“X-Ray Edge” Singularities in Nanotubes and Quantum Wires with Multiple Subbands

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Band theory predicts a \((\epsilon - \Delta)^{-1/2}\) van Hove singularity in the tunneling density of states at the minimum energy \((\Delta)\) of an unoccupied subband in a one-dimensional quantum wire. With interactions, an orthogonality catastrophe analogous to the x-ray edge effect for core levels in a metal strongly reduces this singularity to the form \((\epsilon - \Delta)^{\beta-1/2}\), with \(\beta \approx 0.3\) for typical carbon nanotubes. Despite the anomalous tunneling characteristic, good quasiparticles corresponding to the unoccupied subband states do exist.

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I. INTRODUCTION

It is well known that one-dimensional (1d) metals are profoundly influenced by interactions. The generic behavior for a 1d system with a single conduction band is that of a Luttinger liquid, in which the quasiparticle excitations of the non-interacting system are converted into spin and charge collective modes. These collective modes are largely orthogonal to the bare quasiparticle states close to the Fermi surface, hence leading to a dramatic power-law suppression of the tunneling Density of States (DOS) at the Fermi energy. A similar vanishing occurs in the momentum-dependent single-particle spectral function, signaling complete breakdown of the quasiparticle picture. Indeed, tunneling experiments evidence the novel nature of the Luttinger liquid much more strongly than do other measures such as four-probe resistance and optical conductivity, which are essentially probes of collective modes. There now appears to be increasing evidence for Luttinger liquid behavior in carbon nanotubes, \([1]\) which are perhaps the most ideal probes of collective modes. These collective modes are largely orthogonal to the bare quasiparticle states. Such multiple subband structures exist both in carbon nanotubes and semiconductor quantum wires. \([2]\) which are perhaps the most ideal experimental quantum wires to date. \([3,4]\)

In this paper, we address the behavior of the tunneling DOS far above the Fermi energy. As the voltage bias between a tunneling tip and the quantum wire is increased, it becomes possible to add an electron not only to the conduction band(s), but to higher energy unoccupied subbands. Such multiple subband structure exists both in carbon nanotubes and semiconductor quantum wires. In the former case, the unoccupied subbands are essentially states of different angular momentum around the graphitic cylinder. For semiconductor systems, the higher subbands arise from different standing-wave modes transverse to the wire’s propagation direction in the confinement region. In a non-interacting model, the density of states would exhibit van Hove singularities at the subband edges. In one dimension, these singularities are divergent, giving a contribution \(\rho_0(\epsilon) \sim \sqrt{m(\epsilon - \Delta)^{-1/2}}\) for energies just above the subband edge at \(\epsilon = \Delta\) (\(m\) is the subband effective mass). An asymmetric peak structure has indeed been observed in STM measurements of individual nanotubes on gold surfaces. \([1,5]\)

How do interactions affect these van Hove singularities? A simplified, though unphysical model in which the mass of the higher subband is taken to be infinite provides considerable insight. In this limit the higher energy subbands can be replaced by discrete, localized levels. The “x-ray edge” problem of a localized level interacting with a conduction sea was solved by Nozieres and de Dominicis \([6]\), and is one of the first demonstrations of an orthogonality catastrophe. Physically, the core hole is “dressed” through interactions with conduction electrons, which see the hole as a scattering center. A bare or undressed hole is then orthogonal to its dressed counterpart, since an infinite number of conduction electrons are available to scatter off of it. This leads to a broadening and reduction of the tunneling density of states from a sharp delta-function to a power law singularity. While this effect is superficially similar to the suppression of spectral weight in the Luttinger liquid, it is in fact quite distinct. It is due not to the absence of a well-defined core hole excitation, but due to its mixing with the conduction sea. The distinction is emphasized by the fact that x-ray edge singularities are present in any dimension, not just in 1d.

Suppose now that the mass of the higher subband is taken finite. Since for the tunneling density of states only a single particle is being added to the metal, one is faced with understanding the behavior of a heavy particle in a Luttinger liquid. This problem has been investigated by a number of authors in a different context. \([7,8]\) These authors were primarily concerned with the mobility of the heavy particle in response to an external electric field at finite temperature. For the tunneling DOS, one is interested in a rather different property – essentially, the overlap between the two ground states in the presence and absence of the heavy particle. This overlap may be thought of as a boundary condition changing operator \([9]\), and is completely outside the Hilbert space of the problem in which the heavy particle is always present.

In this paper, we demonstrate that x-ray edge effects persist even for this finite mass case. These reduce the naive van Hove singularities in the tunneling DOS by a
power-law amount. Like the singularities in the original x-ray edge problem (but unlike the the Luttinger singularities at low bias), this modification does not, however, signal the destruction of sharp quasiparticle excitations in the higher subbands. We argue that a necessary and sufficient condition for the presence of such finite-energy singularities is a conserved quantum number distinguishing the states of the higher subband from the conduction states. In the case of the carbon nanotube, this is an angular momentum quanta. For a semiconductor wire, such a good quantum number exists in the ideal case of a symmetric confining potential, in which case the second subband has odd parity with respect to reflection, while the lowest subband has even parity. If such a distinguishing quantum number is absent, we expect the van Hove peak to be rounded and rendered completely nonsingular.

The case when only forward scattering interactions are present between the higher subband particles and the conduction sea is asymptotically exactly soluble by bosonization methods, as we outline here. As discussed in Ref. 10, this forward scattering model is in fact an excellent approximation for single-walled carbon nanotubes with diameters $D \gtrsim 1\, \text{nm}$. Within this model, we predict a reduced density of states singularity

$$
\rho(e) \sim \rho_0 \left( \frac{\Delta}{\epsilon - \Delta} \right)^{\frac{1}{2} - \beta} \Theta(\epsilon - \Delta),
$$

where $\Theta(x)$ is the heaviside step function, and the orthogonality exponent $\beta \approx 0.3$ for typical metallic nanotubes. The form of Eq. 4 is expected to apply to the second subband in semiconductor quantum wires as well (see the concluding remarks for a discussion of experiments).

II. FORWARD SCATTERING CHARGE MODEL

In this section we present a simple Forward Scattering Charge Model (FSCM) describing only forward scattering interactions, i.e. those processes involving small momentum exchange, in the total charge channel. We describe the conduction electrons by a Luttinger model, i.e. those processes involving small power-law amount. Like the singularities in the original x-ray edge problem (but unlike the the Luttinger singularities at low bias), this modification does not, however, signal the destruction of sharp quasiparticle excitations in the higher subbands. We argue that a necessary and sufficient condition for the presence of such finite-energy singularities is a conserved quantum number distinguishing the states of the higher subband from the conduction states. In the case of the carbon nanotube, this is an angular momentum quanta. For a semiconductor wire, such a good quantum number exists in the ideal case of a symmetric confining potential, in which case the second subband has odd parity with respect to reflection, while the lowest subband has even parity. If such a distinguishing quantum number is absent, we expect the van Hove peak to be rounded and rendered completely nonsingular.

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In this section we present a simple Forward Scattering Charge Model (FSCM) describing only forward scattering interactions, i.e. those processes involving small momentum exchange, in the total charge channel. We describe the conduction electrons by a Luttinger model, valid near the Fermi energy, which we take to be $E = 0$,

$$
H_0 = \sum_{i\alpha} \int dx \, v_F \left[ \psi_{Ri\alpha}^\dagger i\partial_x \psi_{Ri\alpha} - \psi_{Li\alpha}^\dagger i\partial_x \psi_{Li\alpha} \right].
$$

Here $v_F$ is the Fermi velocity, and $\alpha = \uparrow, \downarrow$ labels the electron spin. We have also included an additional “flavor” index $i = 1 \ldots N_f$ to allow for extra degenerate bands (with the same Fermi velocity) at the Fermi energy. For metallic carbon nanotubes, $N_f = 2$ and $i$ should be interpreted as a sublattice index. No such special degeneracy is present for a semiconductor quantum wire, so $N_f = 1$ in this case. Eq. 3 can be rewritten using bosonization. We follow the conventions of Ref. 10. One has $\psi_{R/Li\alpha} \sim e^{i(\phi_{i\alpha} \pm \theta_{i\alpha})}$, where the dual fields satisfy

$$
\phi_{i\alpha}(x), \theta_{j\beta}(y) = -i \pi \delta_{ij} \delta_{\alpha\beta} \Theta(x - y) \quad (\Theta(x) \text{ is a heavy-side step function}).
$$

Then $H_0$ is given by

$$
H_0(\theta, \phi) = \frac{v_F}{2\pi} \left[ i(\partial_x \phi) + (\partial_x \theta)^2 \right].
$$

The slowly varying electronic density in a given channel is given by $\rho_{i\alpha} \equiv \psi_{Ri\alpha}^\dagger \psi_{Ri\alpha} + \psi_{Li\alpha}^\dagger \psi_{Li\alpha} = \partial_x \theta_{i\alpha}/\pi$. Physically, $\theta$ can be understood as a displacement or phonon field, while $\phi$ carries the phase of the quantum wavefunction.

It is simplest to work in a rotated basis of collective modes. For $N_f = 1$, define $\theta_{\rho/\sigma} = (\theta_{i\alpha} \pm \theta_{i\beta})/\sqrt{2}$. For $N_f = 2$, let $\theta_{i,\rho/\sigma} = (\theta_{i\uparrow} \pm \theta_{i\downarrow})/\sqrt{2}$ and $\theta_{i,\mu/\nu} = (\theta_{i\mu} \pm \theta_{i\nu})/\sqrt{2}$, with $\mu, \nu = \rho, \sigma$. With similar definitions for the $\phi$ fields, canonical commutators are preserved, and $H_0 = \sum_\alpha \int_x H_0(\theta_{i\alpha}, \phi_{i\alpha})$, where $\alpha$ is summed over the $2N_f$ rotated boson fields.

Because we are interested only in energies near the putative van Hove singularity, the unoccupied 1d subband can be described by a non-relativistic electron operator $d, d^\dagger$:

$$
H_0^d = \int dx \, d^\dagger_i \left[ \frac{1}{2m} \partial_x^2 + \Delta \right] d_i.
$$

Here $\Delta$ is the gap to the first subband and $m$ is an effective mass. The electron field satisfies $\{d_i(x), d^\dagger_{i'}(x')\} = \delta_{ij} \delta(x - x')$. In the case of a carbon nanotube, there are actually multiple degenerate subbands at energy $\Delta$. This degeneracy is unimportant within the FSCM, as the tunneling DOS involves only states with a single excited electron. We therefore neglect this additional degeneracy.

The interactions in the FSCM are written as a single term coupling only the total charge density,

$$
H_{\text{int}} = \frac{1}{2} \int dx dx' \, \rho_{\text{tot}}(x) V(x - x') \rho_{\text{tot}}(x'),
$$

where

$$
\rho_{\text{tot}} = -e(d^\dagger d + \sum_{i\alpha} \rho_{i\alpha}) = -e(d^\dagger d + \sqrt{2N_f}/\pi \partial_x \theta_\rho).
$$

Here and in what follows we abbreviate $\theta_{\rho\uparrow} = \theta_\rho$ for the $N_f = 2$ case. A phenomenological form for the potential is sufficient for our purposes. We take $V(x) = \exp(-|x|/\xi) / \sqrt{x^2 + W^2}$, modeling the smoothing of the interaction on the scale of the wire width by $W$ and including a screening length $\xi$, determined, e.g. by the distance to an external gate (any dielectric constant can be included by rescaling $e^2 \rightarrow e^2/\epsilon$).

While it is possible to proceed directly with the non-local form in Eq. 1, near to the van Hove singularity (within an energy of order $v_F/W$, up to a weak logarithmic factor) it is sufficient to make the local approximation $V(x) \rightarrow \delta(x) \int dx' V(x')$. This gives $H_{\text{int}} = \int_x H_{\text{int}}$, with

$$
H_{\text{int}} = e^2 \ln(\xi/W) \left( \frac{\sqrt{2N_f}}{\pi} \partial_x \theta_\rho + d^\dagger d \right)^2.
$$
III. SOLUTION OF FSCM

To determine the effects of the interaction, it is convenient to employ a path integral formulation. Quantum mechanical expectation values are evaluated as functional integrals over classical fields in imaginary time with respect to a measure \( \exp(-\int dx \tau \mathcal{L}) \), where \( \mathcal{L} \) is a Lagrange density. Standard techniques give

\[
\mathcal{L} = \frac{i}{\pi} \partial_x \theta \partial_x \phi + d^* \partial_x d + \mathcal{H},
\]

with

\[
\mathcal{H} = \mathcal{H}_0^d + \mathcal{H}_0^\theta + \mathcal{H}_{\text{int}}
\]

\[
= \frac{v_p}{2\pi g} \left[ \partial_x \theta + \gamma d^* d \right]^2 + \frac{g v_p}{2\pi} (\partial_x \phi)^2 + \mathcal{H}_0^d.
\]

Here we have defined the plasmon velocity \( v_p = \sqrt{v_F (v_F + (4N_F e^2/\pi \hbar) \ln(\xi/W))} \). Luttinger parameter (“conductance” \( \gamma \)) = \( v_F/v_p \), and \( \gamma = \pi \sqrt{2} \gamma_g \). (1)

It may be tempting to proceed by perturbation theory in \( \gamma \). Indeed, for properties of the conduction electrons at energies small compared to \( \Delta \), this is a perfectly sensible procedure: as no heavy particles are present, the properties of the conduction sea are completely unaffected. However, the same is not true for the tunneling density of states. This is obtained from the heavy particle Green’s function, \( G(x, \tau) \equiv \langle d(0, 0) d^\dagger(x, \tau) \rangle \), via

\[
\rho(\epsilon) = \pi^{-1} \Im \int dk/2\pi \frac{\epsilon - G(k, i\omega \rightarrow \omega + i\delta)}{\omega - \Delta}.
\]

The first perturbative correction to \( G \) is obtained from the self-energy diagram in Fig. 1a, is logarithmically divergent. Although we will not proceed along this route, this logarithmic divergence can be controlled to leading order using a renormalization group procedure which treats in a self-consistent fashion both this self-energy correction and the additional vertex renormalization given by the diagram in Fig. 1b. The results of this calculation (11) are confirmed by a non-perturbative analysis, to which we now turn.

![Diagrams](image)

**FIG. 1.** Diagrams in perturbation theory. A direct attack requires a renormalization group resummation of diagrams (a) and (b), where the solid line is the heavy-particle propagator, the dashed line is the \( \theta \) propagator, and the vertices each carry a momentum factor. After the transformation of Eqs. (10–11), the residual interactions in Eq. (13) generate only irrelevant corrections via diagrams (a) and (c), where now the dashed lines represent \( \phi \) propagators and the vertices carry two momentum factors each.

The model in Eq. (13) is solved by a canonical transformation, or change of variables in the path integral:

\[
\theta \rightarrow \theta - \gamma \int_{-\infty}^\infty dx' d^\dagger(x') d(x'),
\]

\[
d(x) = e^{i\gamma \phi(x)/\pi \delta(x)}.
\]

Eqs. (10–11) embody the physical process in which the conduction sea *adiabatically adjusts to the heavy particle*. In particular, Eq. (10) represents the depletion of the conduction electron density near the heavy particle due to Coulomb repulsion. Eq. (11) represents phase shifts of these conduction electrons when the heavy particle is introduced. Formally, the exponential of the dual \( \phi \) field in Eq. (11) is a Jordan-Wigner “string” operator which has been attached to the heavy particle.

In the new variables, the Hamiltonian density becomes

\[
\mathcal{H} = \frac{v_p}{2\pi g} \left[ \partial_x \theta + \gamma d^* d \right]^2 + \frac{g v_p}{2\pi} (\partial_x \phi)^2 + \mathcal{H}_0^\theta[\delta, d^\dagger] + \mathcal{H}_{\text{int}}.
\]

with a different residual interaction term

\[
\mathcal{H}_{\text{int}} = \left[ \frac{\gamma^2}{2m\pi^2} (\partial_x \phi)^2 - \frac{i}{2m\pi} \partial^2 \phi \phi \right] d^\dagger d.
\]

It might appear that the transformations have actually worsened the problem, as the interaction in Eq. (13) naively appears more complicated than the original in Eq. (1). However, a closer inspection shows that the new couplings in Eq. (13) are dimensionally weaker by one inverse power of length than the original forms. As the original interaction was marginal, the terms in Eq. (13) are in fact *irrelevant* in the renormalization group sense. This can be verified by an explicit calculation of their effects on the \( \delta \) Green’s function. Apart from a constant renormalization of the subband gap, the leading order diagrams (Figs. 1a,1c) give self-energy contributions proportional to \( (\omega - \Delta)^3 \).

The irrelevance of the couplings in Eq. (13) indicates that at long times and distances, the transformed fermion and boson correlation functions asymptotically factorize. Thus at energies close to the threshold energy \( \Delta \), the \( \delta \) operator creates good quasiparticles which propagate independently of the conduction sea. The tunneling DOS, however, involves the addition of a *bare* electron created by the \( d^\dagger \) operator. Factorization implies

\[
G(x, \tau) = G^0(x, \tau)/\Lambda \left[ x^2 + v_p^2 \tau^2 \right]^\beta,
\]

where \( G^0 \) is the non-interacting Green’s function describing free propagation in the unoccupied subband, \( \beta = \gamma^2/2\pi^2 g = (1 - g^2)/(4N_F g) \), and \( \Lambda \) is a momentum cutoff \( (O(k_F)) \). When Fourier transformed, the space-time product above becomes a convolution, which physically represents the emission of plasmon waves by the added electron. Analytic continuation to real frequency gives the modified van Hove singularity in Eq. (13).

IV. DISCUSSION

The preceding analysis demonstrates the persistence of a well-defined edge in the tunneling spectrum in the
presence of forward scattering charge interactions with the conduction electrons. The existence of such a finite energy singularity hinges on the inability of the heavy particle to truly decay or mix with the many other (conduction subband) excitations coexisting at the same energy. This is ensured within the FSCM due to heavy particle charge conservation. If there are no true distinguishing quantum numbers of the excited state, decay is possible and the singularity is rounded, as can be verified by explicit calculation using, e.g. Fermi’s golden rule.

We have already argued that for ideal conducting nanotubes and symmetric semiconductor quantum wires, at least the first excited subband is protected from decay in this way. In any experiment, various non-ideal perturbations will lead to some rounding. Thermal smearing (from thermal excitation both internally and in the tunneling lead) limits the resolution to $\epsilon \gtrsim k_B T$. More significant rounding arises from hybridization of the one-dimensional electronic states with the bulk. This is probably the most significant effect in recent tunneling experiments using nanotubes on metallic gold substrates. This effect could be greatly reduced by using an insulating substrate or better, a freely suspended tube. Even for nanotubes on an insulating substrate, the asymmetry in dielectric constants allows some degree of mixing of different subband states. Fortunately, this is likely to be a weak effect due to the delocalization of the subband states around the circumference of the cylinder. Finally, impurities or defects lead to smearing of the ideal density of states on the scale of the inverse elastic scattering time.

Additional processes left out of the FSCM may lead to significant modifications of the physics, although they cannot remove the edge singularity. The forward scattering assumption itself is always correct at energies sufficiently close to $\Delta$, since the heavy particle cannot accommodate a large change in momentum without a corresponding large increase in its energy. There are, however, forward scattering interactions outside the total charge density at the first subband to $\Delta$. For a typical diameter nanotube, we estimate $\beta \approx 0.3$. The singularities at all higher subbands in metallic quantum wires should be rounded.

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