

Many body effects in carbon nanotube fluorescence spectroscopy

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Abstract

Two dimensional fluorescence spectroscopy on suspensions of carbon nanotubes probes the electronic excitations of carbon nanotubes with unprecedented resolution and reveals systematic deviations from the predictions of conventional one electron theories. We address these problems by formulating a theory of the scaling optical excitation energies with band index, tube radius and chiral angle. This reveals an unconventional scaling relation that arises from a singular self energy contribution to the quasiparticle dispersion relation in the two dimensional graphene sheet. Self energy and excitonic effects from the long range part of the Coulomb interaction for the one dimensional nanotube are separately strong but they largely cancel, exposing the physics of the two dimensional interacting system.

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Soon after the experimental discovery of carbon nanotubes theorists realized that wrapping a graphene sheet into the form of a cylinder could produce one dimensional structures with either conducting or semiconducting electronic character [1]. This occurs because the low energy electronic states of the graphene sheet reside in a narrow range of wavevectors near the corners of its two dimensional Brillouin zone. For semiconducting nanotubes, these regions in phase space are kinematically forbidden by the requirement that the electronic wavefunctions be continuous on the tube circumference. By linearizing the graphene spectrum around its Fermi points one concludes that for semiconducting nanotubes of sufficiently large radius, the energy gaps should scale inversely as the tube radius

$$E_n^0 = \frac{2n\hbar v_F}{3R} \quad (1)$$

where v_F is the slope of the quasiparticle dispersion relation and $n=1, 2, 4, 5$, etc. give the gaps of the 1st, 2nd, 3rd and 4th gapped subbands in the electronic spectrum. This linearized result is the first term in an expansion in powers of $1/R$ and it is exact for noninteracting electrons in the limit of large radius [2]. The leading order corrections to (1) due to the effects of tube curvature and trigonal warping in the electronic spectrum are proportional to $\nu \sin 3\theta/R^2$, where $\nu = \pm 1$ is the chiral index and θ is the chiral angle [2]. Thus for smaller radius tubes the large radius expansion is most accurate for tubes approaching the ‘armchair’ wrapping where $\theta=0$. Interestingly, the signs of the leading order corrections alternate with the sign of the chiral index and therefore they bracket a separatrix where the $1/R^2$ contributions are absent.

Initially, experimental tests of these ideas were attempted by transport measurements: Scanning tunnelling spectroscopy [3,4], and scanning probe imaging of standing wave patterns produced by the backscattering of electron waves from tube ends and defects [5,6]. At the level of accuracy of these measurements the predictions of (1) when

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corrected for the effects of trigonal warping and curvature in the band structure have been regarded as providing at least a semiquantitative account of the data. In particular the alternation of conducting and semiconducting character with the tube structure was verified.

This description is now being challenged by a new generation of experiments that probe the electronic excitations using photoluminescence excitation (PLE) spectroscopy. The experiments are carried out on suspensions of carbon nanotubes that are isolated within micelles [7,9], and on individual nanotubes supported above a substrate [8]. A typical suspension may contain micelles encapsulating individual nanotubes with a distribution of radii and chiral angles. Two dimensional spectroscopy measuring the PLE for fixed emission frequency as a function of the exciting frequency reveals discrete correlations between the two, thus experimentally isolating the first and second optical excitations of individual nanotubes. These measurements are now providing an experimental probe of the optical excitations with unprecedented resolution. Data are available for over 30 different wrapped structures, and for the first time allow one to extract from experiment the scaling of the optical excitation energies with R and θ .

When confronted with these data, one finds that the conventional band theoretic description of the electronic excitations breaks down. These difficulties are noteworthy because they involve violations of theoretical predictions that are very general and essentially model independent. Thus the discrepancy between theory and experiment does not signal a quantitative failure of a specific computational methodology, but instead clearly reveals a systematic failure of the Fermi liquid paradigm applied to these materials. The resolution to this problem requires a more complete treatment of the effects of the electron interaction on the electronic excitations.

In this paper, we will briefly review the aspects of the experimental data that clearly identify the effects of electron interactions. We then briefly outline our work to formulate a general framework for interpreting nanotube optical spectra including the effects of electron interactions, and analyze the scaling of these effects with tube radius R and chiral angle θ .

In the theoretical community, it has been widely anticipated that one dimensional excitonic effects would be large in semiconducting nanotubes and play a dominant role in determining their optical excitation spectra [10]. By analyzing the experimental data we conclude that these excitonic effects, while significant, are largely compensated by an upward band gap renormalization due to the Coulomb self energy. This cancellation in the long wavelength physics then exposes the effects of the Coulomb interaction at shorter scales where this system is more two dimensional in character. In fact, a careful analysis of the experimental data reveals an asymptotic nonlinear scaling with $1/R$ that is

a signature of a marginal Fermi liquid state for interacting electrons in two dimensional graphene [11].

We can classify the three failures of one electron theory applied to the optical excitations as (1) the ratio problem, (2) the blue shift problem and (3) the deviations problem. Before turning to the theory we summarize each of these.

(1) *Ratio problem*: The absorption (E_{22}) and emission (E_{11}) frequencies measured in PLE are thought to arise from excitation and recombination respectively from the first two gapped subbands of semiconducting nanotubes. Thus, using the linearized theory for low energy excitations one expects that in the limit of large radius tubes, the ratio E_{22}/E_{11} should asymptotically approach 2. Experimentally it does not, and instead approaches a value ≈ 1.7 [7]. Interestingly, over the range of tubes studied experimentally, the expected alternating $1/R^2$ corrections due to trigonal warping and curvature are observed, and these bracket a separatrix for the gap ratio for nearly armchair tubes that is nearly radius independent over the entire range $0.6 < R < 1.4$ nm.

(2) *Blue shift problem*: When plotted as a function of $n/3R$ the excitation and emission energies E_{22} and E_{11} fall on a single though nonlinear scaling curve [12]. This is shown in Fig. 1, where these energies, and the differences of the energies from the linearized prediction are plotted as functions of $n/3R$. This scaling curve must pass through the origin since the graphene sheet ($R \rightarrow \infty$) is gapless. Nevertheless the observed energies lie significantly above the predictions of a plausible linearized low energy model. These magnitude of this difference is seen clearly in the difference plot of Fig. 1(b), with a mean value approximately 0.3 eV over a wide range of radii. This shift of the observed excitation energies to higher energy is the blue shift problem. The collapse of the data to a single scaling curve strongly suggests that these data probe the quasiparticle dispersion relation of the graphene sheet mapped onto the surface of the nanotube. It is particularly striking from the difference plot that this dispersion measured experimentally cannot be described by any theory in which interactions simply renormalize the effective Fermi velocity. Any such correction would lead to a renormalized, but linear scaling of these energies.

(3) *Deviations problem*: Using the separatrix identified in these scaling plots (for example by looking at the excitations of the nearly armchair structures) the behavior of individual tubes can also be characterized by their deviations from the behavior of a reference tube on the separatrix at the same radius. Correlating these deviations for the observed E_{11} and E_{22} reveals several important trends. First they are anticorrelated, i.e. a positive deviation at the first band edge is correlated with a negative deviation at the second and vice versa. This is exactly as expected for the band theoretic contributions that depend on $\sin(3\theta)$. Second, they are very large. The scale of these deviations for E_{11} for the nearly identical (9,1) and (9,2) wrapped structures is approximately 0.2 eV! The size of these deviations is at the limit of what can be understood from

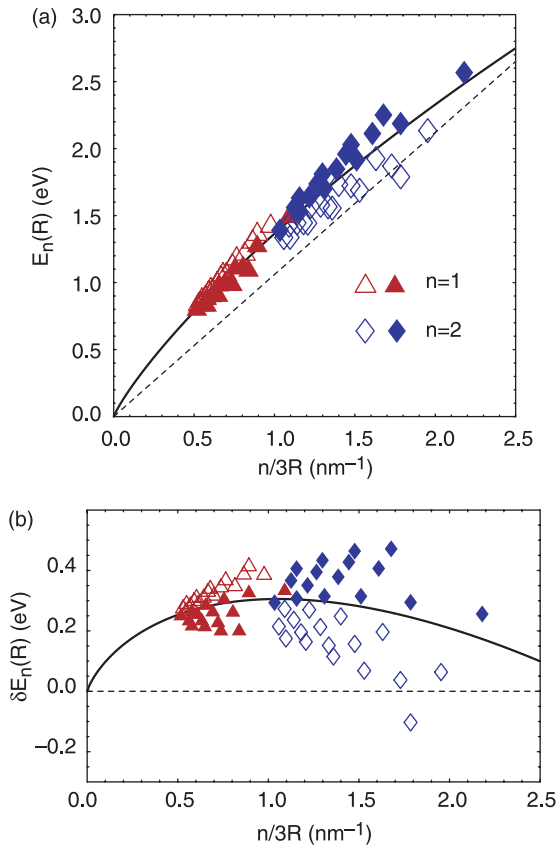


Fig. 1. Observed excitation energies measured in fluorescence spectroscopy from carbon nanotubes plotted as a function of $n/3R$ where $n = 1, 2$ is the band index and R is the tube radius. The open and filled symbols give the results for the two possible chiral indices $\nu = \pm 1$. The dashed lines give the prediction of a linearized theory. The solid curve is derived from a theory developed from a theory of the graphene sheet as a marginal Fermi liquid.

conventional band theoretic contributions, and suggests some important additional contribution to these corrections, possibly from electron interactions. Third, the distribution of these deviations is asymmetric: Deviations that are negative (these reduce the size of the bandgap) are systematically larger than those that are positive for comparable radius. This is inconsistent with simple band theoretic contributions from curvature and trigonal warping that one expects to be nearly symmetrically distributed about a zero mean [13].

Most of these difficulties have as a common origin the effect of the Coulomb interactions on the optical excitations. To study these effects it is useful to parse the interaction into a long range and short range contribution. The long range piece acts on length scales large compared to a tube circumference. This interaction is asymptotically proportional to $1/z$ where z is the interparticle separation measured along the tube axis. This part of the interaction is mediated by electric field lines that spread into the space

outside the tube and therefore in the $q \rightarrow 0$ limit it is unscreened by dielectric properties of the tube (although it may be screened by the dielectric environment in which the tube is embedded). The shorter range part of this interaction acts on length scales of order the tube circumference. This short range potential allows for both intra- and inter-subband scattering, and at this scale the phase space for the electron becomes essentially two dimensional. This part of the interaction is screened by the dielectric properties of the tube.

For two dimensional graphene the latter part of the Coulomb interaction provides a singular correction to the electron self energy [11,12]. To leading order in $g = e^2/\hbar v_F$ the exchange self energy modifies the long wavelength dispersion relation

$$E(q) = \hbar v_F q \left[1 + \frac{g}{4} \log \left(\frac{\Lambda}{q} \right) \right] \quad (2)$$

where q is the magnitude of the two dimensional wavevector and Λ is an ultraviolet cutoff of order an inverse lattice constant. Importantly, the $q \rightarrow 0$ singularity in this expression survives in the effects of screening. This singular contribution to the self energy is most clearly seen by studying the group velocity $(1/\hbar)\partial E/\partial q$. This ‘velocity’ (which is the relevant parameter for correlating the bandgap of a tube with its radius) is thus scale dependent, and diverges as $q \rightarrow 0$.

Eq. (2) is exact, even for a strongly interacting system (large g) in the limit of large wavelengths. Thus the interacting system admits a description in terms of quasiparticles but with an anomalous nonlinear dispersion relation. This singular behavior is a signature of a marginal Fermi liquid. The nonlinear $n/3R$ scaling of the separatrix in Fig. 1 can be understood by including this singular correction to the quasiparticle self energy. The separatrix is well fit by the bold curve obtained by using the parameters $\Lambda = 0.5 \text{ nm}^{-1}$, $\hbar v_F = 7.8 \text{ eV \AA}$ and $g = 0.74$. These values are in reasonably good agreement with expectations for graphene. Interestingly, the nonlinearity in this dispersion relation explains both the blue shift problem and the ratio problem [14]. This is because the quasiparticle dispersion relation is concave ‘downward’ so that twice the first subband gap must exceed the gap for the second subband, as observed. The blue shift problem and the ratio problem are thus unified. They are different symptoms of a single fundamental issue, namely the breakdown of the Fermi liquid description of the low energy quasiparticle excitations.

Nevertheless, the success of this model is unsettling since it completely ignores the effect of the long range part of the Coulomb interactions, which one expects to lead to strong excitonic effects in the optical spectra [10,15,16]. We find that the expected effect of the Coulomb interaction on transition energies is largely offset by a positive bandgap renormalization due to the long range Coulomb interaction

[10,14,15]. The result is a modest reduction of the transition energy from the prediction of the two dimensional theory, so that the 2D theory remains a useful scaling law for the nanotube. In particular, the singular correction to the quasiparticle self energy is not affected by this correction and can be observed in the experimental data.

The cancellation of the band gap renormalization and the excitonic binding can be understood in two ways. The Coulomb contribution to the single particle self energy describes the ‘field energy’ associated with an uncompensated charge, here an added electron. Because the nanotube is a one dimensional object embedded in a three dimensional world, these field lines associated with an isolated electron or hole propagate unscreened in the surrounding space and provide a substantial upward renormalization of the single particle gap. When the electron and hole bind to form an exciton, the charges are compensated on a length scale given by the size of the exciton several tube radii. Thus, the electric field lines for this charge neutral excitation are confined to a narrow region of space around the nanotube and the electrostatic field energy is strongly reduced. Thus, most of the energy ‘paid’ in the single particle bandgap renormalization is ‘recovered’ when the excited electron is screened by its valence band hole.

We quantify these ideas by computing the single particle and particle hole energy gaps for carbon nanotubes within a statically screened Hartree Fock approximation and comparing these with the results obtained by mapping the 2D quasiparticle theory. The calculations are similar to those previously reported by Ando [10]. To avoid complications associated with the $(\nu \sin(3\theta))/R^2$ corrections, we study tubes in the armchair geometry with an artificial phase shifted boundary condition to impose an energy gap and render them semiconducting. The results are summarized in Fig. 2 where various single particle and particle hole gaps are plotted in units of their values for the noninteracting theory. The calculations show that the single particle gaps are strongly enhanced by the interactions. In contrast, the particle hole gaps show only a modest enhancement and their values are well described by the mapping of the 2D quasiparticle theory. In particular, we observe that the slopes of these scaling curves on a log-linear plot are nearly identical with the $\log(A/q)$ contribution inherited from the quasiparticle dispersion of the parent 2D system.

Although the long range interaction has only a minor effect on the excitation energy, it has an enormous effect on the shape of the absorption spectrum. The electron and hole are strongly bound by their Coulomb attraction and as seen in Fig. 2 the lowest bound state of the pair is well separated in energy from the particle-hole continuum. One finds that essentially all of the optical spectral weight is exhausted in the excitonic pole, with only weak absorption remaining in the pair continuum [15]. Thus, while the 2D quasiparticle theory provides a useful scaling formula for the energy of the excitonic bound state, the lowest energy optical

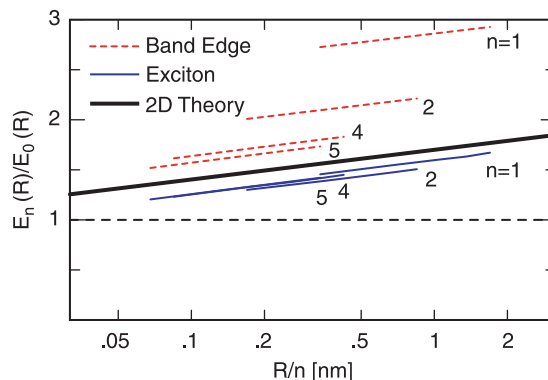


Fig. 2. Normalized optical excitation energies calculated for carbon nanotubes within the static screening approximation are plotted as a function of $\log(R/n)$. All calculated energies are given in units of their noninteracting counterparts, so the deviations from 1 (horizontal dashed line) indicate the effects of electron interactions. The bold curve gives the mapping of the 2D quasiparticle dispersion relation onto the graphene sheet. The dashed lines are higher energy give the renormalized single particle gaps, and the lines at lower energy give the energies of the lowest bound exciton. All the lines show a linear scaling with $\log(R/n)$ with nearly identical slopes that derive from the quasiparticle dispersion of two dimensional graphene.

excitations of the nanotube are not well described as weakly interacting 2D quasiparticles, but rather consist of a strongly bound particle hole pair.

The cancellation of the band gap renormalization and excitonic binding energy can be understood simply by recognizing that it is exact in the limit of an infinite range interaction. This is the constant interaction model studied in the theory of the Coulomb blockade. Consider a system with a bare energy gap $2\Delta_0$ and a constant interaction of strength V_0 . Interactions renormalize the single particle gap $2\Delta = E(N+1) + E(N-1) - 2E(N) = 2\Delta_0 + V_0$, while for the optical gap the particle number is unchanged so that $\Delta E = 2\Delta_0$. The 1D Coulomb interaction is not an infinite range potential, but the constant interaction model is a useful starting point for understanding this effect.

It is becoming increasingly clear that electron interactions play an essential role in nanotube photophysics. There are several areas where their effects need to be further clarified. For example, it is unclear at present whether the relatively low luminescence efficiencies observed in these systems are intrinsic, due to photocarriers relaxing to ‘dark’ low energy many body states in the interacting spectrum, or are simply extrinsic, due to trapping of carriers at defects. Similarly, the presence of a background density of doped electrons or holes seems almost certain to significantly modify the optical properties of the interacting system, and has not yet been carefully explored for these systems. It is interesting that these questions have arisen in research on the optical excitations of semiconductor quantum dots and quantum wires, and a confluence of these two fields now

holds substantial promise for expanding our understanding of quantum and optical phenomena of these new low dimensional structures.

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