Japan
Brazil

South America
Caribbean Sea
North Atlantic Ocean
South Pacific Ocean
South Atlantic Ocean
COLOMBIA
VENEZUELA
GUYANA
SURINAME
French Guiana (FRANCE)
ECUADOR
PERU
BRAZIL
BOLIVIA
PARAGUAY
CHILE
ARGENTINA
URUGUAY
PANAMA
COSTA RICA
Belo Horizonte (NT07)
Rio de Janeiro
Nagano (NT06)
JAPAN
Scale 1:35,000,000
Azimuthal Equal-Area Projection
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802585 (R02108) 6-98

Excitons in Carbon Nanotubes

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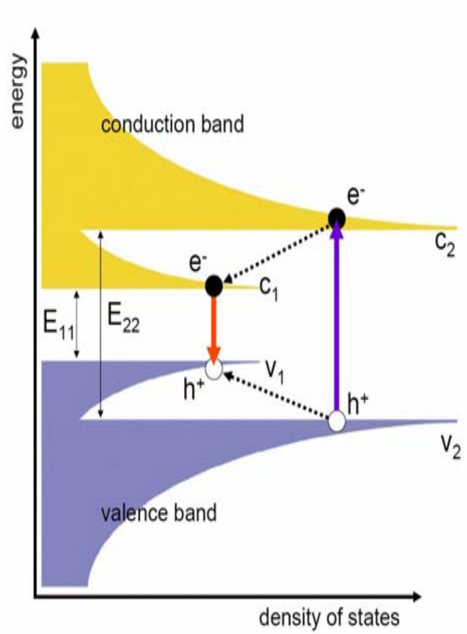
Mildred S. Dresselhaus, MIT, USA

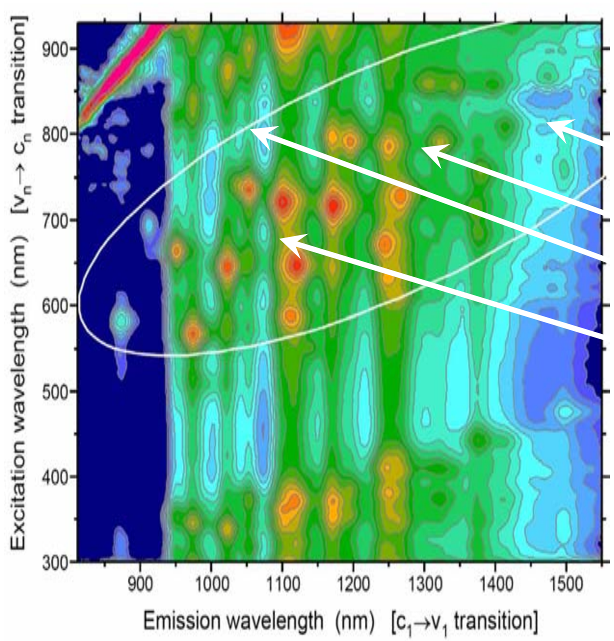
Outline

1. Introduction
2. Symmetries
3. Diameter and chirality dependence of binding energies and sizes
4. Radiative lifetimes

Optical measurements on individual nanotubes: Band-to-band vs. exciton picture

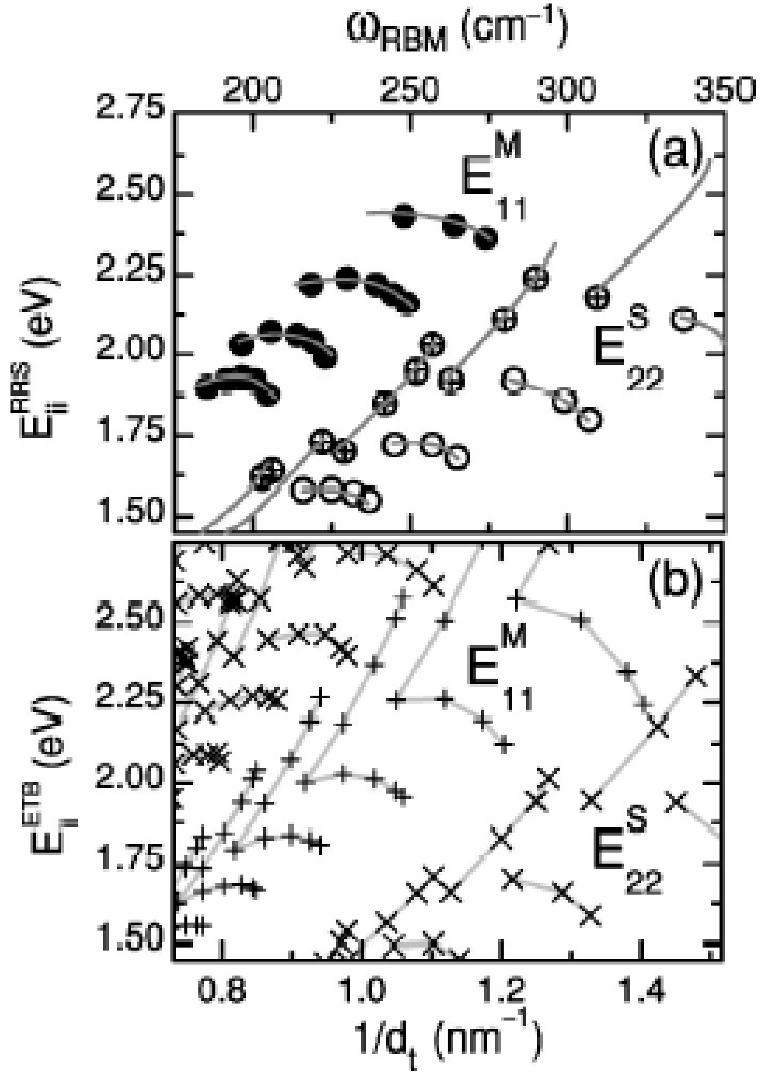
- Resonance Raman Scattering: Jorio et al., Phys. Rev. Lett. **86**, 1118 (2001)
- Photoluminescence: Bachilo et al., Science **298**, 2361 (2002)





(n,m)
(9,5)
(7,6)
(8,3)
(6,5)

Band-to-band picture looked ok...



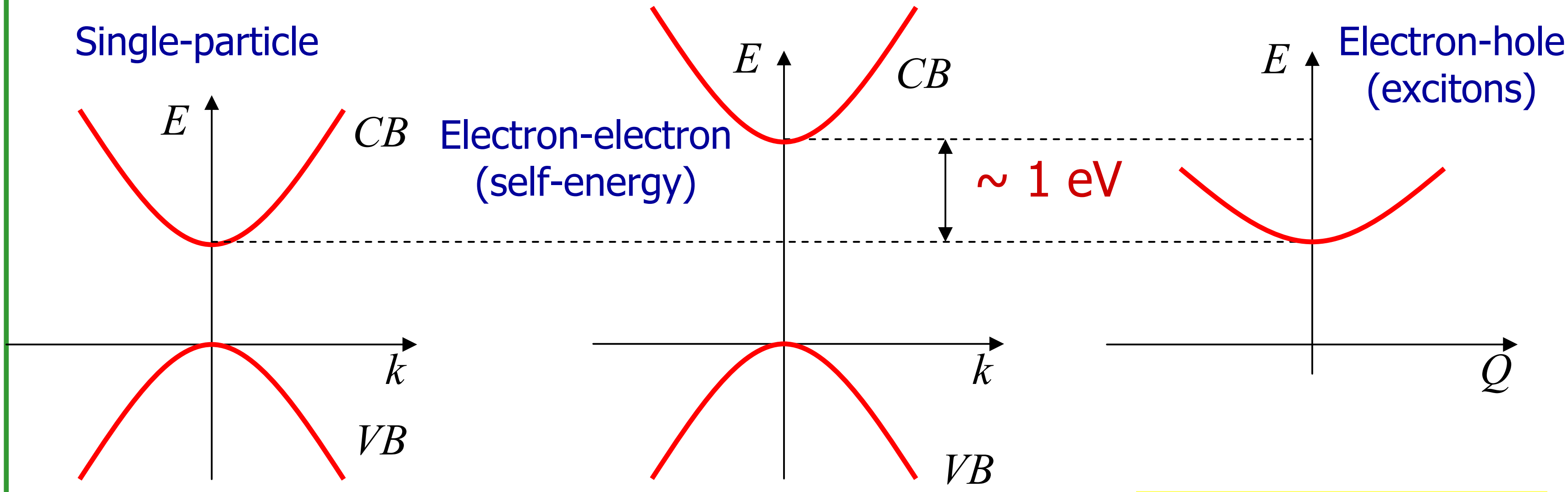
Experiment

Theory

Jorio et al., Phys. Rev. B **71**, 075401 (2005)

… but theorists believed in excitons

- Strong excitonic effects in nanotubes: 1D confinement



	E_{11} (eV)		E_{22} (eV)		E_{22}/E_{11}	
	Theory	Exp.[a]	Theory	Exp.[a]	Theory	Exp.[a]
(7,0)	1.20	1.29	3.00	3.14	2.50	2.43
(8,0)	1.55	1.60	1.80	1.88	1.16	1.17
(10,0)	1.00	1.07	2.39	2.31	2.39	2.16
(11,0)	1.21	1.20	1.74	1.66	1.44	1.38

Partial cancellation of many-body e-e and e-h effects

[a]S. Bachilo, et al., Science (2002) .

C. D. Spataru, S. Ismail-Beigi, L. X. Benedict, and S. G. Louie, Phys. Rev. Lett. **92**, 077402 (2004)

REPORTS

The Optical Resonances in Carbon Nanotubes Arise from Excitons

Feng Wang,[1*] Gordana Dukovic,[2*] Louis E. Brus,[2] Tony F. Heinz[1]†

Optical transitions in carbon nanotubes are of central importance for nanotube characterization. They also provide insight into the nature of excited states in these one-dimensional systems. Recent work suggests that light absorption produces strongly correlated electron-hole states in the form of excitons. However, it has been difficult to rule out a simpler model in which resonances arise from the van Hove singularities associated with the one-dimensional bond structure of the nanotubes. Here, two-photon excitation spectroscopy bolsters the exciton picture. We found binding energies of ~400 millielectron volts for semiconducting single-walled nanotubes with 0.8-nanometer diameters. The results demonstrate the dominant role of many-body interactions in the excited-state properties of one-dimensional systems.

Coulomb interactions are markedly enhanced in one-dimensional (1D) systems. Single-walled carbon nanotubes (SWNTs) provide an ideal model system for studying these effects. Strong electron-electron interactions are associated with many phenomena in the charge transport of SWNTs, including Coulomb blockade (*1*, *2*), Kondo effects (*3*, *4*), and Luttinger liquid behavior (*5*, *6*). The effect of Coulomb interactions on nanotube optical properties has remained unclear, in spite of its central importance both for a fundamental understanding of these model 1D systems (*7–9*) and for applications (*7*, *10*, *11*). Theoretical studies suggest that optically produced electron-hole pairs should, under their mutual Coulomb interaction, form strongly correlated entities known as excitons (*12–18*). Although some evidence of excitons has emerged from studies of nanotube optical spectra (*7*, *19*) and excited-state dynamics (*20*), it is difficult to rule out an alternative and widely used picture that attributes the optical resonances to van Hove singularities in the 1D density of states (*21–23*). Here, we demonstrate experimentally that the optically excited states of SWNTs are excitonic in nature. We measured exciton binding energies that represent a large fraction of the semiconducting SWNT band gap. As such, excitonic interactions are not a minor perturbation as in comparable bulk semiconductors, but actually define the optical properties of SWNTs. The importance of many-body effects in nanotubes derives from their 1D character; similar excitonic behavior is also seen in organic polymers with 1D conjugated backbones (*24*).

We identified excitons in carbon nanotubes using two-photon excitation spectroscopy. Two-photon transitions obey selection rules distinct from those governing linear excitation processes and thereby provide complementary insights into the electronic structure of excited states, as has been demonstrated in studies of molecular systems (*25*) and bulk solids (*26*). In 1D materials like SWNTs, the exciton states show defined symmetry with respect to reflection through a plane perpendicular to the nanotube axis. A Rydberg series of exciton states describing the relative motion of the electron and hole, analogous to the hydrogenic states, is then formed with definite parity with respect to this reflection plane. The even states are denoted as 1*s*, 2*s*, 3*s*, and so on, and the odd wave functions are labeled as 2*p*, 3*p*, and so on (*27*). Because of the weak spin-

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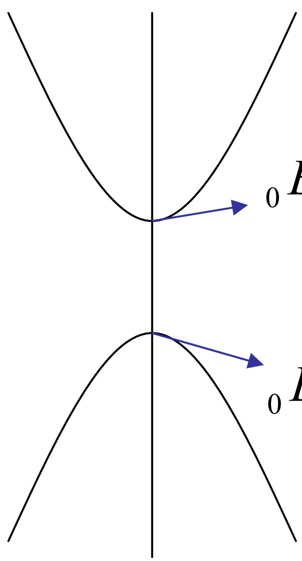
2. Symmetry of Excitons

Exciton wavefunction: $\psi(\mathbf{r}_e,\mathbf{r}_h)=\sum_{cvk} A_{cvk}\varphi_{ck}(\mathbf{r}_e)\varphi^*_{vk}(\mathbf{r}_h)$

- $|vc>$ will belong to the direct product representation of $|v>$ and $|c>$

(n,0) Zig-Zag Tubes



Γ

$_0E_m^+, |k,m,\pi\rangle$ partners : $\begin{pmatrix}|c_1\rangle \\ |c_2\rangle\end{pmatrix}=\begin{pmatrix}|0,+m,+\rangle \\ |0,-m,+\rangle\end{pmatrix}$

$_0E_m^-, |k,m,\pi\rangle$ partners : $\begin{pmatrix}|v_1\rangle \\ |v_2\rangle\end{pmatrix}=\begin{pmatrix}|0,+m,-\rangle \\ |0,-m,-\rangle\end{pmatrix}$

k: wavevector

m: angular momentum

π: σ_h parity

Symmetrized exciton states:

$|{}_0A_0^-\rangle=|v_1c_1\rangle+|v_2c_2\rangle$

$|{}_0B_0^-\rangle=|v_1c_1\rangle-|v_2c_2\rangle$

$|{}_0E_{2n-2m}^-\rangle=\begin{pmatrix}|v_1c_2\rangle \\ |v_2c_1\rangle\end{pmatrix}$

$$_0E_m^-\otimes{}_0E_m^+={}_0A_0^-+{}_0B_0^-+{}_0E_{2n-2m}^-$$

E. B. Barros, R. B. Capaz, et al., PRB (to appear)

Optical activity

$$\langle 0|v_z|S\rangle = \sum_{v}^{hole}\sum_{c}^{elec} A_{vc}^{S}\langle v|v_z|c\rangle$$

${}_0A_0^+$ ${}_0A_0^-$

$$|S\rangle = |{}_0A_0^-\rangle \Rightarrow {}_0A_0^- \otimes {}_0A_0^- = {}_0A_0^+ \rightarrow \text{BRIGHT}$$

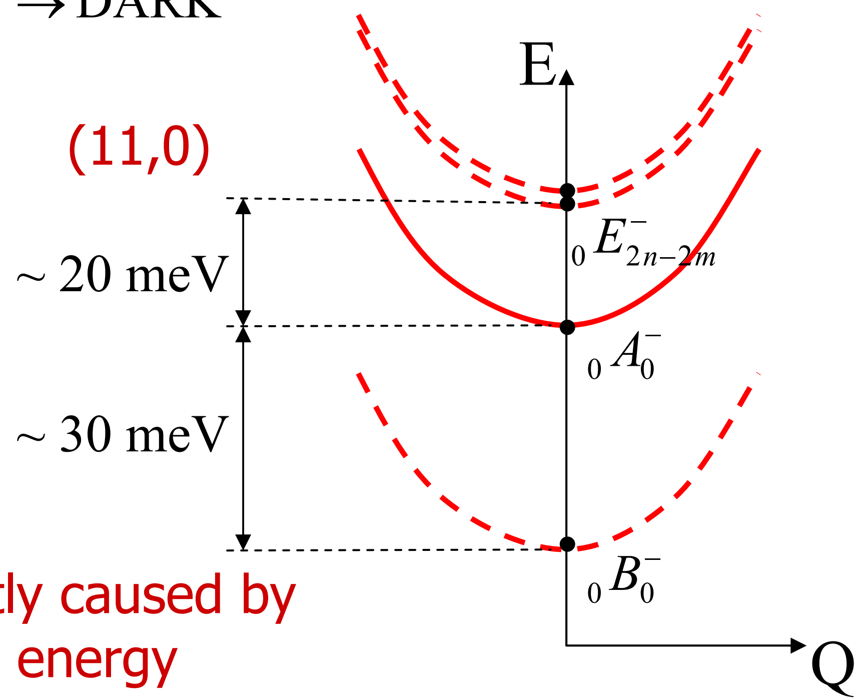
$$|S\rangle = |{}_0B_0^-\rangle \Rightarrow {}_0A_0^- \otimes {}_0B_0^- = {}_0B_0^+ \rightarrow \text{DARK}$$

$$|S\rangle = |{}_0E_{2n-2m}^-\rangle \Rightarrow {}_0A_0^- \otimes {}_0E_{2n-2m}^- = {}_0E_{2n-2m}^+ \rightarrow \text{DARK}$$

1 bright and 3 dark excitons

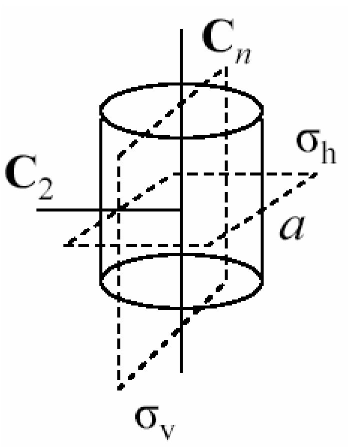
Electronic structure of lowest energy (E_{11}) bound excitons

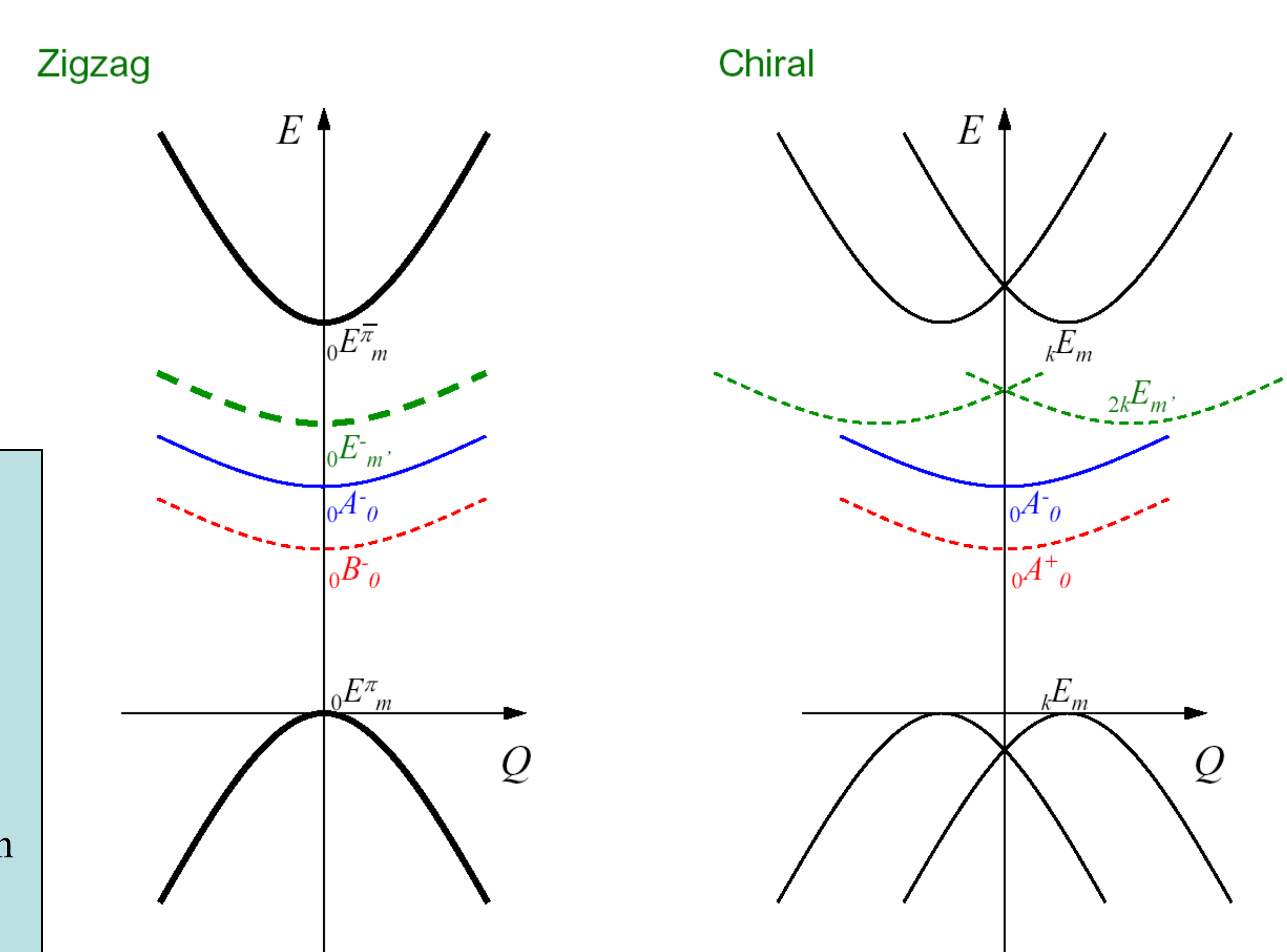
(11,0)



Splittings are mostly caused by the exchange energy

Symmetry of Excitons of Semiconducting CNTs

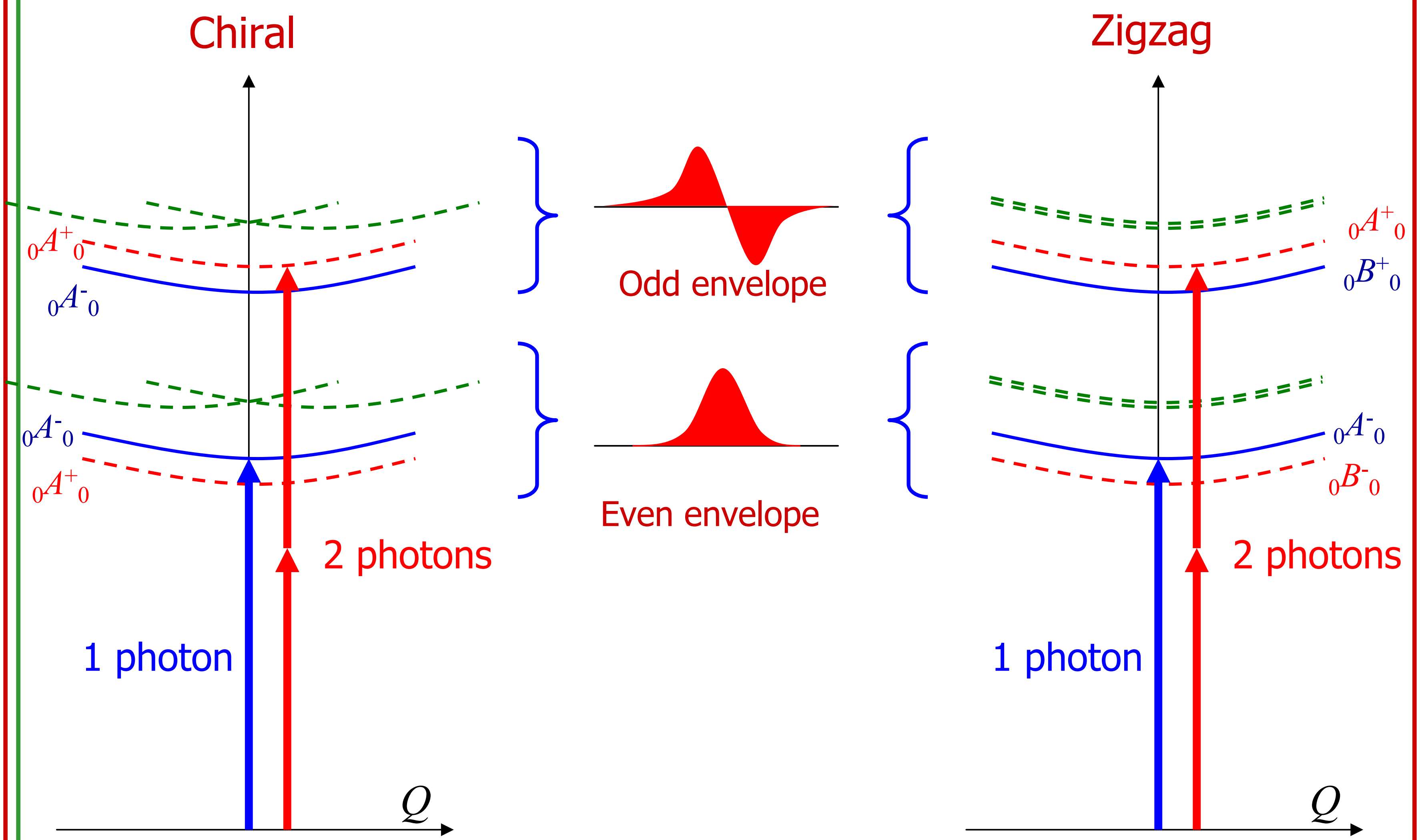




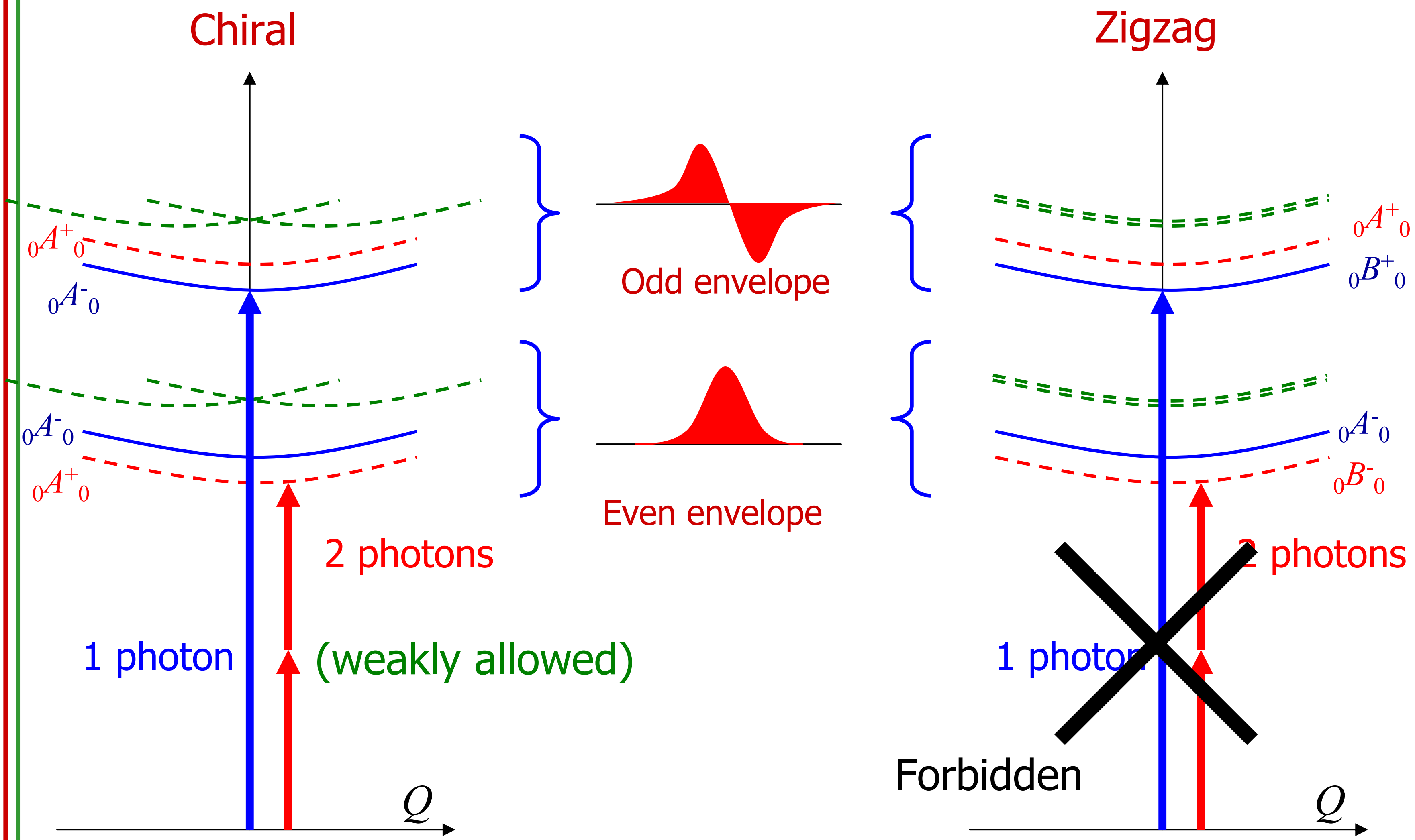
$${}_kX^{\pi}_m$$

k: wavevector
m: angular momentum
X = A, B, E, G, depending on dimensionality & parity with respect to σ_v
π: parity under C_2

Higher-energy states and implications for one- and two-photon spectroscopy



Weakly allowed transitions: Measurements of Bright-Dark Splittings?

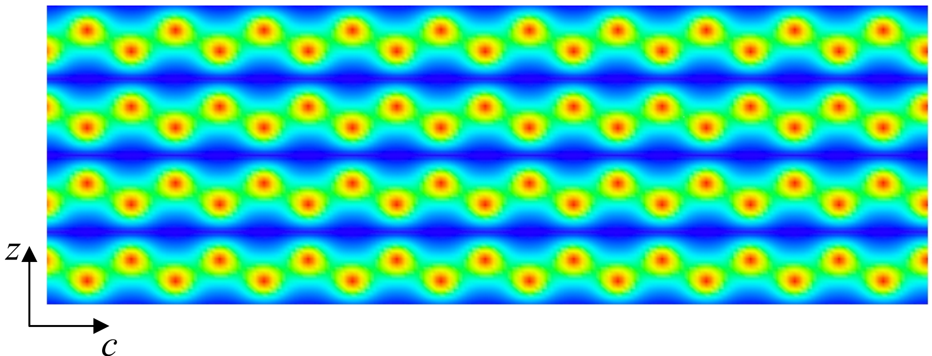


Looking at the exciton wavefunctions

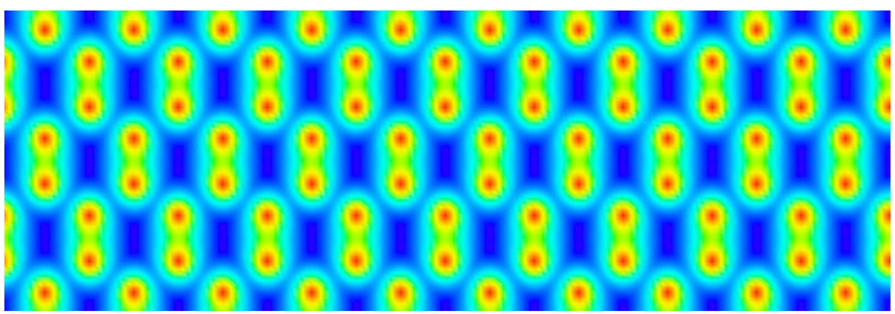
Zig-zag tubes: (10,0)

Hole position is indicated by the black arrow

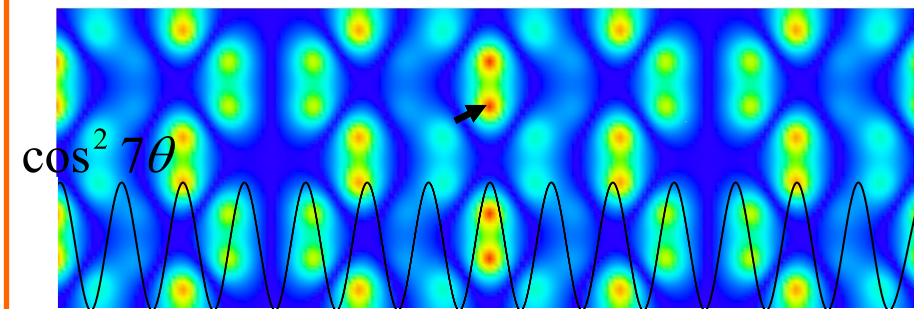
$|\varphi_{v_1}(\mathbf{r}_h)|^2 = |\varphi_{v_2}(\mathbf{r}_h)|^2$



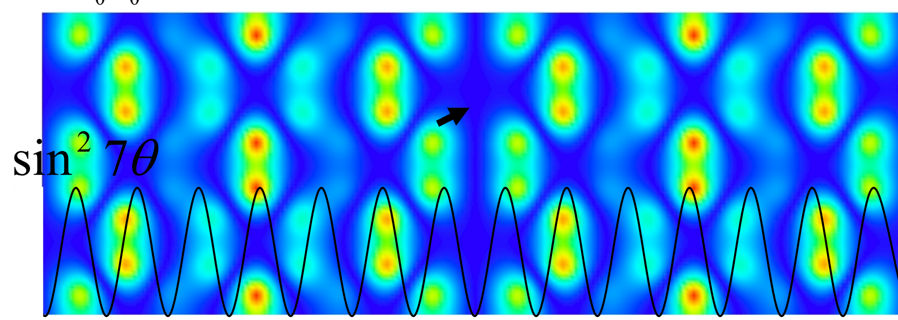
$|\varphi_{c_1}(\mathbf{r}_e)|^2 = |\varphi_{c_2}(\mathbf{r}_e)|^2$



$|\psi_{0A_0^-}(0,\mathbf{r}_e)|^2$ (bright)



$|\psi_{0B_0^-}(0,\mathbf{r}_e)|^2$ (dark)



Optical transition matrix element : $\mu = \int d\mathbf{r}\, z\,\psi(\mathbf{r},\mathbf{r})$

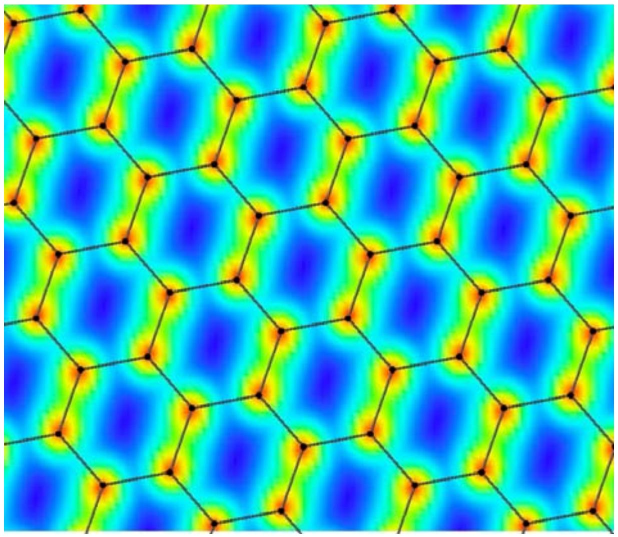
Exchange energy : $E_x = 2\int d\mathbf{r}\int d\mathbf{r}'\,\psi^*(\mathbf{r},\mathbf{r})\dfrac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi(\mathbf{r}',\mathbf{r}')$

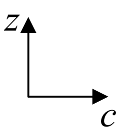
"Groundness" and "darkness": same physics (electron and hole cannot be found at the same position): Low efficiency of CNT light emission

Chiral tubes: (4,2)

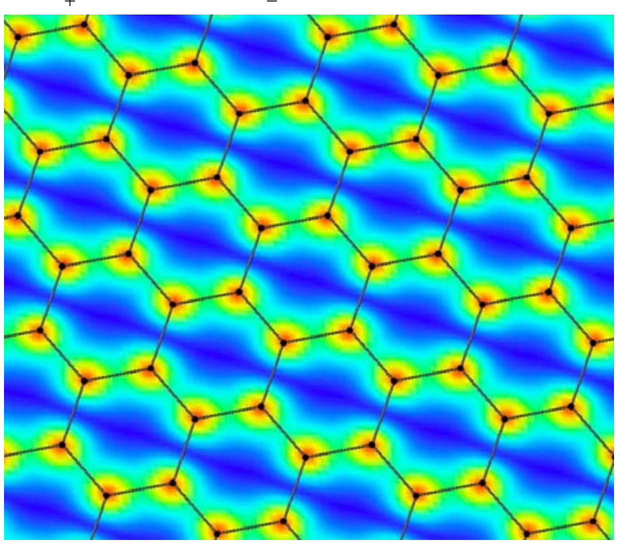
Hole position is indicated by the black arrow

$|\varphi_{v_+}(\mathbf{r}_h)|^2=|\varphi_{v_-}(\mathbf{r}_h)|^2$

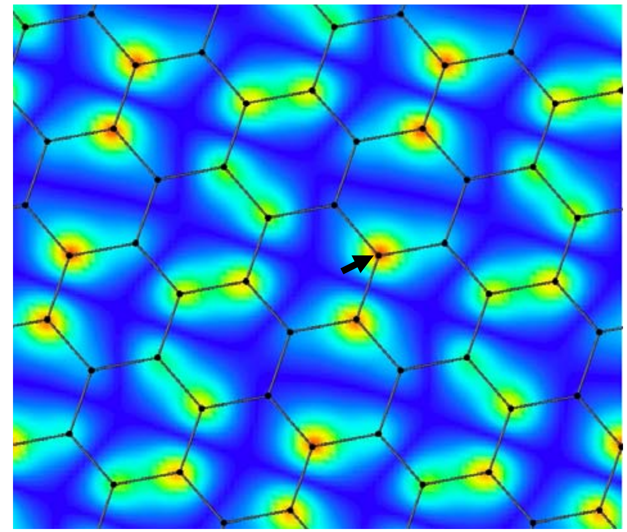




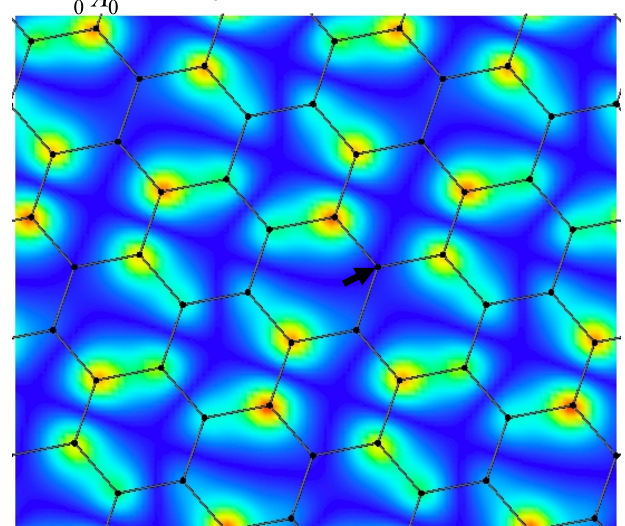
$|\varphi_{c_+}(\mathbf{r}_e)|^2=|\varphi_{c_-}(\mathbf{r}_e)|^2$



$|\psi_{0A_0^-}(0,\mathbf{r}_e)|^2$ (bright)



$|\psi_{0A_0^+}(0,\mathbf{r}_e)|^2$ (dark)



3. Diameter and chirality dependence of binding energies and sizes

R. B. Capaz, C. D. Spataru, S. Ismail-Beigi, and S. G. Louie, cond-mat/0606474 (2006)

- Ab initio calculations of excitons in SWNTs are restricted to small-diameter tubes: Spataru et al., PRL 92, 077402 ('04) (achiral) ; Chang et al., PRL 92, 196401 ('04)

- Recent experimental determinations of exciton binding energies in chiral tubes:

    - Two-photon spectroscopy: Wang et al., Science 308, 838 ('05); Maultzsch et al., PRB 72, 241402 ('05).

    - Raman spectroscopy on electrochemically doped SWNTs: Wang et al., PRL 96, 047403 ('06)

The full diameter and chirality dependences of exciton properties is needed

A variational tight-binding approach

Variational Wavefunction :

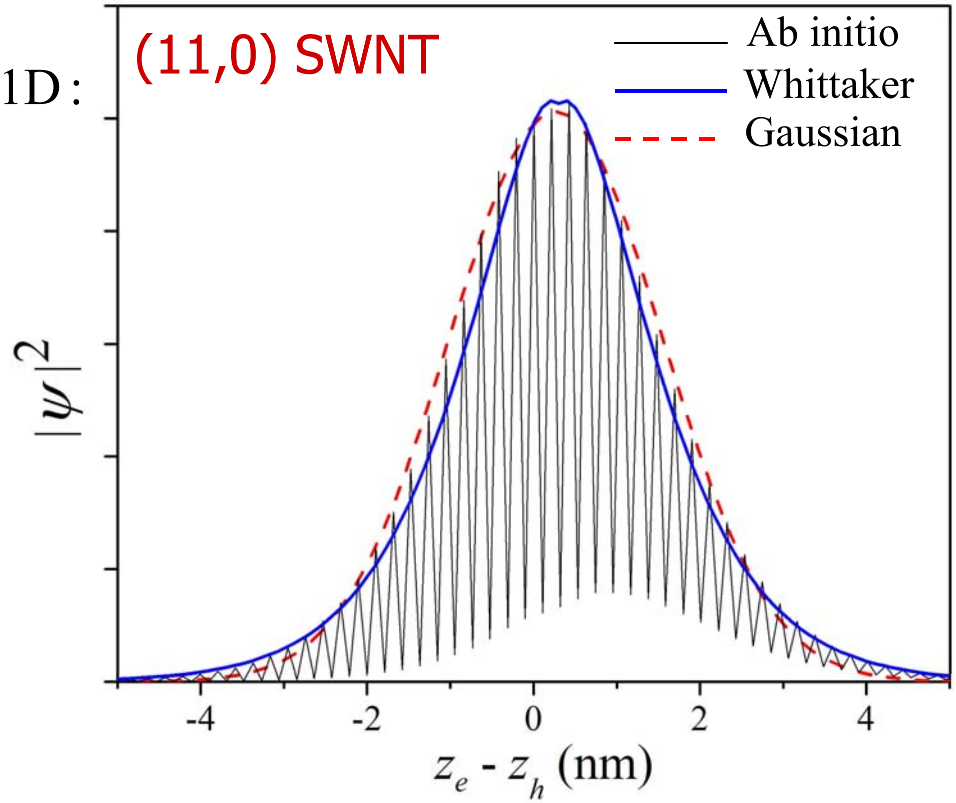
$$\psi_S(\mathbf{r}_e,\mathbf{r}_h) = C\sum_{vc} A_{vc}\varphi_v^*(\mathbf{r}_h)\varphi_c(\mathbf{r}_e)\, e^{\frac{-(z_e-z_h)^2}{2\sigma^2}}$$

σ : variational parameter

"Regularized" Coulomb potential in 1D :

$$U(z) = \frac{1}{|z|+\alpha} \quad , z = z_e - z_h$$

Solution : Whittaker function



Both Gaussian and Whittaker functions fit well the ab initio results

Energy terms

Direct Energy:

$$\langle S|K^d|S\rangle = \int d\mathbf{r}_e d\mathbf{r}_h \psi_S^*(\mathbf{r}_e,\mathbf{r}_h) V_C^{scr}(\mathbf{r}_e-\mathbf{r}_h)\psi_S(\mathbf{r}_e,\mathbf{r}_h)$$

Exchange Energy:

$$\langle S|K^x|S\rangle = 2\int d\mathbf{r}_e d\mathbf{r}_h \psi_S^*(\mathbf{r}_e,\mathbf{r}_e) V_C(\mathbf{r}_e-\mathbf{r}_h)\psi_S(\mathbf{r}_h,\mathbf{r}_h)$$

Kinetic Energy (Gaussian envelope):

$$\langle S|T|S\rangle = \frac{\hbar^2}{4m^*\sigma^2}; \quad \frac{1}{m^*} = \frac{1}{m_e} + \frac{1}{m_h}$$

ε = 1.846

(fitted to the (11,0) tube)

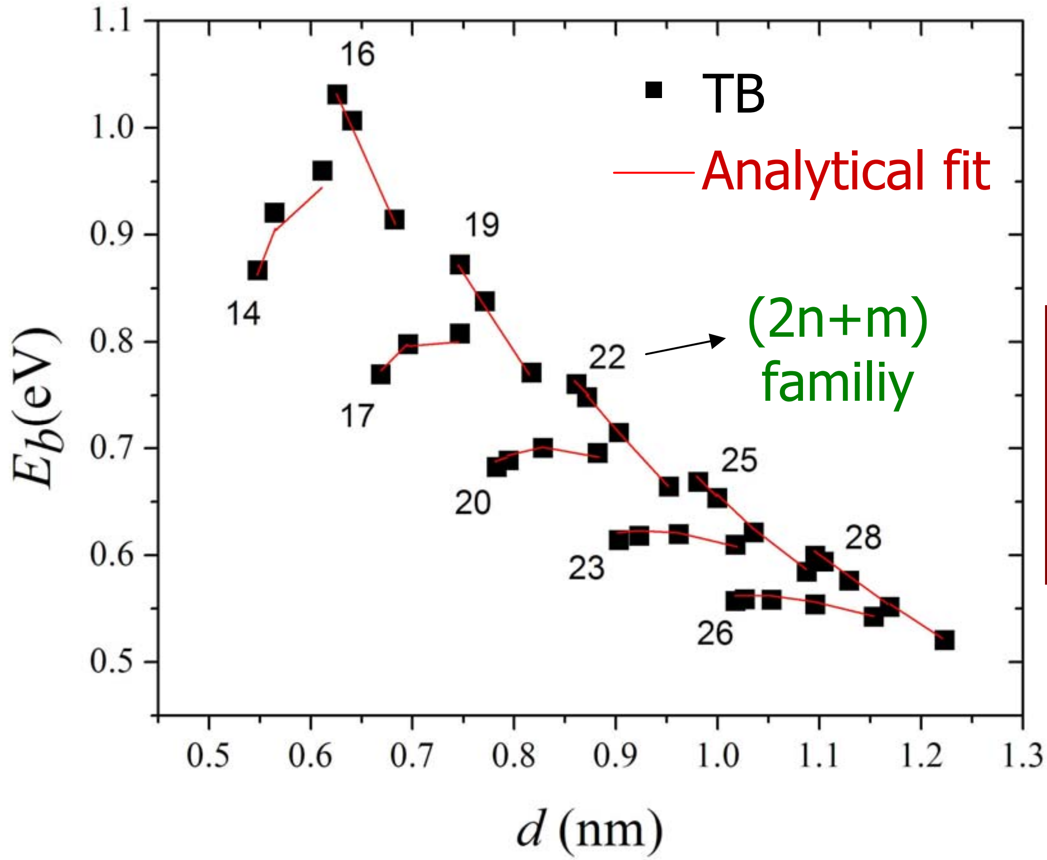
Binding Energies: Ab initio vs. Model

Tube	E_{11}		E_{22}	
	BSE (eV)	TB (eV)	BSE (eV)	TB (eV)
(7,0)	0.89	0.87	1.13	1.61
(8,0)	0.99	1.03	0.86	0.92
(10,0)	0.76	0.68	0.95	1.09
(11,0)	0.76	*0.76 (fitted)*	0.72	0.75

Very localized wavefunction: breakdown of envelope function approximation

(n-m) Mod3 = 1 or 2 oscillation (chirality dependence) is captured by the TB model

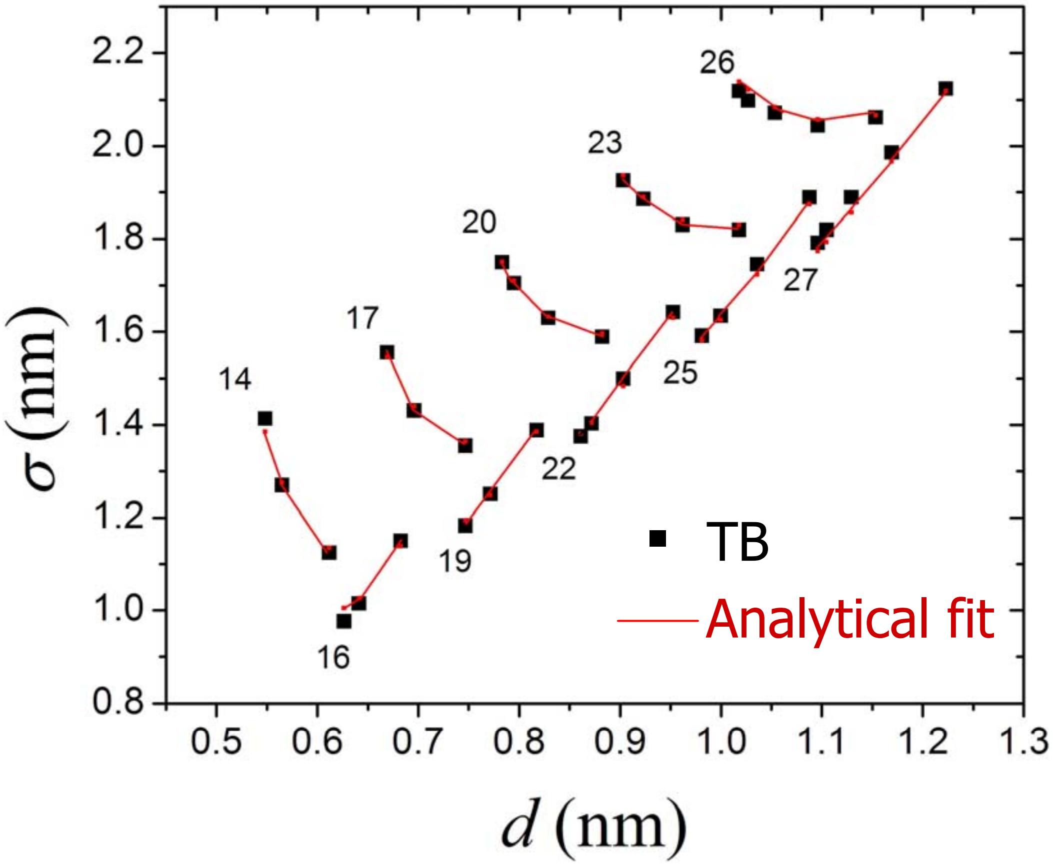
Diameter and Chirality Dependence of Exciton Binding Energies



- Leading decay ~ 1/d
- Chirality spread ~ 20%
- Family Behavior

$$E_b = \frac{1}{d}\left[A + \frac{B}{d} + C\xi + D\xi^2\right], \ \xi = \frac{(-1)^\nu \cos 3\theta}{d}, \quad \nu = (n-m)MOD3$$

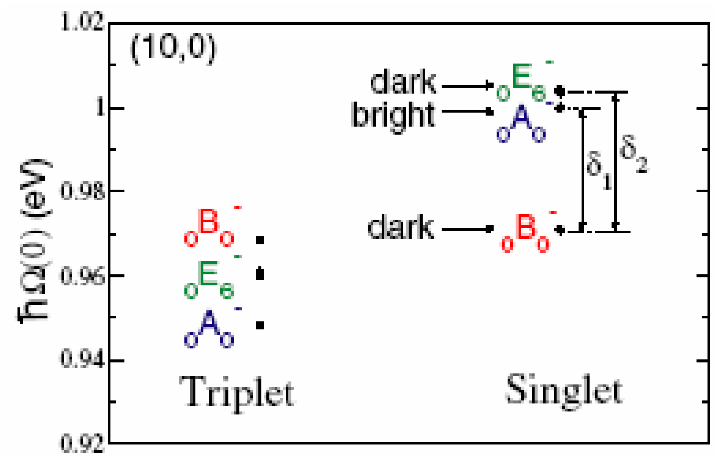
Exciton Sizes



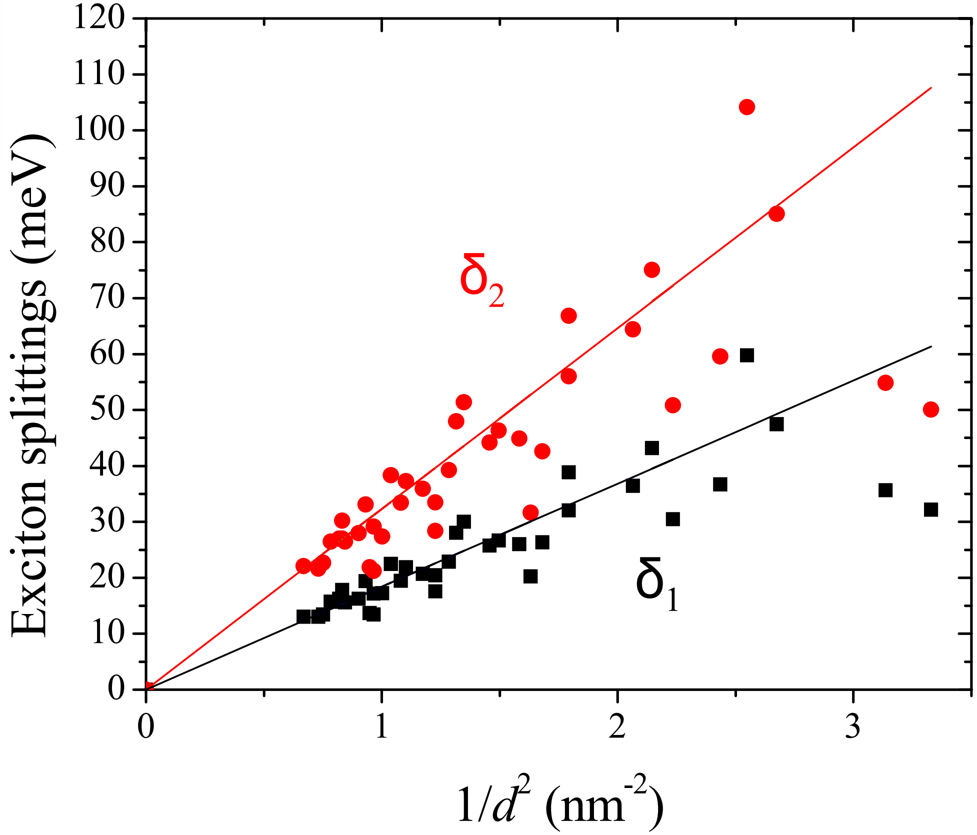
- Leading scaling ~ d
- Family Behavior

$$\sigma = d\left[E + F\xi + G\xi^2\right],\ \xi = \frac{(-1)^\nu \cos 3\theta}{d}, \quad \nu = (n-m)MOD3$$

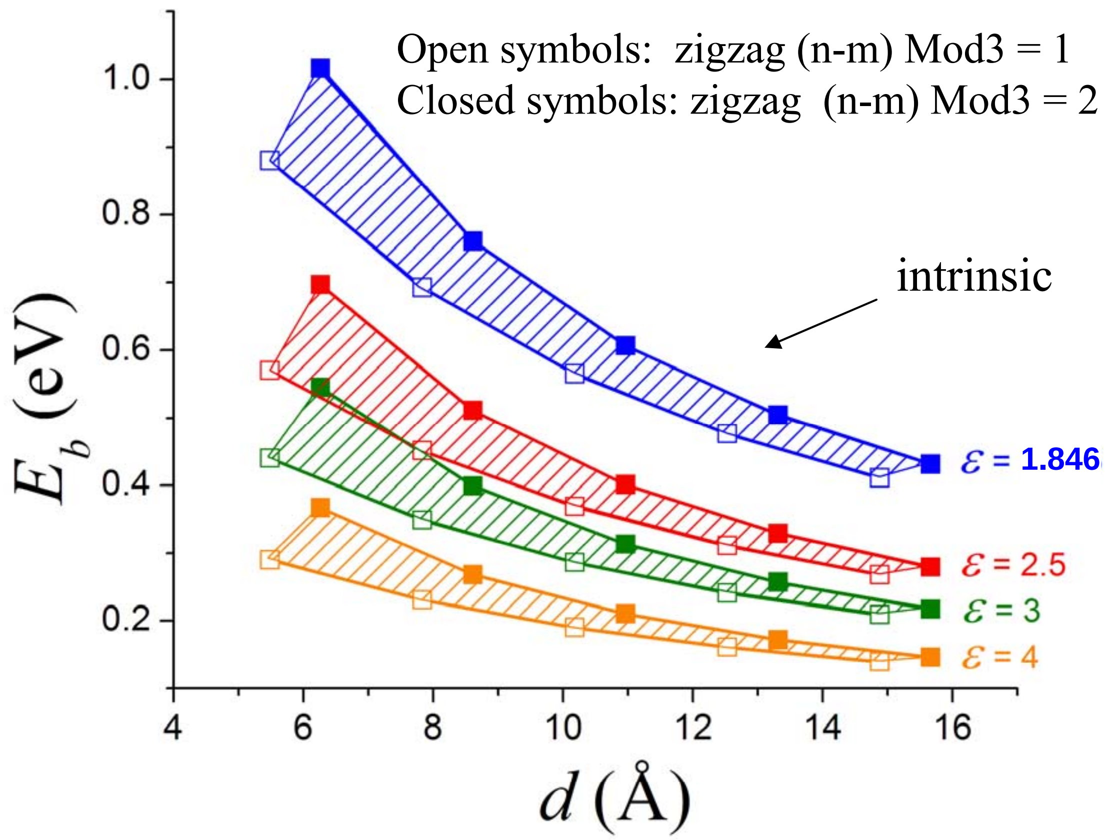
Bright-Dark Splitings



Splittings scale as $1/d^2$



Exciton Binding Energy: Influence of Dielectric Medium



$E_b \propto \varepsilon^{-1.4}$ Perebeinos et al. (2004)

Comparison with experiment

Tube	This work (ε = 3.049) (eV)	2-photon (E_{11}) Dukovic et al. (eV)
(8,3)	0.42	0.42
(6,5)	0.40	0.43
(7,5)	0.38	0.39
(10,2)	0.37	0.34
(9,4)	0.35	0.34
(7,6)	0.34	0.35
(8,6)	0.33	0.35
(11,3)	0.32	0.31
(9,5)	0.31	0.33
(8,7)	0.30	0.29
(9,7)	0.29	0.30
(12,4)	0.29	0.27
(11,6)	0.27	0.27

Dukovic et al., Nano Lett. 5, 2314 (2005)

Tube	This work (ε = 3.208) (eV)	2-photon (E_{11}) Maultzsch et al. (eV)
(6,4)	0.42	0.42
(9,1)	0.40	0.42
(8,3)	0.39	0.38
(6,5)	0.37	0.37
(7,5)	0.36	0.31
(9,4)	0.33	0.38

Maultzsch et al., PRB 72, 241402 (2005)

Tube	This work (ε = 2.559) (eV)	Raman (E_{22}) Wang et al. (eV)
(7,5)	0.54	0.62
(10,3)	0.55	0.49

Wang et al., PRL 96, 047403 (2006)

4. Radiative lifetimes

VOLUME 92, NUMBER 17 PHYSICAL REVIEW LETTERS week ending 30 APRIL 2004

Time-Resolved Fluorescence of Carbon Nanotubes and Its Implication for Radiative Lifetimes

Feng Wang,[1] Gordana Dukovic,[2] Louis E. Brus,[2] and Tony F. Heinz[1]

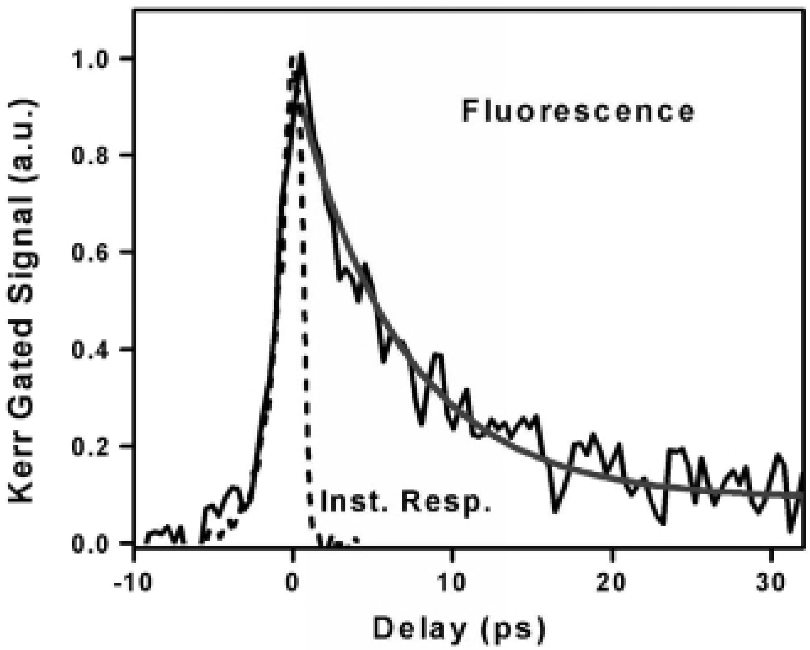


FIG. 3. Fluorescence decay of SWNTs (solid curve) as measured by the Kerr gating technique. The smooth solid line is a fit to a 7-ps exponential decay, with a weaker and slower tail

- Lifetime of excited tubes ≈10 ps
- Quantum efficiency of luminescence > 10^{-4}

⇒

⇒ $\tau_{rad} = 10\text{-}100$ ns

Luminescence decay is dominated by non-radiative processes

Calculating the lifetime

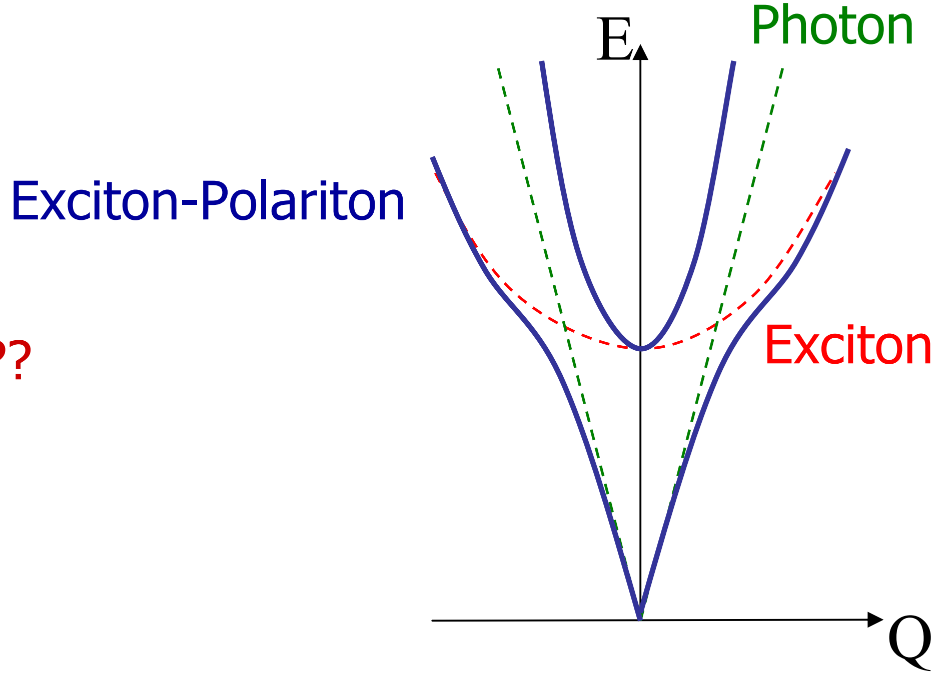
Molecules

$$\tau_{fi}^{-1} = W_{fi}^{s} = \frac{4}{3c^2}\alpha\omega_{fi}^{3}\left|\mathbf{r}_{fi}\right|^2$$

Ingredients: Perturbation theory, Fermi Golden rule, dipole approximation, sum over all final photon states satisfying the conservation laws

3D Solids: Exciton-polaritons – Lifetime is infinite!

How about 1D solids???

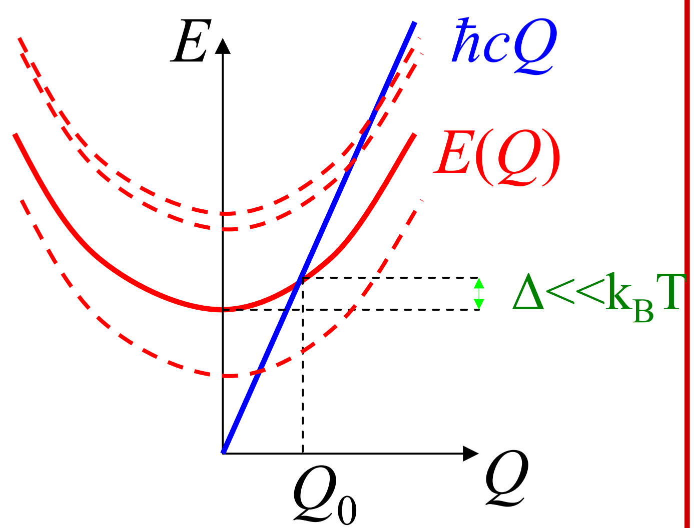


Calculated radiative lifetime of bound excitons

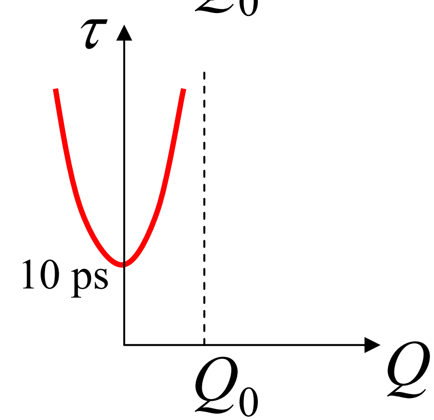
Ab initio intrinsic radiative lifetime of bright excitons:

$$\tau_{rad}^{\mathrm{int}}(Q) = \begin{cases} \dfrac{c^2 a}{2\pi e^2 \mu^2 E^2(0)} \dfrac{E^2(Q)}{E^2(Q) - c^2 Q^2}, \text{ if } |Q| < Q_0 \\ \infty, \text{ if } |Q| > Q_0 \end{cases}$$

$\tau_{rad}^{\mathrm{int}}(0) \approx 10$ ps for the (11,0) tube



Only excitons with energy above the photon line can decay: Momentum conservation

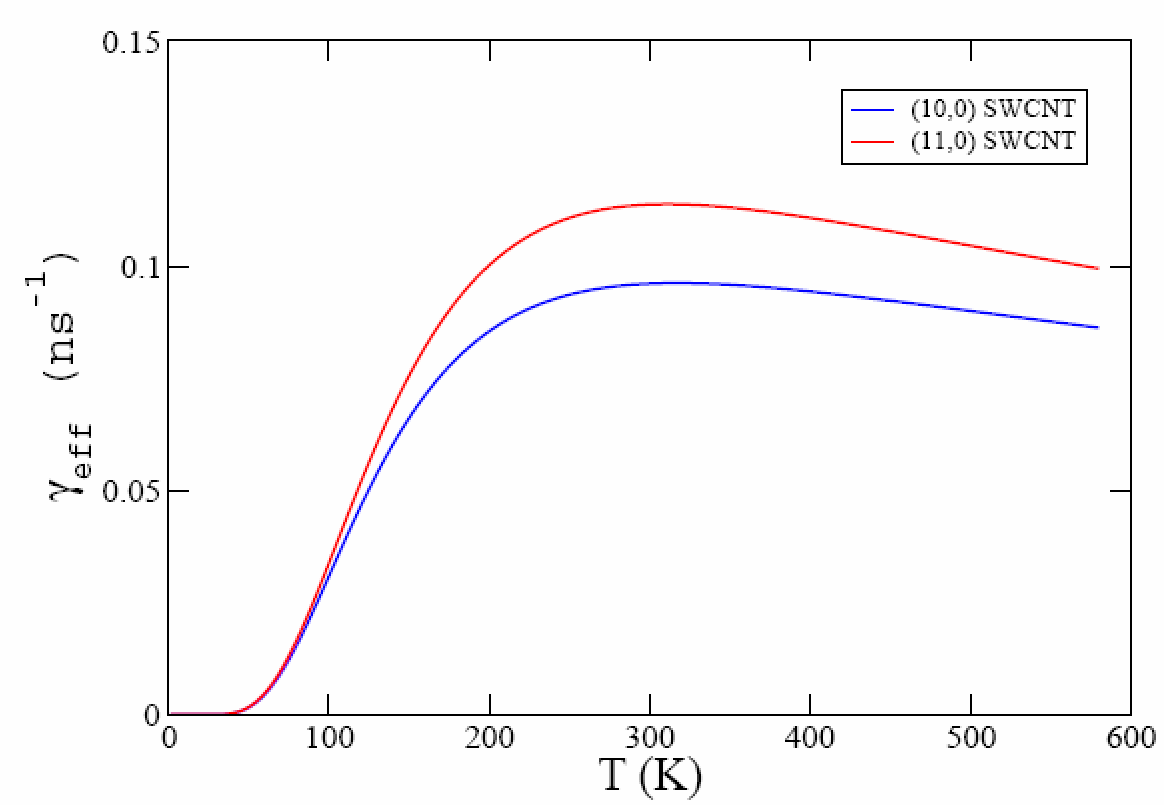


- Temperature and dark-exciton effects:

$$T = 300\,\mathrm{K} \Rightarrow \tau_{rad}^{T} \approx 10\,\mathrm{ns}$$

Spataru, Ismail-Beigi, Capaz and Louie, PRL 94, 247402 (2005).

Temperature dependence of the lifetime



Conclusions

- For each bright exciton in nanotubes, there are other 3 dark ones, separated by a few meV
- The lowest excitonic state is always dark (symmetry): Low efficiency of SWNT light emission
- We calculate diameter and chirality dependence of exciton properties
- We calculate effective radiative lifetimes of ~ 10 ns once temperature and dark-exciton effects are taken into account
- Luminescence decay is dominated by non-radiative transitions to dark exciton states

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