Many body effects in finite metallic carbon nanotubes.

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The non homogeneity of the charge distribution in a carbon nanotube leads to the formation of an excitonic resonance, in a similar way to the one observed in X-ray absorption in metals. As a result, a positive anomaly at low bias appears in the tunnelling density of states. This effect depends on the screening of the electron–electron interactions by metallic gates, and it modifies the coupling of the nanotube to normal and superconducting electrodes.

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Introduction. The addition of single electrons to finite carbon nanotubes induces measurable effects, related to the finite spacing between the energy levels and to the electrostatic energy associated to the electron charge. The standard model for Coulomb blockade assumes that the electrostatic potential inside the system is raised by the addition of an individual electron, preventing tunnelling unless different charge states are degenerate. The potential is supposed to be constant throughout the sample. When it is not the case, non equilibrium effects may occur, which are related to the Fermi edge singularities associated to the sudden ejection of a core electron in a metal. One dimensional systems, like the nanotubes, are good candidates for observing these effects, as screening is suppressed, and the electrostatic potential inside them can be modulated by metallic gates in their proximity. Other effects related to modulations in the electrostatic potential were considered in [17].

We calculate in this paper the changes in the tunnelling density of states due to the non homogeneity of the electrostatic potential, for different possible experimental setups. The effects discussed here look similar, but are different from the Luttinger liquid features expected near a contact [16, 17, 18, 19], which have also been observed in nanotubes [20, 21].

The next section describes the model to be studied. The main results are presented next. Then, we analyze how to incorporate Luttinger liquid effects. The expected behavior at energies comparable to the spacing between individual electronic levels is discussed next. The paper concludes with a section on possible experimental consequences of the effects analyzed here.

The model. We consider only a nearest neighbor hopping, $t$, between $\pi$ orbitals at the C atoms. Each sub-band in a zigzag nanotube can be modelled by a one dimensional tight binding hamiltonian with two sites per unit cell and two different hoppings, $t$ and $t(1 + e^{i\phi_n}) = 2te^{i\phi_n/2}\cos(\phi_n/2)$, where $\phi_n = (2\pi n)/N, n = 1, \ldots, N - 1$ is the transverse momentum associated to the subband, and $N$ is the number of C atoms in a transverse section of the nanotube.

In a metallic nanotube, $N = 3M$, where $n$ is an integer. There are two gapless bands, characterized by $n = \pm M$. Other bands with $n \neq M$ have a gap, $\Delta_n = t|1 \pm 2\cos(\phi_n/2)|$. Thus, the electronic states of the two bands which cross the Fermi level can be described by the simple hamiltonian:

$$H = \sum_{n,s} e_n^\dagger e_{n+1,s} + \text{h.c.}$$

The Fermi velocity can be written as $v_F = 2ta$, where $a$ is the lattice constant. We consider a finite nanotube with $L$ unit cells. When an electron hops into the nanotube its charge will be distributed throughout its length. In a first approximation, this charge can be calculated using the Hartree or Hartree-Fock approximation. As the electrostatic potential is weakly screened in a one dimensional geometry, the charge distribution can be influenced by metallic gates in the vicinity. We first consider the setup depicted in Fig. 1, where the electron is emitted from a metallic electrode at one end of the nanotube. More complicated geometries will be studied later.

We consider the two spin degenerate bands which cross the Fermi level. The polarization of the remaining bands by the potential associated to the charge of a single electron will be small, and it can be treated perturbatively. The radius of the nanotube acts as a short distance cutoff of the Coulomb potential. We describe the effects of the metallic electrode by an image charge induced by the physical charge on the nanotube. We approximate the electrostatic interaction between electrons located at
unit cells $n_1$ and $n_2$ as measured from the gate, as:

$$V_{\text{tot}}(n_1, n_2) = V_{\text{el}}(n_1 - n_2) - V_{\text{el}}(n_1 + n_2 + \frac{d}{a})$$

$$- V_{\text{el}}(-n_1 - n_2 + \frac{d}{a}) + V_{\text{el}}(-n_1 + n_2)$$

$$V_{\text{el}}(n) = \frac{e^2}{\sqrt{n^2a^2 + R^2}} \quad (2)$$

where $d$ is equal to twice the distance between the nanotube and the electrode, and $R$ is the radius of the nanotube.

**Results.** The electrostatic potential and the induced charge when the number of electrons in one of the four subbands at the Fermi level is one above half filling (which is taken as the neutral situation) is shown in Fig. 2.

The calculations have been done using the Hartree approximation. The results are significantly changed if exchange is included. We find enhanced Friedel oscillations, and a sizable gap pinned at the Fermi level. Some of these effects are due to changes in bulk properties which are unrelated to the addition of electrons. In the following, we present results obtained within the Hartree approximation, where the features associated to single charges are easier to isolate.

A non negligible fraction of the charge is localized by its image near the electrode. This leads to a reduction of the repulsive electrostatic potential in that region. This effect is relatively small compared with the gaps of the higher lying subbands of a small carbon nanotube, so that the assumption of neglecting their polarization is justified. We also find substantial Friedel oscillations, which have periodicity two, as $k_F = \pi/a$.

The charge distribution depends strongly on the location of the external electrodes. Fig. 3 compares the potential calculated previously with the one obtained when there are two symmetrically placed electrodes at each end of the nanotube, and in the absence of electrodes, all other parameters being the same.

The effects associated with the non homogeneous charge distribution after the injection of a single electron are described, within the Hartree approximation used above, as a change of all electronic levels. Taking this effect into account, the electronic density of states is changed as: i) The overlap between the initial and final eigenstates is reduced. In the limit of vanishing level spacing, this leads to the orthogonality catastrophe induced by the sudden switching of a local potential. ii) The potential shifts the electrons towards the electrode, enhancing the density of states at the Fermi level in its vicinity. This is the so called excitonic effect and it opposes the orthogonality catastrophe.

The final local density of states, in the limit of vanishing level splitting, goes as $D(\omega) \propto \omega^{(1-\delta)^2-1}$, where $\delta > 0$. Hence, for sufficiently small perturbations, $\delta < 1$, the tunnelling density of states is enhanced at the ends of the nanotube. The effective density of states can be obtained by assuming that the hamiltonian after the charging of the nanotube is modified from an initial expression $\mathcal{H}_0$ to $\mathcal{H}_t = \mathcal{H}_0 + \delta V_{sc}$, where $\delta V_{sc}$ is the modification of the Hartree-Fock potential induced by the extra electron. Assuming that the tunnelling takes place at position 1 and subband 1 near the edge of the nanotube, the tunnelling density of states at zero temperature is:

$$G(\omega) = \prod_{j \neq 1} |f_{j,j}(0, N|0, N)_{0,j}|^2 \times \sum_n |f_{1,1}(n, N + 1|\epsilon_0|0, N)_{0,1}|^2 \delta(\omega - \epsilon_n + \epsilon_0) \quad (3)$$

FIG. 2: Electrostatic potential and charge (inset) at the edge of a nanotube with an additional electron and $L = 1024$ unit cells. The parameters used are $e^2/\epsilon_F = 5.4$, $R/a = 3$ and $d/a = 1$.

FIG. 3: Electrostatic potential induced by a single electron when there is one electrode (full line), two symmetrically placed electrodes (dashed line), and no electrodes (dash-dotted line). The inset shows the non equilibrium density of states for the same three cases.
where the states $|n,N\rangle_{(0,f),j}$ are eigenstates of $H^J_{0,j}$ with $N$ electrons, and $j = 1, \cdots , 4$ is the band index. As these states are Slater determinants, the calculation is reduced to a sum of determinants of overlaps between one particle wavefunctions.

Results obtained for the injection in a neutral nanotube with $L = 1024$ unit cells and the parameters which lead to the electrostatic potentials shown in Fig. 3 are shown in the inset of Fig. 3, and, in more detail, in Fig. 4, where they are also compared with the results obtained neglecting $\delta V_{sc}$.

**Luttinger liquid effects.** The calculation discussed above takes into account, in an approximate way, the interaction corrections expected at the boundary of a Luttinger liquid. The anomalous exponent in the density of states can be estimated using first order perturbation theory, and it is finite within Hartree-Fock theory 29. Note that the calculations also describe approximately the crossover to a Fermi liquid behavior at sufficiently high energies 29.

For sufficiently long wires, we can use the bosonization approach. The calculation of the final state effects leading to eq. 4 can be extended without too much difficulty to the case of a Luttinger liquid with forward interactions. The initial and final bosonized hamiltonians are 29:

$$H_0 = \frac{1}{2} \int_{x>0} dx 4\pi v_F \Pi^2(x) + \frac{v_F}{4\pi} [\partial_x \Phi(x)]^2$$
$$+ \frac{e^2}{8\pi^2} \int_{x>0} dx \int_{y>0} dy \partial_x \Phi(x)V_{tot}(x,y)\partial_y \Phi(y)$$
$$H_f = H_0 + \frac{1}{2\pi} \int_{x>0} dx \delta V_{sc}(x)\partial_x \Phi(x)$$

The hamiltonians $H_0$ and $H_f$ differ by a term which is linear in the boson fields, and there is a simple unitary transformation, $\mathcal{U}$ which transforms one into the other. The calculation of the density of states can be written as the Fourier transform of the expression:

$$G(t) = \langle 0\vert \psi(x=0) e^{iHt} \psi^\dagger(x=0) \vert 0 \rangle$$
$$= \langle 0\vert \psi(x=0) e^{iH_0t} \mathcal{U} \psi^\dagger(x=0) \vert 0 \rangle$$

(5)

where $|0\rangle$ is the ground state of $H_0$, and we are assuming that the end of the nanotube is at position $x = 0$.

The hamiltonians in eq. 4 are quadratic in the bosonic fields, and the expression in eq. 5 can be calculated by normal ordering the operators, which depend exponentially on the bosonic degrees of freedom. If we neglect the breakdown of translational symmetry induced by the gates, and the long range effects of the Coulomb potential, the tunnelling density of states becomes:

$$D(\omega) \propto |\omega|^{\frac{1}{2} \left(1-g^2 \frac{\delta V}{v_F}\right)^2-1}$$

(6)

where $g$ is the parameter which describes the Luttinger liquid properties, and $\delta V = (2\pi)^{-1} \lim_{k \to 0} \int_0^\infty e^{ikx} \delta V_{sc}(x)dx$. For repulsive interactions, $g < 1$, and Luttinger liquid effects tend to suppress the positive anomaly studied here.

In the presence of gates, the electron–electron potential is not translationally invariant. The screening effects of the gates reduce locally the interactions, which are unscreened away from the gate. A related situation was considered in 27, a Luttinger liquid connected to non interacting gates. The quadratic hamiltonian, eq. 4, which is defined on a half line, $x,y > 0$, can be solved by defining a related problem on the entire axis 29. We can estimate in a simple way the value of the parameter $g$ at the edge of the nanotube from the energy associated to a fluctuation of the charge density on a scale $l < L$ in that region. This estimate, in the thermodynamic limit, leads to the charge compressibility and to the bulk value of $g$. In the absence of screening by gates, the inverse compressibility diverges logarithmically with the size of the system. It is easy to show that, in the geometry depicted in Fig. 1, the energy associated to a fluctuation of size $l$ is given by a term which diverges logarithmically as $l \to \infty$ minus a term which tends to a constant. The second term describes the screening effects of the gate. Thus, for large nanotubes and at sufficiently low energies, bulk effects determine the value of $g$, and the tunnelling density of states will be given by eq. 6. At high energies, on the other hand, the screening of the electron–electron interactions by the gate makes $g \to 1$ and the non equilibrium effects described here will dominate. The crossover between these two regimes depends on the limiting value of the interaction, which, in turn, is influenced by screening by other parts of the system (see below).

**Single electron properties.** At sufficiently low energies or temperatures, a finite nanotube behaves like a quantum dot 1, 2, 4, 5, 6, 8, 29, 30. For the parameters used here, $e^2/v_F = 5.4$, the level splitting and the charging energy are comparable. The Hartree calculation described above allows us to estimate the charging energy, $E_C = E_{N+1} + E_{N-1} - 2E_N$. The Coulomb potential considered here, in the absence of gates, leads...
to $E_C \approx e^2 L^{-1} \log(L/R)$. The screening by the vertical gates, as in Fig. 1, reduces this value by a quantity which scales as $L^{-1}$. For the parameters used in Fig. 2 we find a level spacing (in units of $v_F/a$) of $\Delta E = 0.00306$, and a charging energy $E_C = 0.0196$.

The final state effects considered here manifest themselves, at the scale of the level spacing, as a dependence of the tunnelling amplitude on the charge state. This effect can be included by adding assisted hopping terms to the hamiltonian $H_{12}$ (see also $H_{34}$). This effect, in our case, is rather small. Using the parameters in Fig. 2, the value of the square of the renormalized creation operator $\langle \hat{N}^2 \rangle$ at zero energy is 0.002616 for the transition $N \rightarrow N + 1$ and 0.002612 for $N + 1 \rightarrow N + 2$ (note that these transitions involve the same electronic level). The smallness of the final state effects on single particle levels shows that the enhancement of the effective tunnelling of states is a collective phenomenon, which arises from the cumulative changes in many levels near the Fermi energy.

Conclusions. We have analyzed, semi–quantitatively, the appearance of a low energy peak in the tunnelling of states in nanotubes due to the inhomogeneous potential induced by the charge of a single electron. This zero bias anomaly is closely related to the excitonic resonance which appears in X-ray absorption in metals [14, 24]. The formation of this resonance enhances the tunnelling density of states, although it is induced by the Coulomb interaction. The strength of this anomaly depends on the screening of the nanotube by metallic contacts and gates, and, presumably, it can be tuned experimentally.

The strength of the enhancement of the tunnelling density of states can be suppressed by Luttinger liquid effects, for repulsive electron–electron interactions. Luttinger liquid effects are reduced when the interaction is screened, which, on the other hand, favors the existence of the excitonic resonance. The effects discussed here should also be present in multiwall nanotubes. In a system with many bands at the Fermi level, only one contributes to the resonance, while the others induce an orthogonality catastrophe (note that we have considered four bands here, see eq. 2).

The presence of an excitonic resonance makes the transport properties of the nanotube similar to those of Luttinger liquids with attractive interactions. It can lead to the enhancement of the proximity effect in nanotubes attached to superconducting electrodes [35, 36, 37], and increase, in general, the tendency towards superconductivity in these systems [38].

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