Many Body Effects in Carbon Nanotube Fluorescence Spectroscopy

E.J. Mele and C.L. Kane

Sheets and Cylinders of Graphene

Photophysics of NT's (mainly exptl)

<u>Scaling Relations</u> in Optical Properties from e-e Interactions

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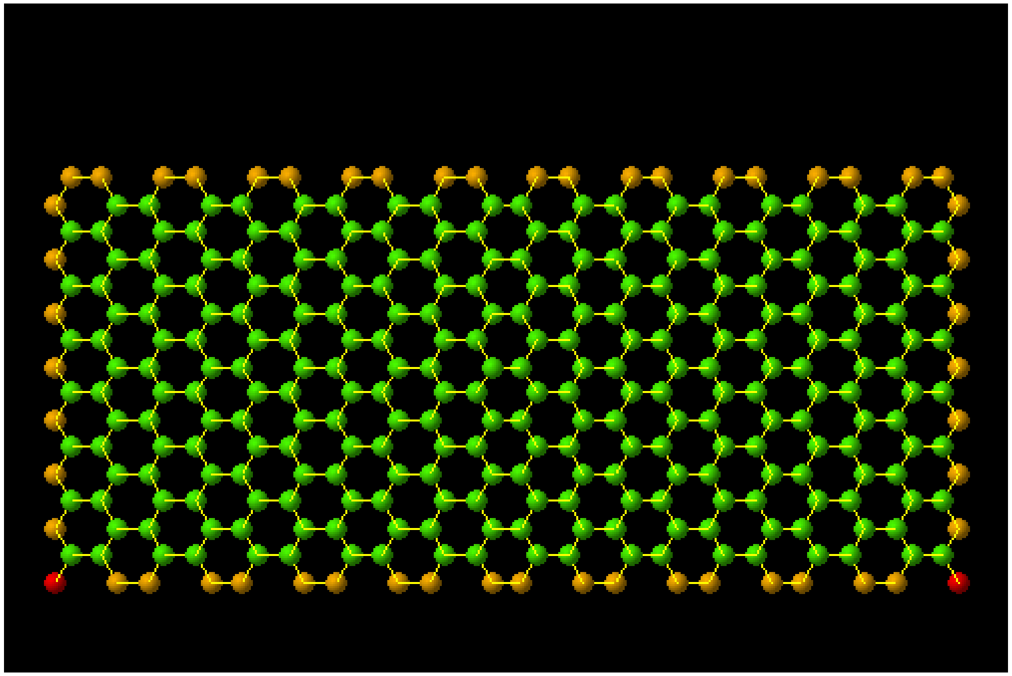
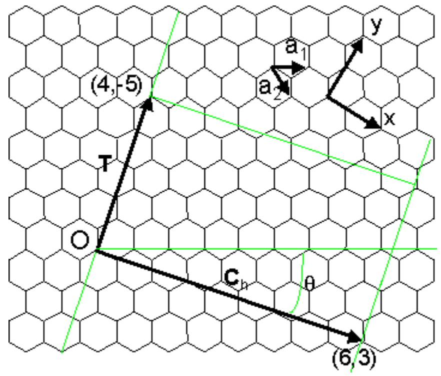
Nanotubes from wrapped graphene

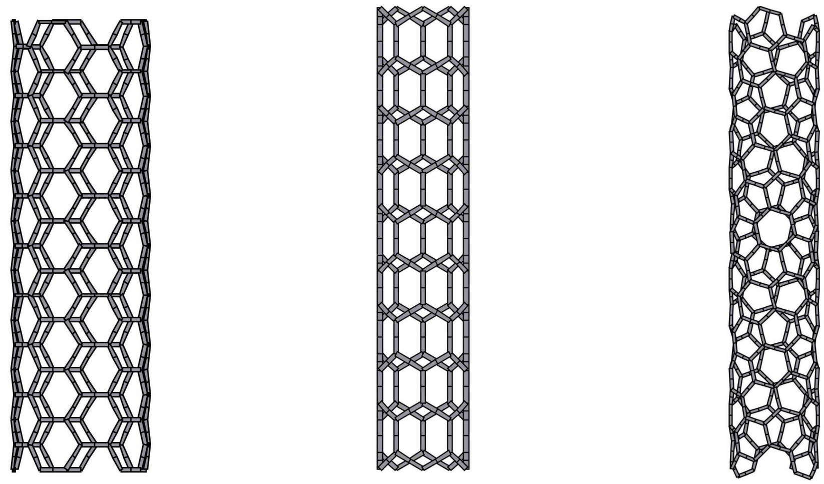


Each tube is indexed by the translation vector around its circumference

NT as a molecule, a 1D wire, a quantum dot, a semiconductor, an interconnect…

Rolling-up a graphene sheet



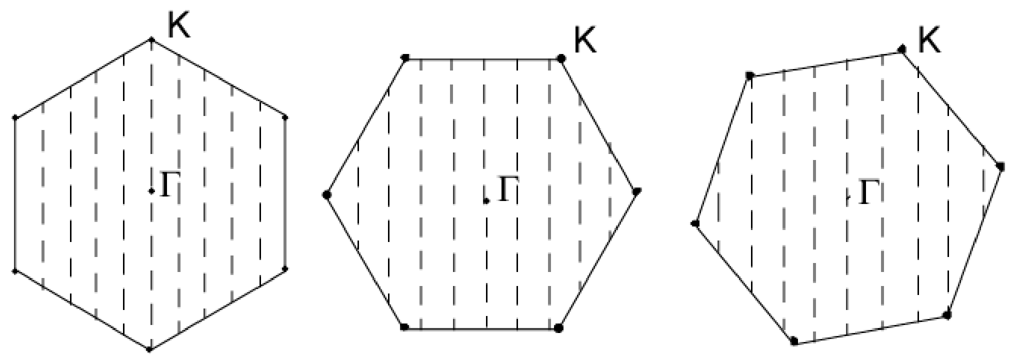


(5,5) Armchair Tube
Metal

(5,0) Zigzag Tube
Semiconductor

(5,-1) Tube
Metal
(small-gap SC)

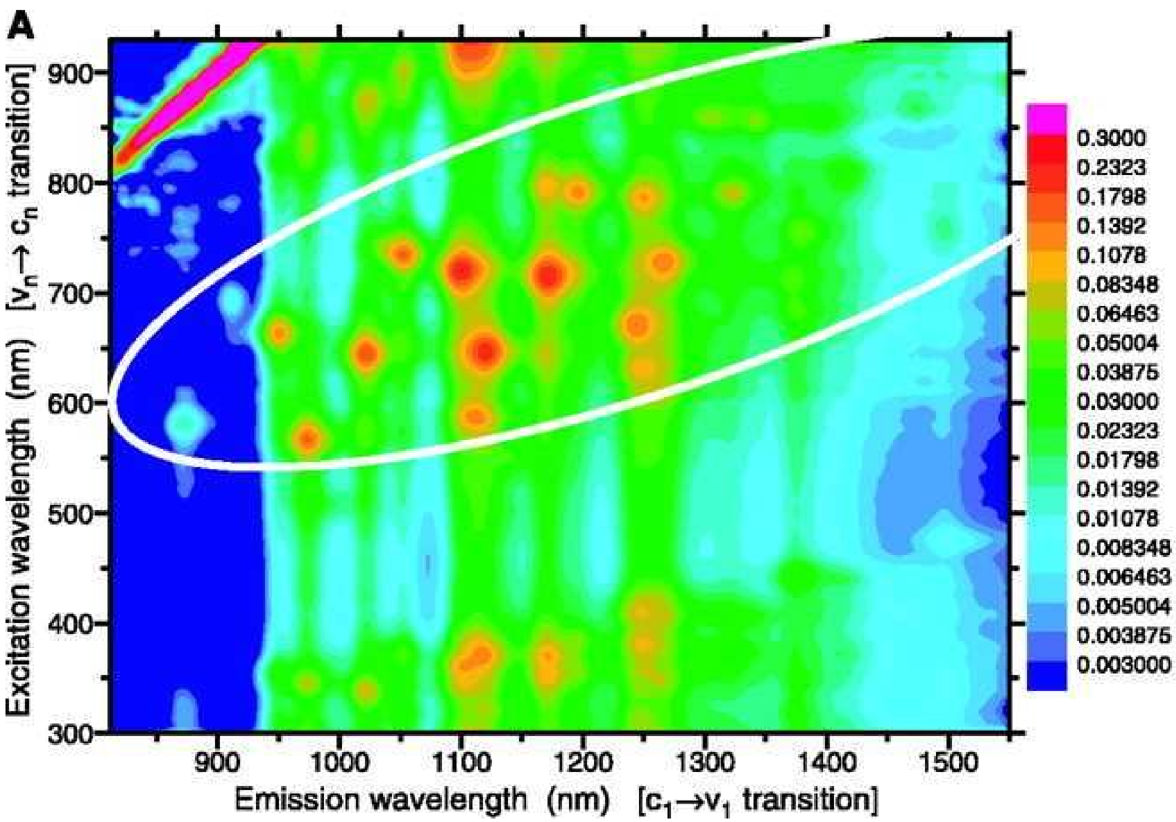
The (m,n) wrapping specifies a translation vector of the graphene lattice.



m=n **mod(m-n,3) = ±1** **mod(m-n,3) = 0, m≠n**

Two Dimensional PLE Spectroscopy

Discrete Peaks are Excitations of <u>Individual</u> SWNT's



- **The Ratio Problem**

  Anomalous scaling of <u>gap ratios</u> in large R limit

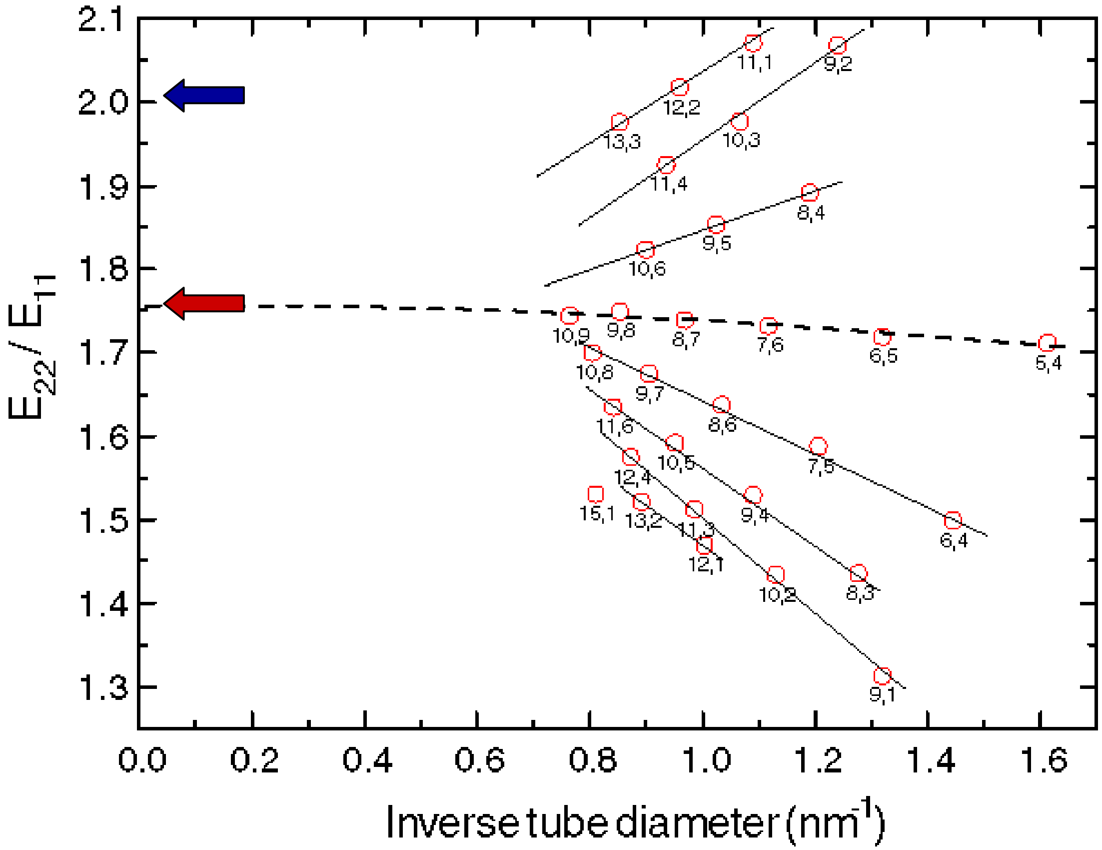
- **The Blue Shift Problem**

  The observed gaps are <u>blue shifted</u> with <u>nonlinear 1/R scaling</u>

- **The Deviations Problem**

  Anomalies in period-3 deviations from scaling

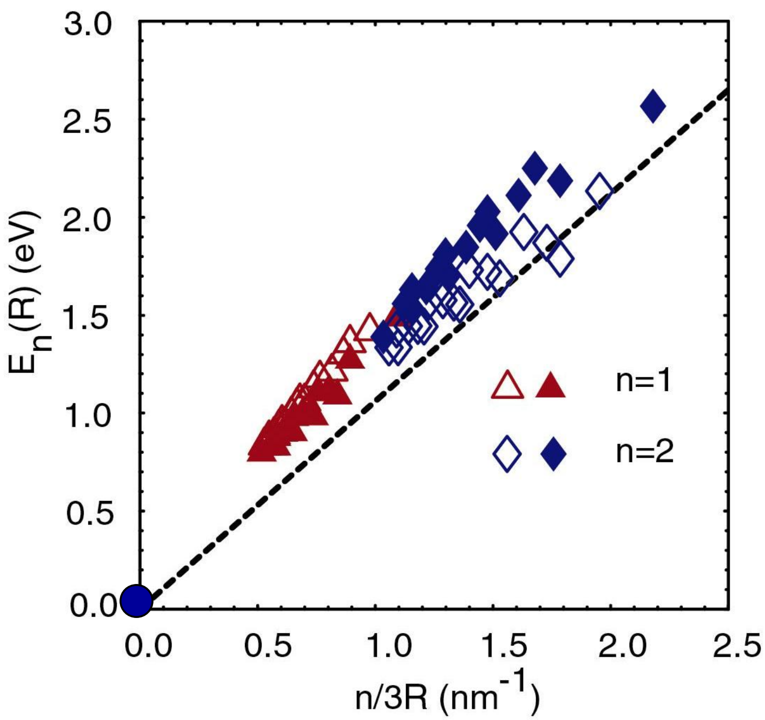
Ratio Problem: the ratio of absorption/emission frequencies < 2 in Large R Limit

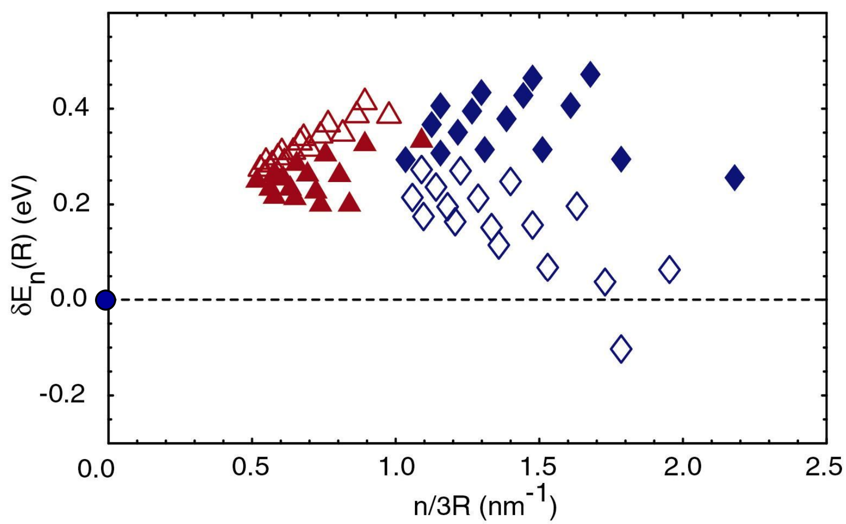


Data: S.M. Bachilo et al. Science 298, 2361 (2002)

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

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

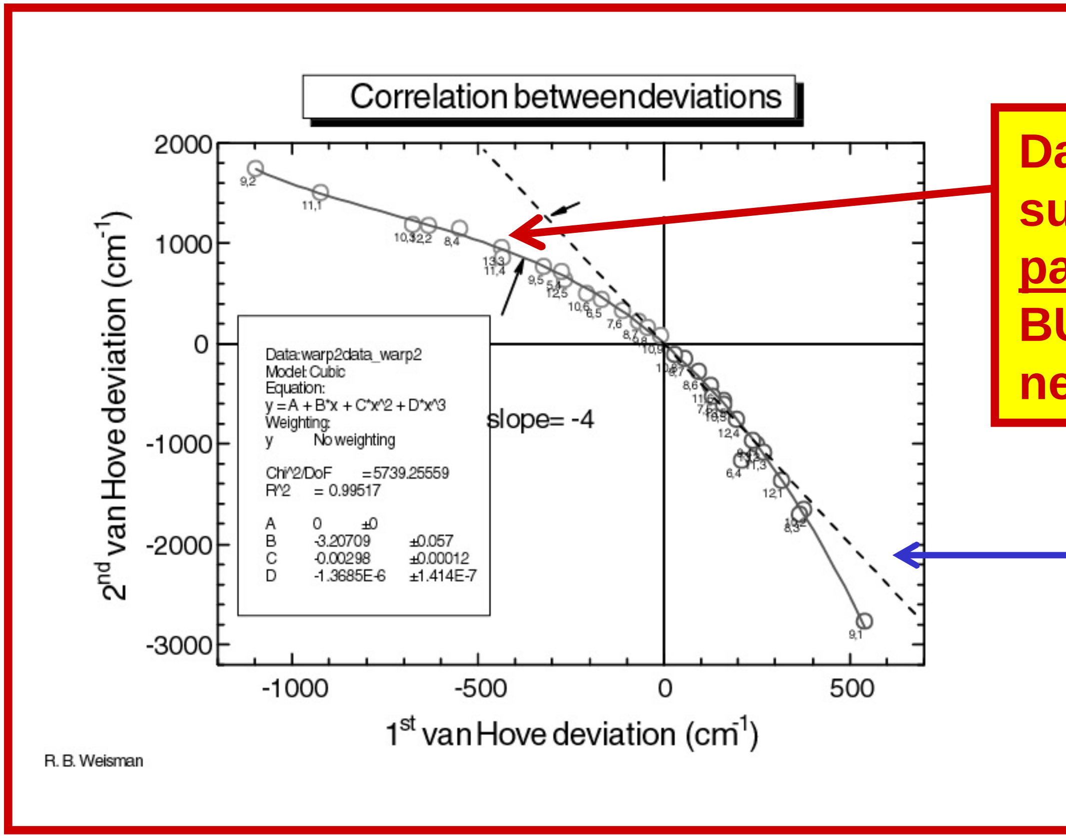




(nearly armchair tubes at border)

<u>Ratio Problem</u>: Scaling of Deviations from Scaling

(ref: Structure Assigned Optical Spectra of Single Wall Carbon Nanotubes, S. Bachilo et al., Science <u>298</u>, 2361 (2002))



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

trig.warping line

(This is still a puzzle..band effects? interactions? multiplet effects?)

<u>*Electron-Electron Interactions*</u>
<u>*are responsible for all three anomalies*</u>

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 <u>simplest</u> way)

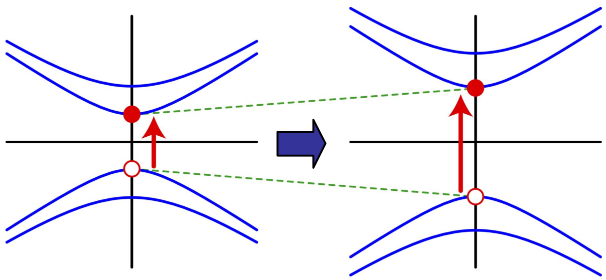
Separate 1D and 2D Interaction Effects

(the NT is actually a 2D structure)

Rule 1 There are competing interaction effects

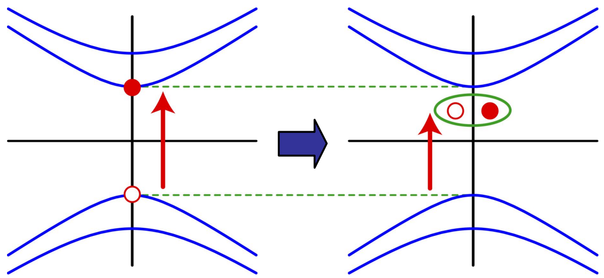
Coulomb Interaction gives a positive self energy…

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

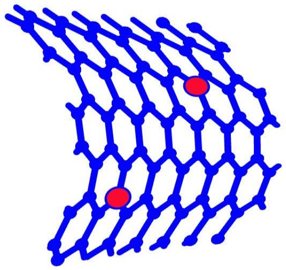
Rule 2 The tube radius sets a fundamental length scale: separation of 1D and 2D interaction effects

$$\boxed{V(r) = \frac{e^2}{r} = V_{\mathrm{long}}(r) + V_{\mathrm{short}}(r)}$$

Long Range Interaction : (r > 2πR)

One Dimensional
Unscreened for large separation

Short Range Interaction : (a < r < 2πR)



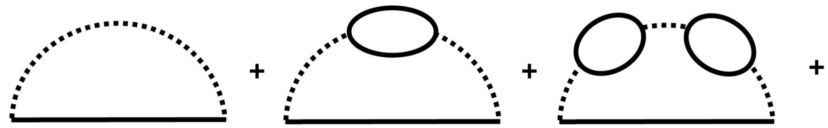
Two Dimensional

Leads to nonlinear q log q shift in dispersion of graphene, and nonlinearity in $E_{nn}(1/R)$

Interactions renormalize quasiparticle dispersion E(q) of two dimensional graphene

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

Interacting:



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

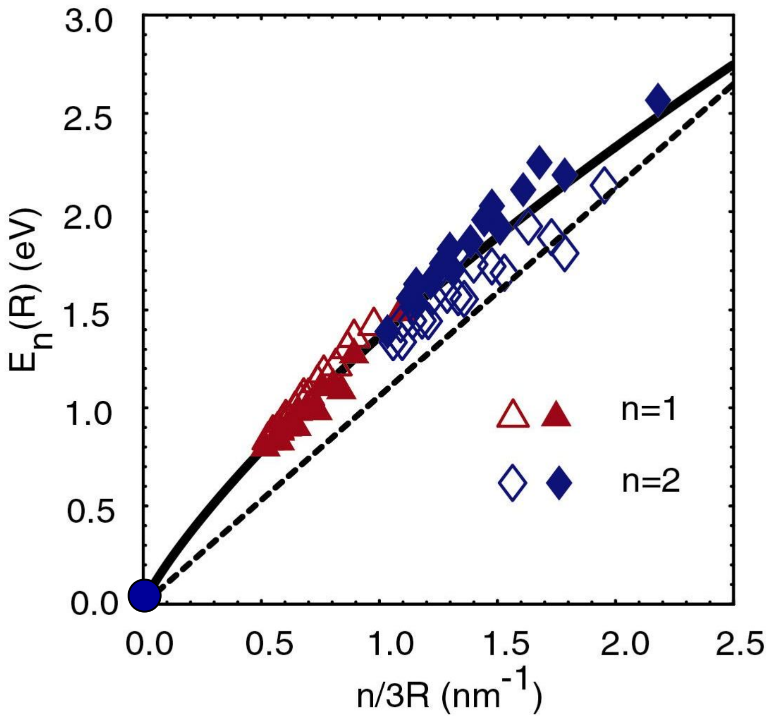
$$g = e^2 / \hbar v_F$$

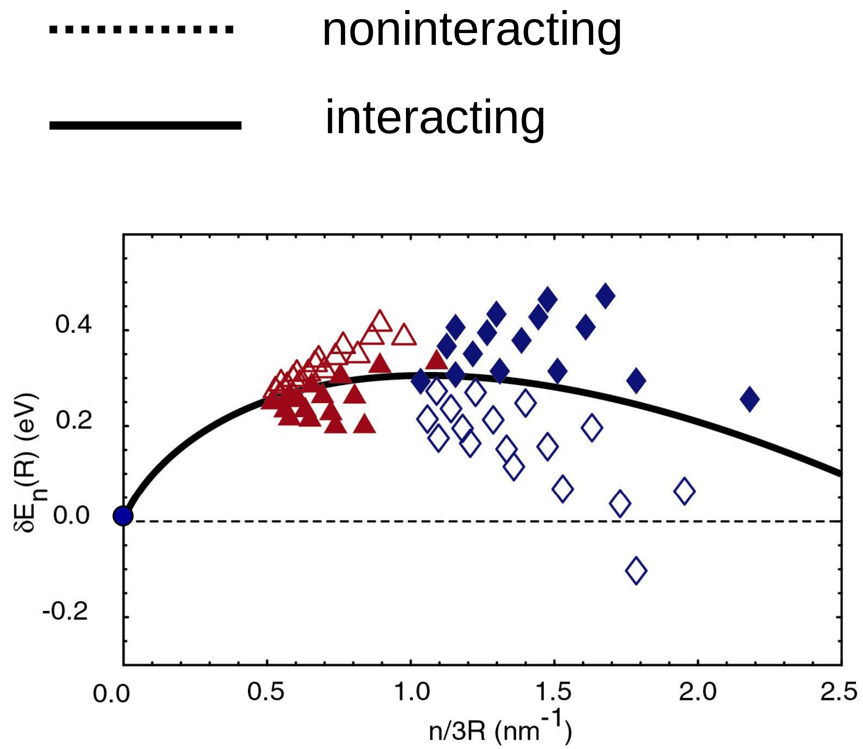
This is <u>exact</u> for q -> 0, with a scale dependent v_F and g :

(scales to perturbative regime at small q)

Earlier work: J. Gonzalez, F. Guinea and M.A.H. Vozmediano Phys. Rev. B 62, 4273 (2002)

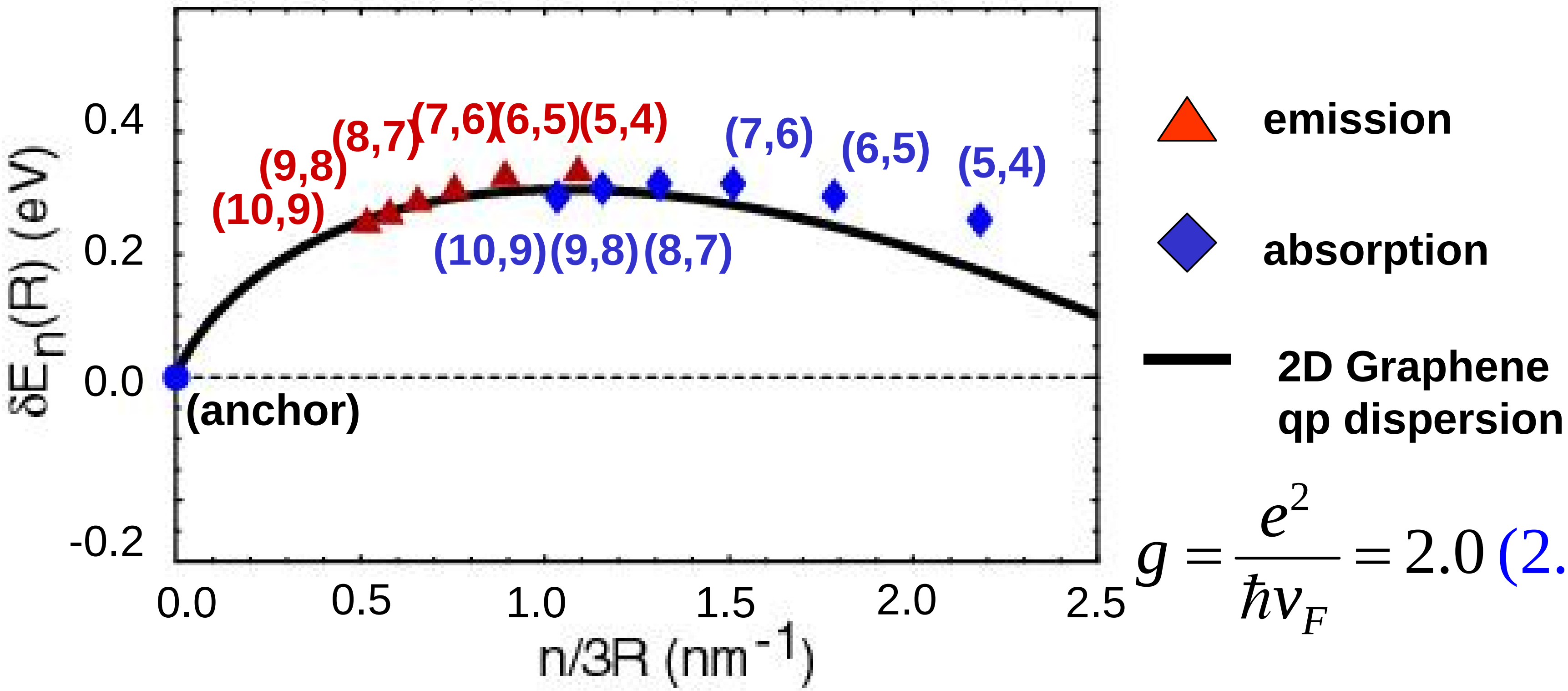
Map graphene quasiparticle energies to nanotube





Resolves (by unifying!) ratio problem and blue shift problem

sin(3θ) Effects Are Small Near The Armchair Structures



$$g = \frac{e^2}{\hbar v_F} = 2.0\ (2.7)$$

But how would (could) this survive with even stronger 1D interaction effects

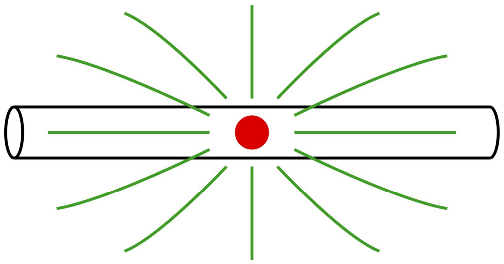
Rule 3. The long(est) range effects nearly balance each other

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

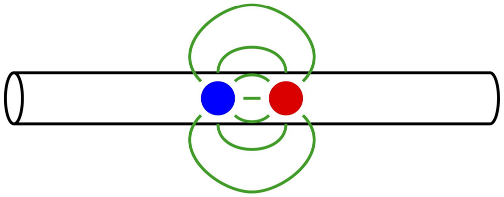
schematically for r > 2πR

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: 2Δ **Interaction Energy:** $V_o N^2/2$

Quasiparticle Gap:

$$E(N+1) + E(N-1) - 2E(N) = 2\Delta + V_o$$

N+1 + N-1 -2 N

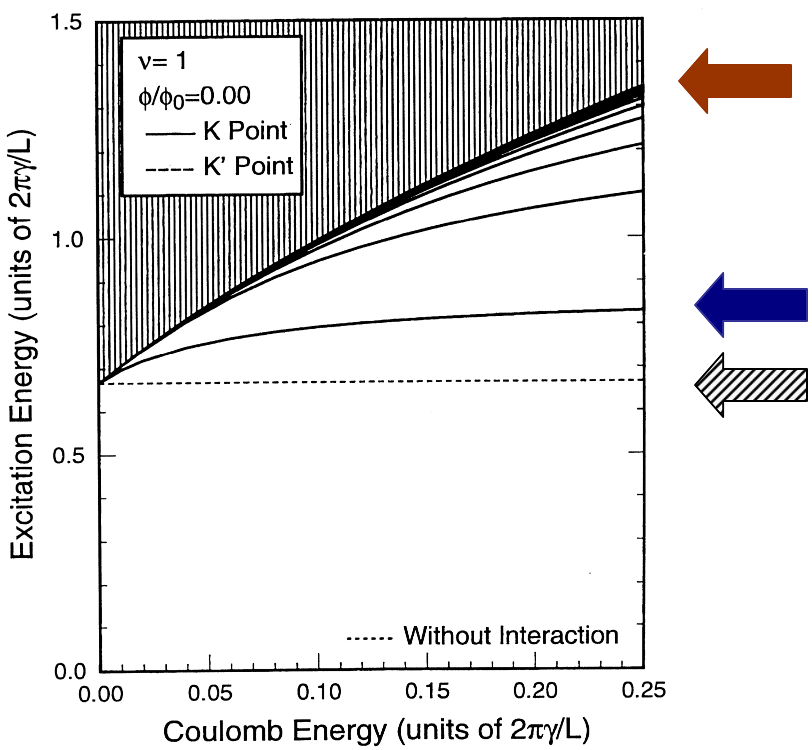
Electron-Hole Gap: 2Δ

e-h

Near Cancellation for Screened NT Interaction

T. Ando, J. Phys. Soc. Japan 66,1066 (1997)

Numerical Calculation in Screened Hartree Fock Approximation



Quasipartlce gap

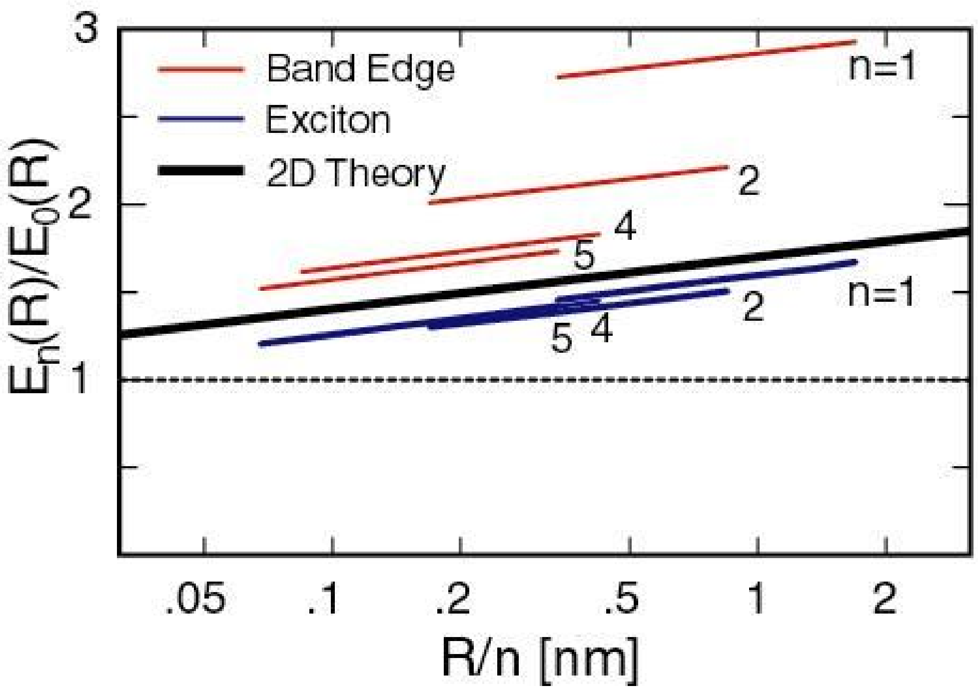
Lowest Exciton

Noninteracting

Interaction strength

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

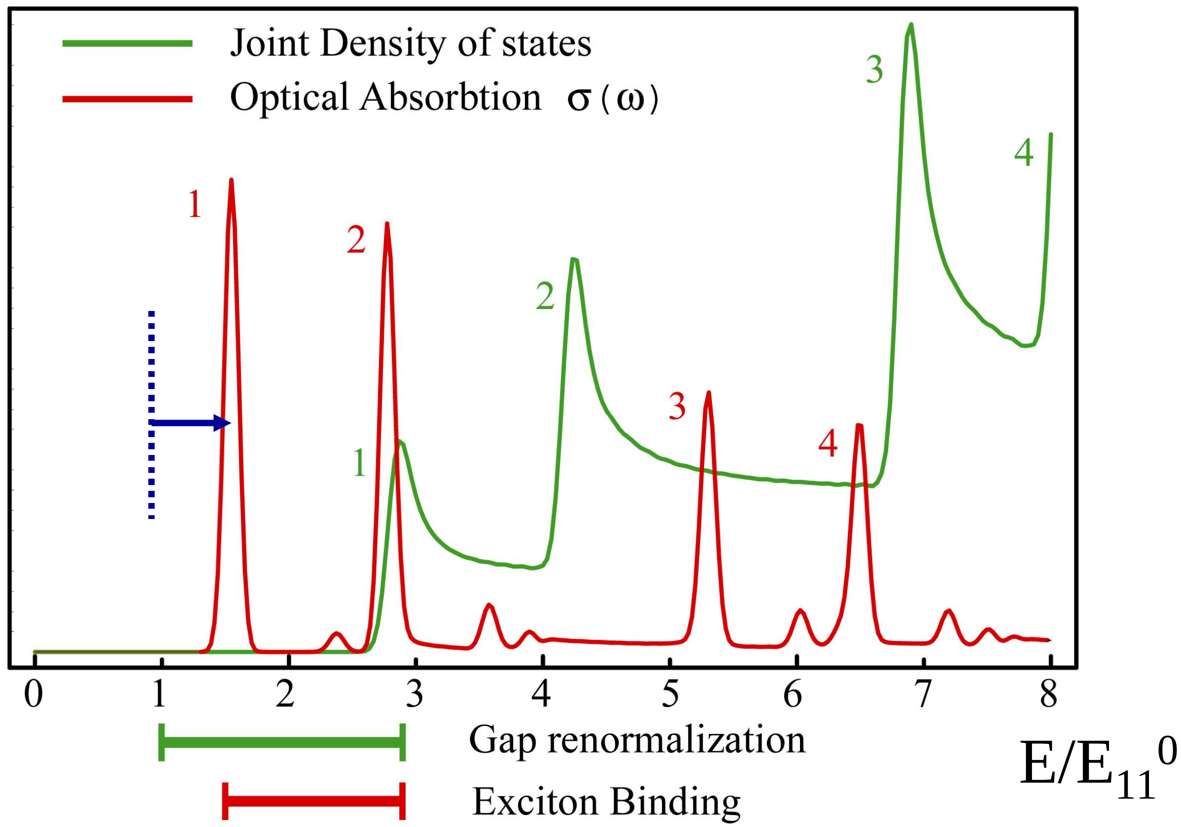
2D qp's

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.

Properties of NT Excitons

They are strongly bound

size ~ few tube radii, $\Delta E/E$ ~ 30% ! Nearly all spectral weight in bound state

they carry <u>spin</u> (0,1) and <u>valley</u> (K,K') indices

these degeneracies are lifted by intervalley and exchange

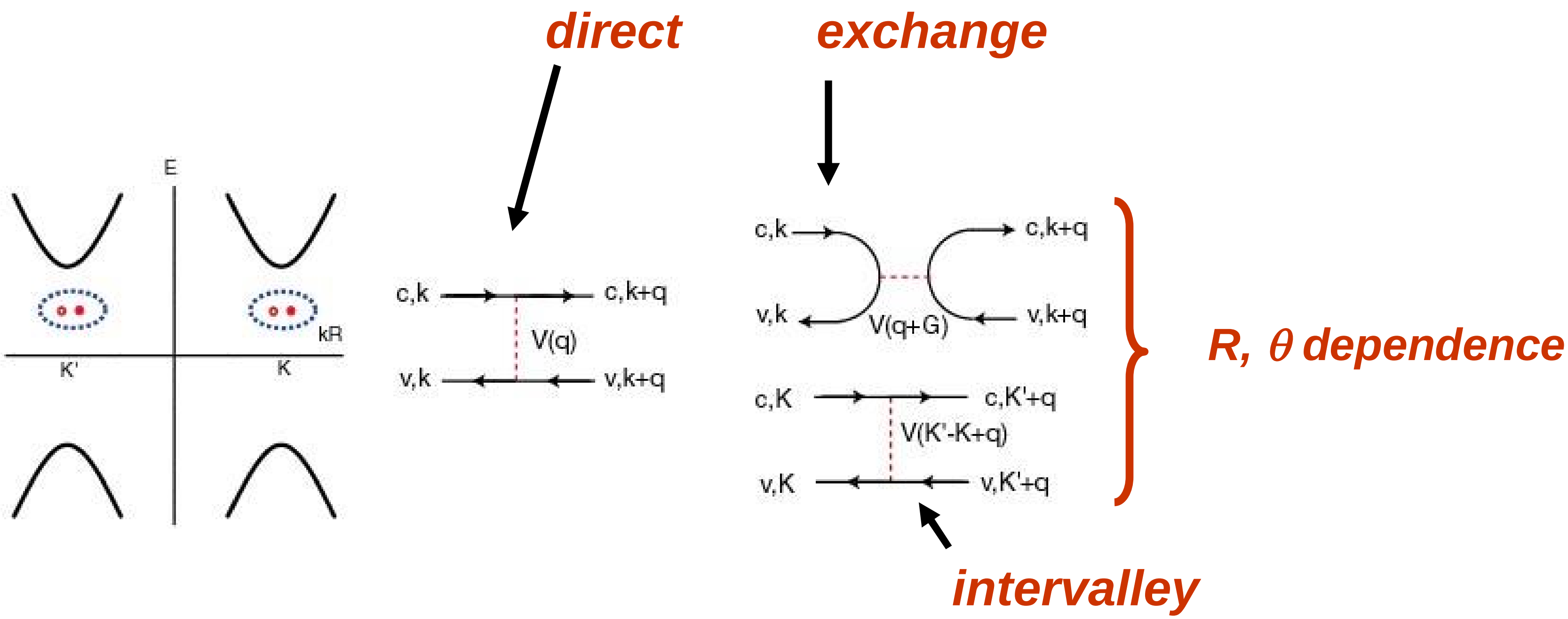
⟹ <u>spectrum</u> of dipole allowed and dark (forbidden) states

possibly stable to high density (?)

power law decay of transient absorption

⟹ long lived diffusing species

Spin and Valley Degeneracies Broken by Interactions



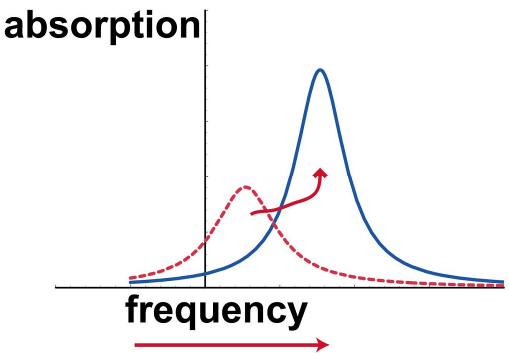
Exchange and Intervalley at finite momenta (θ –dependent)

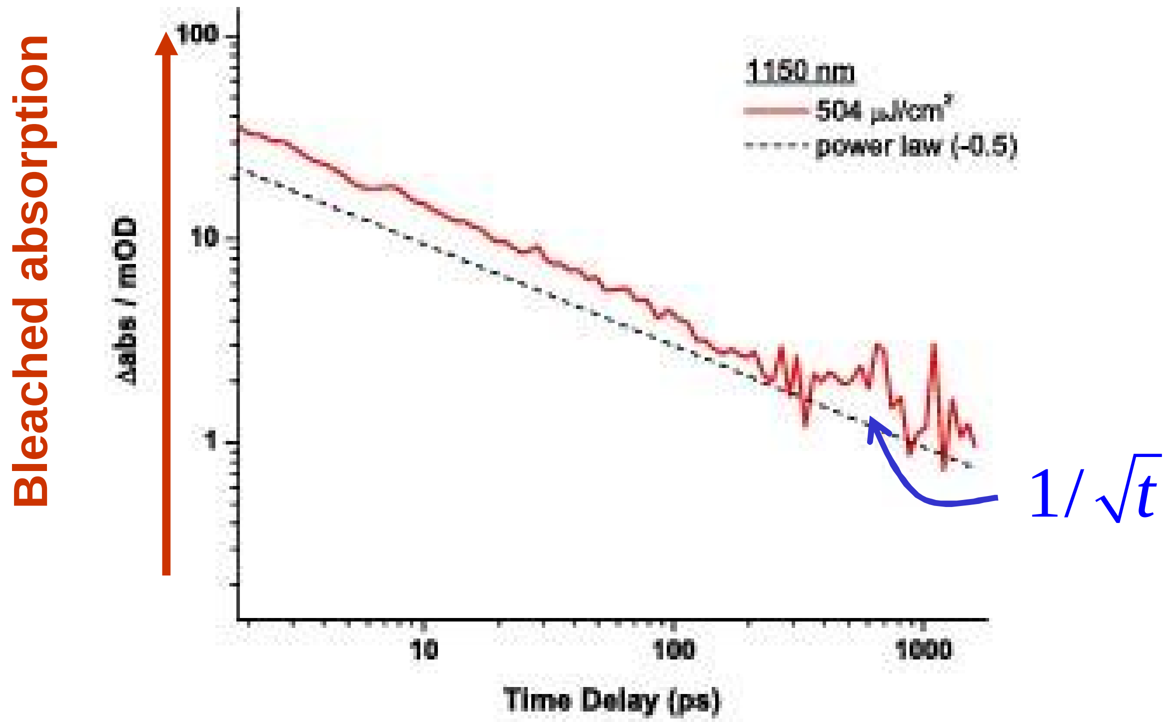
<u>Low Energy</u> Triplet & "Dark" Singlet Excitons

Time Resolved Photo-Absorption Spectroscopy

R. Russo, EJM, CLK, D.E. Luzzi, I.B. Rubstov and M.J. Therien

Physical Review B 74, (R) 041405 (2006)





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 3θ dependence?

Scale of extrinsic effects: dielectric environment, doped carrier density…

Collaborators

Charlie Kane (theory)

Dave Luzzi, Rich Russo
Mike Therien, Igor Rubstov

Dina Zhabinskaya
Jesse Kinder

Bruce Weisman (Rice)

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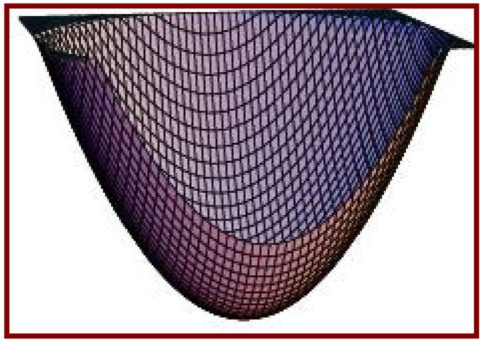
Physics
Chemistry
Mat. Science

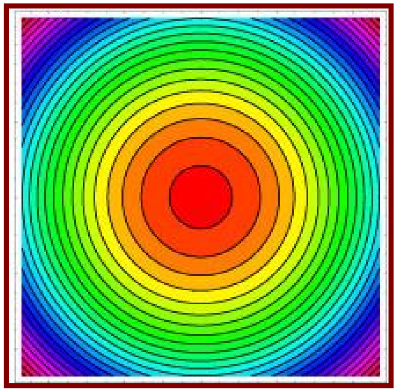
Penn
UNIVERSITY of PENNSYLVANIA

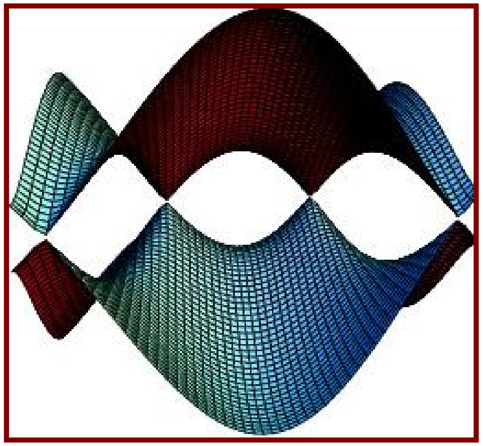
LRSM
the University of Pennsylvania's
Materials Research Science
and Engineering Center

Graphene has a critical electronic state

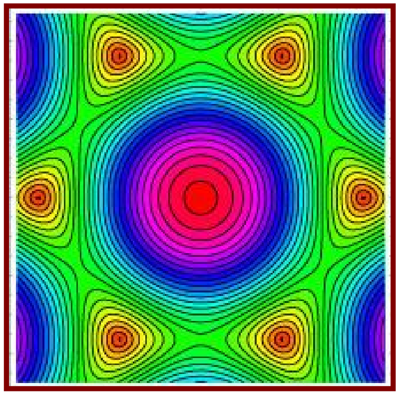


Dispersion of a
free particle in 2D..

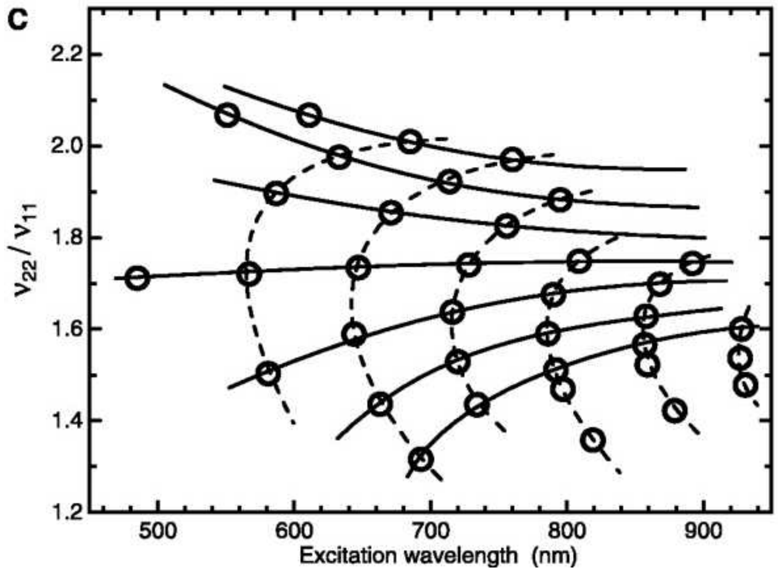




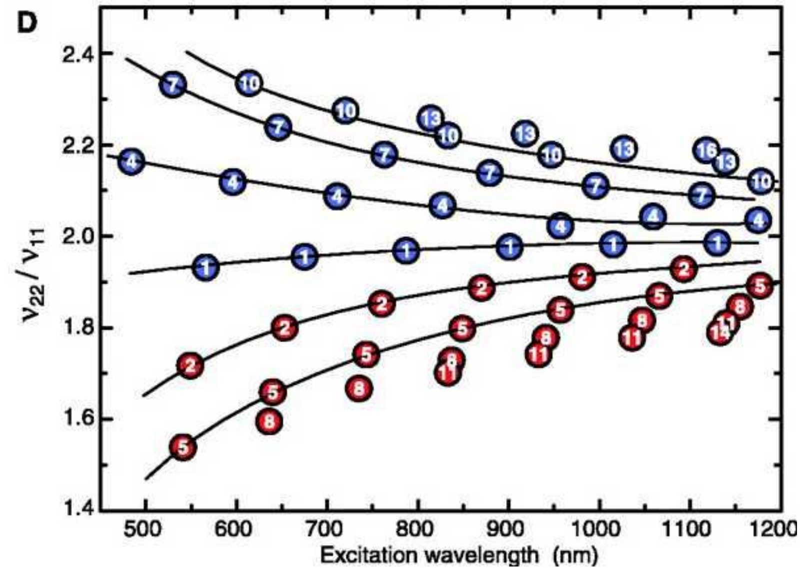
…is replaced
by an unconventional
E(k) relation on the
graphene lattice



Experimental "Ratio Plot"



Theory (Reich, 00)



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

Corroborated by Raman spectroscopy of the radial breathing mode.

- **The Ratio Problem**

  Anomalous scaling of <u>gap ratios</u> in large R limit

- **The Blue Shift Problem**

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- **The Deviations Problem**

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Deviations Problem

(ref: Structure Assigned Optical Specta of Single Wall Carbon Nanotubes, S. Bachilo et al., Science 298, 2361 (2002))