Electron Interactions and Nanotube Fluorescence Spectroscopy

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Large radius theory of optical transitions in semiconducting nanotubes derived from low energy theory of graphene

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• Brief Introduction to nanotubes
• Independent electron model for optical spectra
• 2D interactions: nonlinear scaling with 1/R
• 1D interactions: excitons
• Short Range Interactions: exciton fine structure
Carbon Nanotubes as Electronic Materials

- Ballistic Conductor
- Field Effect Transistor
- Logic Gates

A Molecular Quantum Wire

Tans et al. (Nature 1998)
Carbon Nanotubes as Optical Materials

Photoluminescence

- Nanotubes in surfactant micelles
  Bachillo et al. (2002).

- Photoluminescence from individual suspended nanotubes
  Lefebvre et al. (2003).

Electroluminescence & Photoconductivity

- Infrared Emission, photoconductivity in individual nanotube field effect devices
Carbon Nanotube : Wrapped Graphene

\[ C = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 \]

Tubes characterized by \([n_1,n_2]\) or

- **Radius**: \( R = |C|/2\pi \)
- **Chiral Angle**: \( 0 < \theta < 30^\circ \)
- **Chiral Index**: \( \nu = n_1-n_2 \mod 3 = 0,1,-1 \)
Electronic Structure

Metal
• Finite Density of States (DOS) at Fermi Energy

Semiconductor
• Gap at Fermi Energy

Graphene
• Zero Gap Semiconductor
• Zero DOS metal
Low Energy Theory of Graphene

“Effective Mass” Model: Massless Dirac Hamiltonian

\[ H_{\text{eff}} = \hbar v_F \psi^\dagger \sigma \cdot \nabla \psi \]

\[ E(q) = \pm \hbar v_F |q| \quad \hbar v_F = 0.53 \text{ eV nm} \]

Tight Binding model: \( \hbar v_F = \sqrt{3} \gamma_0 a / 2 \); \( \gamma_0 = 2.5 \text{ eV} \)
Wrap it up......

- **Flat Graphene:**
  A zero gap semiconductor

- **Periodic boundary conditions on cylinder:**

  \[ n_1 - n_2 = 0 \mod 3 \]
  1D Metal

  \[ n_1 - n_2 = +/-1 \mod 3 \]
  Semiconductor
Near-infrared Photoluminescence from Single-wall Carbon Nanotubes

O’Connel et al. (Science 02)
Bachillo et al. (Science 02)

Excitation (661 nm)  Emission (> 850 nm)
Each peak in the correlation plot corresponds to a particular species \([n_1,n_2]\) of semiconducting nanotube.

**GOAL:**

Understand observed transition energies in terms of low energy properties of an ideal 2 dimensional graphene sheet.
Free Electron Theory of Nanotube Bandgaps

Systematic expansion for large radius, $R$

• Zeroth order:

$$E_n^0 = \frac{2\hbar v_F}{3} \frac{n}{R} \quad (n = 1, 2, 4, 5, \ldots)$$
Free Electron Theory of Nanotube Bandgaps

Systematic expansion for large radius, $R$

- **Zeroth order:**
  \[ E_n^0 = \frac{2\hbar v_F}{3} \frac{n}{R} \quad (n = 1, 2, 4, 5, \ldots) \]

- **Trigonal Warping Correction**
  \[ \Delta E^{T,W}_n \propto (-1)^n \nu \frac{n^2 \sin 3\theta}{R^2} \]

- **Curvature Correction**
  \[ \Delta E^C_n \propto (-1)^n \nu \frac{\sin 3\theta}{R^2} \]

Curvature and Trigonal Warping:
- Vary as $1/R^2$
- Alternate with band index $n$
- Alternate with chiral index $\nu$
- Vanish for armchair tubes, $\theta = 0$

Different dependence on $n$

The large $R$ limit is most accurate for nearly armchair tubes: $\theta \sim 0$

$E_n^0$ describes tight binding gaps accurately for $R > .5$ nm
Nanotube Assignments from Pattern of sin 3θ/R² Deviations

Experimental “Ratio Plot”

• By comparing the experimental and theoretical ratio plots the [n₁,n₂] values (and hence R and θ) for each peak can be identified.

• Corroborated by Raman spectroscopy of the radial breathing mode.
The Ratio Problem

- Free electron theory predicts $E_{22} / E_{11} \to 2$ for $R \to \infty$
- Consequence of linear dispersion of graphene

Increasing diameter
Scaling of Optical Transition Energies

(Kane, Mele ’04)

- Free electrons for $\theta=0$
  \[ E_{nn}^0 (R) = 2\hbar v_F n / 3R \]

- $v \sin 3\theta / R^2$ deviations are clear

- Separatrix between $v=+1$ and $v=-1$ describes nearly armchair tubes with $\theta=0$, where $\sin 3\theta/R^2$ deviations vanish.
Scaling of Optical Transition Energies

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- Nearly armchair \([p+1,p]\) tubes

![Graph showing the scaling of optical transition energies.](image)
Scaling of Optical Transition Energies

(Kane, Mele ’04)

- Free electrons for θ=0
  \[ E_{nn}^0(R) = \frac{2\hbar v_F n}{3R} \]

Ratio Problem:
  \[ E_{22} / E_{11} < 2 \]

Blue Shift Problem:
  \[ E_{nn}(R) > E_{nn}^0(R) \]
  Worse for large R

Nonlinear scaling \( E_{nn}(R) = E(q_n = n/3R) \) accounts for both effects.
Electron Interactions in large radius tubes

For $2\pi R >> a$ electron interactions can be classified into three regimes, which lead to distinct physical effects.

- **Long Range Interaction**: $(r > 2\pi R)$
  - One Dimensional in character
  - **Strongly bound excitons**

- **Intermediate Range Interaction**: $(a < r < 2\pi R)$
  - Two Dimensional in character
  - **Nonlinear Scaling with n/R**

- **Short Range Interaction**: $(r \sim a)$
  - Atomic in character
  - **Exciton “Fine Structure”**
Long Range Interaction: \((r > 2\pi R)\)

\[
V(z) = \frac{e^2}{\varepsilon |z|}
\]

- Renormalize Single Particle Gap
  - Increase observed energy gap
- Leads to exciton binding
  - Decrease observed energy gap
- Single Particle and Particle hole gaps both scale linearly with \(1/R\):

\[
E_G^0 \sim \hbar v_F / R
\]

\[
\frac{\hbar^2}{2m^*} \sim \hbar v_F R
\]

\[
E(R) \sim \left(\frac{\hbar v_F}{R}\right) f \left(\frac{e^2}{\varepsilon \hbar v_F}\right)
\]

- Gap renormalization and exciton binding largely cancel each other.
Cancellation of gap renormalization and exciton binding:

- **Single Particle excitation:**
  
  Self energy $\sim \frac{e^2}{\varepsilon R}$
  
  Depends on dielectric environment

- **Particle-hole excitation:**
  
  Bound exciton is unaffected by the long range part of the interaction.

The cancellation is *exact* for an infinite range interaction

- **Coulomb Blockade Model:**
  
  Bare gap: $2\Delta$
  
  Interaction energy: $U \frac{N^2}{2}$

- Single particle gap: $2\Delta + U$

- Particle-hole gap: $2\Delta$
Intermediate Range Interaction: \((a < r < 2\pi R)\)

- Leads to nonlinear \(q \log q\) dispersion of graphene.
- Responsible for nonlinear scaling of \(E_{11}(n/R)\).

Short Range Interaction: \((r \sim a)\)

- Leads to “fine structure” in the exciton spectrum: \(S=0,1,\text{ etc.}\)
- Splittings \(\sim e^2 a / R^2\)
Interactions in 2D Graphene  

\[ H = \frac{\hbar v_F}{2} \int d^2 r \psi^\dagger \psi \sigma \cdot \nabla \psi + e^2 \int d^2 r d^2 r' \frac{n(r)n(r')}{2 |r - r'|} \]

- Renormalized Quasiparticle Dispersion:

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

Singularity due to long range Coulomb interaction \( V(q) = 2\pi e^2/q \).
Interactions in 2D Graphene  

\[ H = \hbar v_F \int d^2 r \psi^+ \sigma \cdot \nabla \psi + e^2 \int d^2 r d^2 r' \frac{n(r)n(r')}{2|r-r'|} \]

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• “Dielectric Screening” in 2 Dimensions

\[ \varepsilon_{\text{screened}} = \frac{g}{\varepsilon} \quad \Pi_{\text{static}}(q) = q/4v_F \quad \varepsilon_{\text{static}} = 1 + g\pi/2 \]
Interactions in 2D Graphene  

\[ H = \hbar v_F \int d^2r \psi^+ \frac{\sigma \cdot \nabla}{i} \psi + e^2 \int d^2r d^2r' \frac{n(r)n(r')}{2 |r - r'|} \]

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- “Dielectric Screening” in 2 Dimensions

\[ g_{\text{screened}} = g/\varepsilon \quad \Pi_{\text{static}}(q) = q/4v_F \quad \varepsilon_{\text{static}} = 1 + g\pi/2 \]

- Scaling Theory \( g = g(\Lambda); \quad v_F = v_F(\Lambda) \)

\[ \frac{dg}{d \ln \Lambda} = -\frac{1}{4} g^2 \quad \text{Marginally Irrelevant} \]

- \( q \ln q \) correction is exact for \( q \neq 0 \)
Compare 2D Theory with Experiment

\[ E_{nn} = E(q_n = n / 3R) \]

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

\( \hbar v_F = .47 \text{ eV nm} \)

\( g = \frac{e^2}{\varepsilon \hbar v_F} = 1.2 \quad \Rightarrow \quad \varepsilon \sim 2.5 \)
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Compare 2D Theory with Experiment

\[
\begin{align*}
E_{nn} &= E(q_n = n / 3R) \\
E(q) &= 2\hbar v_F q \left(1 + \frac{g}{4} \log \frac{\Lambda}{q}\right) \\
\hbar v_F &= 0.47 \text{ eV nm} \\
g &= \frac{e^2}{\varepsilon \hbar v_F} = 1.2 \quad \Rightarrow \quad \varepsilon \sim 2.5
\end{align*}
\]

The optical spectra reflects the finite size scaling of the 2D Marginal Fermi Liquid
Exciton effects: Compute particle-hole binding due to statically screened interaction (similar to Ando ‘97).

- Lowest exciton dominates oscillator strength for each subband.
- Lineshape for absorption is not that of van Hove singularity.
- Large bandgap renormalization mostly cancelled by exciton binding.

Related Work:
- Spaturu et al (Berkeley) PRL 03
- Perebeinos et al (IBM) PRL 04
Scaling behavior: \( E_n(R) = E \left( q_n = n/3R \right) \)

\[
\frac{3R}{v_F n} E_{nn}(R) = \log \left( \frac{3R \Lambda}{n} \right)
\]

\[
E_{\text{exciton}}^{nn}(R) = \frac{v_F n}{3R} \left[ c_n + \frac{e^2}{4 \epsilon \hbar v_F} \log \frac{3R \Lambda}{n} \right]
\]

\( c_n \sim \text{independent of } n \)
Exciton Fine Structure

Degenerate exciton states:

\[
\begin{align*}
\text{e : } & \quad k = K \text{ or } K' \quad ; \quad s = \uparrow \text{ or } \downarrow \\
\text{h : } & \quad k = K \text{ or } K' \quad ; \quad s = \uparrow \text{ or } \downarrow
\end{align*}
\]

16 states

Degeneracy lifted by short range \((q\sim 1/a)\) interactions:

Effective 2D Contact Interaction:

\[
H_C = \int d^2r \sum_{\alpha\beta\gamma\delta} U_{abcd} \psi_{a\alpha}^{\dagger}(\vec{r}) \psi_{b\beta}(\vec{r}) \psi_{c\gamma}^{\dagger}(\vec{r}) \psi_{d\delta}(\vec{r})
\]

\[
U \sim e^2a
\]

\[
\langle H_C \rangle \sim \frac{e^2a}{4\pi R\xi}
\]

\(
\xi \sim \text{exciton size } \sim 2\pi R
\)
Exciton Eigenstates:

Classify by momentum, spin, parity under $C_2$ rotation

- $q = \pm K ; \ S = 0$
- $q = 0 ; \ S = 0 ;$ odd (Optically Allowed)
- $q = 0 ; \ S = 0 ;$ even
- $q = 0 ; \ S = 1 ;$ odd
- $q = \pm K ; \ S = 1$
- $q = 0 ; \ S = 1 ;$ even

~30 meV (R~.5nm)

“Dark States”

See also Zhao, Mazumdar PRL 04
Conclusion

Fluorescence spectroscopy data for nearly armchair tubes is well described by a systematic large radius theory.

- **2D interactions:**
  - q log q renormalization of graphene dispersion.
  - Non linear scaling with 1/R.
  - Explains ratio problem and blue shift problem.

- **1D interactions**
  - Lead to large gap enhancement AND large exciton binding
  - Largely cancels in optical experiments revealing 2D effects.

- **Short Range interactions**
  - Lead to fine structure in exciton levels
  - Dark Ground State

**Experiments:** measure single particle energy gap

- Tunneling (complicated by screening)
- Photoconductivity
- Activated transport