Many Body Effects in Carbon Nanotube Fluorescence Spectroscopy

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Sheets and Cylinders of Graphene

Photophysics of NT’s (mainly exptl)

Scaling Relations in Optical Properties from e-e Interactions
Nanotubes from wrapped graphene

Each tube is indexed by the translation vector around its circumference

NT as a molecule, a 1D wire, a quantum dot, a semiconductor, an interconnect...
The (m,n) wrapping specifies a translation vector of the graphene lattice.

Rolling-up a graphene sheet

(5,5) Armchair Tube Metal
(5,0) Zigzag Tube Semiconductor
(5,-1) Tube Metal (small-gap SC)

\[ m = n \quad \text{mod}(m-n,3) = \pm 1 \quad \text{mod}(m-n,3) = 0, \ m \neq n \]
Two Dimensional PLE Spectroscopy

Discrete Peaks are Excitations of Individual SWNT’s
• The Ratio Problem
  Anomalous scaling of gap ratios in large R limit

• The Blue Shift Problem
  The observed gaps are blue shifted with nonlinear 1/R scaling

• The Deviations Problem
  Anomalies in period-3 deviations from scaling
**Ratio Problem:** the ratio of absorption/emission frequencies < 2 in *Large R Limit*

**Blue Shift Problem**: $E_{11}$ and $E_{22}$ are blue shifted wrt linearized theory

**BUT with separatrix on single scaling curve ($n/R$)**

(nearly armchair tubes at border)
**Ratio Problem: Scaling of Deviations from Scaling**


Data collapse suggests a one parameter scaling - BUT nonlinearity needs f (R) & g(θ)

*trig.warping line*

(This is still a puzzle..band effects? interactions? multiplet effects?)
**Electron-Electron Interactions**
*are responsible for all three anomalies*

**NT Exciton Effects are Large**
*(binding energies are a substantial fraction of bandgap)*

**Absorption/Fluorescence Frequencies Scale**
*in a Simple Way with Inverse Tube Radius*
*(but not in the simplest way)*

**Separate 1D and 2D Interaction Effects**
*(the NT is actually a 2D structure)*
Rule 1 There are competing interaction effects

Coulomb Interaction gives a positive self energy...

exchange increases the observed gap

... and an attractive e-h interaction:

with particle-hole bound state at lower energy

Both effects are strong in NT’s but subtle since they partially compensate
**Rule 2** The tube radius sets a fundamental length scale: separation of 1D and 2D interaction effects

\[ V(r) = \frac{e^2}{r} = V_{\text{long}}(r) + V_{\text{short}}(r) \]

Long Range Interaction: \((r > 2\pi R)\)

One Dimensional
Unscreened for large separation

Short Range Interaction: \((a < r < 2\pi R)\)

Two Dimensional

Leads to nonlinear q log q shift in dispersion of graphene, and nonlinearity in \(E_{\text{nn}}(1/R)\)
Interactions renormalize quasiparticle dispersion $E(q)$ of two dimensional graphene

Noninteracting: \[ E(q) = \hbar v_F q + O(1/R^2) \]

Interacting:
\[
E(q) = \hbar v_F q \left[ 1 + \frac{g}{4} \log\left(\frac{\Lambda}{q}\right) \right] + O(1/R^2);
\]
\[ g = \frac{e^2}{\hbar v_F} \]

This is exact for $q \to 0$, with a scale dependent $v_F$ and $g$:

(scales to perturbative regime at small $q$)

Earlier work: J. Gonzalez, F. Guinea and M.A.H. Vozmediano
Map graphene quasiparticle energies to nanotube

Resolves (by unifying!) ratio problem and blue shift problem
**sin(3θ) Effects Are Small Near The Armchair Structures**

But how would (could) this survive with even stronger 1D interaction effects?
Rule 3. The long(est) range effects nearly balance each other

\[ V(r) = \frac{e^2}{r} = V_{\text{long}}(r) + V_{\text{short}}(r) \]

schematically for \( r > 2\pi R \)

One Dimensional
(unscreened at large \( r \))

Renormalizes the Band Gap

Binds the Exciton
An Exactly Solveable Model: Infinite Range Interaction

e.g. simplest model of a “quantum dot”

Bare Gap: $2\Delta$  
Interaction Energy: $V_0N^2/2$

Quasiparticle Gap:  
$E(N+1) + E(N-1) - 2E(N) = 2\Delta + V_0$

Electron-Hole Gap: $2\Delta$
Near Cancellation for Screened NT Interaction
Numerical Calculation in Screened Hartree Fock Approximation

Interaction strength

Quasiparticle gap
Lowest Exciton
Noninteracting
Size-Scaling of Single Particle and Particle - Hole Energies

C.L. Kane and EJM (PRL 93, 197402 (2004))

multiband mixing with screened interaction

- single particle gaps
- 2D qp’s excitons
- noninteracting

(Logarithm of tube radius)
Excitonic v. Interband Spectra

Oscillator strength in bound state
Suppress continuum van Hove singularity
Bandgap renormalization nearly cancelled by exciton binding.
They are strongly bound
size ~ few tube radii, $\Delta E/E \sim 30\%$ ! Nearly all spectral weight in bound state

they carry spin $(0,1)$ and valley $(K, K')$ indices

these degeneracies are lifted by intervalley and exchange

$\rightarrow$ spectrum of dipole allowed and dark (forbidden) states

possibly stable to high density (?)

power law decay of transient absorption

$\rightarrow$ long lived diffusing species
Spin and Valley Degeneracies Broken by Interactions

Exchange and Intervalley at finite momenta ($\theta$–dependent)

Low Energy Triplet & “Dark” Singlet Excitons
Power law decay of PA from a long lived diffusive but nonemissive excited state
Conclusions…

Large NT Excitonic/Interaction Effects

Anomalies From “2D” Graphene Self Energy
(nontrivial scaling with inverse tube radius)

… and Questions

Why are comparable qp effects “missing” in STS?
Modification by multiplet effects, and $3\theta$ dependence?
Scale of extrinsic effects: dielectric environment, doped carrier density…
Charlie Kane (theory)

Dave Luzzi, Rich Russo
Mike Therien, Igor Rubstov

Dina Zhabinskaya
Jesse Kinder

Bruce Weisman (Rice)

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LRSM
the University of Pennsylvania’s Materials Research Science and Engineering Center
Graphene has a critical electronic state

Dispersion of a free particle in 2D...

...is replaced by an unconventional E(k) relation on the graphene lattice
Experimental “Ratio Plot”

By comparing the distributions of gap ratios the $(n_1,n_2)$ values (hence $R$ and $\theta$) for each peak are assigned.

Corroborated by Raman spectroscopy of the radial breathing mode.

Theory (Reich, 00)
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Deviations Problem