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Numerical Study of Transport in Carbon Nanotubes with Lattice Vacancy

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The conductance is calculated for approximately 1.6×10^5 armchair carbon nanotubes (CN's) with a different lattice vacancy in a tight-binding model using a multi-channel Landauer's formula. When the vacancy is much smaller than the circumference of CN, the conductance is quantized into zero, one, and two times the conductance quantum $e^2/\pi\hbar$ depending only on the site-number difference between removed A and B sublattice sites.

KEYWORDS: graphite, carbon nanotube, vacancy, conductance, Landauer's formula, recursive Green's function technique

After the discovery of carbon nanotubes (CN's) in 1991 by Iijima[1], much attention has been focused on carbon networks of the nanometer scale. One important aspect of these systems is that their π electronic structure is critically controlled by the topological structure of sp^2 carbon networks. For example, carbon nanotubes become either metallic or insulating depending on the tubular circumferential vector.[2−11] Because of their unique geometric and electronic structure, they are considered to be a new type of quantum wire. The purpose of this work is to demonstrate a general rule of conductance quantization in the presence of a vacancy.

Recently, effects of scattering on the impurity potential were studied theoretically and it was proved that a Born series for back-scattering vanishes identically for scatterers having a potential with a range larger than the lattice constant.[12] This intriguing fact was related to Berry's phase acquired by a rotation in the wave-vector space in the system described by a $\boldsymbol{k}\cdot\boldsymbol{p}$ Hamiltonian.[13] The conductance was calculated in a tight-binding model by varying the strength of the potential.[14]

Some experiments suggest the existence of defective nanotubes of carpet-roll or papier-mâché forms.[15,16] These systems have many disconnections in the π electron network governing the transport of CN's, and therefore are expected to exhibit properties different from those in perfect CN's. In a graphite sheet with a finite width, for example, localized edge states are formed near the Fermi level in the undoped case, chosen at $\varepsilon=0$, when the boundary is in a certain specific direction.[17−22]

Effects of scattering by a vacancy in armchair nanotubes in the presence and absence of a magnetic field have been studied.[23−25] It has been shown that the conductance at $\varepsilon=0$ in the absence of a magnetic field is quantized into zero, one, or two times the conductance quantum $e^2/\pi\hbar$ for three typical vacancies.[24,25] In this paper we shall perform numerical calculations for approximately 1.6×10^5 vacancies and demonstrate that such quantization is quite general.

To study the conductance of armchair CN's with a lattice vacancy, we use a tight-binding model of a single π band with a nearest-neighbor hopping integral γ_0 and a lattice constant a. The hybridization of σ and π states may be ignored in CN's with a large diameter. An armchair nanotube is known to be always metallic and has two bands in the vicinity of the Fermi energy crossing at $k_y=2\pi/3a$ (K point) and $k_y=-2\pi/3a$ (K' point), where k_y is the wave vector in the axis direction. The energy dispersion near the Fermi energy is approximately given by $\varepsilon=\pm\gamma|k|$, where k is the wave vector measured from the K and K' point and $\gamma=\sqrt{3}a\gamma_0/2$. For a given energy, $\varepsilon=\gamma k\geq0$, for example, there are two channels denoted as K and K' with positive velocity $\gamma/\hbar$ and two with negative velocity $-\gamma/\hbar$.

A unit cell of two-dimensional graphite contains two carbon atoms denoted as A and B constituting a honeycomb network, as shown in Fig. 1. We first consider circular vacancies with a radius w centered on (a) the center of a six-membered ring (ring-center vacancy) illustrated in Fig. 1(a), and (b) an atomic site (site-center vacancy) illustrated in Fig. 1(b), where removed A and B sublattice sites are denoted by open and closed circles. The ring-center and site-center vacancies have six-fold and three-fold symmetry, respectively. Next, we examine the conductance of CN's with a more general vacancy having an arbitrary shape to eliminate effects specific to symmetry. We shall confine ourselves to vacancies in which removed sites are all connected to each other.

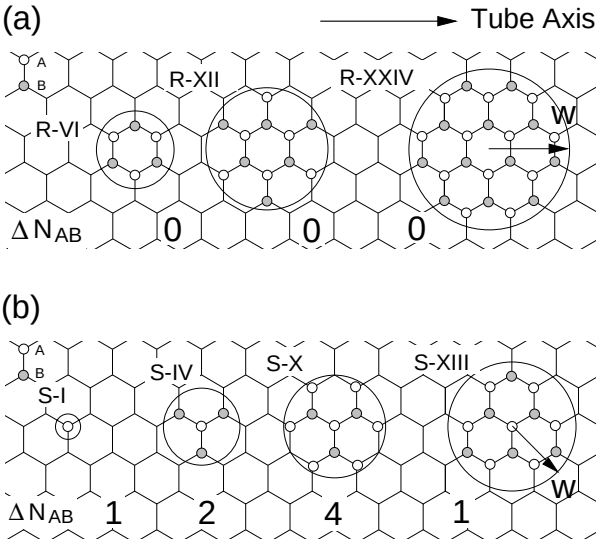

Fig. 1 Examples of (a) ring- and (b) site-center vacancies. Removed A and B sublattice sites are denoted by open and closed circles, respectively, w is the radius of the circle encircling the vacancy, and ΔN_{AB} is the site-number difference between removed A and B sublattice sites.

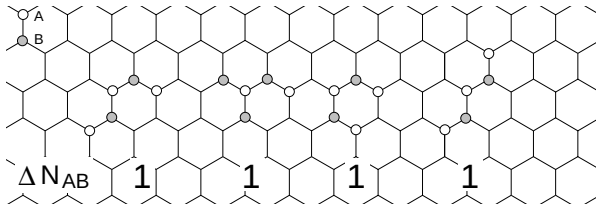

Fig. 2 Examples of vacancies consisting of five carbon atoms. Only "molecules" are shown and the actual number of different vacancies is 12, 12, 6, and 6, from left to right.

Examples of such vacancies consisting of five carbon atoms are shown in Fig. 2. In this case there are only four different shapes, each of which will be called a "molecule." Each molecule usually generates six vacancies having a different configuration by the rotation $\pm 2\pi/3$ and a mirror reflection and a further six by the exchange of A and B sublattice points. Some of these generated vacancies are equivalent particularly for molecules with a certain symmetry and therefore the actual number is usually less than twelve times the number of different molecules. In the case of five-atom vacancies, as shown in Fig. 2 for example, the total number of vacancies is 36. The number of molecules and that of vacancies increases explosively with the number N of removed carbon atoms. We have approximately 14000 molecules and approximately 1.6×10^5 vacancies in total for $5\le N\le 13$. In armchair nanotubes we are concerned with the many vacancies generated from a molecule which give identical conductance because of the presence of the mirror symmetry around a plane containing the axis and around a plane perpendicular to the axis.

An important parameter of the vacancy is ΔN_{AB} defined as $\Delta N_{AB}=|N_A-N_B|$, where N_A and N_B are the number of removed A and B sublattice sites, respectively. For a ring-center vacancy, we have $\Delta N_{AB}=0$ because of the six-fold symmetry. For a site-center vacancy, we have $\Delta N_{AB}\ge 1$. In the case of a general vacancy, $\Delta N_{AB}\ge 1$ and $\Delta N_{AB}\ge 0$ for odd and even N, respectively. For $5\le N\le 13$, approximately 25000 vacancies have $\Delta N_{AB}=0$, 106000 have $\Delta N_{AB}=1$, and 31000 have $\Delta N_{AB}\ge 2$.

The vacancies can be simulated by two models. In the first model (1), we consider the explicit disconnection of bonds around the vacancy. In the second model (2), on-site energy V is introduced at vacancy sites on the perfect network of CN's. It has been shown that model (2) becomes equivalent to model (1) in the limit $V\to\infty$.[25] We use model (1) for ring-center and site-center vacancies and model (2) for general vacancies.

The conductance is calculated by a multi-channel Landauer's formula[26] given by $G=(e^2/\pi\hbar)\sum_{\mu,\nu}|t_{\mu\nu}|^2$, where μ and ν are out-going and in-coming channels, respectively. The transmission $t_{\mu\nu}$ and reflection coefficients $r_{\mu\nu}$ are calculated by a recursive Green's function technique.[27,28] In the following, we shall exclusively consider the case $\varepsilon=0$. In this case, the combinations of $\{\mu,\nu\}$ are given by $\{\mathrm{K},\mathrm{K}\}$, $\{\mathrm{K}',\mathrm{K}'\}$, $\{\mathrm{K}',\mathrm{K}\}$, and $\{\mathrm{K},\mathrm{K}'\}$. The former two correspond to intra-valley scattering within the K point or the K' point and the latter two correspond to inter-valley scattering between K and K' points.

In CN's with a ring-center vacancy, the calculated conductance depends on both the vacancy radius and the circumference of CN's. If the vacancy is much smaller than the circumference of CN's, the conductance is slightly smaller than the perfect conductance $2e^2/\pi\hbar$. The deviation from $2e^2/\pi\hbar$ decreases with the increase of the circumference L in proportion to $(a/L)^2$ for a fixed w and increases with the increase of w. For sufficiently thick nanotubes, it is quite natural to expect that the conductance is a universal function of w_{eff}/L, where w_{eff} is an effective radius of a vacancy and is close to w. More explicitly, for a small w_{eff}/L we can assume:

$$G=\frac{2e^2}{\pi\hbar}\left[1-\alpha\Big(\frac{2w_{\mathrm{eff}}}{L}\Big)^2\right], \tag{1}$$

where α is a constant. In order to determine α and w_{eff} uniquely, we assume that the actual and effective number of removed sites becomes equal to each other when being fitted to a straight line. The latter is given by $4\pi w_{\mathrm{eff}}^2/\sqrt{3}a^2$, where $\sqrt{3}a^2/4$ is half the area of a six-membered ring. Such a procedure gives $\alpha=9.8$.

We calculate the conductance for $10\le L/\sqrt{3}a\le 150$ and $0<\sqrt{3}w/a\le 10$, where $a/\sqrt{3}$ is the distance between nearest-neighbor carbon atoms, and determine the value of w_{eff} by fitting the results to eq. (1) in the region of small w corresponding to $1.9\le G/(e^2/\pi\hbar)\le 2$. The results given in Fig. 3 show that the conductance is given by a universal function of $2w_{\mathrm{eff}}/L$ in the whole range of w_{eff}, as has been expected.

The inset of Fig. 3 shows the resulting effective number of removed sites given by $4\pi w_{\mathrm{eff}}^2/\sqrt{3}a^2$ as a function of the actual number, which shows clearly that they are well correlated to each other. It should be noted that the intra-valley backscattering r_{KK} and $r_{K'K'}$ and inter-valley transmission $t_{KK'}$ and $t_{K'K}$, are always absent for ring-center vacancies because of a mirror symmetry about a plane containing the axis.[29]

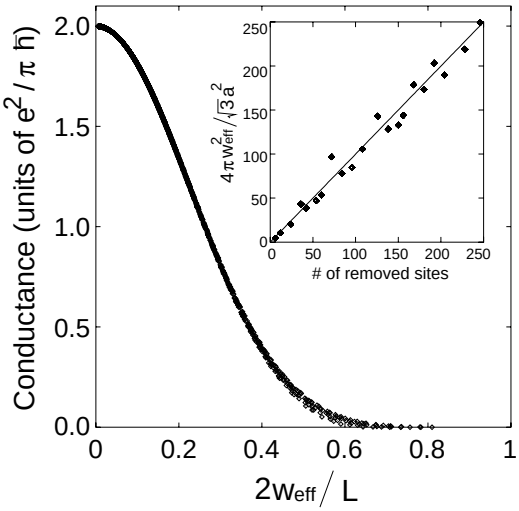

Fig. 3 Calculated conductance as a function of $2w_{\rm eff}/L$ for CN's with a ring-center vacancy. The inset shows the effective number of removed atoms corresponding to $w_{\rm eff}$ as a function of the number of actual removed atoms.

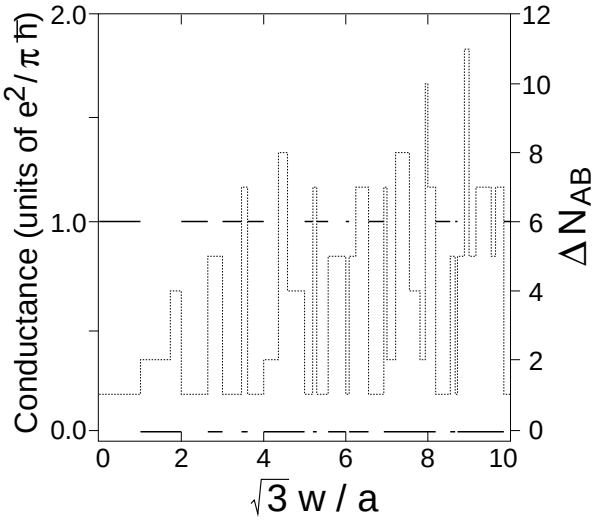

Fig. 4 Calculated conductance as a function of $2w_{\rm eff}/L$ for CN's with a ring-center vacancy. The inset shows the effective number of removed atoms corresponding to $w_{\rm eff}$ as a function of the number of actual removed atoms.

Figure 4 shows an example of calculated conductance and ΔN_{AB} for CN's with a site-center vacancy as a function of $\sqrt{3}w/a$ for $L/\sqrt{3}a=100$ and $0<\sqrt{3}w/a\leq 10$. In this case, the conductance is always quantized into zero or one times the conductance quantum $e^2/\pi\hbar$, in contrast to ring-center vacancies. In fact, we have $G=e^2/\pi\hbar$ for $\Delta N_{AB}=1$ and $G=0$ for $\Delta N_{AB}\geq 2$. These results do not depend on the radius of a vacancy and the circumference of CN's, but depend only on ΔN_{AB}. For $\Delta N_{AB}=1$, both intra- and inter-valley components have an equal amplitude for both transmission and reflection processes, i.e., $|t_{\mu\nu}|=|r_{\mu\nu}|=1/2$. When the conductance vanishes for $\Delta N_{AB}\geq 2$, a perfect reflection occurs within the same valley, i.e., $|r_{\rm KK}|=|r_{\rm K'K'}|=1$.

Figure 5(a) shows the histogram giving the distribution of the conductance for CN's with a general vacancy for $L/\sqrt{3}a=50$. The histogram has a width 5.0×10^{-2} in units of $e^2/\pi\hbar$ and is normalized by the total number of vacancies with specified ΔN_{AB}. The calculated conductance is almost completely quantized into two, one, or zero times the conductance quantum $e^2/\pi\hbar$, depending exactly on whether $\Delta N_{AB}=0$, $\Delta N_{AB}=1$, or $\Delta N_{AB}\geq 2$. In fact, the conductance always vanishes, independent of the shape and configuration of a vacancy, when $\Delta N_{AB}\geq 2$ and the distribution function has a sharp peak at $G=e^2/\pi\hbar$ for $\Delta N_{AB}=1$ and at $G=2e^2/\pi\hbar$ for $\Delta N_{AB}=0$. It has a very small tail on the left-hand side for $\Delta N_{AB}=0$ and 1. This deviation from the quantized conductance arises mainly from vacancies which are exceptionally long in the circumference direction. An example of such vacancies is illustrated in an inset of Fig. 5(a).

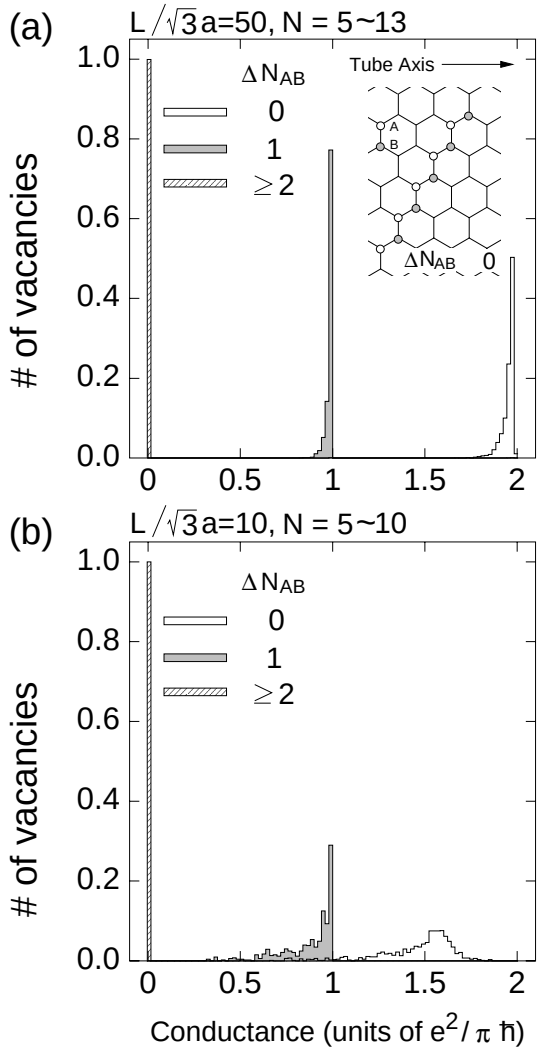

Fig. 6 Calculated distribution of the conductance of C-N's with a general vacancy for (a) $L/\sqrt{3}a=50$ and $5\leq N\leq 13$ and for (b) $L/\sqrt{3}a=10$ and $5\leq N\leq 10$. Open, shaded, and hatched portions denote results for $\Delta N_{AB}=0$, 1, and ≥ 2, respectively. The histogram has a width 5.0×10^{-2} in units of $e^2/\pi\hbar$ and is normalized by the total number of vacancies having specified ΔN_{AB}. The inset shows an example of a vacancy which causes a large deviation from the quantized conductance.

When the circumference of CN's is not large enough compared with the size of a vacancy, the conductance quantization is destroyed, as shown in Fig. 5(b) for $L/\sqrt{3}a=10$. In this case, the distribution function has a broad peak around $G=1.6\times e^2/\pi\hbar$ when $\Delta N_{AB}=0$ and

has a sharp peak at $G = e^2/\pi\hbar$ accompanied by a long tail for $\Delta N_{AB} = 1$. When $\Delta N_{AB} \geq 2$, however, the conductance is always given by $G = 0$ and a perfect reflection occurs.

Recently, effects of strong and short-range scatterers on the conductance were studied using an effective-mass approximation developed earlier.[12] The resulting conductance was shown to be quantized into zero, one, and two times of the conductance quantum, in agreement with the general rule obtained in this paper. This will be reported elsewhere.[30]

In this letter, we have studied the effects of a lattice vacancy on the quantum transport in carbon nanotubes. The conductance has been calculated for approximately 1.6×10^5 CN's with a different lattice vacancy using a multi-channel Landauer's formula. The results have demonstrated clearly that for vacancies much smaller than the circumference, the conductance vanishes for $\Delta N_{AB} \geq 2$ and is quantized into one and two times $e^2/\pi\hbar$ for $\Delta N_{AB} = 1$ and 0, respectively, where ΔN_{AB} is the difference in the number of removed A and B sublattice sites.

Acknowledgments

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