Exciton Dynamics in Carbon Nanotubes: From the Luttinger Liquid to Harmonic Oscillators

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We show that the absorption spectrum in semiconducting nanotubes can be determined using the bosonization technique combined with mean-field theory and a harmonic approximation. Our results indicate that a multiple band semiconducting nanotube reduces to a system of weakly coupled harmonic oscillators. Additionally, the quasiparticle nature of the electron and hole that comprise an optical exciton emerges naturally from the bosonized model.

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Many of the properties of single-walled carbon nanotubes (SWNTs) are deeply rooted in the physics of strongly interacting electrons in low spatial dimensions [1]. In SWNTs, the low-energy fluctuations in the electron density are dominated by one-dimensional excitations of the electrons in the \( \pi \)-energy bands. SWNTs can transport electrons like a nearly ideal one-dimensional conductor, but more like molecules than solid-state materials, display sharp lines in their absorption spectra [2, 3]. These two faces: part solid-state and part molecular, make SWNTs unique nanoscale systems. The bands made from these orbitals are characterized by a wavevector and band index (Fig. 1). The lowest energy bands can be semiconducting or metallic, depending on the chirality of the tube [4]. Because the susceptibility is related to the density-density correlation function through the continuity equation, optical excitations probe the quantum mechanical electronic density fluctuations of the SWNT. A consistent and comprehensive picture of the optical excitations and electronic dynamics in semiconducting SWNTs is important at a fundamental level. Such a picture may have practical consequences in certain applications, because one might exploit novel properties that emerge from strong electron-electron interactions. Because semiconducting SWNTs absorb strongly in the near-IR of the spectrum, they are also promising candidates for solar energy applications. In such applications one needs to understand not just how and where the SWNT will absorb light, but about the subsequent electronic dynamics following absorption, such as interband scattering, Auger recombination, and multiple exciton generation (MEG) [5–7].

The quasiparticle approach has made some remarkably accurate predictions for the absorption spectra of SWNTs [3, 14, 15]. These fluctuations are described naturally within Luttinger liquid (LL) theory [16, 17]. Here too, some of the predicted transport properties have been reported in experiments [18, 19]. The LL approach has also been applied to study transport in semiconducting SWNTs [20], but only recently been applied to study optical excitations in SWNTs [21].

In this letter we analyze optical excitations and relaxation dynamics in SWNTs by applying Luttinger liquid theory to SWNTs with multiple bands. We present a mean-field and variational treatment of a bosonized multiband gapped Luttinger liquid model that clarifies some outstanding issues about the nature and dynamics of electronic excitations in a gapped one-dimensional system. The resulting theory makes predictions for optical transition energies, the \( E_{\text{tr}} \), in SWNTs that agree well with experimental measurements, and we comment on the relaxation dynamics of the excitations between bands. We find that the Luttinger liquid is fragile to gaps of any size, and that once a gap is introduced into the SWNT, electron-electron interactions widen it and the correlation length for the electronic density fluctuations becomes finite. At any finite gap these fluctuations resemble particles (electrons), antiparticles (holes), and an excitonic state that can all be classified according to their topological charge. While terms that give rise to MEG and Auger relaxation are in the model, these are interband processes. Such processes become progressively weaker relative to the intraband Coulomb interaction as the length to diameter ratio for the SWNT gets larger, consistent with the findings in Ref. 22.

The usual methods to solve for optical excitations in nanotubes begin with dressed electron and hole states, typically at the level of Hartree-Fock mean-field theory [1, 12]. In essence this method takes the dressed states, or quasiparticles, of the gapped bands as a reference Hamiltonian. The complete Hamiltonian with the Coulomb interaction is solved approximately with respect to the reference Hamiltonian. The method we employ shares some similarities to this approach. For the gapless case, bosonizing the free-particle energy with the (for-
Coulomb interaction gives an exactly solvable Hamiltonian. The solution is a Luttinger liquid, a system that lies along a line of quantum critical points, where density-density correlation functions follow a nonuniversal power law. In this work the LL Hamiltonian is used as the reference. Relative to this reference an intrinsic gap is relevant in the renormalization group (RG) sense. Interband scattering is marginal. At long wavelengths, fluctuations widen a bare gap, while the interband scattering matrix element tends towards a constant value [23]. The gap term is the strongly interacting part of the Hamiltonian in the bosonized representation and cannot be treated perturbatively [20, 21]. We solve for the intraband gapped LL using mean-field theory and a variational harmonic Ansatz. The excitonic nature of the excitations emerges from the mean-field result (Fig. 2). The corresponding energies are nearly exactly reproduced by the harmonic approximation, and they are in good agreement with experimental results (Fig. 3). The harmonic Ansatz greatly facilitates analysis of interband processes. The last step in our theory is to analyze the marginal interband scattering within the harmonic approximation.

SWNTs inherit the degeneracy of the $K$ and $K'$ points from graphene's dispersion relationship. We refer to the resulting degenerate band pair (sometimes referred to as valleys) by the band index $n$ for the nanotube, illustrated in Fig. 1. In semiconducting tubes the bare gaps are $\Delta_0^{(n)} = 2n v_F / 3R$ ($n = 1, 2, 4, 5$ for the first four bands) according to the nearest neighbor tight-binding, zone-folding approximation [4, 24]. In this relationship $v_F$ is the graphene Fermi velocity and $R$ is the tube radius. We assume that the tube radius is not so small that backscatter and Umklapp processes become relevant [14]. Reference 25 derived an effective low-energy theory for metallic SWNTs using the bosonization technique and we refer the reader to this work for details on the fermion to boson mapping. The bosonized reference Hamiltonian, $H_0^{(n)}$, is the LL Hamiltonian. It includes the free-particle and Coulomb interaction and is expressed in terms of pairs of dual bosons $\theta_{\nu}^{(n)}(x)$ and $\phi_{\nu}^{(n)}(x)$. For a given band, $n$, the reference Hamiltonian is a sum of four sectors.

$$H_0^{(n)} = \frac{1}{2} \sum_{\nu} u_{\nu} \int dx \frac{1}{K_{\nu}} \left( \partial_x \theta_{\nu}^{(n)}(x) \right)^2 + K_{\nu} \left( \partial_x \phi_{\nu}^{(n)}(x) \right)^2,$$

(1)

with $h = 1$. We follow the conventions of Ref. 25 where the $\theta_{\nu}$ fields are associated with density fluctuations, and the $\phi_{\nu}$ fields act as a corresponding phase. The subscript $\nu = c\pm, s\pm$ indicates charge and spin modes for the sum and difference from the two degenerate bands. The Coulomb interactions determine the values of the Luttinger parameters, $K_{\nu}$. Only the total charge sector, $\nu = c+$, is interacting, with a Luttinger parameter value less than unity. Typically in nanotubes $K_{c+} \approx 0.2$ [25]. The $c+$ sector gives the long wavelength fluctuations of the total electron density: $\rho(x, t) = \frac{2}{\sqrt{\pi}} \sum_{n} \partial_x \theta_{c+}^{(n)}(x, t)$. The Coulomb interaction increases the velocity for the $c+$ sector, $u_{c+} \approx v_F / K_{c+}$. The remaining sectors have $u_{\nu} = v_F$, and we will refer to these $\nu \neq c+$ sectors as the neutral sectors.

The resonances in the current-current time correlation function correspond to peaks in the absorption spectrum. They occur at the gaps, $\Delta^{(n)}$, of the $c+$ sector in the fully interacting theory. The gap terms that are quadratic in fermion fields have a complicated form in the bosonized representation [20],

$$H_{\text{gap}}^{(n)} = \frac{4 \Delta_0^{(n)}}{\pi a} \int dx \prod_{\nu} \cos \sqrt{\pi} \theta_{\nu}^{(n)} + \prod_{\nu} \sin \sqrt{\pi} \phi_{\nu}^{(n)}.$$

(2)

The parameter $a$ is the short distance cutoff of the theory [25]. Under RG each cosine and sine term has a scaling dimension $K_{\nu} / 4$ [26]. $H_{\text{gap}}^{(n)}$ therefore has the scaling dimension $\sum_{\nu} K_{\nu} / 4 < 1$. A scaling dimension of 2 would indicate a marginal perturbation, but $H_{\text{gap}}^{(n)}$ is far from this value and is relevant. It should not be treated using perturbation theory.

This result also implies that the LL line in SWNT is fragile. Metallic zigzag and chiral tubes can have a curvature induced gap [29]. These gaps are small, on the order of tens of meVs [30], but the RG flow moves the system rapidly away from the line of LL critical points at zero gap. While perturbation theory is unreliable at $K_{c+} \approx 0.2$, the system becomes amenable to a semiclassical approximation.

$H_{\text{gap}}$ includes only the $\theta_{\nu}^{(n)}$ fields. One can obtain a description of the gapped tube, $H_0^{(n)} + H_{\text{gap}}^{(n)}$, solely in terms
The electronic quasiparticle behaviors and the relative difference between breathers/excitons for different bands [28]. The electronic gap energy is determined to be an important parameter when the coupling constants are solved self-consistently, and the $\nu_{c+}$ then determine the energies of the breathers, $m_{c+}^{(n)}$ [21, 33, 34]. The breather solutions of the $c+$ sector, formed from pure solitons and antisolitons, are the semiclassical result that correspond to the excitons of the optical transitions.

While the soliton solutions to the $\theta_{c+}$ fields jump between ground states, the breather solutions oscillate narrowly about a minimum in the cosine function. In analogy to a particle in a potential well, the coupled sine-Gordon (sG) model describes a coupled sine-Gordon (sG) model. While the soliton solutions to the $\theta_{c+}$ fields are inherently scale dependent. Their values depend on the short distance cutoff $\xi$. To make progress, we proceed as in Ref. 21 and make a mean-field approximation that assumes the $\theta_{c+}^{(n)}$ from different sectors are uncorrelated. Within a given band, $n$, the theory is one of four scalar sG actions, $S^{MF} = S_0 + S_{\text{gap}}$, for each boson sector. Written in canonical form [33], $S_{\text{gap}}$ for each sector within each band, in the mean-field approximation, becomes

$$S_{\text{gap}}[\theta_{c+}^{(n)}] = -2\mu_{c+}^{(n)} \nu_{c+} \int dx d\tau \cos \sqrt{\pi} \theta_{c+}^{(n)}.$$  \hspace{1cm} (3)

The coupling constants are solved self-consistently, and the $\mu_{c+}^{(n)}$ then determine the energies of the breathers, $m_{c+}^{(n)}$ [21, 33, 34]. The breather solutions of the $c+$ sector, formed from pure solitons and antisolitons, are the semiclassical result that correspond to the excitons of the optical transitions.

While the soliton solutions to the $\theta_{c+}$ fields jump between ground states, the breather solutions oscillate narrowly about a minimum in the cosine function. In analogy to a particle in a potential well, $S_{\text{gap}}$ can be replaced by its harmonic approximation, $1 - \cos \sqrt{\pi} \theta_{c+} \sim \theta_{c+}^{2}$. In this form, the decoupled sG action describes a theory of free massive bosons, or quantum harmonic oscillators, whose dispersion relationship is determined by the full gaps [16]

$$\Delta^{(n)} = u_{c+} \left[ 2\pi \mu_{c+}^{(n)} K_{c+} \right]^{1/(2-K_{c+}/4)}.$$  \hspace{1cm} (4)

The application of the RG in nanoscale systems often results in cutoff-dependent parameters [35]. The same is true here. The coupling constants $\mu_{c+}^{(n)}$ are inherently scale dependent. Their values depend on the short distance cutoff $a$ [see Eq. (2)]. We use a normalization scheme that first determines the value for $\Delta^{(n)}$ in the noninteracting case, $K_{c+} = 1$. The ratio $\Delta^{(n)} / \Delta^{(0)}$ gives a single normalization factor applied to solutions with $K_{c+} = 0.2$. The full gaps $\Delta^{(n)}$ in the quantum harmonic approximation are within half a percent of the breather energies $m_{c+}$ evaluated in the semiclassical approximation. The correlation length in the free massive
boson theory is inversely proportional to the mass term, $\Delta^{(n)}$, and we find that the ratio of correlation lengths follows from the “ratio problem,” $\xi^{(1)}/\xi^{(2)} \approx 1.78$ [36]. When estimated from the semiclassical particle density (Fig. 2) the ratio of the full widths at half maximum, gives $\xi^{(1)}/\xi^{(2)} \approx 1.76$, which implies that the dynamics for the lowest energy excitations in the quantum harmonic approximation are nearly indistinguishable from those evaluated with semiclassical methods.

The full gaps from Eq. (4) give the optical transition energies. Just as in Ref. [35], we plot them alongside the experimental data in Fig. 3. Since we set $K_{c+} = 0.2$ for the interacting case and we fix the short distance cutoff to be the carbon-carbon distance, our theory has a single free parameter: the radius $R$, or equivalently, the bare gaps $\Delta^{(n)}_0$. The agreement between our theory and experiment is quantitative for the $E_{11}$ transition in large radius tubes and semiquantitative otherwise. The largest disagreements between our theory and experiment occur when $R$ is small, which is to be expected for a field-theoretical treatment. For small radius tubes, short wavelength behavior and a host of marginal and irrelevant terms, ignored in the field theory, contribute.

In addition to our calculated optical transition energies in Fig. 3 we also show theoretical results from Ref. 35. The tight-binding prediction is that $\Delta_0 \propto R^{-1}$. Kane and Mele [35] used RG arguments and Bethe-Salpeter calculations and found a logarithmic dependence on the tube radius $\Delta/\Delta_0 \propto \ln R$. The results from the harmonic approximation show a power law relationship $\Delta/\Delta_0 \propto R^\gamma$ with a small nonuniversal exponent $\gamma = (1 - K_{c+}) / (5 - K_{c+})$.

Having identified and analyzed the strongly interacting parts of the theory, we turn to the interband scattering dynamics. In the Fourier basis, the vertex of the Coulomb interaction on a cylinder of radius $R$ and wave vector $q$ behaves as $V_0(q) \sim |\ln(qR)|$ for intraband scattering, and $V_f(q) \sim 1/2 + q^2 R^2$ for scattering between adjacent bands at small $q$. A 3 $\mu$m length, 1 nm diameter tube has $V_0/V_f \sim 20$. For simplicity we look at scattering between the lowest two energy bands. The interband term involves only densities from the total charge sector in each band and contains no anharmonicities:

$$S_I \left[ \theta_{c+} \right] = \frac{1}{2} \frac{4V_f}{\pi} \int dx \partial_x \theta^{(1)}_{c+}(x) \partial_x \theta^{(2)}_{c+}, \quad (5)$$

and is exactly solvable in the harmonic approximation. It leads to a small hybridization between bands, equivalent to a redefinition of the normal modes, but nothing more. The strongly-interacting low-dimensional aspect of the Coulomb interaction is manifest between carriers within the same band, but between carriers in different bands, it is a relatively small effect. This conclusion is consistent with other atomistic calculations based on the Bethe-Salpeter equation [38].

The boson fields can be quantized in terms of boson creation and annihilation operators [16, 17]:

$$\partial_x \theta^{(n)}_\nu(x) \sim \sum_{k \neq 0} e^{-a|k|/2} e^{-ikx} \left( b^{(n)}_k \right)^\dagger + b^{(n)}_k \right). \quad (6)$$

The interband scattering includes $b^{(1)}_k b^{(2)}_k$, and its Hermitian conjugate, but no higher order terms that could lead to multiple exciton generation. Reference 15 also considers an interband forward scattering model in carbon nanotubes, they find a MEG-like term in the Hamiltonian but it is determined to be irrelevant. It is significant that semiconducting SWNTs are well described as a system of harmonic oscillators (Fig. 3). Within our approximations, long wavelength interband scattering does not lead to multiple exciton generation.

In this work we show that the optical transition energies for semiconducting SWNTs can be determined with a minimal number of parameters using a forward scattering bosonization model, mean-field theory, and a harmonic approximation. The multiband SWNT reduces to a system of weakly coupled harmonic oscillators. We have shown that the LL phase of metallic SWNTs are unstable in the presence of a bare gap of any size. These gaps may be introduced by curvature effects [39], magnetic fields [20], or strain [40]. Under the influence of a bare gap, correlation lengths become finite. The electron fluctuations, localized in space, may be thought of as quasiparticles. This may be related at a fundamental level to the success of quasiparticle based Bethe-Salpeter theories for excitons in SWNTs.

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![Figure 3](image-url)
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