Localization in carbon nanotubes within a tight-binding model

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We analyze the influence of defects on conductance, density of states, and localization in (N_a, N_a) armchair carbon nanotubes within a tight-binding model. Using the transfer-matrix method, we calculate the reflection (related to the conductance) from a sequence of defects and relate its energy dependence near the Fermi level to the appearance of a quasibound state. This state is also seen in the density of states and in the energy dependence of the quasiparticle lifetime. We compute the localization length $\xi(\omega)$ as a function of energy ω. Comparison of $\xi(0)$ with the mean free path l_{mfp} in the limit of small defect concentration c and small defect strength E leads to a simple approximate relation $\xi(0)\approx 3l_{\mathrm{mfp}}=3\times 3aN_at^2/2cE^2$ (t— hopping integral, a—lattice constant). [S0163-1829(99)12939-4]

The discovery of carbon nanotubes (NT's) (Ref. 1) (see Refs. 2 and 3 for a review) provides a unique opportunity to study the influence of disorder on electronic structure and transport properties of genuine one-dimensional systems of almost macroscopic size. The role of disorder in these systems is a controversial issue. On one hand, there are observations of ballistic conductance in individual single[4] and multiwall[5] tubes. On the other hand, temperature dependence of the conductivity of the NT ropes suggests possible onset of weak localization[6] in low-T region. The measurements performed on the seemingly similar tubes tend to differ significantly in transport behavior,[7–9] depending on the conditions of sample preparations or—perhaps—the number of defects in the samples.

The purpose of the present paper is to provide simple quantitative criteria to estimate importance of the disorder effects in single wall armchair NT's. We study localization of electronic wave functions for different defect strengths E and concentrations c. Electronic properties of the NT's are shown to be determined by the presence of quasibound states near the Fermi energy. This result is supported by our calculation of the electronic conductance and density of states.

In contrast to some earlier works,[10] we study spatially restricted (pointlike) defects, which do not change the global topology of the NT lattice. This category includes chemical substitutions (e.g., nitrogen or boron substitution of carbon), vacancies, and 5-77-5 (bond rotation[11]) defects. Our starting point is a tight-binding Hamiltonian with one p-orbital per carbon atom[12] and with the hopping integral $t\approx -3$ eV. The defects are modeled by random modulation (with δ distribution) of the site energy. Various defect strengths representing typical defects are $E\approx -2.5$ eV for C→N substitution,[13] $E\approx 6t$ for 5-77-5 defect,[12] and $E/t\gg N_a$ to mimic a vacancy.

First, we calculate the reflection coefficient of the electron incident on a barrier made by a sequence of unit cells containing defects. The reflection coefficient $R\leqslant 1$ is directly related to the conductance Γ (Ref. 14), $\Gamma/\Gamma_0=(1-R)$, where $\Gamma_0=e^2n_c/h$, and n_c is the number of conducting channels. The reflection is calculated using the transfer-matrix method, as described in detail in Ref. 12.

Typical result for R in the case of 12 defects distributed randomly on 300 unit cells of (5,5) NT is presented in the Fig. 1. The reflection shows rapid oscillations as a function of energy of the incident electron. They depend on the particular arrangements of the defects. Apart from these oscillations, the overall energy dependence of R is related to the single defect results. In general, the bigger the reflection R_1 from a single defect, the bigger is R for a sequence of the defects. Noticeable enhancements of R correspond to boundaries of the energy regions with a different number of conducting channels: the increase of R is due to the reduced velocity of electrons near the top or bottom of consecutive bands.

The fluctuations of R, characteristic for a given defect arrangement, are quantum effects related to interference of the electron waves scattered from different defects. Let us neglect for a moment these quantum effects and treat the scattering electrons as classical particles reflected from a point defect with a probability R_1.[15,16] We then get an estimation of the reflection from N identical defects:

$$R_N=\frac{NR_1}{1+(N-1)R_1}. \tag{1}$$

This is plotted in the Fig. 1 against the exact result. One can see that Eq. (1) explains quite well the energy dependence of reflection from a small number of defects in terms of that from a single defect, except that it does not show the oscillations. In the case of a single defect, we found previously[12] that the reflection at $\omega=0$ can be well described by the scaling law

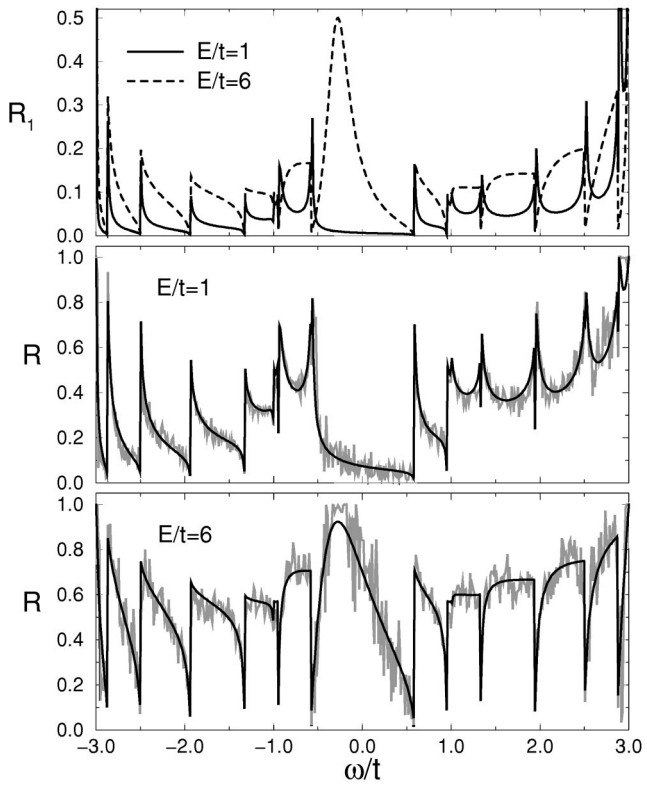

FIG. 1. Reflection from a single point defects (top panel) and from 12 point defects in (5,5) nanotube of the length of 300 unit cells. Black heavy lines—the result obtained neglecting interference effects, Eq. (1).

$$R_1(0)=\alpha\left(\frac{E}{N_a t}\right)^2, \quad \alpha\approx 1/6 \tag{2}$$

which holds for $|E/t|\ll N_a$. Note that $\omega=0$ coincides with the value of the chemical potential at $T=0$ K for the half-filled band case, corresponding to undoped NT. Although Eq. (2) can be strictly established for a point defect only, it is a good approximation for more extended defects, provided that their size is much smaller than the NT radius. If the system is large enough, we can define a defect concentration c per carbon atom: $c=N/4N_aL$ (L is the NT length in units of the lattice constant $a=0.14\times\sqrt{3}/2$ nm). We then find, using Eq. (1), an estimation of conductance for $|E/tN_a|c\ll 1$, neglecting interference effects (Ref. 15):

$$\frac{\Gamma_N}{\Gamma_0}\approx\frac{l_e}{l_e+aL}, \quad l_e=\frac{a}{4cN_aR_1}\overset{\omega\to 0}{\to}\frac{a}{4\alpha}\frac{N_a}{c}\left(\frac{t}{E}\right)^2 \tag{3}$$

which defines a scattering length l_e (Ref. 16). For $l_e\gg La$ the conductance is almost equal to the ideal limit Γ_0—this is the ballistic range. In the opposite limit, when $l_e\ll La$, the conductance goes as inverse of L—this is the limit of validity of Ohm's law.

Let us discuss now the energy dependence of R upon the defect strength E. For a weak defect ($E/t=1$), one can see an apparent depression of the reflection in the central, two-channel per spin region near $\omega=0$, and a relatively large reflection outside this region. For the strong defect ($E/t=6$), there is a clear increase of R to almost complete reflection ($R=1$) in a region close to $\omega=0$. At the same time

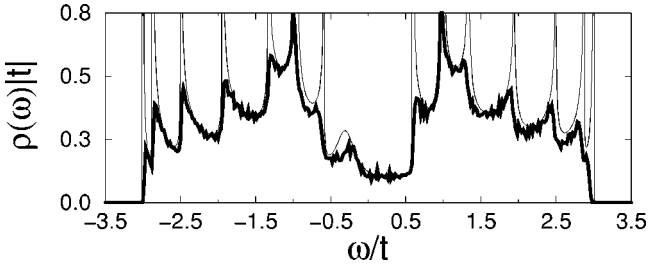

FIG. 2. DOS for (5,5) NT with concentration $c=5\%$ of point defects having strength $E/t=6$. Heavy solid line—exact diagonalization of a chain of $L=3000$ unit cells. The thin solid line is obtained using a single defect solution. Bands of localized states, existing for $5<\omega/t<7$, are not shown here.

the reflection in the rest of the energy range increases moderately only, as compared to the weak defect case. These results agree with those of Ref. 17, where almost complete suppression of the conductance in the case of a very strong defect was found.

The maximum of $R(\omega)$ in the region near $\omega=0$ moves towards $\omega=0$ with the increase of defect strength. In the case of a single point defect, the reflection coefficient is equal to $R_1^{max}=1/n_c$ at its maximum. The maximum is due to the appearance of a quasibound state.[12,18] This state is also seen in the density of states (DOS). Exact to terms linear in defect concentration c, the change in DOS due to point defects reads

$$\pi\delta\rho(\omega)=cE\ \mathrm{Im}\frac{[dF(\omega)]/d\omega}{1-EF(\omega)}, \tag{4}$$

$$F(\omega)=\frac{1}{4LN_a}\sum_{k\nu}\frac{1}{\omega+i0^+-\varepsilon_{k\nu}}, \tag{5}$$

where $\varepsilon_{k\nu}$ denotes the νth band of the perfect NT. Total DOS, obtained by adding $\delta\rho(\omega)$ and the perfect lattice DOS, is shown in the Fig. 2 together with the result of exact diagonalization of the Hamiltonian corresponding to a NT of the length $L=3000$ and $E/t=6$. One can see a pronounced peak of the quasibound state, centered at $\omega\approx-0.2t$, corresponding to a maximum in R in Fig. 1. We note that the resonance peak cannot be obtained if we restrict the sum in Eq. (5) to only two conducting bands. In this case, the two band model[13] does not describe correctly the energy dependence of DOS and of R. This is due to the fact that the scattering processes to other bands become important as the defect strength increases.

For strong defects, the usual Born approximation is insufficient to describe the frequency dependence of dynamics of quasiparticles, especially near the quasibound state. In the case of diluted strong scatterers, one has to include exactly all processes corresponding to multiple scattering on the same site. The self-energy of the quasiparticle, exact up to linear term in c, is then given by

$$\Sigma=\frac{cE}{1-EF(\omega)}. \tag{6}$$

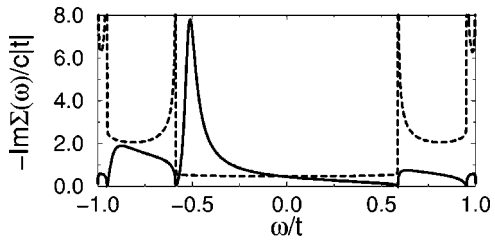

FIG. 3. Energy dependence of $-\mathrm{Im}\,\Sigma/c|t|$ for the (5,5) NT and point defects of strength $E/t=2$. Heavy line is obtained from Eq. (6), and dashed line from the Born approximation.

Note that in the case of point defects, Σ does not depend on the band index and on the wave vector. The imaginary part of the self-energy gives the lifetime of the quasiparticle due to the scattering by defects.

The imaginary part of $F(\omega)$, which gives the density of states of a perfect NT, can be obtained explicitly for any N_a. It is an even function of ω, $\mathrm{Im}\,F(-\omega)=\mathrm{Im}\,F(\omega)$. As a result, the real part of F vanishes at $\omega=0$. This leads to the expression for the lifetime,

$$\hbar\tau^{-1}(\omega=0)=\frac{cE^2}{\sqrt{3}N_a|t|}\left[1+\frac{E^2}{3N_a^2t^2}\right]^{-1}, \tag{7}$$

exact up to linear term in c. This result is a generalization of the one obtained in Ref. 13 to the case of arbitrary strong defects. In fact, keeping only terms linear with respect to E^2 in Eq. (7) makes a good approximation (exact to within 10%) for $|E|$ as large as ≈ 15 eV for (10,10) NT.

The energy dependence of the lifetime may be important in estimation of more subtle transport properties of the system such as the thermoelectric power. The Born approximation gives a symmetric $\tau(\omega)$. On the other hand, the ω dependence of τ obtained from Eq. (6), and presented in Fig. 3, shows substantial asymmetry. We note a maximum in $\tau^{-1}(\omega)$, corresponding to the position of the quasibound state found in Fig. 2.

Using the results for the quasiparticle lifetime, we find an explicit expression for the mean-free path at $\omega=0$ in the limit of weak defect strength and small c. For the two bands intersecting at the Fermi wave vector $k_F=2\pi/3$, we have

$$\varepsilon_{k\pm}=\pm t\left(1-2\cos\frac{k}{2}\right), \quad v_F=\frac{a|t|}{2\hbar}\sqrt{3} \tag{8}$$

and the mean-free path $l_{\mathrm{mfp}}=v_F\tau$ reads

$$l_{\mathrm{mfp}}=\frac{3aN_a}{2c}\frac{t^2}{E^2}. \tag{9}$$

This coincides with the expression for the scattering length l_e, derived above. The agreement is due to the neglect of interference effects from scattering from different defects both in Eqs. (6) and in (3).

We now examine the role of quantum interference effects in scattering by comparing l_e with results of numerical computations which exactly include these effects. A synthetic measure of the role of disorder is given by a localization length ξ, which is related to the spatial extent of the electron wave function. In many-band systems, the localization length can be calculated from the smallest positive Lyapunov exponent λ_L^{min}, obtained from product of the transfer matrices:[19] $\xi_L^{-1}=\lambda_L^{min}$. In Fig. 4, we present the results for the localization length as a function of energy. They were obtained for systems of length of $10^5,\ldots,10^7$ unit cells, depending on parameters c, E. Further increase of L did not noticeably change ξ_L. The presented results were calculated by averaging over 50 different realizations of the disorder. The accuracy of $\xi=\lim_{L\to\infty}\xi_L$, estimated from the standard deviation, was of the order of a few percent.

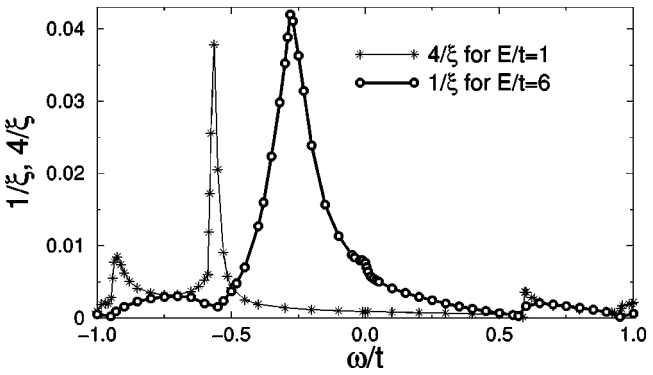

FIG. 4. Energy dependence of inverse of the localization length for (5,5) NT's with the concentration $c=0.5\%$ of point defects of strengths $E/t=1$ and $E/t=6$.

The energy dependence of the inverse of the localization length in general follows the corresponding dependence of the reflection R. In particular, the regions of sharp increase of ξ^{-1} are due to the enhanced scattering near the band top or bottom. The pronounced maximum in ξ^{-1} near $\omega=-0.2t$ for $E/t=6$ is related to the existence of the quasibound state. The localization length for weak defects is a smooth function of ω near $\omega=0$. With increase of E, a tiny maximum in $\xi(\omega)$ emerges near $\omega=0$, suggesting appearance of more complex quasibound states, possibly due to neighboring defects.

It is interesting to compare the value of the localization length with the calculated mean-free path l_{mfp} for $\omega=0$. In Fig. 5, the value of $l_{\mathrm{mfp}}/\xi(0)$ is plotted as a function of the concentration c. For $|E/tN_a|<1$ the points corresponding to different values of E and N_a fall onto lines which all converge to a common point at $c=0$, where $l_{\mathrm{mfp}}/\xi(0)\approx 0.33$. The $c=0$ limit of the ratio $l_{\mathrm{mfp}}/\xi(0)$ is similar to that for the one-band Anderson model,[20] where $l_{\mathrm{mfp}}/\xi(0)=0.5$. Our result can be applied to determine if a given NT sample should

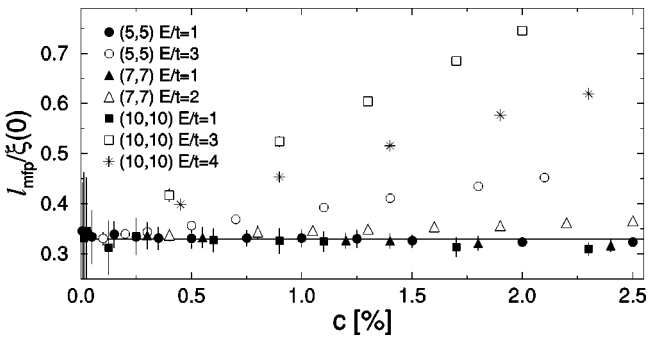

FIG. 5. Ratio $l_{\mathrm{mfp}}/\xi(0)$ vs concentration c of defects of various strengths in NT's of various radii. Solid line corresponds to the relation $l_{\mathrm{mfp}}=0.33\xi(0)$.

exhibit properties characteristic for ballistic, Ohmic, or localized regime.[15] In the particular case of ''5-77-5'' defect corresponding to $E/t \approx 6$, with equilibrium defect concentration $c \approx 1.5 \times 10^{-5}$ (Ref. 11) we find $\xi(0) \approx 10\,\mu$m for (10,10) NT. This shows that a NT of length 2 μm (Ref. 4) can be well in the ballistic limit if no other strong defects are present.

In application of the above results to a real NT, one should be aware of some effects not included in the present approach. First, electron interactions are neglected here and we assume that the NT can be treated as a Fermi liquid. While a thorough discussion of the effects of Coulomb interaction is beyond the scope of the present paper, we expect that our results are valid for systems where disorder effects dominate over electron correlations. A numerical example of such a case is provided by exact calculation of the Kubo conductivity at $T=0$ K obtained for a model of interacting electrons on a small two-dimensional cylinder with disorder.[21] These results suggest that in the weak interaction limit, the conductivity only slightly depends on the interaction.

Second, the results obtained for the individual NT may not be directly applied to ropes composed of NT's. Indeed, upon doping with electron donors and acceptors, the conductivity of NT ropes shows an increase by more than one order of magnitude.[22] It is difficult to reconcile this with the rather smooth dependence of the localization length on the energy at $\omega=0$. One may speculate that an interplay of the intertube interaction (leading to formation of a pseudogap[23]) and the intrinsic disorder in ropes reduces the localization length near the Fermi level.

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