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Abstract
Theoretical studies of how the electronic properties of carbon nanotubes are affected by foreign adsorbed atoms are commonly done by *ab initio* electronic structure calculations in which a single impurity atom is considered. Although these calculations are essential to understand how the system responds to doping, they are by no means sufficient, since, in reality, a large disordered array of adatoms must be considered. It is then necessary to combine *ab initio* techniques with less computationally demanding methods if one wishes to describe the real effect of doping on the electronic properties of nanotubes. Here we propose a method that makes use of *ab initio* results for single impurities as an input to generate the parameters of the less demanding tight-binding technique. It is based on suitable sum rules for the Green functions of the impurity-free nanotubes and does not rely on band-structure fitting. The resulting parameterization allows us to describe disordered systems without missing the important contributions due to charge transfer and screening. The method is illustrated with hydrogen atoms adsorbed to a nanotube, for which the transport properties are subsequently investigated.

1. Introduction

The use of carbon nanotubes (CNs) as functional electronic devices is currently the focus of much research, and is primarily driven by the miniaturization strategies of the electronics and computer industries. Such strategies require an understanding of the transport properties of nanotube-based materials with the aim of tuning their conductivities through controlled doping processes. Substitutional impurities, chemisorbed and physisorbed adatoms, nanoparticles and molecules are some of the examples that have already been considered as possible doping agents both on the experimental and theoretical fronts [1–4].

The experimental achievements in this field have been outstanding. For instance, nitrogen-doped CNs have been carefully synthesized and characterized by scanning tunnelling

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spectroscopy [5]. Regarding the doping effect on the transport properties, a strong n-type donor state near the Fermi level was identified as primarily responsible for modulating the conductance of the doped structure, in agreement with theoretical predictions. Field-effect transistors with n-type current were produced using single-walled CNs doped with randomly dispersed potassium atoms [6]. It has been argued that the n-type doping may contribute to the enhancement of on-currents of those transistors due to the chemically suppressed Schottky barriers at the contacts, suggesting that a device comparable to a silicon n-MOSFET could be designed. Furthermore, the ability to change the conductance of a nanotube exposed to dispersed gaseous molecules is driving the search for sensitive devices capable of detecting minute concentrations of certain substances.

The advances on the theoretical front have not progressed at a similar pace, mainly due to the large computational complexity of calculations involving doped structures. The complexity increase results from the need to include a large number of impurity atoms, together with the greater accuracy required to treat systems reliably at the nanoscale. Whereas modern *ab initio* techniques based on density functional theory (DFT) can achieve a good degree of accuracy to describe the electronic structure of pristine crystalline materials, it is somewhat restricted when dealing with disordered systems. In fact, DFT calculations for doped nanotubes have been attempted but have always been limited to a very small number of impurities. For instance, studies of transition-metal-doped nanotubes investigated their electronic and magnetic properties both in isolation and in bundles but were restricted to fewer than four impurities per unit cell [7]. DFT was again used to investigate the encapsulation of Li^+ ions to assess whether nanotubes could be used as lithium-based batteries, but in this case only a single Li atom was considered [8]. Such calculations may be indicative of the effects that doping brings to certain electronic properties, but as far as the conductance of a doped system is concerned, the limitation to a small number of impurities can be misleading. Multiple scattering events that naturally reduce the extended character of the electronic wave functions are not fully accounted for in the case of very few impurities, which suggests that the effect of disorder on the transport properties would be somewhat underestimated in those cases. Even when large unit cells are considered, which in principle allows calculations with an increased number of impurities, the results bear little statistical significance since many configurations are needed to truly represent the statistical ensemble of the disordered system.

To overcome this problem, less computationally demanding techniques must be used. A combination of tight-binding (TB) methods and *ab initio* calculations is one natural choice. The advantage of this type of combination is in the simplicity with which one can include scattering effects generated by randomly distributed impurities without major compromises to accuracy. One of the suggested methods for combining the two techniques is by fitting the zone-folded TB band structure to that obtained by DFT calculations [9, 10]. While this is a possible strategy, it may involve fitting eigenvalues that do not necessarily contribute directly to the ground-state energy, a quantity known to be the most reliable output in first-principles calculations. Moreover, the fitting is not unique since it is dependent on the choice of points of the Brillouin zone that the band structure must be matched to. Rather than band-structure fitting, here we suggest an alternative method that relies on *ab initio* evaluations for the binding energy and for the charge transfer to provide the appropriate values for the tight-binding parameters.

We focus on nanotubes doped with adsorbed atoms attached to their walls, but it is worth emphasizing that the method is quite general and, in principle, can be applied to any low-dimensional system in the presence of impurities. Depending on the degree of interaction between the nanotube host and the impurity adatoms, the transport properties of the former can be modified quite significantly. Our method is based on a set of equations that relate the change in the global density of states to changes in both the local charge and the total energy.

By relating all these quantities under a common framework we not only obtain the appropriate model parameters, but may also see the effects that doping may bring to the physical properties of a nanotube in a transparent fashion. In what follows, we introduce the method in the next section, followed by its application to the illustrative case of hydrogen-doped nanotubes. Their transport properties are subsequently calculated.

2. Description of the method

We start by considering, first, a situation in which a nanotube and a single adatom are decoupled. As we shall see, one of the advantages of our method is that it uses information about the system in its decoupled configuration. The system is described by a Hamiltonian $\hat{H}_0 = \hat{h}_0 + \hat{h}_a$, where $\hat{h}_0$ and $\hat{h}_a$ correspond to the individual Hamiltonians for the tube and the impurity atom, respectively. For the sake of simplicity, we choose to represent the electronic structure of the nanotube by a single π-band Hamiltonian. This is known to be the relevant electronic orbital at the Fermi level, which consequently determines the transport properties of nanotubes. It is worth mentioning that the use of such a simplified Hamiltonian for $\hat{h}_0$ is primarily chosen to ease the presentation of the method and bears no limitation to its applicability. In fact, it is straightforward to generalize the procedure described here to a multiorbital representation of the nanotube. The Hamiltonian $\hat{h}_0$ is written in operator form as

$$\hat{h}_0 = \sum_i \left[|i\rangle \epsilon_0 \langle i| + \sum_j |i\rangle \gamma_0 \langle j| \right] \tag{1}$$

where $|i\rangle$ is a Hilbert-space vector representing an electron localized on a carbon atom labelled by the index i. The quantities ϵ_0 and γ_0 are the on-site energy and hopping integral parameters for the carbon atoms of the pristine tube, respectively. The sum over j extends over nearest neighbours only. The Hamiltonian $\hat{h}_a$ for the isolated atom is concisely written as $\hat{h}_a = |a\rangle \epsilon_a \langle a|$, where $|a\rangle$ represents the atomic orbital associated with the level ϵ_a. Once again for the sake of simplicity, we choose to represent the electronic structure of the atomic impurity by a single level. This too is an easily relaxable constraint that brings no limitation to the methodology here presented.

When decoupled, both the nanotube and the impurity atom can be accurately described by suitable TB parameters for the Hamiltonians $\hat{h}_0$ and $\hat{h}_a$ that reproduce well the features of their individual electronic structures. However, changes in those parameters are expected when they are no longer in isolation. It is reasonable to assume that the parameters to be corrected should lie within the vicinity of the contact between the tube and the impurity. As a first approximation, we assume that the nanotube is efficient in screening any local charge variation and that only the on-site energy of the carbon atom nearest to the impurity is to be affected. We hereafter refer to this assumption as the efficient-screening hypothesis. As we shall see, this is not essential in our method, and it will later be relaxed to account for imperfect screening. Likewise, the on-site potential energies on the impurity atom are also allowed to change. Finally, the actual coupling between tube and the impurity atom is modelled by an added electronic hopping between them. In summary, the interaction between the nanotube and the impurity is represented by the following perturbing potential:

$$\hat{V} = |0\rangle \delta_0 \langle 0| + |a\rangle \delta_a \langle a| + |0\rangle \tau \langle a| + |a\rangle \tau^* \langle 0| \tag{2}$$

where δ_0 and δ_a are the corrections to the on-site potentials on the nearest carbon site (labelled 0) and on the impurity atom (labelled a), respectively. The hopping τ is responsible for coupling the nanotube to the impurity atom.

The knowledge of the perturbing potential $\hat{V}$ fully determines the effect that the coupling brings to the electronic structure of the system and consequently how it affects the transport properties of the structure. It is our goal to introduce a simple procedure to determine this contact-induced perturbation in terms of quantities that are evaluated by *ab initio* calculations, like the binding energy and the charge transfer, for instance.

The binding energy is defined as the difference of total energies between the coupled and decoupled configurations, and it reflects how strongly the objects interact. In mathematical terms, the binding energy $\Delta\mathcal{E}$ is defined as the difference of total energies given by $\Delta\mathcal{E} = E_T(NT + A) - E_T(NT) - E_T(A)$, where $E_T(NT + A)$ represents the total energy for the coupled configuration, $E_T(NT)$ is the total energy for the isolated nanotube and $E_T(A)$ the total energy for the impurity atom. It is clear from the definition above that contributions to the total energy that are common to both configurations play no role in the binding energy because of cancellations. Bearing in mind that those individual total energies are usually large compared to the binding energy, there is a large degree of unnecessary cancellations that could be avoided if only the relevant contributions to the binding energy were taken into account. Instead of using the Hamiltonian explicitly, in this paper we describe all the relevant quantities in terms of the corresponding single-particle Green functions, which are extremely convenient in dealing with total energy variations and in avoiding such cancellations. For instance, the Green function $\mathcal{G}_{i,j}$ between arbitrary sites i and j of a pristine tube is obtained by simple renormalization techniques based on Dyson's equation [11, 12]. Likewise, equally simple expressions are also available for the Green functions associated with the impurity adatoms.

The parameters associated with the potential $\hat{V}$ in equation (2) are obtained by solving a set of equations, traditionally associated with the so-called Lloyd's formula method [13, 14]. This method is based on the existence of special sum rules for the total density of states in the presence of a localized perturbation. In our case, the localized nature of $\hat{V}$ leads to an expression for the variation of the total electronic density of states $\Delta\rho$ that reads

$$\Delta\rho(E) = -\frac{1}{\pi} \, \text{Im Tr} \, \frac{d}{dE} \ln[\hat{1} - \hat{G}(E)\hat{V}], \tag{3}$$

where Tr is the trace operator, Im represents the imaginary part and $\hat{G}(E)$ contains the decoupled Green functions in block-diagonal form for electrons of energy E. More specifically, the matrix $\hat{G}(E)$ is given by

$$\hat{G}(E) = \begin{bmatrix} \mathcal{G}_{0,0}(E) & 0 \\ 0 & \mathcal{G}_{a,a}(E) \end{bmatrix}, \tag{4}$$

where $\mathcal{G}_{0,0}(E)$ and $\mathcal{G}_{a,a}(E)$ are the Green functions $\hat{\mathcal{G}} = (E - \hat{H}_0)^{-1}$ projected on sites $|0\rangle$ and $|a\rangle$, respectively. In matrix form, equation (2) is rewritten as

$$\hat{V} = \begin{bmatrix} \delta_0 & \tau \\ \tau^\dagger & \delta_a \end{bmatrix}. \tag{5}$$

In the framework of the so-called tight-binding total energy methods, one can write the total energy as the electronic structure contribution added to a repulsive energy term [15–17], in which the latter has been given a formal correspondence with modern density functional theory [18]. Moreover, as shown by Papaconstantopoulos and co-workers [15], this latter contribution is easily accounted for by including it in the electronic on-site potential associated with the tight-binding Hamiltonian. In this way, the total energy can be written as a sum over the eigenvalues of the Hamiltonian, which in turn allows us to express the binding energy as a function of $\Delta\rho$.

Making use of the energy derivative in equation (3), both the total energy variation $\Delta\mathcal{E}$ and charge variation $\Delta\mathcal{N}$ are easily derived. The former is obtained by a simple integration by

parts, which gives

$$\Delta\mathcal{E} = \frac{1}{\pi} \int_{-\infty}^{E_F} \mathrm{d}E \ \mathrm{Im} \ \mathrm{Tr} \ \ln[\hat{1} - \hat{G}(E)\hat{V}], \tag{6}$$

whereas the latter is written as

$$\Delta\mathcal{N} = -\frac{1}{\pi} \ \mathrm{Im} \ \mathrm{Tr} \ \ln[\hat{1} - \hat{G}(E_F)\hat{V}]. \tag{7}$$

E_F in the equations above stands for the Fermi level of the system. Equations (6) and (7) are fundamental expressions in our method in the sense that they describe the change of two key quantities, namely total energy and total number of particles, as a result of the interaction between the tube and the impurity atom. At this point it is worth mentioning that they are valid not only for $\hat{h}_0$ and $\hat{h}_a$ defined above but for whichever Hamiltonian is chosen to represent the electronic structure of the system, the only difference being in the precise form of the matrix elements of the operators $\hat{G}$ and $\hat{V}$. Moreover, we are not limited to impurity adatoms, in the sense that doping agents of different nature can be easily included if the appropriate form for the corresponding Green function $\mathcal{G}_{a,a}$ is considered.

Substituting equations (4) and (5) into equations (6) and (7), we have

$$\Delta\mathcal{E} = \frac{1}{\pi} \int_{-\infty}^{E_F} \mathrm{d}E \ \mathrm{Im} \ \ln\left[(1 - \mathcal{G}_{0,0}\,\delta_0)(1 - \mathcal{G}_{a,a}\,\delta_a) - \mathcal{G}_{0,0}\,\mathcal{G}_{a,a}\,\tau^2\right] \tag{8}$$

$$\Delta\mathcal{N} = -\frac{1}{\pi} \ \mathrm{Im} \ \ln\left[(1 - \mathcal{G}_{0,0}(E_F)\delta_0)(1 - \mathcal{G}_{a,a}(E_F)\delta_a) - \mathcal{G}_{0,0}(E_F)\mathcal{G}_{a,a}(E_F)\tau^2\right] \tag{9}$$

In deriving equations (8) and (9), one must explicitly use the fact that $\mathrm{Tr} \ \ln(\hat{X}) = \ln \det(\hat{X})$. Since we have three unknowns (δ_0, δ_a and τ), a third equation must be derived by taking into account the charge transfer between the tube and the impurity. Dyson's equation allows us to obtain the change in the local density of states on the impurity site, which can be further integrated to express the charge transfer $\Delta\mathcal{C}$ between the tube and the impurity as follows:

$$\Delta\mathcal{C} = -\frac{1}{\pi} \int_{-\infty}^{E_F} \mathrm{d}E \ \mathrm{Im} \left\{ \left[\mathcal{G}_{a,a}^{-1} - \delta_a - (1 - \mathcal{G}_{0,0}\,\delta_0)^{-1} \ \mathcal{G}_{0,0}\,\tau^2\right]^{-1} - \mathcal{G}_{a,a} \right\}. \tag{10}$$

The set of equations (8), (9) and (10) relates three basic quantities, namely the binding energy, the change in the total number of particles and the charge transfer, with the parameters δ_0, δ_a and τ associated with the potential $\hat{V}$. Bearing in mind that equation (9) must reflect the charge neutrality of the system, we must impose that the total charge be conserved, i.e., $\Delta\mathcal{N} = 0$. Therefore, the knowledge of $\Delta\mathcal{E}$ and $\Delta\mathcal{C}$ is in principle sufficient to fully determine the potential $\hat{V}$. Rather than relying on band-structure fitting, which depends on which portions of the Brillouin zone are chosen to be reproduced, here we propose to use *ab initio*-evaluated binding energies and charge transfers as input values to obtain the correct parameters of the potential $\hat{V}$. In this way, the parameterization of the perturbing potential is done in a unique fashion and does not depend on any particular choice of fitting points.

3. Results

In what follows, we test the method described above by applying it to hydrogen atoms adsorbed to metallic nanotubes. We start by considering a (6, 6) armchair nanotube in the presence of a single hydrogen atom. *Ab initio* calculations were used to evaluate the binding energy and charge transfer between the tube and the impurity atom. The calculations were done using the SIESTA code [19] within the local-density approximation (LDA) approach for the exchange and correlation potential [20]. All the structure comprising the nanotube plus the
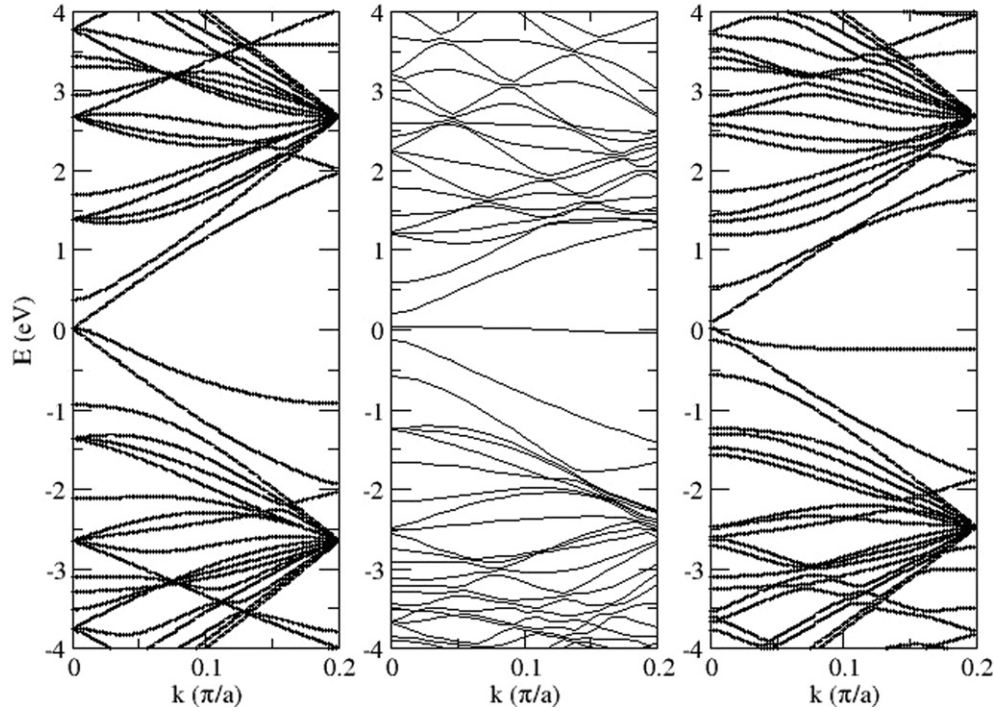
Figure 1. Folded band structures for a doped $(6, 6)$ nanotube with a single H atom per unit cell. The left and right panels are obtained by the Lloyd's formula method, the former within the efficient-screening assumption and the latter considering a screening cloud up to second-nearest neighbours. The middle panel is the *ab initio* result.

adsorbed hydrogen atom is fully relaxed. The calculation shows that the sp^2 hybridization of the carbon atom linked to the hydrogen is converted to sp^3-type, allowing a light distortion of the carbon lattice from its equilibrium position. The C–H bond length is 1.149 Å, which does not differ much from typical hydrocarbons such as the methane molecule ($\sim$1.10 Å) [21]. The calculated values for the total energy variation and the charge transfer are $\Delta\mathcal{E} = -2.74$ eV and $\Delta\mathcal{C} = 0.154e$, respectively. Using them as input values in equations (8) and (10), we can obtain the corresponding values of $\delta_0 = 1.63\gamma_0$, $\delta_a = -2.36\gamma_0$ and $\tau = 2.14\gamma_0$, where $\gamma_0 = 2.66$ eV.

Although the Lloyd's formula method does not rely on band-structure fitting, it is illustrative to compare the *ab initio* energy bands with those obtained by our scheme. With the set of parameters δ_0, δ_a and τ fully determined, we can reproduce the periodic boundary conditions used in the DFT calculations and obtain the corresponding energy dispersion. Such a comparison is shown in figure 1, in which the DFT band structure (middle panel) is juxtaposed with the energy levels obtained by the Lloyd's formula method (left panel). Both diagrams display unmistakable similarities in the way their energy bands are distributed, which places the efficient-screening hypothesis of the Lloyd's formula method as an excellent first approximation to describe the effect of impurity atoms on the electronic structure of nanotubes.

Despite the overall resemblance in the dispersion relations in the left and middle panels, the Lloyd's formula bands are not able to reproduce the detailed features of the band structure, particularly around the Fermi energy. It is worth recalling that the use of equation (2) with only three undetermined parameters relies on the assumption of efficient screening by the nanotube conduction electrons. In other words, it assumes that any charge imbalance in the

system is screened to the extent that only the on-site potential on the atom nearest to the perturbation is affected. This is not a good assumption, as indicated by the local charge distribution that results from the DFT calculation. In fact, the calculations point to a distribution that is not entirely concentrated around a single atom but to one that is spread around a few nearest neighbours. The efficient-screening assumption must therefore be relaxed if we wish to improve the agreement between the band structures.

Imperfect screening can be easily included in our formalism if we consider that the perturbing potential $\hat{V}$ can now affect the next-nearest neighbours surrounding the contact region. Although this increases the size of the matrix $\hat{V}$, equation (3) is still valid in expressing the change in the total density of states due to the contact between the impurity and the tube. The potential $\hat{V}$ will now involve two more matrix elements, namely δ_0^1 and δ_0^2, which are corrections to the on-site potentials on the two non-equivalent nearest-neighbour carbon atoms. To comply with the extra undetermined matrix elements, an equal number of additional equations are required. In this case, the two additional equations are expressions for the local charge variations on the nearest-neighbour atoms, which can also be read out from the DFT results. It turns out that the efficient-screening hypothesis is not a limitation of our approach, in the sense that we can always consider screening clouds of arbitrary sizes, the only difference being in the number of equations required to obtain the adequate parameters. The set of five equations is straightforwardly derived from equation (3), but they are not displayed here, for brevity. When solved, the equations provide the following results: $\delta_0 = 1.26\gamma_0$, $\delta_0^1 = -1.20\gamma_0$, $\delta_0^2 = -0.25\gamma_0$, $\delta_a = 0.28\gamma_0$ and $\tau = 0.76\gamma_0$, which lead to the band structure depicted in the right panel of figure 1. The improvement is considerable when compared with the efficient-screening results of the left panel. Not only is the general trend of the dispersion reproduced but also the small energy gap and the weakly dispersive level that appears near the Fermi energy [22]. Despite the remaining differences, mainly due to the lack of σ–π hybridization, the resemblance between the two graphs is remarkable.

As mentioned previously, the key advantage of mapping the first-principles results with a set of corrected parameters is that we do not have to restrict ourselves to a single impurity, and can in principle include a finite concentration of adsorbed atoms in a truly disordered configuration. We are then able to investigate how the transport properties of carbon nanotubes are affected by a given concentration of impurity atoms along their length. Using our recipe for correcting the Hamiltonian parameters, we include a large number of impurities randomly dispersed within a section of the nanotube. Each added impurity requires parameter corrections according to the size of the screening cloud. The only constraint in the random distribution is that impurities are always sufficiently apart to avoid overlap between the screening clouds. The conductance across such a disordered structure is then calculated using the Kubo formula [11, 12] and averaged over a large number of disorder configurations [23]. This ensemble averaging is crucial in providing results with meaningful statistical significance and could not be done without a less computationally demanding scheme, such as the one suggested in this paper. Figure 2(a) shows the conductance as a function of the energy for two distinct concentrations of H atoms adsorbed on the surface of a (6, 6) nanotube. It is evident from the conductance results that the H atom acts as a strong scattering centre for the charge carriers. Figure 2(b) shows the logarithm of the average conductance as a function of concentration indicating how a nanotube responds to H doping. As expected, an exponential dependence on the impurity concentration is observed [24].

Although the results here presented were based on a simplified description for the electronic structure of both the nanotube and the atomic impurity, it is straightforward to generalize our procedure to account for more degrees of freedom, like, for instance, the multiorbital character of the unperturbed Hamiltonian $\hat{H}_0$ or by including spin-resolved
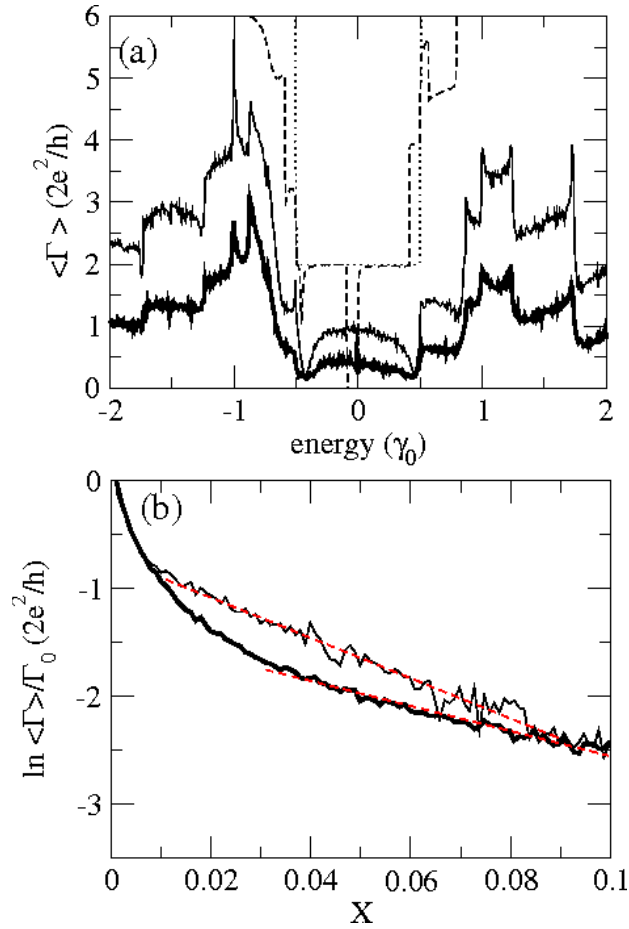
Figure 2. (a) Average conductance as a function of the Fermi energy for distinct concentrations of H atoms distributed randomly along a (6, 6) carbon nanotube: dotted line for pristine tube, dashed line for a carbon nanotube with only 1 adsorbed atom, full line for $x = 1\%$ and broad full line for $x = 3\%$. (b) Logarithm of the average conductance scaled by the conductance for the pristine tube (Γ_0) as a function of the concentration for distinct Fermi energies: full line for $E_F = 0.0\gamma_0$ and broad full line for $E_F = 1.2\gamma_0$. Dashed lines are linear fittings.

(This figure is in colour only in the electronic version)

perturbations typically associated with magnetic impurities [25]. In this case, the only difference lies in the expressions for the Green function in equation (4) and in the matrix elements of the perturbation $\hat{V}$ in equation (5). The parameters τ, δ_0 and δ_a acquire a matrix character that reflects the additional degrees of freedom of the constituent parts. The set of equations needed to obtain the corrected parameters is still based on the fundamental equations (6) and (7). Once again, an increase in the number of parameters requires more equations, this time involving the extra degrees of freedom. Following the same steps as before, we can use quantities from a simple DFT calculation as input to our set of equations. In addition to the binding energy and the overall charge transfer, we may require information about how the charge is distributed in their respective degrees of freedom, which again is readily available from DFT calculations.

4. Summary

In summary, we have presented a method that provides a simple way of accounting for disorder effects on the transport properties of doped nanotubes. *Ab initio* evaluations of the electronic structure of a nanotube with a single doping atom are used as input to generate the corresponding changes to the tight-binding-like parameters surrounding the impurity. Our method makes use of special sum rules for the single-particle Green functions that provide a closed-form expression for the variation of the total density of states, which in turn can be used to relate the desired parameters with quantities like binding energy and charge transfer. These latter quantities, when evaluated by first principles, give a direct way of determining the unknown parameters. It is worth stressing that, unlike band-structure fitting, we do not depend on the choice of Brillouin zone points to be matched against. On the contrary, a finite number of equations give unique solutions to the parameters that can be used to evaluate the corresponding conductances. By averaging over a large ensemble of disordered configurations, we can obtain results with statistical significance that are likely to reproduce the measurable results of transport in doped nanotubes.

Acknowledgments

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