Backscattering in carbon nanotubes: Role of quantum interference effects

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The backscattering contribution to the conductivity, irrelevant for metallic single-walled carbon nanotubes, is proved to become more significant for doped semiconducting systems, in agreement with experiments. In the case of multiwalled nanotubes, the intershell coupling is further shown to enhance the contribution of backscattering for “metallic” double-walled, whereas it remains insignificant for “metallic/semiconducting” double-walled systems. © 2001 American Institute of Physics. [DOI: 10.1063/1.1421643]

Single-walled carbon nanotubes (SWNTs) can be either metallic or semiconducting depending on their helicities, i.e., how the graphene sheet is rolled up.1 For weak uniform disorder, the application of the Fermi golden rule for metallic SWNTs have demonstrated micron long mean free paths2 in agreement with experiments, clearly pointing towards ballistic transport.3–5

Notwithstanding, quantum transport in SWNTs is richer than in the one-dimensional chain, given the implication of additional symmetries of electronic eigenstates associated to the circumferential helicity. This has been widely illustrated through the theoretical study of conduction upon introduction of single defects such as vacancies, impurities or topological defects.6 In particular, the absence of backscattering was demonstrated for single impurity with long range potential in metallic tubes7 and a stepwise reduction of the conductance was inferred from multiple scattering on a few lattice impurities.7,8 Resonant electronic scattering by defects was recently confirmed experimentally.9

On the other hand, electrostatically or chemically doped semiconducting SWNTs have been reported to behave as diffusive conductors with short mean free paths, several orders of magnitude lower than the ones of reported structurally equivalent metallic SWNTs.5,10,11 In all these experiments, the mean free path (l_e) is deduced from the measured conductance using G~(e^2/h)l_e/L_tube (L_tube the length of the SWNTs) and values range from 2 nm10 to ~30 nm,5 Upon doping, the position of the chemical potential (Fermi energy) with respect to the charge neutrality point is shifted downward (hole doping) or upward (electron doping) and hence may come closer to a Van Hove singularity. This may result in a factor \sqrt\langle v_F^2\rangle much smaller than the typical v_F deduced from the metallic SWNTs. Moreover, quantum interference effects (QIE) responsible for localization in 1D systems need to be clarified in the context of carbon nanotubes. Indeed, on multiwalled carbon nanotubes (MWNTs), Bachtold et al.,12 have reported negative magnetoresistance and Aharonov–Bohm oscillations, consistent with the manifestation of quantum interferences in the weak localization regime. This experiment was interpreted by assuming a current predominantly carried in the outermost shell (taken metallic), and mean free path and coherence lengths were deduced from conventional theory. It is surprising that quantum interferences that have been described for the two-dimensional propagation (with many more conducting channels), still account properly for the behavior of a single metallic nanotube shell, which only presents two conducting channels at the charge neutrality point. In that perspective, the debate of ballistic13 against diffusive12,14 conduction in MWNTs is a great issue of concern.

All these considerations can be addressed by rewriting the conductance as

\[
G \sim \frac{e^2}{h} \sqrt{\langle v_F^2\rangle} \tau_e m |\delta\sigma| \sum_j \frac{N_j}{s} \left| \psi_j(E) \right|^4
\]

as long as \xi \sim N_j l_e > L_tube (with \tau_e the mean free time of eigenstates given by the Fermi golden rule, N_j the number of conducting channels, and \xi the selected localization length) and by evaluating properly the contribution of backscattering. The quantum correction (|\delta\sigma|) to the Bloch–Boltzmann conductivity (\sigma_{BB}), is related to the probability of return to the origin of electronic wavepackets, that is connected to the participation ratio (PR), an energy dependent quantity which measures the “spreading” of the electron eigenstates commonly used to address QIE in weak or strong localization regimes.15,16 For an eigenstate \psi(E) described by its N coefficients \psi_j(E) in a tight-binding basis set, the PRs read

\[
PR(E) = \left( \sum_j \left| \psi_j(E) \right|^2 \right)^2 \sum_j \left| \psi_j(E) \right|^4
\]

and it can be shown that an average of the probability of return to the origin in real space is equivalent to an average of the inverse PR on the spectral bandwidth. Accordingly, the amplitude of the quantum correction to the electronic con-
ductivity can be estimated as\textsuperscript{17} $\sigma_{\parallel}^{\parallel} \sim \sigma_{\parallel}^{\parallel} \sim \text{PR}^{-1}$ (for $N \to \infty$). Eigenstates characterized by a linear scaling in $N$ are uniformly extended and associated with a vanishing contribution of QIE, i.e., $\sigma_{\parallel}^{\parallel} \sim \sigma_{\parallel}^{\parallel} \sim 0$. Instead, localized states are related to strong contributions of QIE, i.e., $\sigma_{\parallel}^{\parallel} \sim \sigma_{\parallel}^{\parallel} \sim 1$, whereas scaling laws PR$(N) = N^\alpha$, with $0 < \alpha < 1$, indicate the relative strength of QIE in the diffusive regime.

In this letter we present detailed calculations of the PRs for different tubes, addressing the role of disorder and intertube coupling on their transport properties. We use the standard and reliable one-electron tight binding model including intertube interactions (for MWNTs) fitted to \textit{ab initio} calculations.\textsuperscript{18} Disorder is included by a random modulation of onsite energies within the range $[-W/2, W/2]$ ($W = 0.054, 0.135, 0.98$ eV) that simulate chemical disorder. The mean free path associated for a given disorder is deduced from $l_n \sim (\gamma_0/W)^2 d_{nt}$, ($d_{nt}$ is the nanotube diameter, $\gamma_0 = 2.67$ eV the hopping between carbon sites).\textsuperscript{2}

Effect of disorder in SWNTs: The density of states together with the PRs of several metallic chiral and achiral SWNTs are reported in Fig. 1 (results are nearly identical for $W = 0.054$ and 0.135 eV). For Fermi energies at the charge neutrality point, PR$=N$ for armchair and achiral tubes, whereas PR$=2N/3$ for zigzag SWNTs. An energy dependence relation between the position of Van Hove singularities and the amplitude of PRs is also found. For the Bloch states of zigzag and armchair tubes (the central subband of armchairs excepted), there is a degeneracy due to mirror-inversion symmetry. Each value of the wave vector is associated with two Bloch states with the same energy, but with an opposite phase variation along the circumference: $\psi_n^+ = \exp(i k \theta / 2 \pi)$ and $\psi_n^- = \exp(-i k \theta / 2 \pi)$, where $k > 0$ is a positive integer and $\theta_n$ is the polar angle of the site $n$ located on a given ring. By a linear combination of $\psi^+$ and $\psi^-$, a Bloch state with any PR value between $2N/3$ and $N$ can be constructed. The lowest value is given by the combination $\sqrt{\psi^+ + \psi^-}/\sqrt{2}$, which is a “standing wave” along the circumference: $\psi_n^+ + \psi_n^- = 2 \cos(k \theta_n/2 \pi)$, leading to PR = $N[(\cos^2(k \theta_n/2 \pi))^2]/\cos^4(k \theta_n/2 \pi)) = 2N/3$. Due to this uncertainty, the PR is thus not a well-defined quantity for degenerate eigenstates, but a small amount of disorder is enough to split degeneracy and the PRs shown in Fig. 1 become meaningful. For nondegenerate eigenstates (as found in chiral metallic SWNTs and armchair SWNTs close to Fermi energy), perturbation theory applies, so that the PRs are not much reduced by disorder and remain close to $N$. Instead, for degenerate states (zigzag metallic SWNTs), disorder favors standing waves, i.e., states with a real wave function, because the Hamiltonian is real and symmetric. Thereby the PRs are close to $2N/3$, which explains the general behavior shown in Fig. 1. Values much smaller than $2N/3$ are attributed to standing waves along the tube axis $z$, obtained by mixing $k$ and $-k$. Bloch states close to the Van Hove singularities. At the charge neutrality point of the metallic SWNT (6,6), the eigenstates are basically insensitive to disorder and follow the linear scaling expected for fully extended states (inset Fig. 2). Note that the absence of backscattering demonstrated by Ando \textit{et al.}\textsuperscript{7} corresponds to long range scatters, simulated by identical onsite energies in a given cell (2 atoms), and uncorrelated energies from one cell to another. Here our results (random onsite energies from one atom to another) go further demonstrating that even for short range scatters, the effect of small disorder on backscattering and QIE still remain purely marginal in metallic SWNTs.

The stronger contribution of QIE for doped semiconducting SWNTs is demonstrated by the scaling behavior of PRs as reported in Fig. 2 (main frame). The chemical potential chosen for the doped semiconducting nanotube (7,5) is upshifted artificially by 0.333 $\gamma_0 = 0.89$ eV with respect to the charge neutrality point, to simulate a doping that can be obtained experimentally by means of an anthraquinone–lithium redox chemical reaction\textsuperscript{19} (it is assumed that the shift of the position of the Fermi level scales linearly with the doping concentration).

![FIG. 1. PRs (solid lines) and density of states (dashed lines) for metallic armchair (6,6), zigzag (18,0), and chiral (9,6) tubes. PRs are normalized to the number $N$ of atoms, and have been averaged over a few disorder configurations ($W = 0.054$ eV). The densities of states are given in arbitrary units.](image1)

![FIG. 2. Comparison of the scaling of the PRs for metallic (6,6) (inset) and doped semiconducting (7,5) single-walled nanotube (for which the chemical potential lies nearby a Van Hove singularity, $E_F = \gamma_0/3.333$ upshifted with respect to the charge neutrality point). The dashed lines indicate the linear scaling (PR$=N$). Comparison is made for two values of disorder strength $W = 0.054$ eV (open circles) and 0.136 eV (filled circles). The third disorder strength $W = 0.98$ eV (filled diamonds) taken for (7,5) at the same Fermi energy leads to $l_n \sim 20$ nm.](image2)
concentration). Deviation from the linear scaling are found (PR=∗N) with an increasing contribution of QIE with disorder strength (α∼0.98, 0.95 for W=0.054 and 0.136 eV, respectively). For a much larger disorder strength (W=0.98 eV), that corresponds to a mean free path l=20 nm, the saturation of the PR provides an approximate localization length of ξ≈40 nm, that follows the Thouless relation.20 Hjort and Stafström21 found that for the same disorder, the localization length of the (6,6) at charge neutrality point is ξ≈100 nm. Hence, for doped semiconducting tubes, the mixing between quantum channels induced by disorder, results in an enhanced contribution of QIE, when compared to the metallic tubes at charge neutrality point. This also points towards a chemical potential dependent sensitivity of the transport regime of a MWNT, whenever conduction is restricted to the outermost shell.12,13 To complete this argument, we add the effect of intershell coupling as it promotes charge transfer between shells in MWNTs.

**Effect of disorder and intershell coupling in commensurate MWNTs:** The characteristic sensitivity to disorder of QIE in MWNTs is illustrated in Fig. 3 for small disorder (W=0.054 eV). For the double-walled metallic armchair tube (6,6)@11,11)), the average PR close to the charge neutrality point is roughly half the value for the isolated armchair tube, for same disorder parameter. According to the previous discussion, the [δσ] contribution is now nonnegligible and contributes to a reduction of the conductivity (confirmed by the scaling analysis of PR—not shown here). Such effect is similar in double-walled metallic zigzag tube, but is reduced when the outer shell is semiconducting. This can be understood from the fact that there exist states in the metallic/semiconducting undoped double-walled nanotube that are mainly weighted in the inner metallic shell, so they are less affected by disorder as in a single metallic SWNTs. As MWNTs typically consist of ~2/3 of semiconducting shells, the effect of disorder may be limited in such systems.13

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17. [δσ] is related to (2e2/h)2D∫r dr(τ=0, t)e−iτt(τ=0, t) , with D = u2 τ τ = l/τ y the mean free time, and τ y the inelastic time which limits the contribution of the probability of return to the origin (τ = 0). Such quantity is given by [(τ e−(iθt)/(h))/τ]2.