Effect of bending and vacancies on the conductance of carbon nanotubes

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(Received 15 February 2000; revised manuscript received 15 May 2000)

Electron transport through nanotubes is studied theoretically using the Landauer formalism. The studies are carried out for finite metallic nanotubes that bridge two contacts pads. The current is observed to increase stepwise with the applied voltage. Each step corresponds to resonance tunneling including one single-particle eigenstate of the nanotube. Moderate bending of the nanotube results in a shift of the single-particle levels but the overall current remains essentially unaffected. For large bending, however, the π electron system becomes more disturbed, which introduces backscattering and a marked decrease in the conductivity along the tube. A single carbon vacancy in the nanotube is shown to have very small effect on the conductivity in the center of the metallic band whereas, by increasing the defect concentration the conductivity decreases in the same way as for the strongly bent tubes.

I. INTRODUCTION

Molecular electronics has had an enormous development during the last decade.[1] At the microscopic level this has led to the possibility to measure currents through individual molecules using scanning probe microscopy[1] or mechanically controlled break junctions.[2] In the case of carbon nanotubes (NT's), it was shown that electrodes with a spacing at the submicrometer scale can be used to contact individual, single wall carbon nanotubes[3] (SWNT's). Several other experiments dealing with the conductance of individual nanotubes have followed.[4]

Theoretically, a great number of studies of conductance in NT's have been published during the recent years.[5–10] These studies all deal with the effect of various types of structural defects on the transport properties of SWNT's, in most cases calculated using the Landauer formula[11] combined with various techniques to calculate the transmission coefficient.

In this paper we address the issue of quantized conductance which has been observed in metallic SWNT's by Tans *et al.*[3] The steps in the measured *IV* curves were in that case observed at the mV regime and could be rationalized in terms of the Coulomb blockade effect and/or resonance tunneling induced by individual molecular orbitals of the nanotube. Based on this type of *IV* characteristics for the perfect system we have studied the changes due to bending of the NT. We have also calculated the change in the conductance due to the presence of vacancies on the NT. In contrast to several other studies,[5,12] we focus on tubes with a finite length since this is the most relevant architecture for molecular electronics applications. The finite length also introduces quantized conductance, which is relevant to experimental work on carbon NT's.[3]

Section II of this article introduces the model used to describe the electronic properties of the molecules and the method to calculate the conductance. Results and discussion are presented in Sec. III and a summary of the results is given in Sec. IV.

II. METHODOLOGY

The conductance through a finite carbon NT connected by two metallic lattices coupled to the surface of the tube is calculated from the many-channel Landauer formula[13,14]

$$G=\frac{2e^2}{\pi\hbar}\mathrm{Tr}[t(E)t(E)^{\dagger}], \tag{1}$$

where $t(E)$ represents the amplitudes for electron transmission between the metallic contacts for an electron with energy E. In the results presented below, we have excluded the prefactor, giving a dimensionless conductance, which is identical to the transmission probability $[T(E)]$.

To calculate the conductance we have to specify the Hamiltonians for the NT and the metallic contacts as well as the Hamiltonian that describes the coupling between these two parts. The Hamiltonian of the molecule is described within the tight-binding approximation and treats the π electron system with a basis of orthogonal atomic orbitals. Calculations of the conductance through the C_{60} molecule by Chavy *et al.*[15] show that the main part contributing to the conductance comes from the π electrons and only a very small part from the σ electrons. This restriction to treat only the π system is also well justified in the case of NT's and has been extensively used recently. The work of Nardelli[8] opens up for the possibility to include also the σ electrons and the coupling between the π and σ systems. In a recent paper by Rochefort *et al.*,[10] the extended Hückel method is applied to carbon NT with an emphasis on the coupling between the π and σ electron systems for bent tubes. Indeed, for large bending angles, there is an effect of this coupling, which has been neglected in this work.

By choosing the onsite energy of the carbon atoms to zero the energy offset is determined. The intratubular interactions are restricted to electron hopping between nearest-neighbor (n,n) atoms only. The values of the hopping, $t_{l',l}$ is described by a simple exponential relation to the C-C bond length $R_{l',l}$:

$$t_{l',l}=t_0 e^{-\alpha(R_{l',l}-R_0)} \tag{2}$$

R_0 is the reference bond length, which is fixed to 1.40 Å for the systems discussed here. The value of the constants used were $\alpha=2.0\,\text{Å}^{-1}$ and $t_0=-2.5$ eV. To obtain realistic values of $R_{l',l}$ in Eq. (2), the semiempirical Austin model one (AM1) method[16] was used to optimize the geometry of the

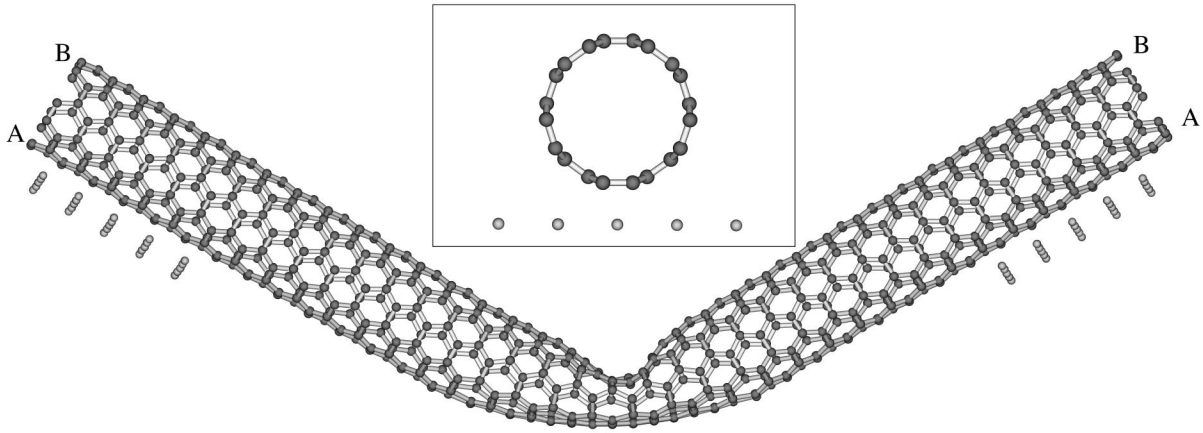

FIG. 1. Bent carbon NT with bending angle 62° together with the 5×5 atoms of the top layer of the two contacts. The letters *A* and *B* point out the endpoints of the *A*-*A* and *B*-*B* all *trans* chains for which the bond lengths are presented in Fig. 2. The inset shows one end of the NT viewed along the tube axis.

NT's at various bending angles. The optimization is performed on a (5,5) NT with 160 carbon atoms. To impose bending, the 10 carbon atoms at each end of the NT are fixed to ensure a chosen bending angle. These angles are set to 62°, 74°, and 85° corresponding to bending radii of 16.7 Å, 14.3 Å, and 12.5 Å, respectively. The positions of all other carbon atoms are optimized. The results of these optimizations are summarized at the beginning of Sec. III. Each end of these optimized bent NT's are then connected to segments of straight tubes to form (5,5) tubes with a total of 700 carbon atoms (in the absence of vacancies). In the case of carbon vacancies, we have not performed any optimization, instead the geometry of these tubes are obtained simply by removing individual carbon atoms from a straight NT with 700 carbon atoms and thereby excluding these sites from the Hamiltonian.

Transmission through SWNT's involves the coupling between the metal contacts and the tube as well as the transport along the molecules. Here the focus is on the changes in the properties of the NT. Therefore, the metal contacts are described in a simple way by cubic tight-binding lattices. The lattice properties are described by a lattice parameter a (2.8 Å simulating the lattice constant of gold), hopping t_l (-2.5 eV) and an onsite energy ϵ_l (0 eV). To obtain a finite number of equations we use a finite lattice ($N\times N$) in the directions parallel to the metal surface. We have tested the dependence of the conductivity on the value of N and found that for N of the order of 5 or larger, the contact size plays a minor role for the qualitative behavior of the conductance. The results presented in this paper are therefore calculated for a contact size of 5×5 atoms (see Fig. 1).

The geometry of coupling between the NT and the two contacts is chosen as realistic as possible, the metal wire contacts the carbon NT from the side as shown in Fig. 1. This setup resembles very much that used in conductance measurements.[3,17] The interaction between the contacts and the NT is described by a hopping term similar to that in Eq. (2), with a nearest-neighbor contact-NT hopping that has been varied to fit experimental contact resistance data (see Sec. III).

Calculation of the transmission amplitudes are performed in a similar way as by Cerdá *et al.*[18] By dividing the system into three parts, the two metal surfaces and the molecule, we can write the wave function of the metal parts as a linear combination of the known stationary solutions in the metals, with special care taken to include the closed decaying channels in the metal surfaces. To obtain the transmission amplitudes we make an anzats with unit flux incoming from one contact and unknown reflected and transmitted amplitudes. The interactions within the NT and the metallic leads as well as between the leads and the NT gives a set of linear equations for the transmission and reflection amplitudes that were solved numerically using the Green function of the molecule.[19]

The transmission amplitudes are multiplied according to results of Eq. (1), which results in the transmission probability $T(E)$ as a function of the energy of the incoming electron E. The current I through the structure can be approximated by integrating the transmission in the range $[E_f-eV/2,E_f+eV/2]$ where V is the applied voltage and E_f is the Fermi energy. In Sec. III, IV curves are presented for V up to 2 V. It should be noted that for (5,5) tubes, this corresponds to an energy range covering only the central part of the band structure in which there are only two electronic bands.

III. RESULTS AND DISCUSSION

Bending of the NT in the way described above introduces a rather localized defect as shown in Fig. 1. The bond lengths on the outer surface of the bent tube are elongated whereas the inner surface gets buckled. The optimized bond lengths along the tube are shown in Fig. 2 for the *A*-*A* and *B*-*B* all *trans* chains (see Fig. 1) with a tube bending angle of 62°. The effect of bending is to elongate the bond lengths along the *A*-*A* chain. The bonds at the two ends of the bend show the maximum elongation, 0.35 Å in the case of 62° bending. For larger bending angles, these bonds will break completely and thus cause an almost complete interruption of the π conjugation along the *A*-*A* chain. The *B*-*B* chain, on the other hand, exhibits optimized bond lengths that are essentially unaffected by the bending. Therefore, there is no major reduction in the π conjugation along this chain in our model. Note that in our case we do not include the effect of buckling of the NT surface, which might cause an additional small

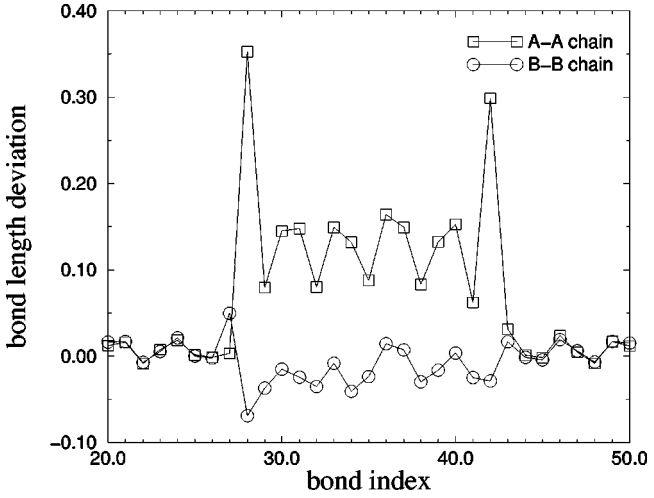

FIG. 2. Deviations in bond length along the *A*-*A* (□) and *B*-*B* (○) lines (see Fig. 1), with reference to a bond length of 1.42 Å.

reduction in the hopping between neighboring C atoms (see below).

Out of the ten all *trans* chains along the (5,5) NT, there are two that have the property of the *A*-*A* chain shown in Fig. 2. The remaining chains show, like the *B*-*B* chain, quite small changes in the bond lengths. Also the carbon-carbon bonds that are perpendicular to the tube axis are essentially unaffected by the bending. The effect of the bending is therefore quite localized both along the tube direction and over the cross section of the NT.

Below we also report results for straight defect free NT's as well as NT's with vacancies. The defect free NT has also been optimized at the AM1 level producing essentially constant bond length along the NT with a bond length of 1.42 Å. The structure of the vacancies, on the other hand, are not optimized; we have only removed carbon atoms at the randomly chosen positions of the vacancies. Based on the structures for these three kinds of NT's (defect free, bent and NT with vacancies) we will now discuss their transport properties.

According to Eq. 2, we translate the optimized bond lengths to a nearest-neighbor hopping strength. Based on the values for the hopping interaction as well as the contact/tube interaction, we calculate the transmission probability spectrum $[T(E)]$. $T(E)$ is shown in Fig. 3 for a bending angle of 62° as a function of the Fermi energy of the metal contacts. In our case the contact/tube interactions are rather restricted in space compared to the full extension of the NT. The electronic system of the NT couples, therefore, only weakly to the contacts (high-resistance contacts) which results in sharp resonances for energies close to the eigenenergies of the tube. For other energies, the transport is an ordinary tunneling process that results in very low conductance. The energy regime shown in Fig. 3 corresponds to the central part of the π electronic structure of the NT. In this region there are two bands that cross each other.[20] For the infinite (5,5) tube with the values of the hopping parameters given in Eq. (2), this region extends between ± 1.4 eV, and each energy in this region corresponds to two delocalized orbitals. In the present case with a finite NT and no periodic boundary conditions, this degeneracy is lifted and each peak in the transmission spectrum corresponds to one eigenstate only. We note that a

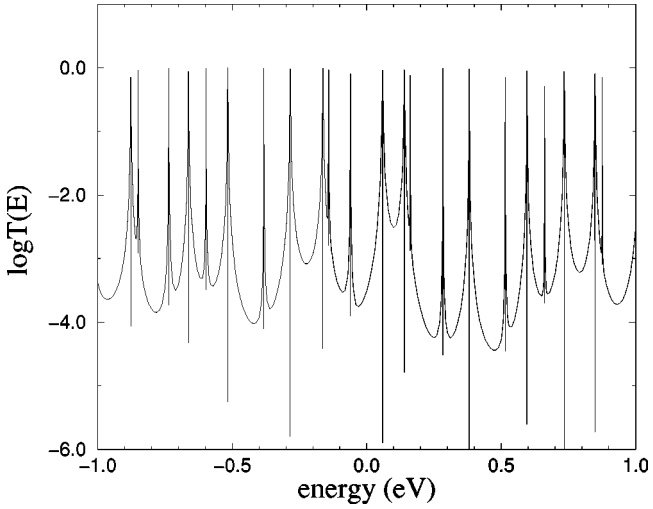

FIG. 3. Conductance spectrum of a NT with bending angle 62°. The very sharp dips at the conductance peaks are caused by numerical problems as described in the text.

dip in the transmission occurs exactly at the eigenenergy. This is a numerical error originating from the Green function of the NT, which is singular exactly at eigenenergies of the NT. However, the dip is very sharp and does not affect the *IV* curves shown below.

By integration of the conductance over the energy regime accessible at a certain potential (see Sec. II) we obtain the *IV* characteristics of the (5,5) NT containing 700 carbon atoms (length approximately 9 nm). In Fig. 4 is shown the *IV* curves for the straight NT together with the NT with three different bending angles, 62°, 74°, and 85°. The presentation is restricted to energies ± 1 eV around the Fermi energy. In the calculations, however, the molecular Green function involves also (nonresonant) effects from all π eigenstates of the (5,5) NT. We will now discuss the general properties of the *IV* curves, in particular that of the straight NT, followed by discussion of the bent NT and finally NT's with vacancies.

The steps in the curves in Fig. 4 occur as a result of resonance tunneling and correspond exactly to the peaks in

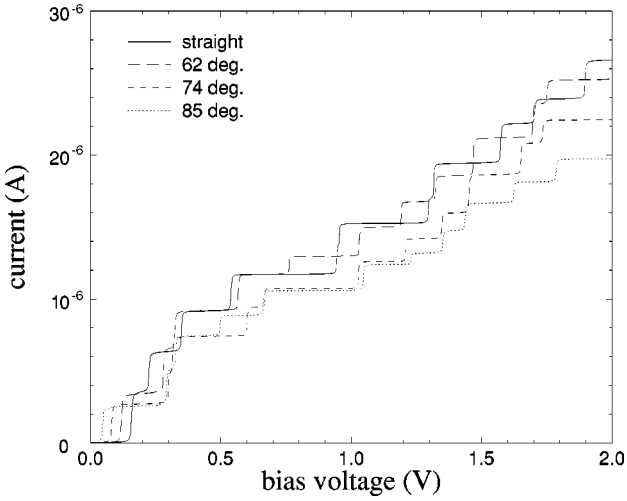

FIG. 4. Current-voltage characteristics of NT's; straight (solid line), bending angle 62° (long-dashed line), bending angle 74° (dashed line), and bending angle 85° (dotted line).

the conductance spectrum. In our case of a (5,5) tube with 700 carbon atoms and one basis function per site this results in a total of 700 eigenstates. The interlevel spacing in the half-filled bands around the Fermi energy is approximately 0.1 eV in this case. If the tube length is increased by a factor of 100 compared to our test tube (then reaching a length of the order of 1 μm), the level spacing would be approximately 1 meV which is of the same order as the step separation in the experimental data by Tans *et al.*[3] It is however not possible to make a direct comparison between our calculated step size and the measured data since the total tube length in measurement was 3 μm whereas the contacts were placed approximately 0.1 μm apart. However, by this simple example, we would like to point out that the experimental data are not inconsistent with a resonant tunneling picture.

A second feature of the data of Tans *et al.*[3] is the existence of a conductivity gap in the bias regime ± 0.1 meV, which has been argued to be due to the Coulomb blockade effect.[21] Unfortunately, at present we are not able to calculate a value for the Coulomb gap of the NT and it is therefore not possible to fully address the question of the origin of the conductivity gap at zero-bias voltage. Our calculated one-particle energy spectra show that the presence of a gap is dependent on the number of carbon atoms in the tube. For the NT with 700 atoms, it is evident from Fig. 2 that there is a gap around the Fermi energy of the order of the average eigenenergy separation. However, for a NT with for example 800 carbon atoms, two degenerate states appear exactly at the Fermi energy and in this case there is no gap in the one-particle transmission spectrum. There are two possible explanations for a conductivity gap in this case. Either it results from the Coulomb blockade effect or the degeneracy at the Fermi energy is lifted by a Jahn-Teller distortion. We have initiated studies of both these effects, studies that hopefully can lead to a more detailed understanding of this issue.

An increase in tube length increases the density-of-states of the NT. For ballistic transport along the tube axis this increase would result in an increase in the number of peaks in the conductance spectrum. However, each peak will at the same time get more narrow since the off resonance conductance drops exponentially with the tube length. In total, the conductance becomes length independent, which in principle should allow for direct comparison between our calculated resistance and those obtained experimentally.[3] The resistance of the NT itself is, however, not the limiting factor in this situation. Instead the resistance comes mostly from the contacts. Here, the interaction between the metal contacts and the surface of the NT is described in terms of a hopping between nearest-neighbor atoms of the metal contact surface and the NT. This hopping strength is 0.6 eV in the results presented above. By changing the hopping strength we can fit our resistance to that obtained by Tans *et al.*[3] The best agreement is observed for a nearest-neighbor hopping strength of 0.2 eV. This type of empirical fit of the hopping gives important information of the type of interaction and could be further analyzed from detailed quantum chemical studies of a NT on a metal surface.

We now turn to the results for the bent NT's. The steps in the *IV* curves occur at slightly different energies in all four cases shown in Fig. 4, indicating a shift of the eigenenergies of the NT as a result of bending. For a bending angle of 62°, the major effect is to redistribute the energy levels slightly. Each level has approximately the same transmission coefficient (i.e., the same step height) as in the case of a perfect tube, indicating that the backscattering of the bent region is very small. This produces an overall slope of the curves, which is essentially unaffected by the bending. This slope corresponds to the inverse of the resistance of the structure and our results thus show that the change in resistance is very small for moderate bending.

At larger bending angles, the slope of the *IV* curves decrease. In this regime the transport along the NT is no longer ballistic between the two contacts, but rather described in terms of a wave scattered by the bond length defects on the NT. It is important to notice that the effect of this scattering on the conductance becomes important only at very high bending for which individual C-C bonds start to break (see Fig. 2 above). It must also be kept in mind that the NT in our calculation is only around 9 nm long. This is an adequate length scale in real nanoelectronics. However, for applications with longer NT's, the relation between the localization length of the electronic states and the length of the NT will be important. Clearly, the tube length studied here is shorter than the localization length in the case of weak disorder (no bond breaking). If the tube gets longer, eventually this situation will change and we expect an increase in the resistance even for weak disorder in that case.[10]

A similar type of study of the effect of tube bending on the conductance was performed by Rochefort *et al.*[10] but with geometries based on molecular mechanics calculations and with the electronic structure determined using the extended Hückel (EH) method. Also in their case, the conductance remained essentially unaffected until the bending exceeded 60°. The slightly higher sensitivity to bending obtained in this EH calculation is partially due to the fact that buckling as well as coupling between the π and σ systems is included in their study and omitted in our case. However, as pointed out above, calculations of the conductance through the C_{60} molecule show that the main contribution to the conductance comes from the π electrons even for this highly curved structure.[15] The effect of the σ electrons is therefore not expected to be significant unless the buckling is very strong. Another reason for the discrepancy is the use of high-resistance contacts in our case and the low resistance contacts used in Ref. 10. As discussed below in connection with the studies of vacancies, the scattering at the contacts has a significant effect on the sensitivity to disorder. We believe that this effect is more important than the neglect of σ electrons in order to explain the difference between our results and those of Rochefort *et al.*[10]

The *IV* curves in the case of carbon vacancies are shown in Fig. 5. Again, we have used a (5,5) NT with 700 carbon atoms in the perfect tube. The result for two different positions (on the same side and on the opposite side of the contacts, respectively) of a single vacancy are shown (dashed lines), together with three different randomly chosen distributions of five vacancies (dotted lines). Clearly, the overall effect of these vacancies is to reduce the current through the NT. For a single vacancy this effect is extremely small. A small difference between the case of the vacancy put on the same side of the tube as the contacts, as compared to the case when the vacancy is placed on the opposite side, is observed.

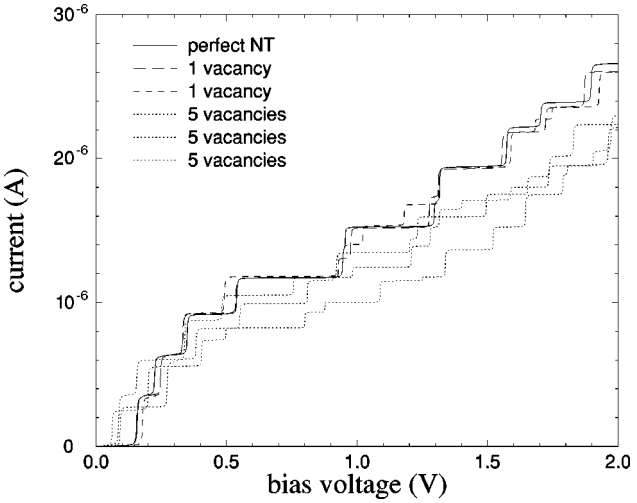

FIG. 5. Current-voltage characteristics of NT's; straight (solid line), one vacancy on the same side of the tube as the contacts (long-dashed line), one vacancy on the opposite side of the tube as the contacts (dashed line), three examples with different distributions of five vacancies (dotted line).

This indicates a difference in the extent of delocalization of the wave functions at different energies. The current distribution over the tube is thus dependent on the bias voltage.

For higher-defect concentrations the scattering of the electrons becomes more important, which results in a clear decrease in the current. The step height varies in this case very much over the studied voltage regime as well as between the three vacancy distributions. The step height gives information about the sensitivity of a particular eigenstate to the disorder and shows clearly the correlation between the positions of the defects and the structure of the wave functions. Apparently, a particular vacancy distribution can cause strong scattering or weak scattering depending on the structure of the wave function. If this distribution is changed it might change the scattering dramatically as is evident from the difference between the three dotted curves.

The results presented here for a finite NT stand in sharp contrast to other studies of vacancies on infinite tubes.[5,12] In our case there are essentially four scattering centra in addition to the vacancies, namely, both ends of the NT and the two high-resistance contacts. In the case of infinite tubes, on the other hand, the only sources of scattering are the vacancies. It is expected, therefore, that our results should differ considerably from those presented earlier. More precisely, the effect of the vacancies becomes much smaller in our case since the total scattering of the wave penetrating the system is dominated by scattering from the tube ends and from the contacts themselves. The extra (weak) scattering caused by a single vacancy has only a very small effect in this type of system. Naturally, when the number of vacancies is increasing, the effect on the transmission becomes more apparent, which here is illustrated by the case of five vacancies. Another way to describe the transmission properties of our system is to consider an incident wave that is reflected on a defect inside the NT. This backscattered wave will experience another reflection at the tube end and/or at the contact and consequently it will be incident another time at the defect. Such multiple reflections reduce the effect of backscattering of the defect as compared to the ideal case of no chain ends or no external contacts.

Note that our approach applies to systems at nanometer length scale (nanoelectronics). For this type of systems, the results presented here clearly show that low-vacancy concentrations will not produce any dramatic effect on the conductance through the NT.

IV. SUMMARY AND CONCLUSIONS

In this paper we presented a method to calculate the *IV* characteristics of finite carbon NT contacted by two metal electrodes to the surface of the NT. The coupling between the contact and the NT is set to a small value that results in a high-contact resistance and a resonant tunneling type of conductance through the NT. For the pristine NT, the transport along the tube is ballistic at low temperatures. Introducing defects along the tube will cause scattering of the electrons and localization of the electronic wave functions. However, it appears that disorder in the form of moderate bending of the tubes or single vacancies does not cause any additional backscattering of the states, at least not in the central part of the conduction band. Thus, at low-bias voltage, we observe essentially the same resistance in this case as compared to the defect free NT.

ACKNOWLEDGMENTS

Financial support from the Swedish Research Council for Engineering Science (TFR) and the Swedish Natural Science Research Council (NFR) are gratefully acknowledged.

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