenyl single-molecule junctions with carbon nanotubes electrodes: The role of molecular conformation and chirality

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(Received 8 July 2010; published 2 August 2010)

We investigate, by means of *ab initio* calculations, electronic transport in molecular junctions composed of a biphenyl molecule attached to metallic carbon nanotubes. We find that the conductance is proportional to $\cos^2 \theta$, with θ the angle between phenyl rings, when the Fermi level of the contacts lies within the frontier molecular orbitals energy gap. This result, which agrees with experiments in biphenyl junctions with nonorganic contacts, suggests that the $\cos^2 \theta$ law has a more general applicability, irrespective of the nature of the electrodes. We calculate the geometrical degree of chirality of the junction, which only depends on the atomic positions, and demonstrate that it is not only proportional to $\cos^2 \theta$ but also is strongly correlated with the current through the system. These results indicate that molecular conformation plays the preponderant role in determining transport properties of biphenyl-carbon nanotubes molecular junctions.

DOI: [10.1103/PhysRevB.82.085402](https://doi.org/10.1103/PhysRevB.82.085402)

PACS number(s): 73.63.-b, 36.20.Ey, 11.30.Rd, 85.65.+h

I. INTRODUCTION

Since the pioneer work by Aviram and Ratner, understanding electronic transport properties of single molecules attached to electrodes has been a major challenge to the implementation of molecular scale electronics.^{1,2} A wealth of theoretical and experimental work over the past decade has revealed that this constitutes a complex task, as the transport characteristics in single-molecule junctions depend on many factors: the intrinsic molecular properties, such as their geometrical conformation and length, the nature and details of the contacts, environment (e.g., temperature, stress, and UHV), the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the relative position of this gap to the contact's Fermi level. The precise control of all these factors is usually difficult so that the majority of experiments in single-molecule transport recur to a statistical treatment.³⁻⁹ One important strategy to extract information about single-molecule junctions from ensemble measurements is that of "molecular families" in which a systematic variation in a single element of the junction (e.g., molecular length and conformation, electronic structure, anchoring group) is carefully performed and analyzed (see Ref. 10 and references therein).

Despite this sensitivity to several parameters, it seems remarkable that a general behavior in the transport properties of a family of molecules exists. Indeed, experiments reveal that molecular conformation can affect electronic transport.¹¹ Another important example is the observation that the conductance of biphenyl-derived molecules scales linearly with $\cos^2 \theta$, where θ the tilt angle between the two phenyl rings.⁷ This law follows from an effective π -orbital coupling model in which the overlap between the two π orbitals, which is expected to be optimal when the biphenyl is planar ($\theta=0$),

leading to the maximal conductance.¹²⁻¹⁴ In contrast, when the rings are rotated relative to each other, which was achieved by chemically modifying the side groups, the overlap between the π orbitals decreases, resulting in the $\cos^2 \theta$ law. This result, which is remarkable since it ultimately suggests that molecular geometry actually governs electronic transport, has been stimulating a lively debate to elucidate the role of the substituents and geometry.^{9,10,14-17}

The aim of the present paper is to theoretically investigate the role of geometry and chirality in molecular junctions composed of single-wall carbon nanotube-biphenyl derivative-single-wall carbon nanotube (CNT-BD junction). In contrast to previous studies on similar systems (metal-biphenyl derivative metal),^{9,10,14-17} we consider metallic CNT contacts, i.e., all-organic electrodes constituted by the same chemical species (carbon) as the molecular bridge. CNTs have been demonstrated to be an ideal material for electrodes in single-molecule devices,¹⁸⁻²⁰ as they exhibit many advantages in comparison to ordinary metallic contacts: they show higher conductivity,²¹ permit better contact to organic molecules,²⁰ and reduce the screening of the gate electric fields due their smaller size.¹⁹ In addition, recent advances in nanofabrication techniques permit a precise control of the gap size in between the CNT leads,²² which is crucial in the development of single-molecule junctions. These reasons have motivated us to investigate electronic transport in CNT-BD junctions by means of *ab initio* density-functional theory calculations coupled with nonequilibrium Green's-function (DFT+NEGF) formalism. Using this formalism, we show that the conductance in these systems follows the $\cos^2 \theta$ law, as in other studies where nonorganic metallic contacts were considered,^{9,10,14-17} provided that the Fermi level of the contacts lies within the HOMO-LUMO gap. This result suggests the general applicability of the $\cos^2 \theta$ law, which seems to be robust against the modifica-

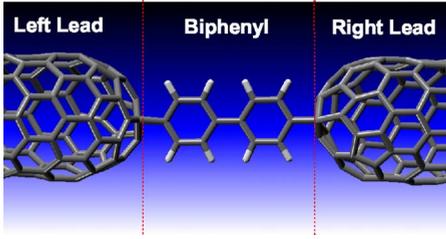


FIG. 1. (Color online) Model geometry for DFT+NEGF calculations consisting of a biphenyl derivative bridging the gap between single-wall metallic carbon nanotubes.

tions of the electrodes structure. We also calculate the geometrical degree of chirality of the whole CNT-BD junction, a purely geometrical quantity that only depend on the position of the atoms, to show that it also follows the $\cos^2 \theta$ law. These results indicate that molecular geometry is the major factor in determining the electronic transport in CNT-BD junctions.

This paper is organized as follows. In Sec. II we describe the electronic transport calculations and detail the methodology used. Section III is devoted to the main results and discussions, whereas Sec. IV is reserved for the conclusions.

II. TRANSPORT CALCULATIONS AND METHODOLOGY

Figure 1 schematically illustrates the system under study: a single biphenyl molecule as central resistive region bridging two single-wall CNTs, used as semi-infinite electrodes with different chemical potentials (reservoirs). As in previous works,²³ we investigate the electronic transport properties of the system by means of first-principles calculations based on DFT coupled with the NEGF method. This methodology has been demonstrated to be highly reliable in describing electronic transport properties of single-molecule devices.^{23–25}

The calculations utilize the local-density approximation (LDA) with norm-conserving pseudopotentials. Several basis sets were tested but this has not qualitatively modified the results. To accomplish the self-consistency, the charge density is obtained by integrating the contributions from scattering states between the lead's chemical potentials given by the Fermi-Dirac distribution. After that, a new charge density is calculated until the self-consistency is achieved.

In order to characterize the transport properties of individual CNTs used as leads, in Fig. 2 the current-voltage (I - V) characteristics of two capped CNTs, characterized by the Hamada indexes (6,0) and (9,0), are calculated by means of DFT+NEGF method as a function of the external bias voltage V_e . Figure 2 reveals a typical ohmic, nonresonant behavior, demonstrating that both (6,0) and (9,0) CNTs are metallic, given consistency to our methodology. We have investigated electronic transport in larger CNTs and no qualitative differences from the results shown in Fig. 2 were found. As a result, these CNTs can be considered as bulklike and hence adequate to be utilized as leads in a Landauer transport calculation.

The current calculation is composed of two procedures: (i) a molecular relaxation of the organic structure is done by

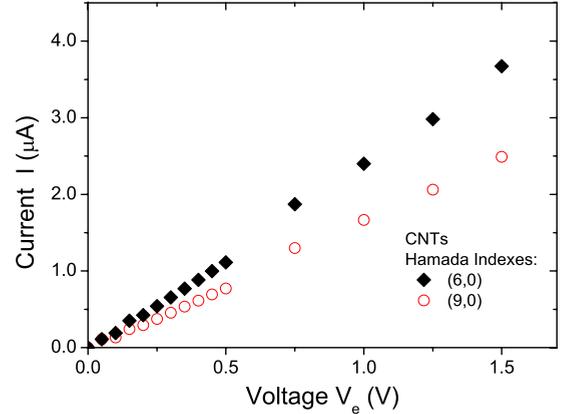


FIG. 2. (Color online) Current-voltage characteristics of individual capped carbon nanotubes used as electrodes, calculated by means of the DFT coupled with NEGF method. CNTs with Hamada indexes (6,0) (black diamonds) and (9,0) (open red circles) were considered.

quantum-mechanical methodologies with specific functional and basis set. To simulate the molecular junction, each optimized molecule, including the carbon atoms of the leads, was translated into a semi-infinite junction with several carbons. The supercell consists of two metallic zigzag carbon nanotubes as the left and right layers (with 184 atoms) and the biphenyl bridging them. In the beginning of the calculation, the molecule is set in a twisted configuration (i.e., with an initial angle between the phenyl rings $\theta \neq 0$) and then is allowed to freely relax with the application of external bias. When the external bias is applied, a structural rearrangement of the whole junction occurs as a result of the optimization procedure of the *ab initio* calculation. Therefore there is a (optimized) molecular configuration and a torsional angle θ for each value of the applied bias. In the calculation, a double- ζ plus polarization basis set is used for all carbon atoms within a LDA. All atoms are relaxed including a very tight optimization process, resulting in a force field less than 0.11 eV/Å; (ii) using the NEGF formalism, the electronic current is calculated after molecular relaxation by applying an external voltage V_e ranging from 0.0 to 0.7 V between the leads. The current is given by the Landauer-Büttiker formula,²⁶

$$I(V_e, \theta) = \frac{2e}{h} \int_{U_L(V_e)}^{U_R(V_e)} T(E, V_e, \theta) dE, \quad (1)$$

where $T(E, V_e, \theta)$ is the transmission coefficient at energy E , and $U_R(V_e)$ and $U_L(V_e)$ are the energies corresponding to the right and left leads, respectively.

It is known that the issue of band alignment is very important in single-molecule transport, i.e., the computation of the current via Eq. (1) depends on the relative position of the Fermi level of the leads with respect to the frontier molecular orbitals of the central molecule (in the present case biphenyl). This is particularly crucial for single molecules attached to nonorganic electrodes, such as gold. In this case, the use of DFT to describe the alignment of the Fermi level and the frontier molecular orbitals is a common source of error in the

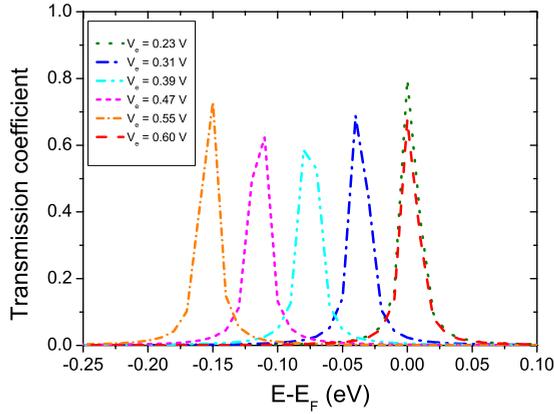


FIG. 3. (Color online) Electrical transmission coefficient as a function of energy for different values of the external applied voltage V_e .

calculation of transport properties (see for instance Ref. 27 and references therein). However, in the present case the issue of band alignment is less relevant since we consider organic CNTs as electrodes so that the biphenyl-lead coupling naturally occurs via the chemical bonding between the regular covalent bond of the biphenyl and the CNTs. From the chemical point of view, this is the main advantage to consider an organic electrode, which by the way does not require the use of a “clip-alligator” molecule to facilitate the lead-central molecule coupling. In other words, the use of an organic electrode facilitates the mismatch between the Fermi level of the leads and the frontier molecular orbitals of the central molecule.

III. RESULTS AND DISCUSSION

To characterize electronic transport through the junction, in Fig. 3 the transmission coefficient $T(E, V_e, \theta)$ is computed by means of *ab initio* calculations as function of the energy E for several values of the external bias voltage V_e . It is important to emphasize that the application of the external voltage induces structural changes in the molecular geometry so that each value of V_e corresponds to a different molecular conformation. To understand the transport properties of the junction, let us consider the coherent transport model based on molecular levels, energy broadened due the coupling to the organic electrodes. Within this model, the voltage drops fully at both CNT-biphenyl contacts. The situation where the HOMO crosses the Fermi level E_F occurs for $V_e \approx 0.25$ V, whereas the LUMO crosses the Fermi level for $V_e \approx 0.6$ V. These situations correspond to transmission peaks at $E \approx E_F$ in Fig. 3. Figure 3 reveals that the widths of the resonances in transmission do not vary significantly as V_e varies, which means that the couplings between the biphenyl molecule and the leads are approximately constant as V_e varies. From this fact and recalling that each value of V_e corresponds to a distinct molecular geometry, and hence to a different angle θ between the phenyl rings, we conclude that modifications in the transport properties are mainly due to intramolecular processes. Confirming that this conclusion holds is important

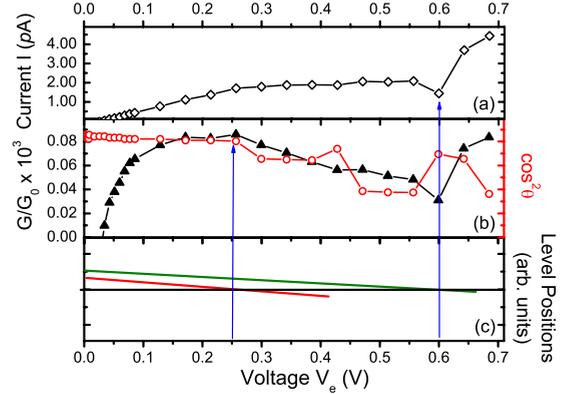


FIG. 4. (Color online) (a) Current-voltage characteristics; (b) conductance (full black triangles), in units of the conductance quantum $G_0 = 2e^2/h$, and the square of the cosine between the phenyl rings $\cos^2 \theta$ (open red circles), multiplied by a constant, as a function of the external bias V_e . The actual values of θ range from 30° up to 45° ; (c) positions of the HOMO (red line), LUMO (green line), and Fermi energy (horizontal black line) as function of V_e . The vertical blue arrows indicate the positions of resonances.

before investigating the applicability of the $\cos^2 \theta$ law in CNT-BD junctions.

In Fig. 4 the current I (a), the conductance $G = dI/dV$ and the square of the cosine of the angle θ between the two phenyl rings (b), as well as the level positions of the frontier molecular orbitals calculated via the NEGF formalism, are shown as a function of the external bias V_e (c). Figure 4(c) allows one to follow the behavior of the position of the HOMO and LUMO as V_e increases, and hence to investigate the effects of resonant tunneling within the coherent transport model on the current and conductance, exhibited in Figs. 4(a) and 4(b), respectively. Notice that at zero bias the Fermi level of the contacts lies outside the frontier molecular orbitals energy gap. From Fig. 4, one can see that there is a strong correlation between the current, the conductance, and $\cos^2 \theta$. Indeed, Figs. 4(b) and 4(c) reveal that the conductance is approximately a linear function of $\cos^2 \theta$ when the Fermi energy sits in between the HOMO-LUMO energy gap, which occurs for $0.25 \text{ V} \lesssim V_e \lesssim 0.6 \text{ V}$. This result is in agreement with experiments⁷ and *ab initio* calculations,¹⁷ where electronic transport in single biphenyl junctions was studied with nonorganic, gold contacts. Therefore, our finding suggests the $\cos^2 \theta$ law has a more general applicability, irrespective of the type of the contacts. This result is somehow surprising since it is known that the electronic molecular structure in single-molecule devices is significantly perturbed by the type of coupling between the molecule and the electrodes.^{28,29} However, when the Fermi level approaches either the HOMO or the LUMO, which occurs for $V_e \approx 0.25$ and ≈ 0.6 V, the linear relation between the conductance and $\cos^2 \theta$ is lost, a result that again agrees with transport calculations in biphenyl junctions with nonorganic electrodes.¹⁷ It is interesting to point out that the relation between the conductance (or the transmission coefficient) and $\cos^2 \theta$ also manifests itself in the behavior of the current. Indeed, one can identify signatures of resonant processes that show up in the I - V characteristics on molecular geometry: whenever the

HOMO or the LUMO crosses the Fermi level, the behavior of $\cos^2 \theta$ is significantly modified. Since the linear dependence between the transmission coefficient and $\cos^2 \theta$ does not hold for every position of the Fermi level relative to the HOMO-LUMO gap, and recalling that the current is obtained by integrating the transmission coefficient over the energies in the Landauer-Büttiker formula (1), the proportionality between the current and $\cos^2 \theta$ does not occur. However, the correlation between the current and $\cos^2 \theta$ remains as a manifestation of the $\cos^2 \theta$ law for the conductance. As an important example where this correlation between the current and $\cos^2 \theta$ comes into play, we identify the region around $V_e \approx 0.6$ V, where a negative differential resistance (NDR) (Ref. 30) occurs, i.e., the current decreases as the bias voltage increases. In fact, one can identify in Fig. 4(b) a strong correlation between the current and molecular conformation at $V_e \approx 0.6$ V, where $\cos^2 \theta$ exhibits an evident change in behavior. Hence we conclude that the NDR has its origin at modifications in molecular conformation. These results suggest that molecular conformation plays a crucial role in determining the transport properties of the CNT-BD junctions.

In order to further understand the influence of molecular geometry on electronic transport, we investigate the geometrical degree of chirality of the molecular junction by calculating the chiral parameter ψ . ψ , defined in Refs. 31 to quantify the degree of chirality of an arbitrary molecule, is a pseudoscalar that only depends on the atomic positions. The chiral index ψ has been shown to be related to physical observables, such as the pitch of a cholesteric liquid crystal³¹ and the optical rotatory power.³² More recently, the connection between ψ and electronic transport through single molecules has been established.²⁴ Specifically, it has been demonstrated that ψ is strongly correlated with the I - V characteristics of PPV derivatives.²⁴ For molecules composed of a single atomic species, ψ is defined in Refs. 24 and 31. The definition of other chiral indexes for molecules composed of different atomic species exists and takes into account different weight functions that reflect the atomic weight.³¹ However, for the system under study, CNT-BD junction, the difference between the values of these indexes and ψ is negligible due to the small atomic weight of the hydrogen relative to the carbon atoms.

In Fig. 5(a) the current I and the chiral index ψ are exhibited as function of the external bias V_e . As a result of the application of the external bias voltage V_e , the atomic positions vary leading to different values of ψ . It is possible to notice a clear correlation between ψ and I , which demonstrates that the connection between ψ and electronic transport is not restricted to a specific system, namely, PPV derivatives²⁴ but seems to be a more general feature in single-molecule transport. Furthermore, in contrast to our previous studies,²⁴ here we explicitly include the contacts in the calculations. This applies not only for transport calculations but also to the chiral index calculations so that here we are probing the geometrical degree of chirality of the whole molecular junction, i.e., ψ has contributions from both the biphenyl molecule and the CNT leads. It is important to emphasize that the contacts give an important contribution to the degree of chirality of the whole junction since CNTs have

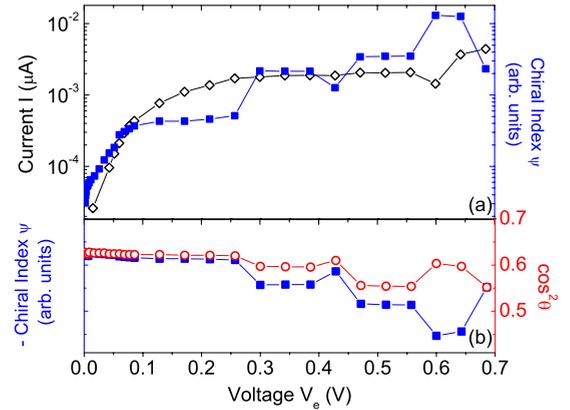


FIG. 5. (Color online) (a) Current (open black diamonds) and chiral parameter ψ (full blue squares) as a function of the external applied voltage V_e . (b) Cosine squared of the angle between the two phenyl rings $\cos^2 \theta$ (open red circles) and $-\psi$ as a function of V_e .

a well-defined chirality.³³ The fact that the purely geometrical parameter ψ is strongly correlated with the I - V characteristics of the CNT-BD junction corroborates the previous conclusion that molecular conformation is indeed the preponderant factor in determining the transport properties of this system.

The connection between the chiral index ψ and $\cos^2 \theta$ is investigated in Fig. 5(b), where both ψ and $\cos^2 \theta$ are exhibited as a function of the external bias V_e . Figure 5(b) reveals that ψ and $\cos^2 \theta$ are proportional for small values of V_e . For larger V_e , the relation of proportionality is lost but the correlation between ψ and $\cos^2 \theta$ remains evident. The fact that, on average, ψ increases as θ increases ($\cos^2 \theta$ decreases) is expected since large values of the torsional angle θ means that the molecule has a large out-of-plane component and hence a larger degree of chirality. This result shows that the behavior of ψ is governed by a single parameter: the torsional angle θ . The variation in ψ as V_e increases is mainly a result of modifications in the geometry of the biphenyl molecule (i.e., variations in θ) since the CNT contacts remain approximately static as V_e varies, leading to a constant contribution to ψ . As V_e increases up to $V_e \approx 0.45$ V, the angle θ increases so that the biphenyl acquires a large out-of-plane component, and hence to a larger value of ψ . For some specific values of V_e , both ψ and θ decreases as V_e increases, leading to a nonmonotonic behavior. The fact that the chiral parameter ψ approximately follows the $\cos^2 \theta$ law explains, in physical grounds, the correlation between ψ and the current. Indeed, ψ , being only dependent of the angle θ between the two phenyl rings, describes the extent of the overlap between the π orbitals of the biphenyl molecule, predicted to follow the $\cos^2 \theta$ law.⁷

IV. CONCLUSIONS

In conclusion, we have investigated the influence of molecular conformation on the electronic transport properties of an all-organic molecular junction composed of a biphenyl molecule attached to metallic carbon nanotubes as contacts. By means of first-principles calculations, we have found a

linear dependence of the conductance of the system on $\cos^2 \theta$, with θ the angle of twist between the two phenyl rings, provided the Fermi level of the contacts is located inside the frontier molecular orbitals energy gap. However, in the vicinities of resonances, i.e., when the Fermi level approaches either the HOMO or the LUMO states, the $\cos^2 \theta$ law is lost. This result, which agrees with previous theoretical calculations¹⁷ and experiments⁷ where electronic transport in single biphenyl molecules attached to nonorganic metallic electrodes is investigated, suggests that the $\cos^2 \theta$ law has a more general validity since it applies even if the nature of the contacts is modified. Furthermore, we have calculated a geometrical chiral parameter ψ , which only depends on the atomic positions, and demonstrate that it is not only proportional to $\cos^2 \theta$ but also is strongly correlated with the current through the junction. This finding indicates that the cor-

relation between the electronic current and ψ , recently established for PPV derivatives,²⁴ also constitutes a more general result in single-molecule transport. In contrast to our previous work,²⁴ here we have explicitly considered the contacts in the calculations. This result, together with the dependence of the conductance on $\cos^2 \theta$, demonstrates that molecular conformation is the preponderant factor that governs the electronic properties in single biphenyl molecular junctions with carbon nanotubes electrodes.

ACKNOWLEDGMENTS

This work was partially supported by the Brazilian agencies CNPq, CAPES, FAPERJ, VALE/FAPESP, Rede Nanotubos de Carbono/CNPq, INCT Nanomateriais de Carbono/CNPq, PPGF, and PPGE.

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