Electron Interactions and Nanotube Fluorescence Spectroscopy

C.L. Kane & E.J. Mele

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

Phys. Rev. Lett. in press
cond-mat/ 0403153

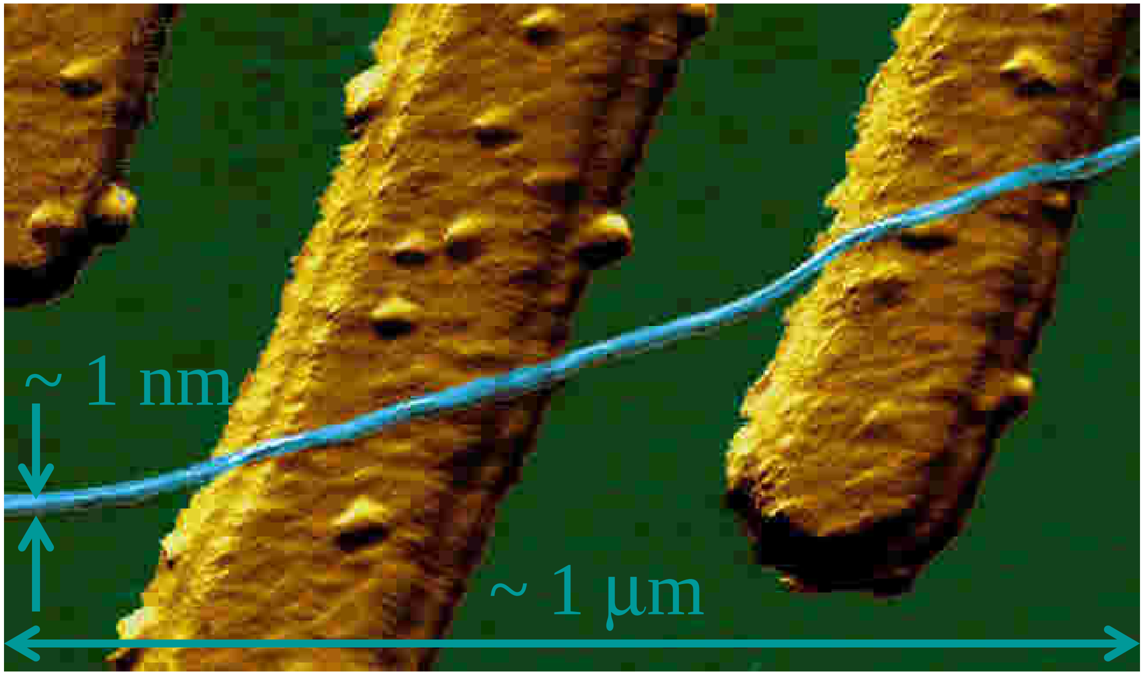
- Brief Introduction to nanotubes
- Independent electron model for optical spectra
- 2D interactions: nonlinear scaling with 1/R
- 1D interactions: excitons
- Short Range Interactions: exciton fine structure

Penn
University of Pennsylvania

LRSM the University of Pennsylvania's Materials Research Science and Engineering Center

Carbon Nanotubes as Electronic Materials

Gate Source Drain



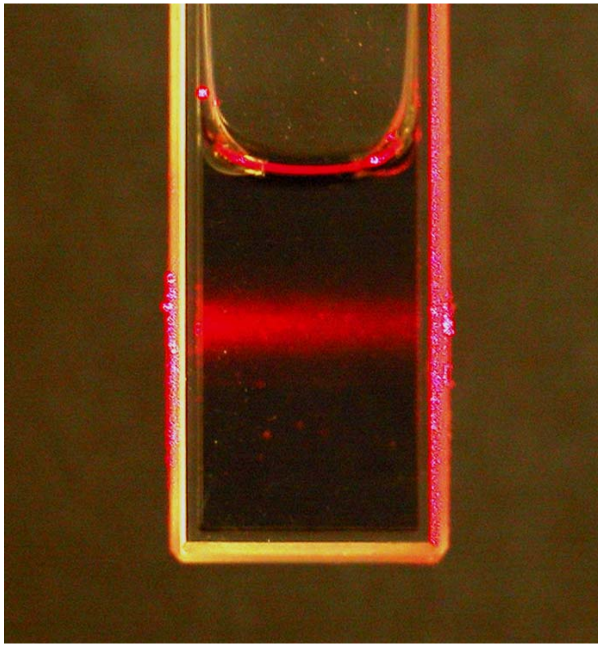
A Molecular Quantum Wire

Tans et al. (Nature 1998)

- Ballistic Conductor
- Field Effect Transistor
- Logic Gates

Carbon Nanotubes as Optical Materials

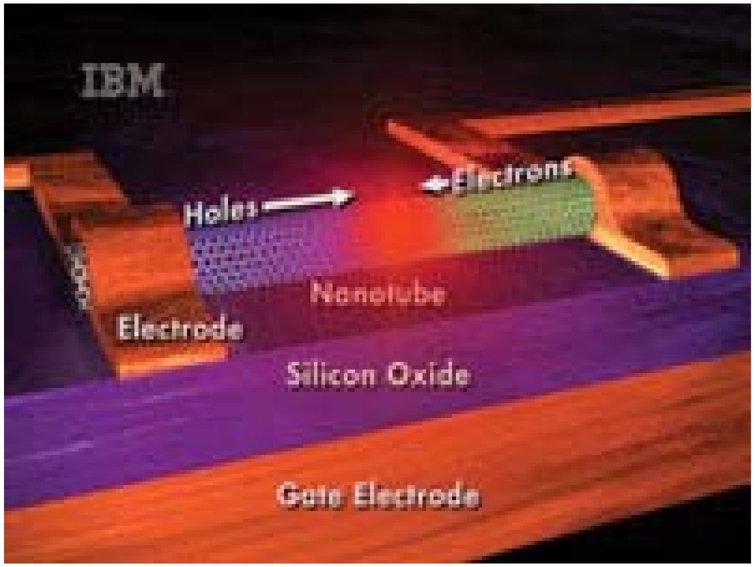
Photoluminescence



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

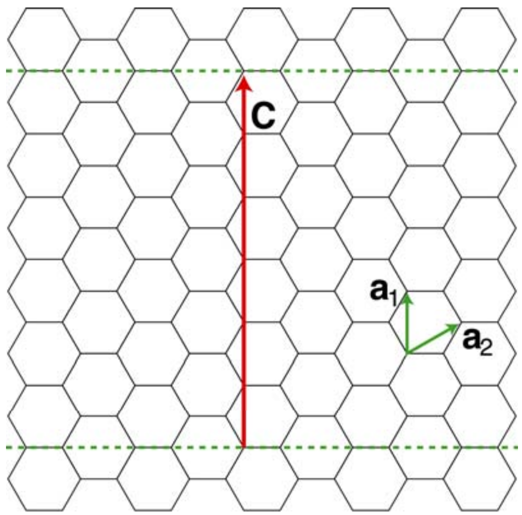
- Photoluminescence from individual suspended nanotubes Lefebvre et al. (2003).

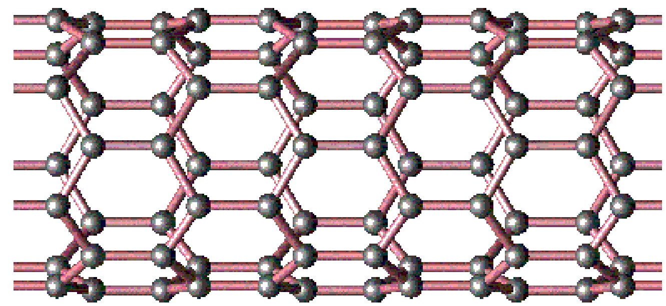
Electroluminescence & Photoconductivity



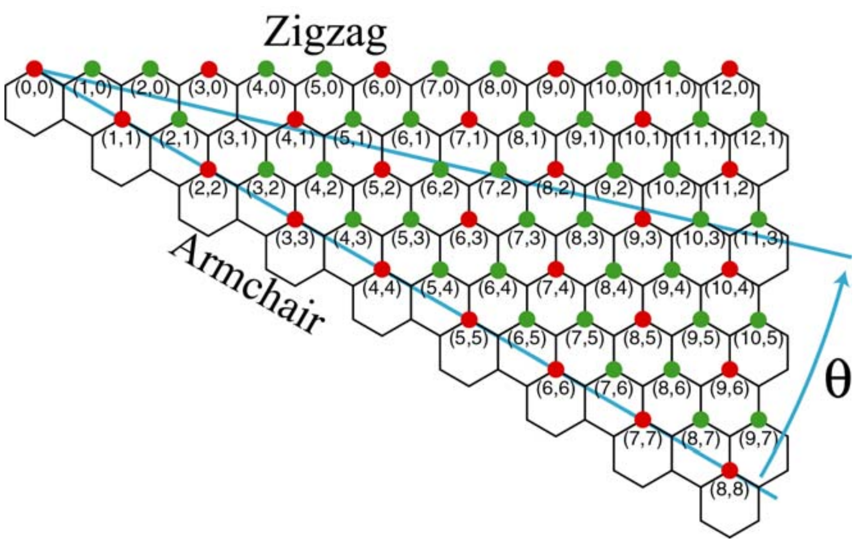
- Infrared Emission, photoconductivity in individual nanotube field effect devices Freitag et al., (IBM) 2004

Carbon Nanotube : Wrapped Graphene





$\mathbf{C} = n_1\,\mathbf{a}_1 + n_2\,\mathbf{a}_2$



Tubes characterized by $[n_1,n_2]$ or

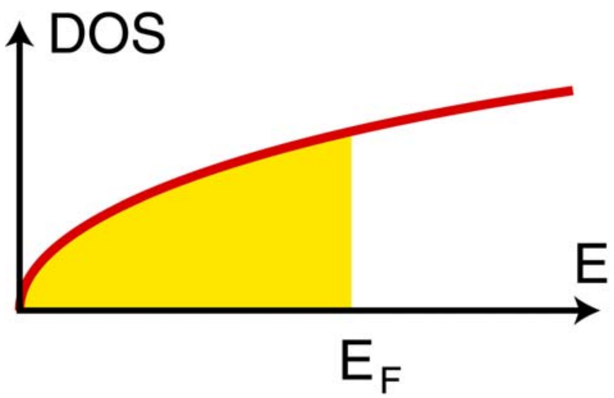
- Radius : $R = |\mathbf{C}|/2\pi$
- Chiral Angle : $0 < \theta < 30^o$
- Chiral Index : $\nu = n_1 - n_2 \bmod 3$

  $= 0,1,-1$

Electronic Structure

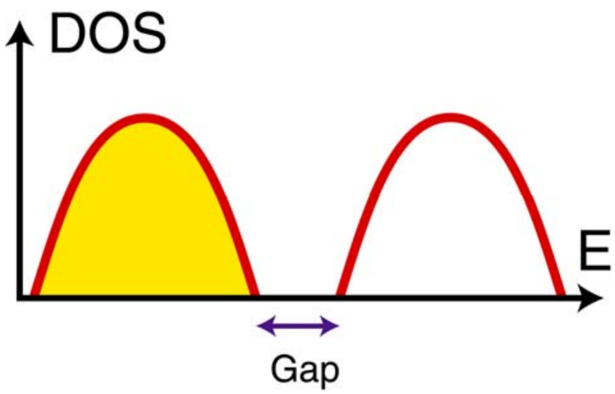
Metal

- Finite Density of States (DOS) at Fermi Energy



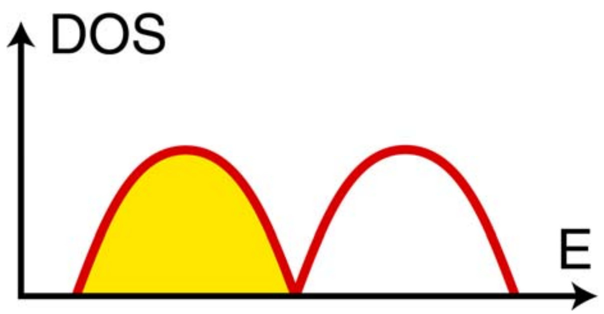
Semiconductor

- Gap at Fermi Energy



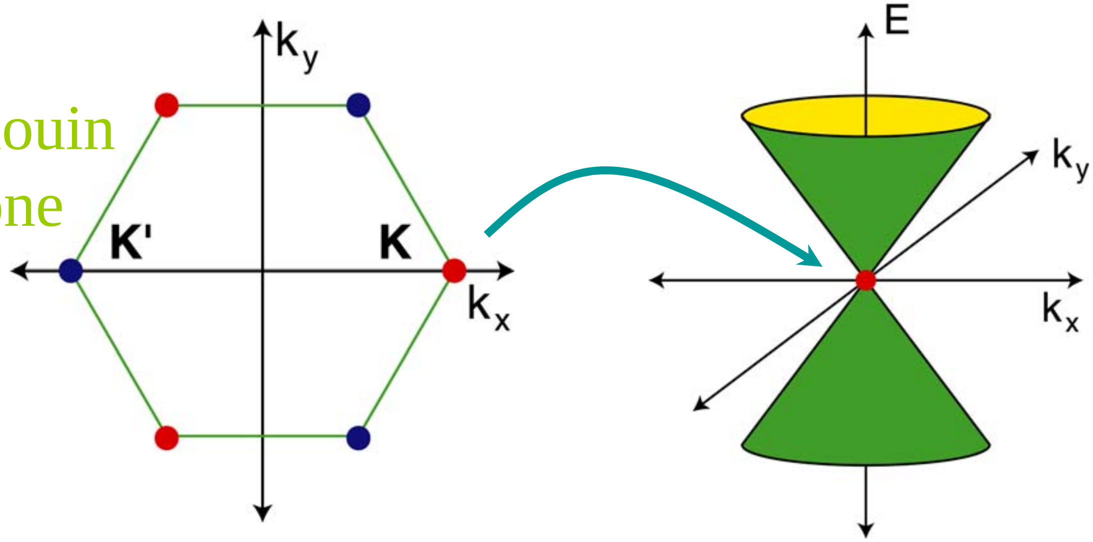
Graphene

- Zero Gap Semiconductor
- Zero DOS metal



Low Energy Theory of Graphene

Brillouin Zone



"Effective Mass" Model: Massless Dirac Hamiltonian

$$H_{eff} = \hbar \mathrm{v}_F \psi^\dagger \frac{\sigma \cdot \nabla}{i} \psi$$

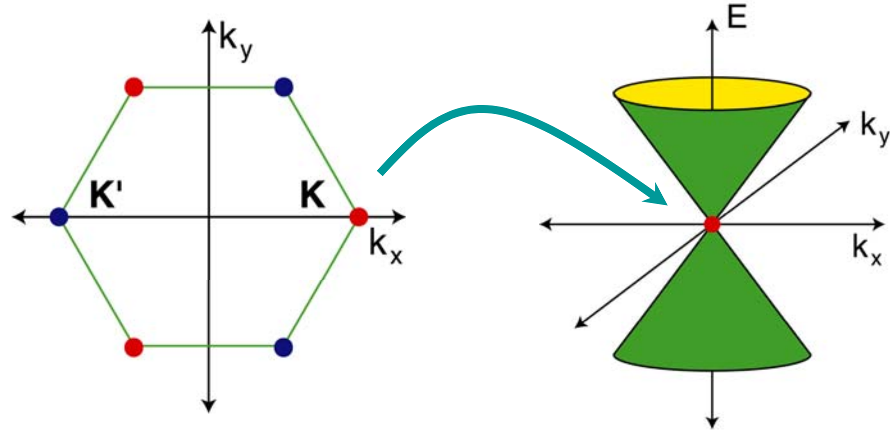
$$E(q) = \pm \hbar \mathrm{v}_F \, | q | \qquad \hbar \mathrm{v}_F = 0.53 \text{ eV nm}$$

Tight Binding model: $\hbar \mathrm{v}_\mathrm{F} = \sqrt{3}\gamma_0 a / 2$; $\gamma_0 = 2.5$ eV

Wrap it up……

- Flat Graphene:

  A zero gap semiconductor



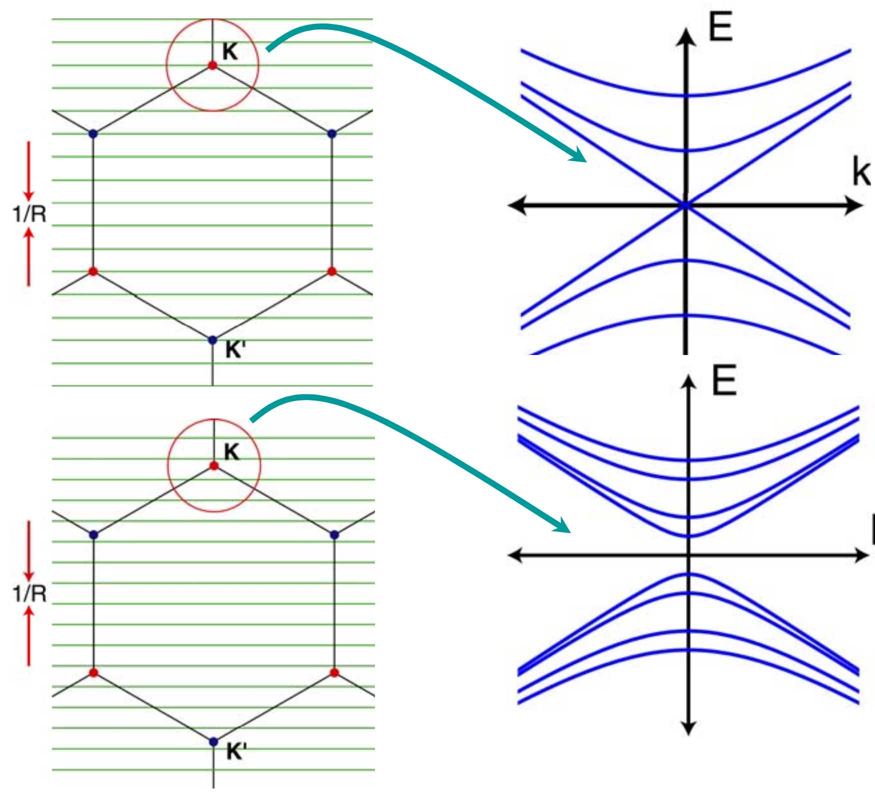
- Periodic boundary conditions on cylinder:

n_1-n_2 = 0 mod 3

1D Metal

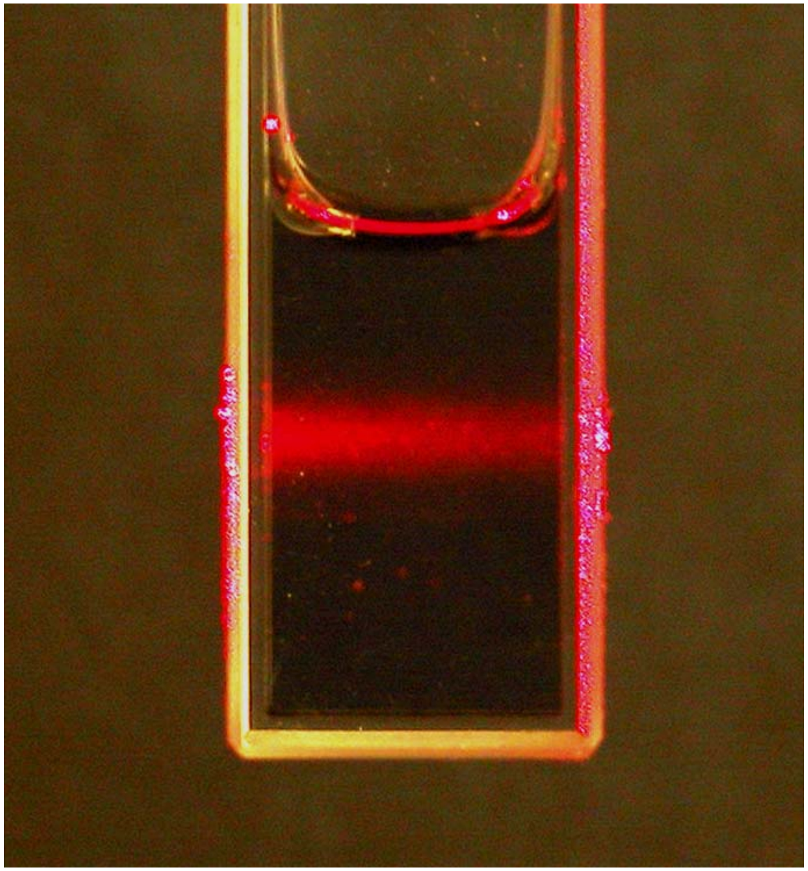
n_1-n_2 = +/-1 mod 3

Semiconductor

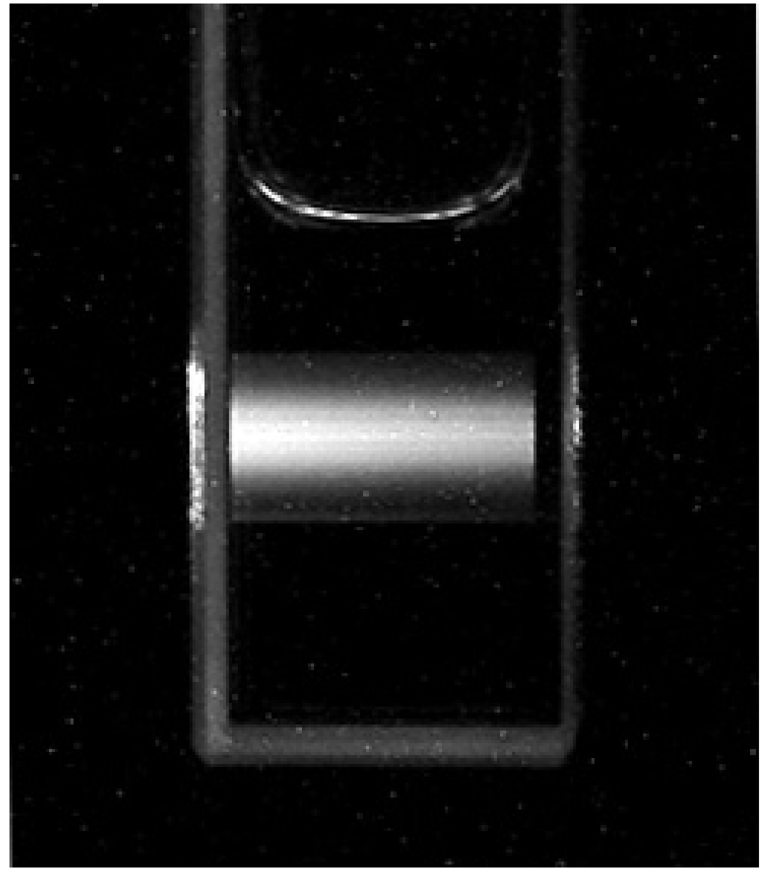


Near-infrared Photoluminescence from Single-wall Carbon Nanotubes

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



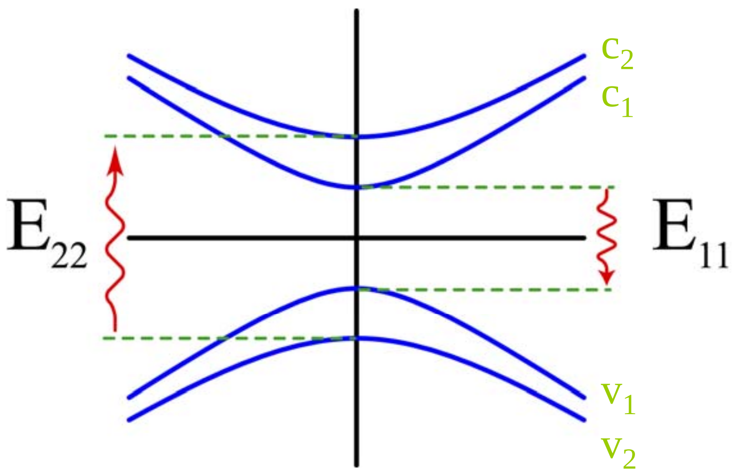
Excitation (661 nm)

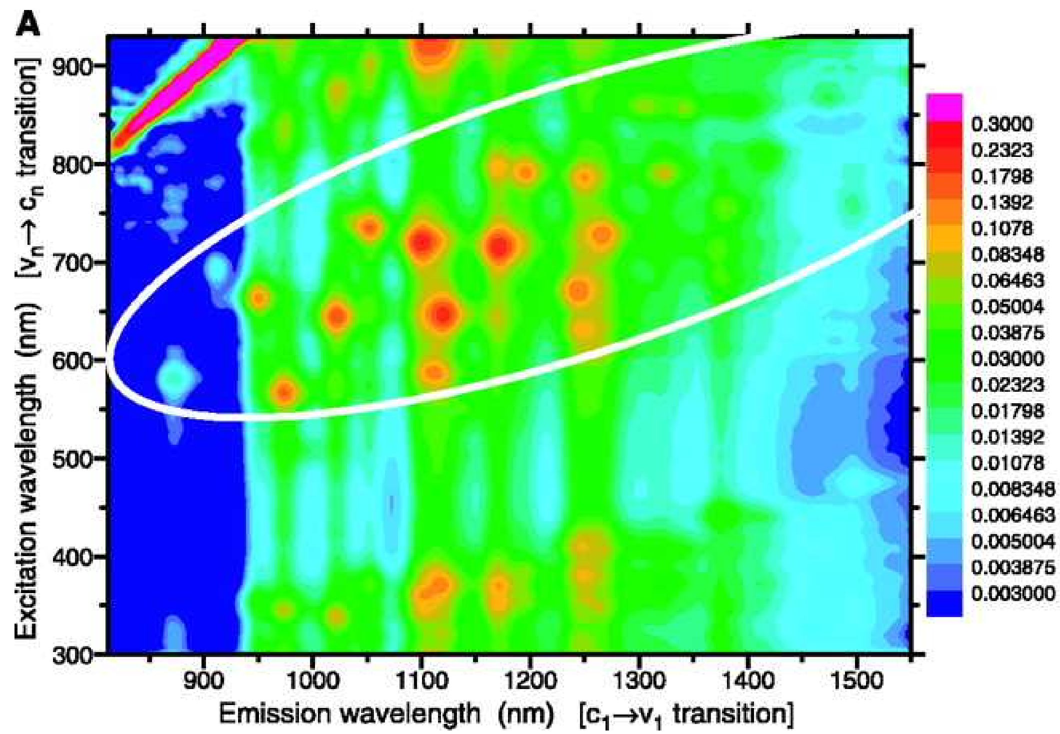


Emission (> 850 nm)

Nanotube Fluorescence Spectroscopy

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





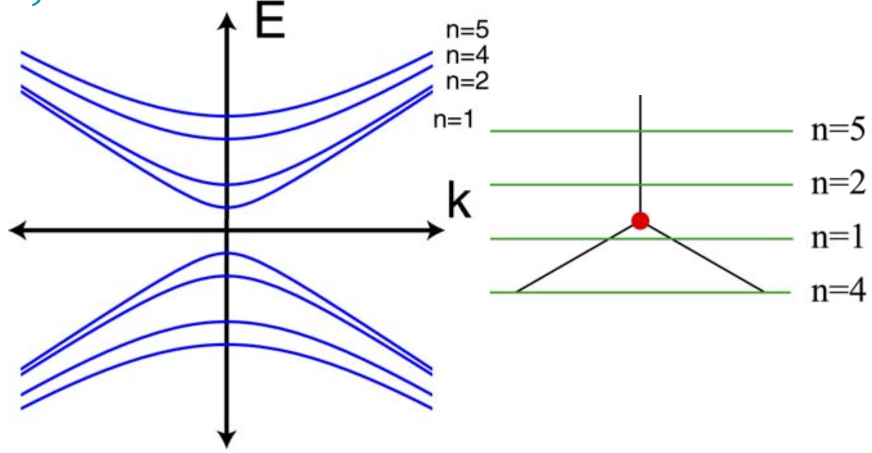
Each peak in the correlation plot corresponds to a particular species $[n_1,n_2]$ of semiconducting nanotube

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

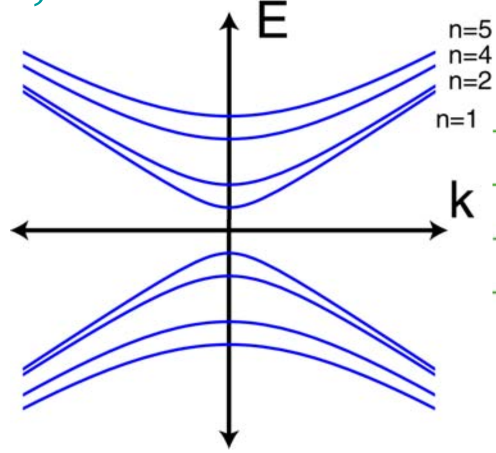


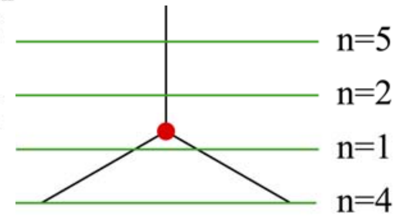
- Zeroth order:

$$E_n^0 = \frac{2\hbar v_F}{3} \frac{n}{R} \qquad (n = 1, 2, 4, 5, \ldots)$$

Free Electron Theory of Nanotube Bandgaps

Systematic expansion for large radius, R



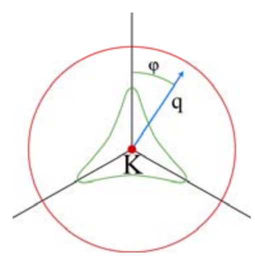


- Zeroth order:

$$E_n^0 = \frac{2\hbar v_F}{3}\frac{n}{R} \qquad (n = 1, 2, 4, 5, \ldots)$$

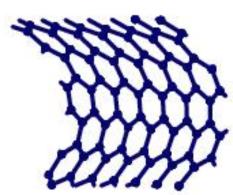
- Trigonal Warping Correction

$$\Delta E_n^{T.W.} \propto (-1)^n \nu \frac{n^2 \sin 3\theta}{R^2}$$



- Curvature Correction

$$\Delta E_n^{C} \propto (-1)^n \nu \frac{\sin 3\theta}{R^2}$$



Curvature and Trigonal Warping:

- Vary as $1/R^2$
- Alternate with band index n
- Alternate with chiral index ν
- Vanish for armchair tubes, θ=0

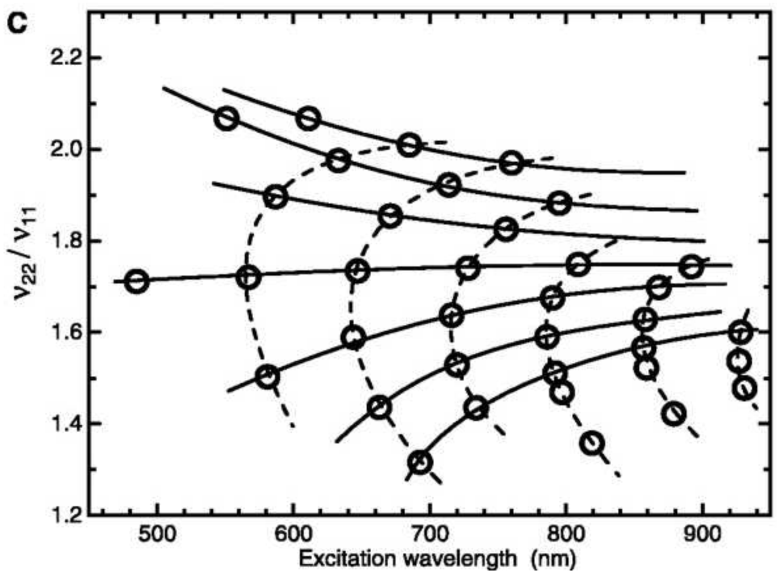
Different dependence on n

The large R limit is most accurate for nearly armchair tubes: θ ~ 0

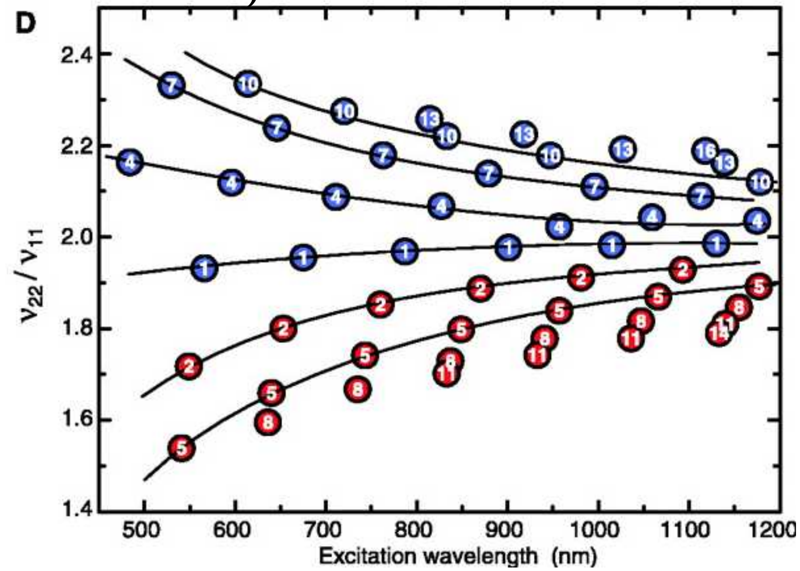
E_n^0 describes tight binding gaps accurately for R > .5 nm

Nanotube Assignments from Pattern of sin 3θ/R^2 Deviations

Experimental "Ratio Plot"



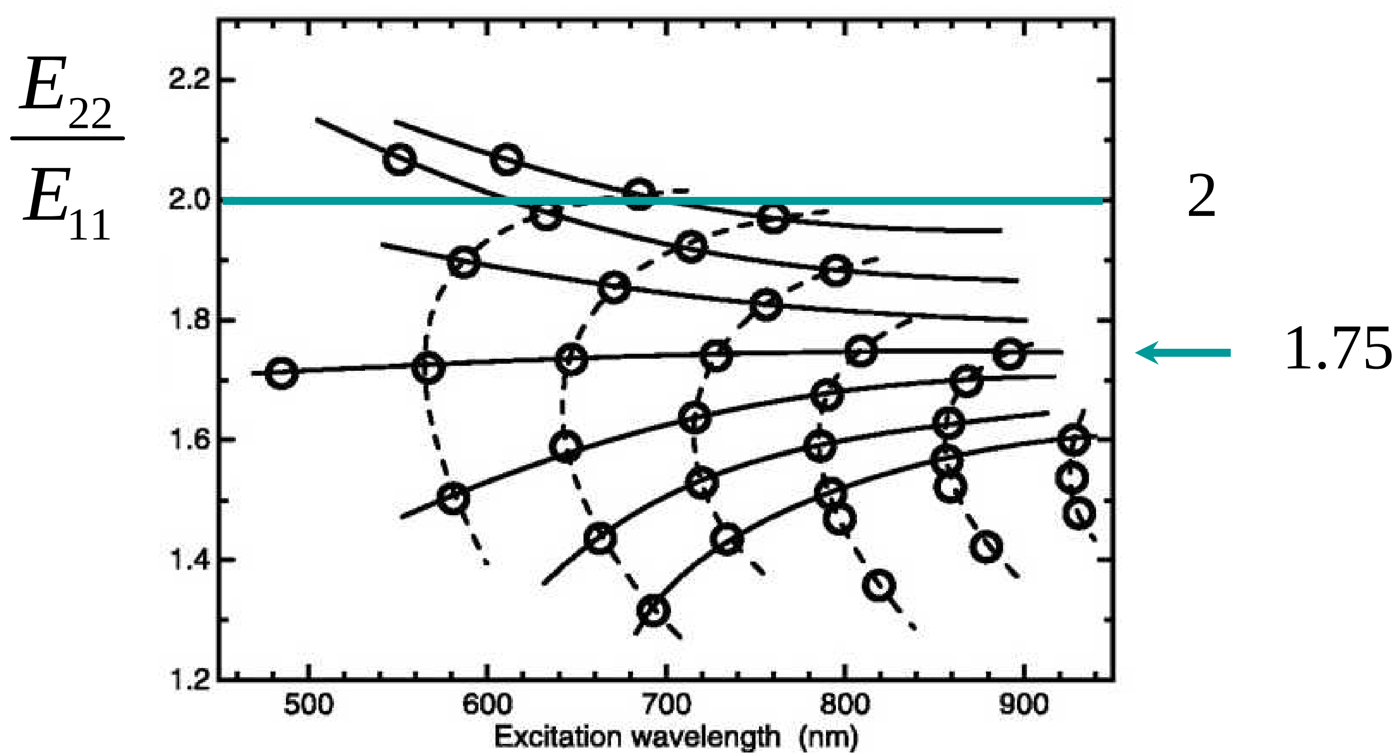
Theory (includes sin3θ/R^2 deviations)



- By comparing the experimental and theoretical ratio plots the $[n_1,n_2]$ values (and hence R and θ) for each peak can be identified.
- Corroborated by Raman spectroscopy of the radial breathing mode.

The Ratio Problem

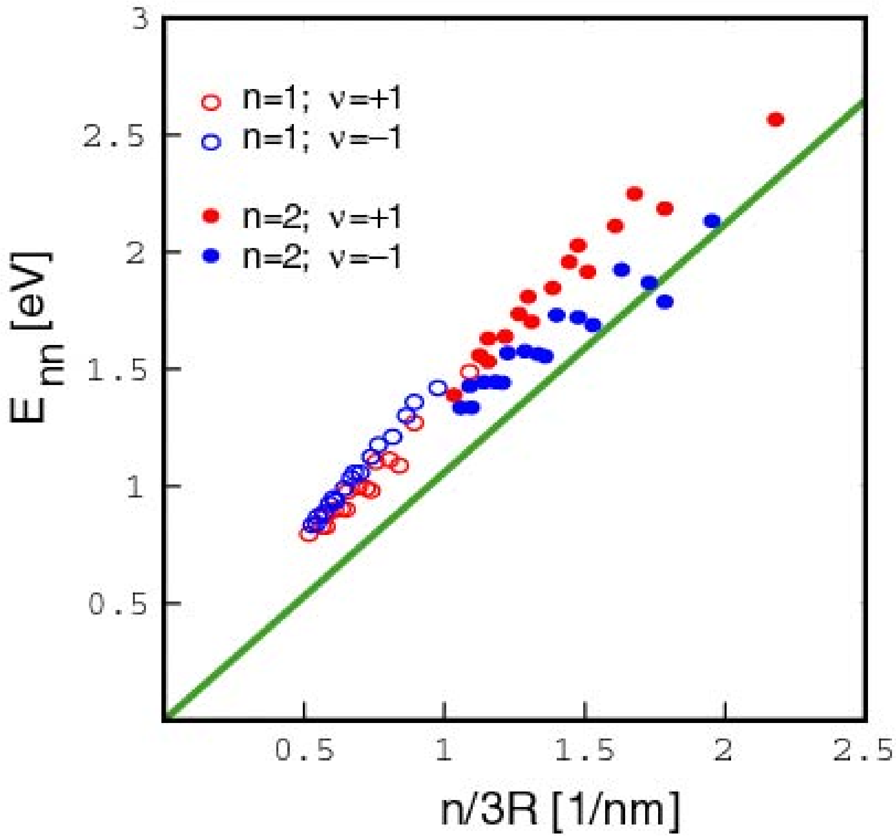
- Free electron theory predicts $E_{22}/E_{11} \rightarrow 2$ for $R \rightarrow \infty$
- Consequence of linear dispersion of graphene



Increasing diameter →

Scaling of Optical Transition Energies

(Kane,Mele ’04)



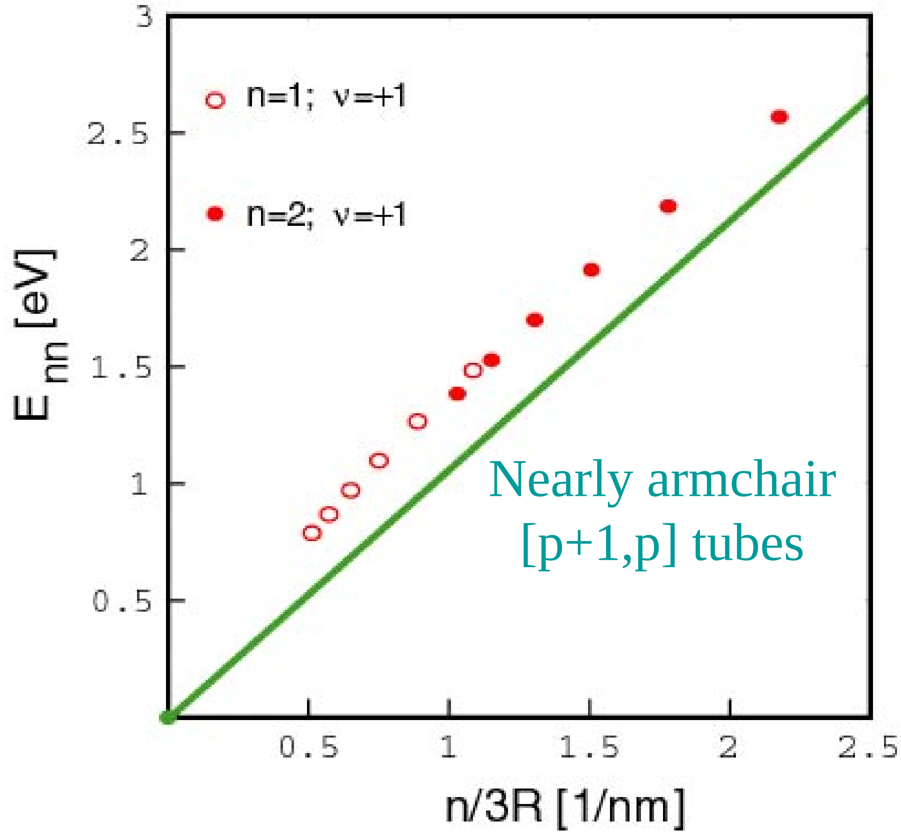
— Free electrons for θ=0

$$E^0_{nn}(R) = 2\hbar v_F n / 3R$$

- ν sin 3θ / R^2 deviations are clear
- Separatrix between ν=+1 and ν=−1describes nearly armchair tubes with θ=0, where sin 3θ/R^2 deviations vanish.

Scaling of Optical Transition Energies

(Kane,Mele ’04)



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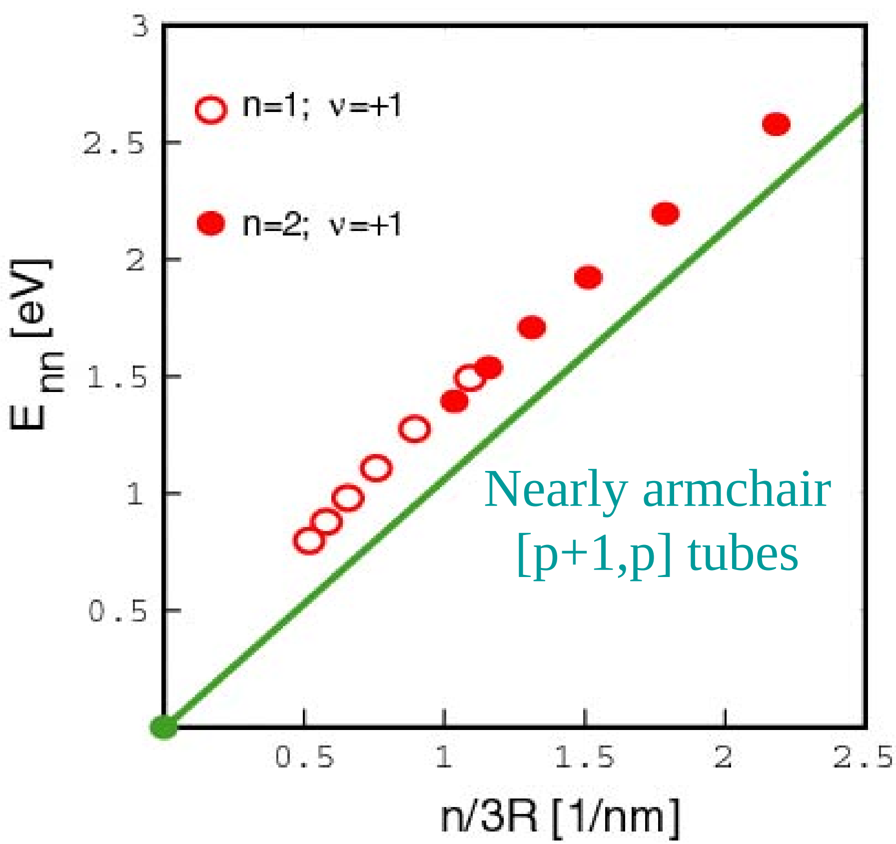


— Free electrons for θ=0

$$E^0_{nn}(R) = 2\hbar v_F n / 3R$$

Ratio Problem:

$$E_{22} / E_{11} < 2$$

Blue Shift Problem:

$$E_{nn}(R) > E^0_{nn}(R)$$

Worse for large R

Nonlinear scaling $E_{nn}(R)=E(q_n=n/3R)$ accounts for both effects.

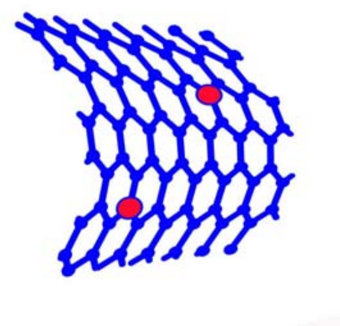
Electron Interactions in large radius tubes

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

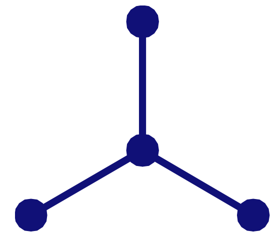


- Intermediate Range Interaction : $(a < r < 2\pi R)$

Two Dimensional in character

➡ Nonlinear Scaling with n/R

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



Atomic in character

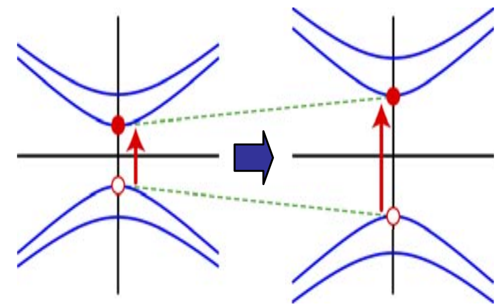
➡ Exciton “Fine Structure”

Long Range Interaction : (r > 2πR)

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

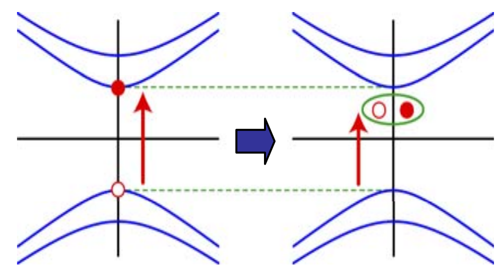
- Renormalize Single Particle Gap

  Increase observed energy gap



- Leads to exciton binding

  Decrease observed energy gap



- Single Particle and Particle hole gaps both scale linearly with 1/R :

$$E_G^0 \sim \hbar v_F / R$$

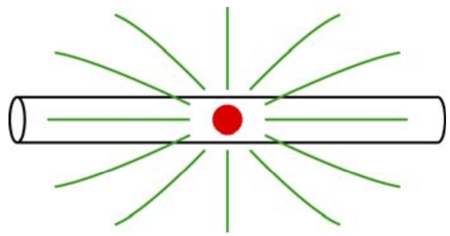
$$\hbar^2 / 2m^* \sim \hbar v_F R$$

$$\Rightarrow \quad E(R) \sim (\hbar v_F / R)\, f\,(e^2 / \varepsilon \hbar v_F)$$

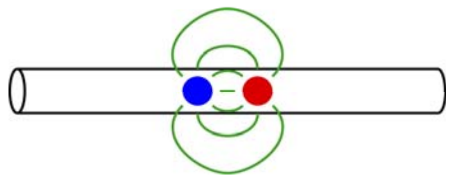
- Gap renormalization and exciton binding largely cancel each other.

Cancellation of gap renormalization and exciton binding:

- Single Particle excitation:
  Self energy ~ $e^2/\varepsilon R$
  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

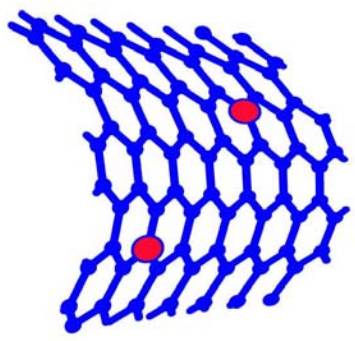
- Coulomb Blockade Model :

  Bare gap: 2Δ Interaction energy: $U N^2/2$

- Single particle gap $2\Delta + U$
- Particle-hole gap 2Δ

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, etc.
- Splittings $\sim e^2 a / R^2$

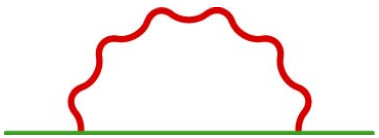
Interactions in 2D Graphene

Gonzalez, Guinea, Vozmediano, PRB 99

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

- Renormalized Quasiparticle Dispersion:

$$E(q) = \hbar v_F q \left(1 + \frac{g}{4} \log \frac{\Lambda}{q} \right) \qquad g = e^2 / \hbar v_F$$



Singularity due to long range Coulomb interaction $V(q) = 2\pi e^2/q$.

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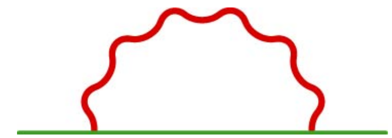

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- "Dielectric Screening" in 2 Dimensions

$g_{screened} = g/\varepsilon \qquad \Pi_{static}(q) = q/4v_F \qquad \varepsilon_{static} = 1 + g\pi/2$

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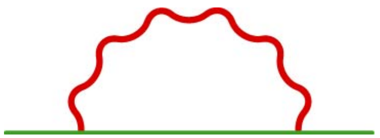

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- "Dielectric Screening" in 2 Dimensions

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

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

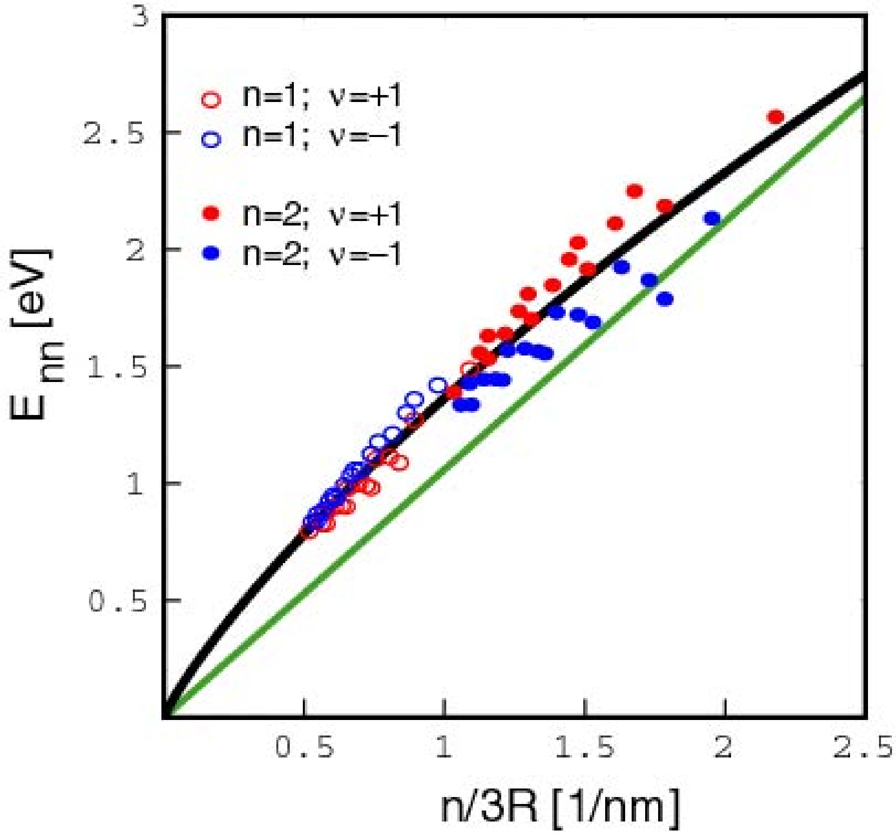
$$\frac{dg}{d\ln\Lambda} = -\frac{1}{4} g^2$$

Marginally Irrelevant

Marginal Fermi Liquid

- q ln q correction is exact for q⌘0

Compare 2D Theory with Experiment



Free electron Theory

2D Interacting Theory

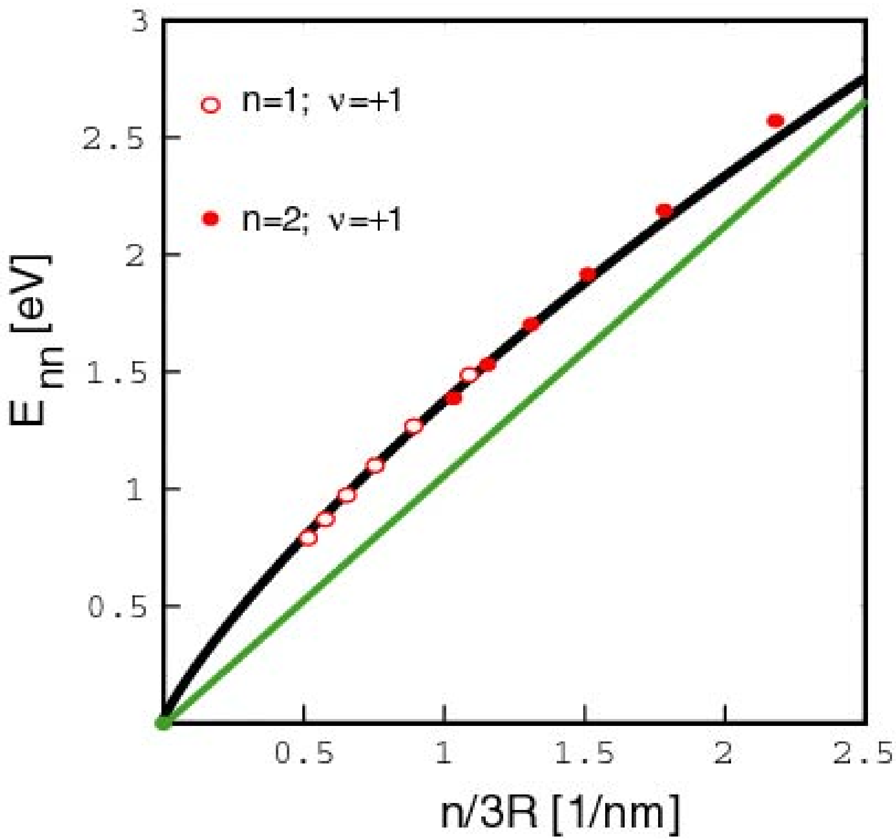
$$E_{nn} = E(q_n = n/3R)$$

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

$$\hbar v_F = .47 \text{ eV nm}$$

$$g = \frac{e^2}{\varepsilon \hbar v_F} = 1.2 \quad \Rightarrow \quad \varepsilon \sim 2.5$$

Compare 2D Theory with Experiment



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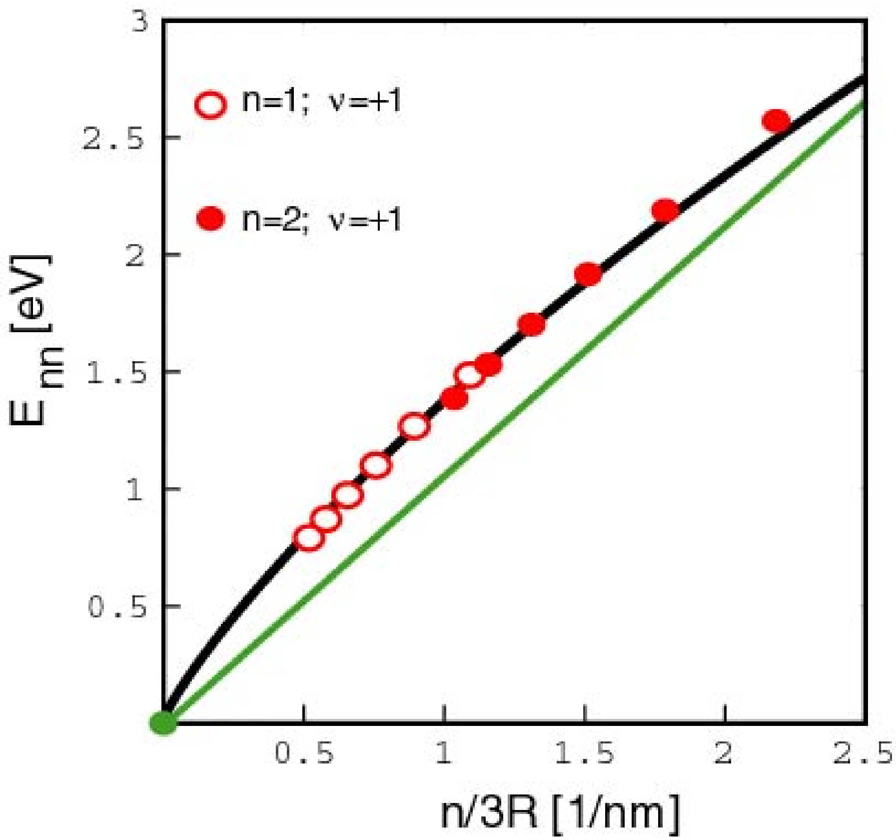

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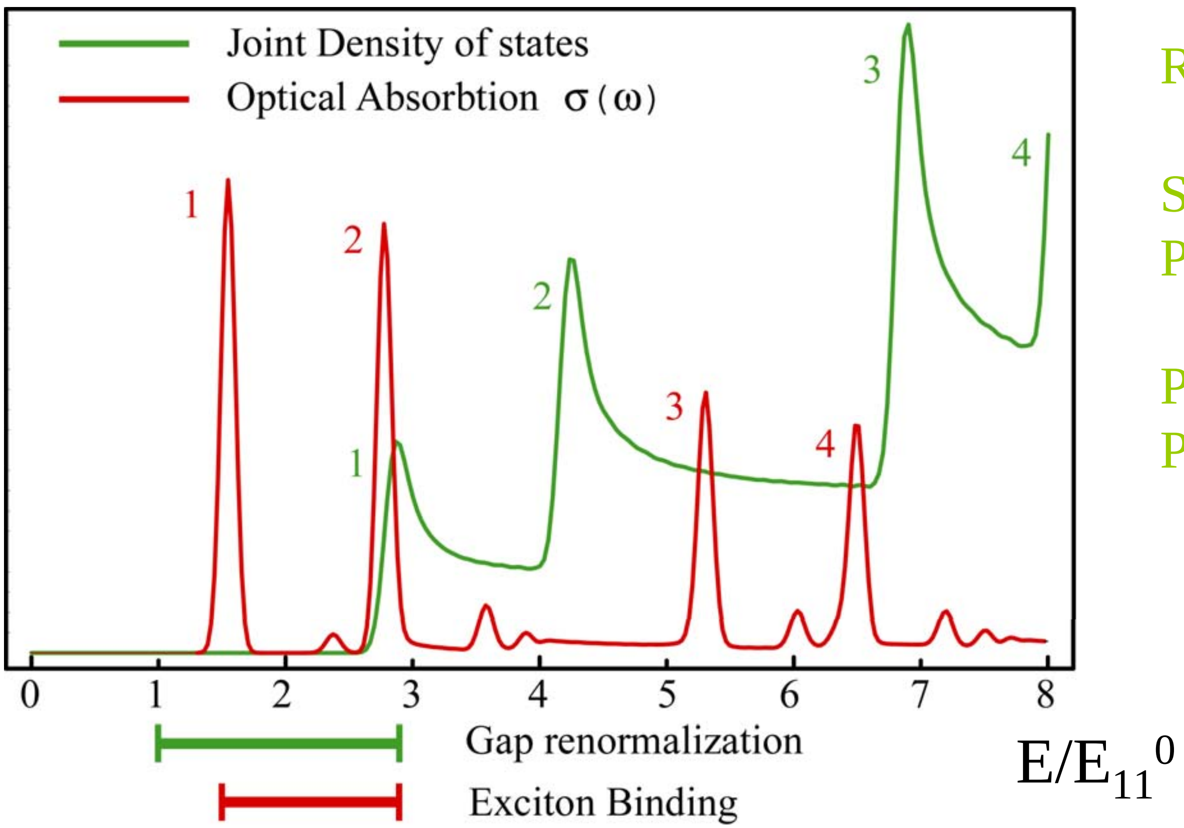
The optical spectra reflects the finite size scaling of the 2D Marginal Fermi Liquid

Exciton effects: Compute particle-hole binding due to statically screened interaction (similar to Ando '97).



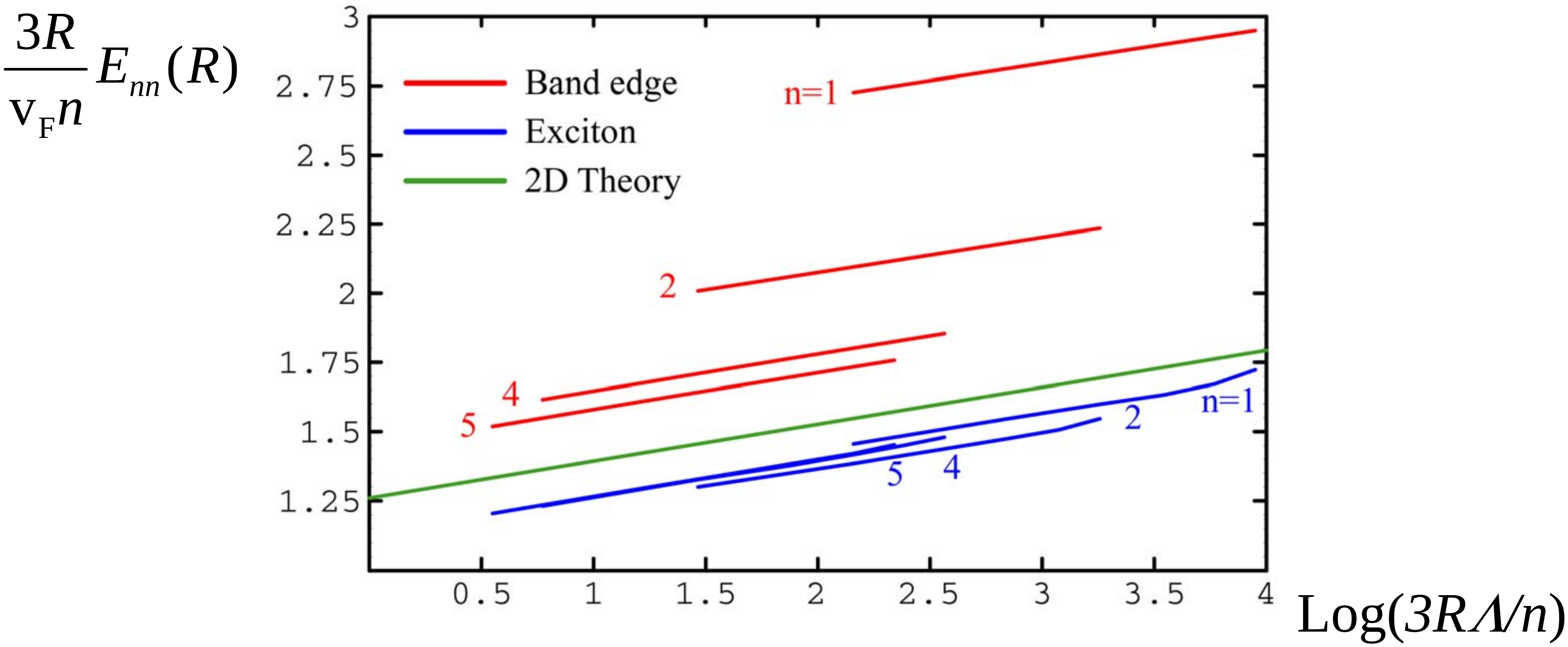
Related Work:

Spaturu et al (Berkeley) PRL 03

Perebeinos et al (IBM) PRL 04

- 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.

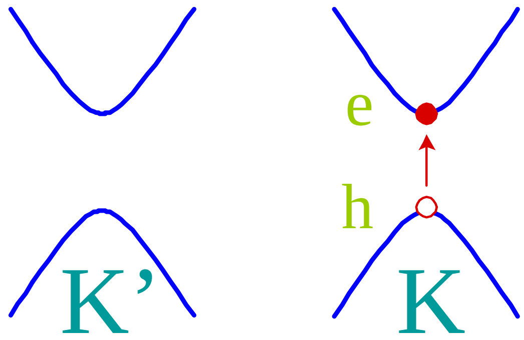
Scaling behavior: $E_n(R) = E(q_n \stackrel{?}{=} n/3R)$



$$E_{exciton}^{nn}(R) = \frac{v_F n}{3R}\left[c_n + \frac{1}{4}\frac{e^2}{\varepsilon\hbar v_F}\log\frac{3R\Lambda}{n}\right]$$

c_n ~ independent of n

Exciton Fine Structure

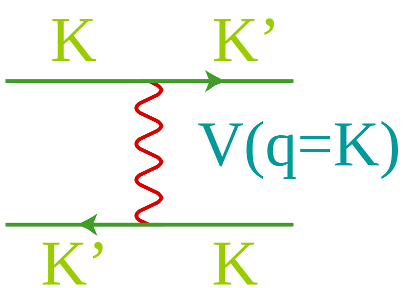


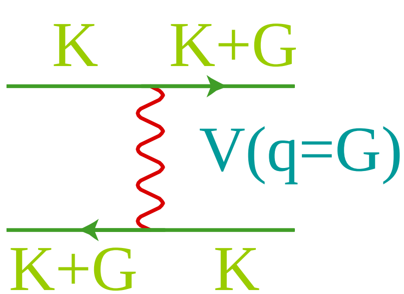
Degenerate exciton states:

$$\left.\begin{array}{l} \text{e}: \; k = K \text{ or } K' \;\; ; \quad s = \uparrow \text{ or } \downarrow \\ \text{h}: \; k = K \text{ or } K' \;\; ; \quad s = \uparrow \text{ or } \downarrow \end{array}\right\}$$

16 states

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





Effective 2D Contact Interaction:

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

$$U \sim e^2 a$$

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

ξ ~ exciton size ~ $2\pi R$

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

~30 meV
(R~.5nm)

$q = 0 \;;\; S = 1$; odd

$q = \pm K \;;\; S = 1 \;;$ — "Dark States"

$q = 0 \;;\; S = 1$; even

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