Intersubband Edge Singularity in Metallic Nanotubes

E. G. Mishchenko and O. A. Starykh

Phys. Rev. Lett. **107**, 116804 — Published 8 September 2011

DOI: 10.1103/PhysRevLett.107.116804

Intersubband Edge Singularity in Metallic Nanotubes

E. G. Mishchenko and O. A. Starykh
Department of Physics and Astronomy, University of Utah, Salt Lake City, Utah 84112, USA

Tunneling density of states of both the massless and massive (gapped) particles in metallic carbon nanotubes is known to have anomalous energy dependence. This is the result of coupling to multiple low-energy bosonic excitation (plasmons). For both kinds of particles the ensuing effect is the suppression of the density of states by electron-electron interactions. We demonstrate that the optical absorption between gapless and gapped states is affected by the many-body effects in the opposite way. The absorption probability is enhanced compared with the non-interacting value and develops a power-law frequency dependence, $A(\omega) \propto (\omega - \Delta)^{-\gamma}$, where $\gamma \approx 0.2$ for typical nanotubes.

PACS numbers: 73.21.Hb, 73.22.Lp

Introduction. Energy spectrum of metallic carbon nanotubes (MNT) has massless band electrons propagating with velocity $v = 8 \times 10^5$ m/s. Despite degeneracy of the spectrum at the Fermi level the backscattering between the left- and right-movers is suppressed due to the orthogonality of the two species. This makes MNT an ideal application for the Luttinger Liquid (LL) theory [1–5]. Observations of MNTs' low-energy properties [6–8] are consistent with the picture of LL. According to the latter the eigenmodes of the interacting system are bosons, while electrons are represented by coherent combinations of infinite number of those modes. This leads to strong modification of the electron spectral properties close to the Fermi level. A step in the distribution function is replaced with the interaction-dependent power law behavior. Furthermore, the tunneling density of states becomes energy dependent, $\nu(\epsilon) \propto \epsilon^{\alpha}$. The exponent $\alpha = (1-g)^2/2Ng$ depends on the total number of channels N, and the effective coupling constant $g = v/u$ is determined by the velocity u of a collective charged mode – plasmon.

In addition to the linear gapless states MNTs have subbands with the nonzero angular momentum along the NT axis, see Fig. 1. The lowest subband has a gap $\Delta = v/R$ from the Fermi level that depends on the tube radius R. In the absence of many-body effects the corresponding density of states has a one-dimensional van Hove singulary. However, as demonstrated by Balents [9], the interaction with massless electrons decreases the density of states of the massive particle in a way reminiscent of LL supression, $\nu(\epsilon) \sim (\epsilon - \Delta)^{-1/2+\beta}$, with $\beta = (1-g^2)^2/2Ng$. The underlying physics of this nonperturbative modification is indeed the same as in the case of LL: coupling to multiple low-energy excitations. Surprisingly, while technical advances of Ref. [9] have been used to further the theory of one-dimensional systems beyond conventional LL approach [10], its physical implications for nanotubes have not received due attention.

While the edge singularity uncovered in Ref. [9] could potentially be probed by tunneling measurements or via x-ray absorption, it remains unexplored if the underlying many-body physics can be seen with the less experimentally intricate techniques, in particular in the optical absorption. The main difference comes from the fact that an optical transition happens between *two states* strongly affected by the interaction with LL, in contrast to transition from a deep core band, as is the case in the x-ray absorption. Thus knowledge of a single-particle Green's function is insufficient to address this question.

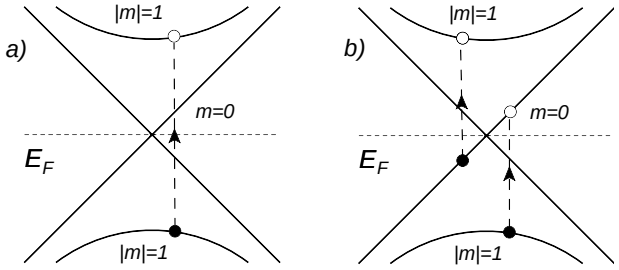

FIG. 1: Processes responsible for the optical absorption in metallic nanotubes. a) Polarization along the NT axis: only transitions with no change of the angular momentum, $m \to m$, are allowed (except $0 \to 0$). The E_{11} transition is indicated by the dashed line, the transition threshold $\omega = 2\Delta$. b) Polarization perpendicular to the NT axis: $m \to m \pm 1$ is required. The processes involving right-moving massless particles are indicated. At zero temperature $T = 0$ the E_{01} and E_{10} transitions are contributing to the optical absorption. The transition threshold $\omega = \Delta$.

In the present paper we demonstrate that the solution to this problem depends strongly on the polarization of the incident electromagnetic field. In the case of *longitudinal* polarization the dipole optical transitions with the change of the azimuthal quantum number are forbidden. The allowed transitions, e.g. E_{11} shown in Fig. 1a), are *not affected* by the interactions with low frequency plasmons. The physical reason for this is the cancellation of the many-body effects in the propagators of the massive electron and hole states by the vertex corrections (which describe plasmon-mediated interactions in the final state of absorption transition). Interaction of the electron and

the hole suppresses their probability to be at the same point via the (essentially single-particle) physics of Sommerfeld factor, leading to strong *suppression* from the free particle density of states [11]. In particular, for a short-range interaction, $A_\parallel(\omega) \propto \sqrt{\omega - 2\Delta}$ [12].

To the contrary, transitions with the change of the angular momentum, see Fig. 1b), are allowed for the *transverse* polarization of electric field. For these transitions the cancellation does not occur and Coulomb interaction leads to a singular deviation of the absorption spectrum from the non-interacting model. According to the latter absorption has a step-like threshold at $T = 0$: e.g. for the E_{01} transition, $A_\perp(\omega) \propto \int dp \delta(\Delta + \frac{p^2}{2m} + v|p| - \omega) \propto \Theta(\omega - \Delta)$. By taking electron-electron interactions into account we obtain the divergent power law behavior,

$$A_\perp(\omega) \propto \frac{\Theta(\omega-\Delta)}{(\omega-\Delta)^\gamma}, \qquad \gamma = \frac{2-g-g^3}{2N}. \tag{1}$$

Since $g < 1$ the effects of Coulomb interaction result in the *enhancement* of the optical absorption, unlike the x-ray absorption which is suppressed by the many-body effects. Below we derive our main result Eq. (1).

Intersubband transitions. Electronic band structure of carbon nanotubes [13] follows from the underlying two-dimensional spectrum of graphene, $\varepsilon(\mathbf{p}) = \pm v|\mathbf{p}|$. The components of the quasimomentum $\mathbf{p}$ are measured from the corresponding Dirac points in the first Brillouin zone. In case of rolled-up graphene sheets the circumferential momentum p_y is quantized giving a set of one-dimensional subbands. For "metallic" folds some cuts pass through the Dirac points, so that $p_y = m/R$, and the resulting spectrum consists of the subbands, $\varepsilon_m(p) = \pm v\sqrt{p^2 + m^2/R^2}$, classified by the angular momentum quantum number, $m = 0, \pm 1, \pm 2, ...$; for (n, n) armchair tubes the NT radius $R = 3na/2\pi$ where $a = 1.4$ Å is the distance between carbon atoms. The following Hamiltonian describes the interaction of band electrons with the external electric field of frequency ω polarized perpendicularly to the MNT axis (we set $\hbar = 1$),

$$\hat{H}_0 = -iv\sigma_x \frac{\partial}{\partial x} - \frac{iv}{R}\sigma_y \frac{\partial}{\partial \theta} + \frac{evE_0}{\omega}\hat{\sigma}_y \cos\theta \sin\omega t, \tag{2}$$

where $\theta = y/R$ is the circumferential angle. We now consider the optical absorption corresponding to a transition from a massless ($m = 0$) right-moving state to a massive particle ($m = 1$) in the first excited subband close to its bottom ($p \ll 1/R$), as indicated by the left dashed line in Fig. 1b):

$$\frac{\hat{\psi}_R(t,x)}{\sqrt{4\pi}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \to \frac{\hat{\Psi}(t,x)}{\sqrt{4\pi}} \begin{pmatrix} 1 \\ i \end{pmatrix} e^{i\theta}, \tag{3}$$

where the operators $\hat{\psi}_{R,L}(t,x)$ and $\hat{\Psi}(t,x)$ describe the one-dimensional propagation of massless and massive particles respectively. The probability of intersubband absorption per unit length of MNT

$$A_\perp(\omega) = \frac{\pi N e^2 v^2 E_0^2}{4\omega^2}\, \mathcal{V}(\omega) \tag{4}$$

is determined by the following correlation function,

$$\mathcal{V}(\omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} dx e^{i\omega t} \langle [\psi_R^\dagger(t,x)\hat{\Psi}(t,x), \hat{\Psi}^\dagger(0,0)\hat{\psi}_R(0,0)] \rangle \tag{5}$$

Note that the overall coefficient in Eq. (4) also takes into account the transitions (all of which have the same probability) to states with $m = -1$ as well as transitions from the left-moving states, and also includes the total channel degeneracy N. The correlator (5) calculated for free electrons yields the Golden Rule probability and reproduces the step-like threshold discussed in the introduction.

Electron-electron interaction. Coulomb interaction in quasi-one-dimensional wires has the form,

$$\hat{H}_i = \frac{1}{2}\int \frac{dq}{2\pi} V(q)\hat{n}(q)\hat{n}(-q), \tag{6}$$

where $\hat{n}$ is the operator of the total electron density. Neglecting backscattering ensures that the formalism of the Luttinger Liquid can be used. Backscattering and Umklapp scattering amplitudes, $\sim e^2 a/R$, are suppressed by virtue of the large radius of a NT, $R \gg a$ [14]. For ungated MNT $V(q) = -2e^2 \ln|q|R$, where $q \ll 1/R$. In case of a metallic gate located a distance d away, the geometry we assume here, the logarithm is cut-off, $V(0) = 2e^2 \ln d/R$.

Coulomb interaction is screened by the electron-hole excitations in the metallic ($m = 0$) subbands, and is given by the RPA dynamic propagator

$$V(0) \to U(\omega, q) = V(0)\frac{\omega^2 - q^2v^2}{(\omega + i\eta)^2 - q^2u^2}, \tag{7}$$

The poles of the expression (7) correspond to collective eigenmodes of LL, plasmons, propagating with the velocity $u = v\sqrt{1 + NvV(0)/\pi} \equiv v/g$. Plasmons are accompanied by electric field and the corresponding scalar potential can be expressed via the plasmon creation $\hat{a}_q^\dagger$ and annihilation $\hat{a}_q$ operators,

$$e\hat{\phi}(t,x) = u(1-g^2)\sum_q \sqrt{\frac{\pi|q|}{2gN}}\Big[\hat{a}_q e^{-i|q|ut+iqx} + c.c\Big], \tag{8}$$

to be in agreement with Eq. (7). In the bosonization scheme plasmons $\hat{a}_q$ represent total charge mode of the system, while the remaining $N-1$ modes $\hat{b}_{iq}$ are charge neutral (they account for spin and/or band degeneracy) and propagate with the Fermi velocity, $\hat{H} = u\sum_q |q|\hat{a}_q^\dagger \hat{a}_q + \sum_{i=1}^{N-1} v\sum_q |q|\hat{b}_{iq}^\dagger \hat{b}_{iq}$.

For the calculation of the correlator (5) we need the bosonized expression for the electron operators. Electrons in gapless subbands are coherent combinations of

bosonic modes, $\hat{\psi}_{R,L}(t,x) = \frac{1}{\sqrt{2\pi R}}\hat{U}_{R,L}e^{\hat{k}_{R,L}(t,x)}$, where $\hat{U}_{R,L}$ are fermionic counting operators; the ultraviolet momentum cut-off $1/R$ is being set by the NT radius. The phase operators are given by,

$$\hat{k}_{R,L}(t,x) = \sqrt{\pi}\sum_q \frac{1 \pm g\ \mathrm{sgn}\ q}{\sqrt{2gN|q|}}\Big[\hat{a}_q e^{-i|q|ut+iqx} - c.c\Big] + \sqrt{2\pi}\sum_{i=1}^{N-1}\sum_q \frac{\Theta(\pm q)}{\sqrt{N|q|}}\Big[\hat{b}_{iq}e^{-i|q|vt+iqx} - c.c\Big], \quad (9)$$

where the upper/lower sign is for the right/left-moving electrons respectively.

Massive particle. We utilize a simple eikonal approach to describe electrons belonging to the upper subband. We first demonstrate how the results of Ref. [9] are recovered with it. Schrödinger equation, describing interaction of the massive particle close to the bottom of the subband with the fluctuating electric field (8) has the form,

$$\left(i\frac{\partial}{\partial t} - \Delta + \frac{1}{2\mu}\frac{\partial^2}{\partial x^2}\right)\hat{\Psi}(t,x) = e\hat{\phi}(t,x)\hat{\Psi}(t,x), \quad (10)$$

where the effective mass is $\mu = 1/vR$. For the heavy particle the solution can be obtained in the form,

$$\hat{\Psi}(t,x) = e^{\hat{K}(t,x)}\hat{\Psi}^{(0)}(t,x). \quad (11)$$

Here $\hat{\Psi}^{(0)}$ is the solution of Eq. (10) for $\hat{\phi} = 0$. Using the identity, $\partial_t e^{\hat{K}} = (\partial_t K + \frac{1}{2}[K, \partial_t K])e^{\hat{K}}$, and *neglecting* spatial derivatives of the phase $\hat{K}$, we obtain the following expression for the latter,

$$\hat{K}(t,x) = (1-g^2)\sum_q \sqrt{\frac{\pi}{2Ng|q|}}\Big[\hat{a}_q e^{-i|q|ut+iqx} - c.c\Big] + it\frac{\pi u(1-g^2)^2}{2Ng}\sum_q 1. \quad (12)$$

The last term while formally divergent simply represents the renormalization of the energy gap Δ. This can be verified directly by a perturbation calculation to the lowest order in the dynamic interaction $U(\omega, q)$. The averaging over fermionic and bosonic operators can now be performed independently in the calculation of the massive particle's Green's function:

$$G_>(t,x) = G_>^{(0)}(t,x)\langle e^{\hat{K}(t,x)}e^{-\hat{K}(0,0)}\rangle = -iR^\beta\sqrt{\frac{\mu}{2\pi t}}\frac{e^{-i\Delta t + i\mu x^2/2t}}{(u^2t^2 - x^2)^{\beta/2}}, \quad (13)$$

where $\beta = (1-g^2)^2/2Ng$, in agreement with Ref. [9].

Edge singularity. Using the electron operators for massless (9) and massive (11)-(12) states we can now express the correlator (5) through the bosonic average,

$$\mathcal{V}(\omega) = \frac{1}{2\pi R}\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}dx e^{i\omega t}G_>^{(0)}(t,x) \times\langle e^{-\hat{k}_R(t,x)}e^{\hat{K}(t,x)}e^{-\hat{K}(0,0)}e^{\hat{k}_R(0,0)}\rangle. \quad (14)$$

As follows from Eq. (13) the spatial integral in Eq. (14) converges on distances $x \sim \sqrt{t/\mu}$. Since $t \sim 1/(\omega - \Delta)$ we observe that $x \ll vt,\ ut$. It is therefore sufficient to set $x = 0$ in the correlation function of bosonic operators in Eq. (14). After straightforward calculation the latter is found to be $(R/vt)^{1-\gamma}$ with γ defined in Eq. (1). Here, as well as in the massive fermion's Green's function (13), it is assumed that $t \to t - i\eta$, a complex plane is cut along the positive half of the imaginary t-axis and the chosen branches assume real values on the negative half of the imaginary t-axis.

Performing now the x-integral in Eq. (14) and then the time integral by deforming the contour to follow the sides of the branch cut we obtain for $\omega > \Delta$,

$$\mathcal{V}(\omega) = \frac{1}{2\pi v\Gamma(1-\gamma)}\left(\frac{\Delta}{\omega - \Delta}\right)^\gamma. \quad (15)$$

For $\omega < \Delta$ the contour can be closed in the lower half-plane, and, because there are no singularities there, the function $\mathcal{V}(\omega)$ vanishes. When the interaction is absent, $\gamma \to 0$ and the function $\mathcal{V}(\omega)$ approaches the one-dimensional density of states, $\mathcal{V}(\omega) = \Theta(\omega - \Delta)/2\pi v$ of the massless electrons. For a MNT $N = 4$. Assuming $R \approx 1$ nm, and thus, $\Delta = 0.5$ eV, and $d \approx 50$ nm, the Coulomb coupling constant $g \approx 0.2$, which gives $\gamma = 0.2$.

It is worth noting that we also derived our results (1) and (15) using the formalism of Ref. [9] as well as with the help of the unitary rotation described in Ref. [18].

Discussion. The physical origin of the singularity (15) is the non-perturbative interaction with multiple low-energy plasmon excitations. As external photon is being absorbed, excitation of an electron and a hole is impeded by the creation of the virtual plasmons. This is reflected in the suppression of each particle's density of states. The interaction in the final state (vertex corrections), to the contrary, *facilitates* propagation of the electron-hole pair [16]. In the LL description fluctuating plasmon field amounts to the additional phase. When both particles belong to massive subbands (e.g. in the E_{11} transitions) the phases accumulated by the electron and the hole are *opposite* (due to opposite charges) and thus cancel each other. Formally this can be seen from Eq. (14): in that case the phase $\hat{k}_R(t,x)$ has to be replaced with $\hat{K}(t,x)$ and the bosonic average drops out. Thus, the absorption lineshape is not affected by many-body effects for the longitudinal polarization.

In case of E_{01} absorption the electron and the hole belong to *different* subbands. Since they propagate with unequal velocities the phases accumulated from *the same* fluctuating electric field are different [15]. The vertex corrections do not exactly cancel the self-energy contributions and the absorption line is modified. What is surprising about the spectrum (15) is that the enhancement by vertex corrections *dominates*. This leads to the overall increase in the optical response.

The increase of the transition probability by interactions is known to occur in the x-ray edge problem in conventional metals [17]. If the interaction is weak enough excitonic contribution dominates, but with the increasing interaction strength the subleading quadratic corrections begin to suppress absorbtion via orthogonality catastrophe mechanism. We emphasize that in our problem the enhancement occurs for any value of the interaction strength g. Moreover, as opposed to the x-ray edge problem, in our case both particles involved acquire non-trivial interaction-induced dynamics.

One can make an interesting connection with the phase diagram of the two-subband quantum wire studied in Ref. [18]. It was found there that for sufficiently small density of electrons in the second (higher) subband *relative* charge fluctuations between the two subbands are gapped. This correlated state is driven by pair-tunneling processes which are strongly enhanced by the intersubband forward scattering (contained in (6)). In our case the second subband is empty but it remains true that optically excited particles there are strongly correlated with charge fluctuations in the lower (Luttinger liquid) subband. This correlation, encoded in the phase factors of (14), is the reason for enhanced response (15).

Effects of finite doping and temperature emphasize the difference between E_{01} and E_{11} transitions. Because typical energy gaps $\Delta \sim 1$ eV the population of the gapped subbands changes insignificantly at room temperatures or small levels of doping the shape of E_{11} should not change appreciably. The behavior of the E_{01} absorption is to the contrary very sensitive due to participation of gappless states. The behavior at $E_F \neq 0$ is easy to infer from Fig. 1b): for small dopings the lineshape is simply given by $\frac{1}{2}[A_\perp(\omega+E_F)+A_\perp(\omega-E_F)]$, and two separate thresholds (with the relative shift of $2E_F$) appear.

To consider finite T effects it is sufficient to do this only for the bosonic operators in Eq. (5) since fermionic Green's function $G_>$ is not affected at $T \ll \Delta$ and $G_< \approx 0$. For $T \sim \omega - \Delta > 0$ the modification of the lineshape is standard for LL problems: $A_\perp \propto [\max(T,\omega)]^{-\gamma}$. Additionally, subgap absorption ($\omega < \Delta$) appears for finite temperatures: the bosonic average in Eq. (14), $(\pi TR/v \sinh[\pi Tt])^{1-\gamma}$, now develops branching points in the lower half-plane at $t = -i/T,\ -2i/T, ..$ The asymptotic behavior at $\Delta - \omega \gg T$ is determined by the first of those points, $\mathcal{V}(\omega) \propto \exp(-\frac{\Delta-\omega}{T})$. The interaction strength only affects the pre-exponential factor.

Summary. We have predicted singular power law enhancement of the optical absorption between gapless and the first gapped subbands of a single-wall metallic nanotube for the perpendicular polarization of the incident radiation. The enhancement is the result of coupling of both states to multiple plasmon excitations of MNT. For typical MNTs the corresponding exponent is $\gamma \approx 0.2$ and depends only weakly on the NT radius. Note that while the singularity should be present in multiwall NTs as well, the larger number of channels N and disorder scattering from intrinsic incommensurability would be detrimental for its experimental observation.

Acknowledgments. Useful discussions with M. Raikh, L. Balents, and A. Imambekov are gratefully acknowledged. This work was supported by DOE, Office of Basic Energy Sciences, Grant No. DE-FG02-06ER46313 (E.M.) and by the NSF Grant No. DMR-0808842 (O.S.).

[1] D. C. Mattis and E. H. Lieb, J. Math. Phys. **6**, 304 (1965).
[2] I. E. Dzyaloshinskii and A. I. Larkin, Sov. Phys. JETP **38**, 202 (1974).
[3] F. D. M. Haldane, J. Phys. C **14**, 2585 (1981).
[4] T. Giamarchi, *Quantum Physics in One Dimension* (Clarendon Press, Oxford, 2004).
[5] for a recent review, see V. V. Deshpande, M. Bockrath, L. I. Glazman and A. Yacoby, Nature **464**, 209 (2010).
[6] M. Bockrath, D. H. Cobden, J. G. Lu, A. G. Rinzler, R. E. Smalley, L. Balents, and P. L. McEuen, Nature **397**, 598 (1999).
[7] Z. Yao, H. W. Ch. Postma, L. Balents, C. Dekker, Nature **402**, 273 (1999).
[8] H. Ishii *et al.*, Nature **426**, 540 (2003).
[9] L. Balents, Phys. Rev. B **61**, 4429 (2000).
[10] M. Pustilnik, M. Khodas, A. Kamenev, and L. I. Glazman, Phys. Rev. Lett. **96**, 196405 (2006); A. Imambekov, L. I. Glazman, Science **323**, 228 (2009).
[11] T. Ogawa and T. Takagahara, Phys. Rev. B **44**, 8138 (1991).
[12] We do not discuss here subgap absorption by excitons that exist even for metallic NTs, as measured by F. Wang *et al*, Phys. Rev. Lett. **99**, 227401 (2007).
[13] R. Saito, G. Dresselhaus (MIT), and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
[14] C. L. Kane, L. Balents and M. P. A. Fisher, Phys. Rev. Lett. **79**, 5086 (1997); R. Egger and A. O. Gogolin, Phys. Rev. Lett. **79**, 5082 (1997).
[15] This is the manifestation of the Doppler effect: indeed, when formally, $u \gg v$ there is no difference in the phase acquired by a "fast" massless particle compared with the "slow" massive one as both the massless and masive particles are slow on the scale of plasmons. As a result both exponents approach each other, $\alpha \approx \beta$.
[16] The competition between self-energy and excitonic contributions in 1D edge problems was first pointed out by T. Ogawa, A. Furusaki, and N. Nagaosa, Phys. Rev. Lett. **68**, 3638 (1992).
[17] G. Mahan, *Many-Particle Physics*, (Plenum Press, New York, 1990).
[18] J. S. Meyer and K. A. Matveev, J. Phys.: Condens. Matter 21, 023203 (2009).