STRONG-COUPLING-MEDIATED QUANTUM NEAR-FIELD EFFECTS IN HYBRID QUASI-1D NANOSTRUCTURES

Igor Bondarev

Math & Physics Department
North Carolina Central University
Durham, NC 27707, USA

US National Science Foundation – ECCS-1306871
US Department of Energy – DE-SC0007117

OUTLINE

- Introduction:

  Interband Plasmons in Individual Single-Wall Carbon Nanotubes

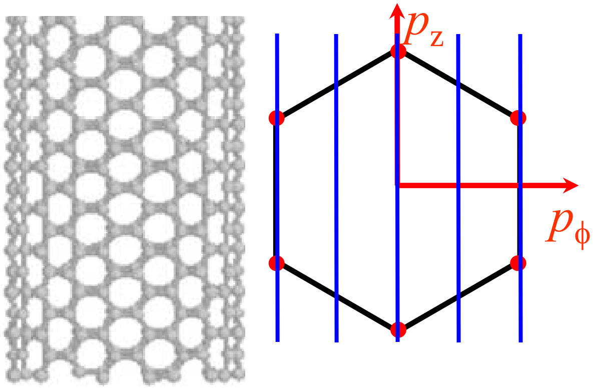
- Hybrid Carbon Nanotube Systems:

  (a.) *Quantum Theory of the Plasmon Enhanced Raman Scattering*
  (b.) *Electron Transport in Metal-Semiconductor Hybrid Systems*

- Summary

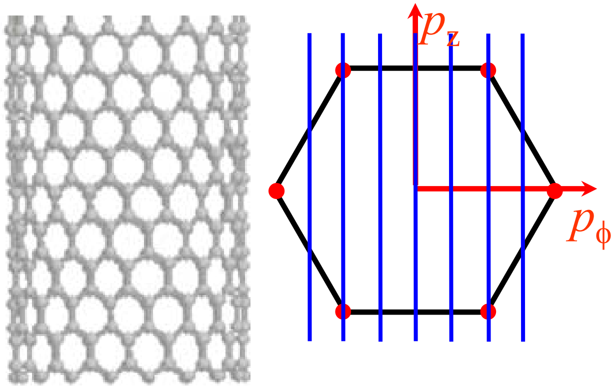
BASIC PHYSICAL PROPERTIES OF SINGLE-WALLED CNs

Brillouin zone structure and longitudinal conductivity

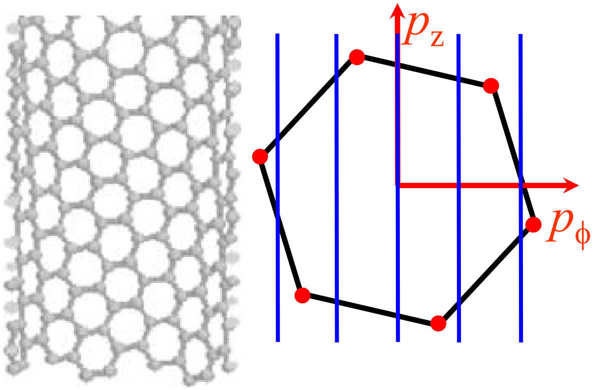


(m,m) – “Armchair”: metallic for all m

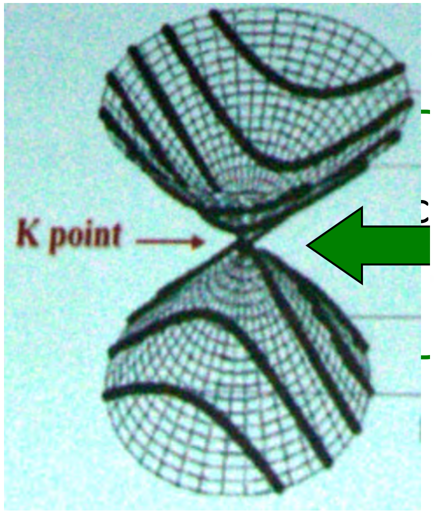
$$p_\phi = \frac{\hbar s}{R_{cn}},\ s = 1,2,\ldots,m$$

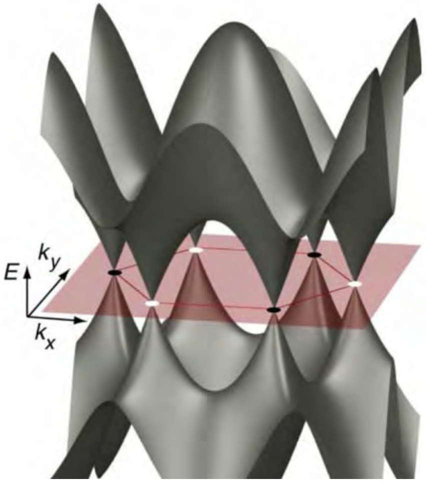


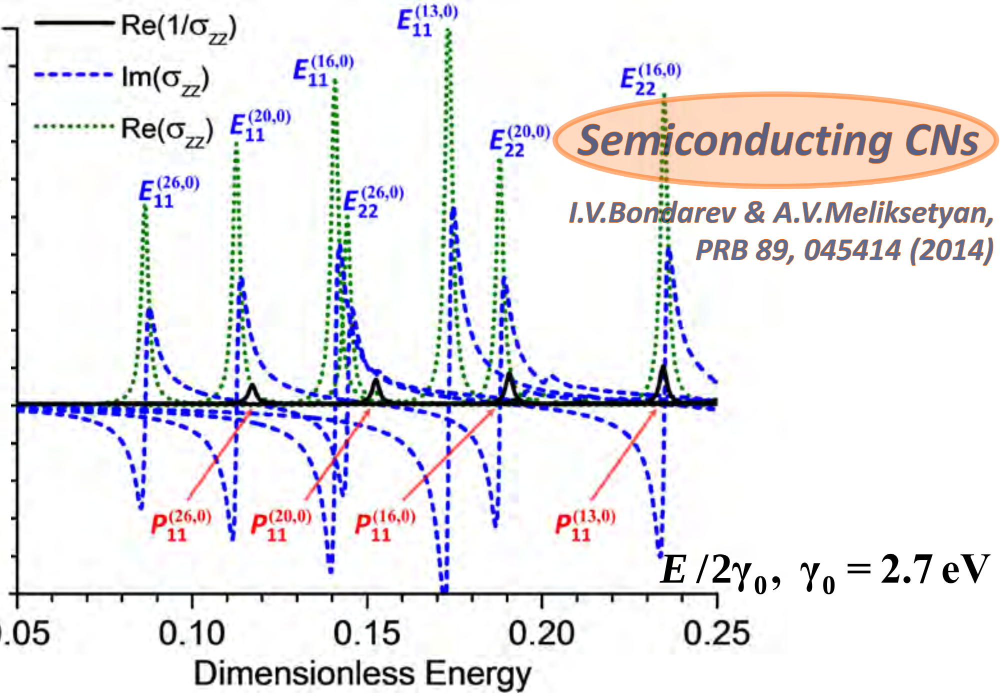
$(m,0)$ – “Zigzag”: metallic for $m=3q$, semiconducting for $m\neq 3q$ ($q=1,2,3,\ldots$)



(m,n) – chiral CN: metallic or semi-conducting depending on the radius and chiral angle





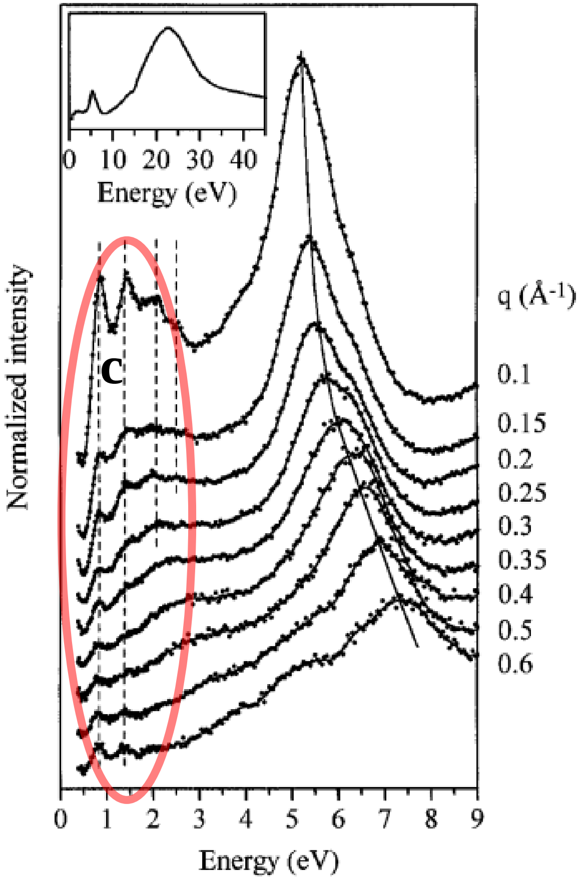


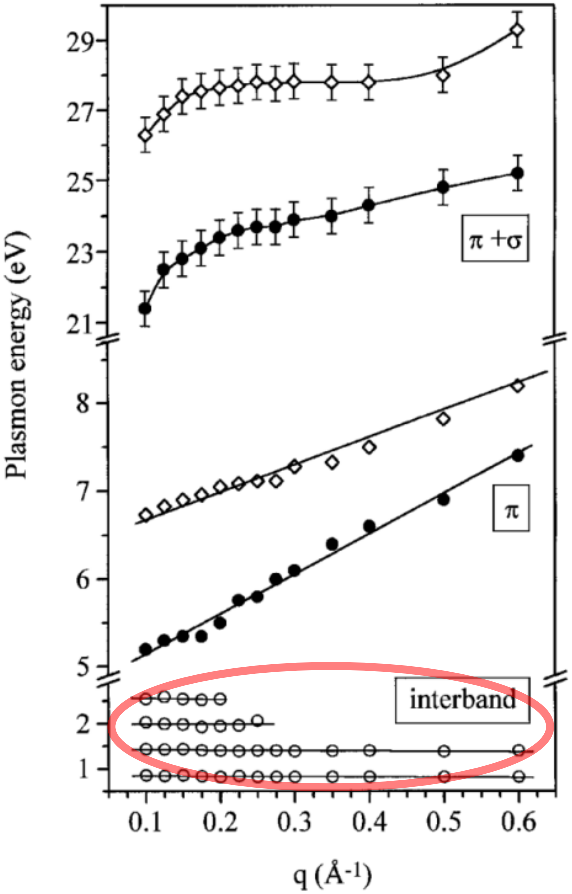
Semiconducting CNs

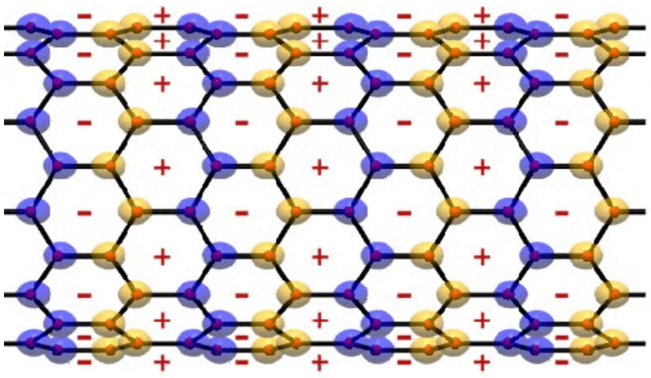
I.V.Bondarev & A.V.Meliksetyan, PRB 89, 045414 (2014)

EXPERIMENTAL ELECTRON ENERGY LOSS SPECTROSCOPY (EELS) SPECTRA OF SINGLE-WALLED CARBON NANOTUBES

T.Pichler, M.Knupher, M.Golden, J.Fink, A.Rinzler, and R.Smalley, PRL 80, 4729 (1998)

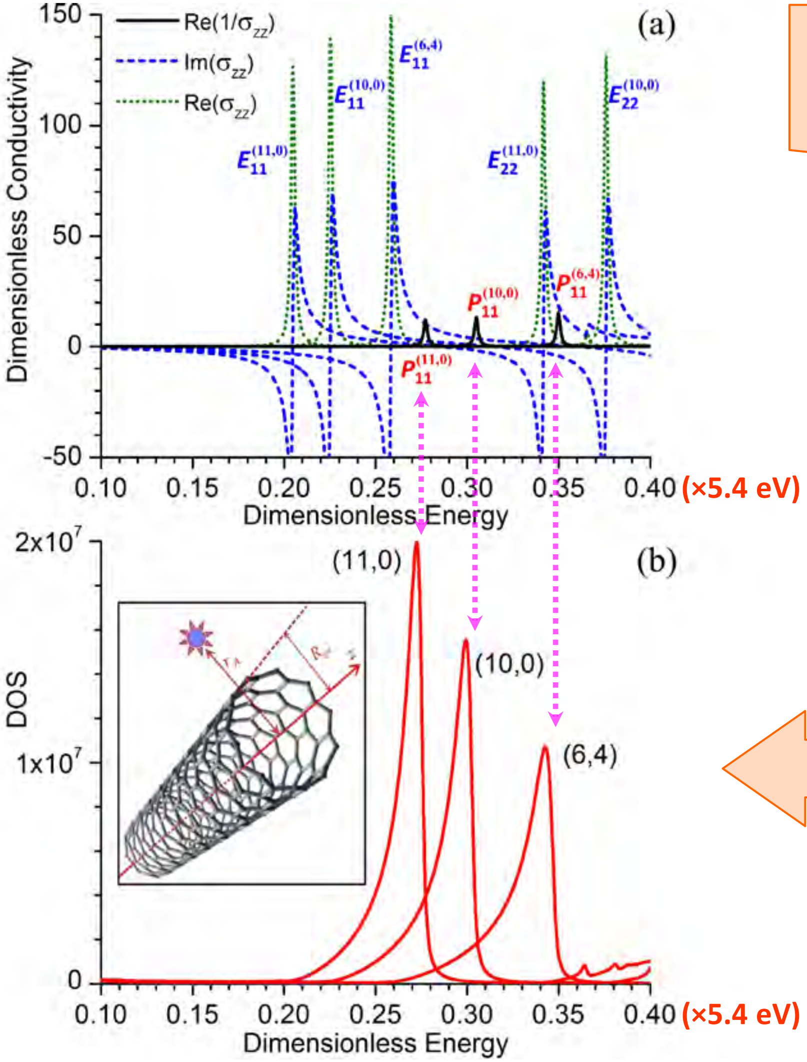






INTERBAND PLASMONS OF CARBON NANOTUBES ARE SIMILAR TO CAVITY PHOTONS IN MICROCAVITY SYSTEMS

I.V.Bondarev & Ph.Lambin, Phys. Rev. B 72, 035451 (2005);
also Ch.6, pp.139-183 in "Trends in Nanotubes Research" (Nova Science, 2006)

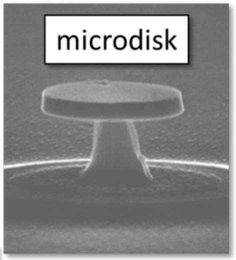


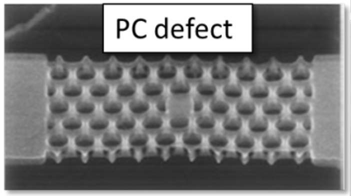
Local Density of Photonic States (DOS) for a two-level emitter coupled to ⊥ (||)-polarized electromagnetic field (same as Purcell factor)

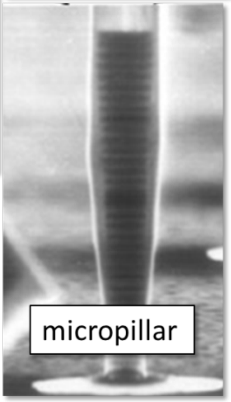
$$\xi^{\perp(\|)}(\mathbf{r}_A,\omega)=\frac{\mathrm{Im}^{\perp(\|)}G_{zz}^{\perp(\|)}(\mathbf{r}_A,\mathbf{r}_A,\omega)}{\mathrm{Im}G_{zz}^{0}(\omega)}$$

$$\xi^{\perp}(r_A\sim R_{CN},\omega)=\xi^{\|}(r_A\sim R_{CN},\omega)=\xi$$

$$\xi=\frac{\Gamma(r_A,\omega)}{\Gamma_0(\omega)},\quad \Gamma_0=\frac{4d_z^2\omega^3}{3\hbar c^3}=\Gamma_{vac}$$







$$F_{Purcell}=\frac{\Gamma_{cav}}{\Gamma_{vac}}=\frac{3\lambda^3}{4\pi^2n^3}\left(\frac{Q}{V_{\mathrm{cav}}}\right)$$

J.M.Gerard, in: ***Single Quantum Dots****, P.Michler, ed., Topics Appl. Phys. 90, 269–315 (2003)*

OUTLINE

- Introduction:

  Interband Plasmons in Individual Single-Wall Carbon Nanotubes

- Hybrid Carbon Nanotube Systems:

  (a.) *Quantum Theory of the Plasmon Enhanced Raman Scattering*
  (b.) *Electron Transport in Metal-Semiconductor Hybrid Systems*

- Summary

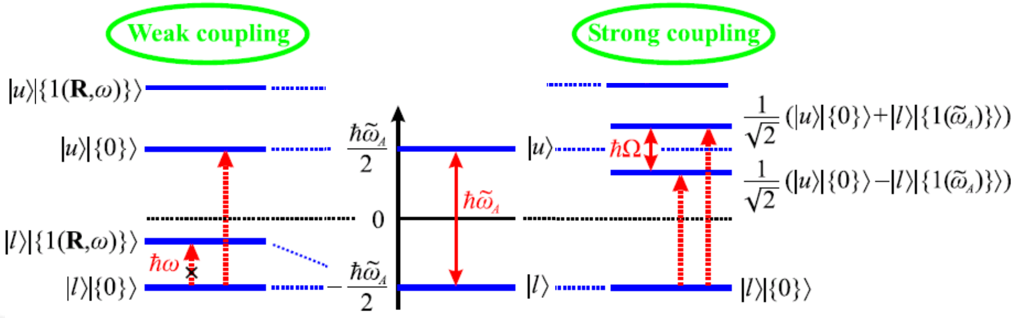
THE MODEL: FOUR-LEVEL SYSTEM OF A TWO-LEVEL ATOM COUPLED TO AN INTERBAND PLASMON RESONANCE

I.V.Bondarev, Optics Express 23, 3971 (2015)

4-level system of a 2-level atom coupled to a plasmon resonance. General case

$$\begin{aligned}|0\rangle &= |l\rangle|\{0\}\rangle,\\ |1,2\rangle &= C_u^{(1,2)}|u\rangle|\{0\}\rangle+\int_0^\infty d\omega\int d\mathbf{R}\,C_l^{(1,2)}(\mathbf{R},\omega)|l\rangle|\{1(\mathbf{R},\omega)\}\rangle,\\ |3\rangle &= |u\rangle|\{1(\mathbf{R},\omega)\}\rangle.\end{aligned}$$

$$C_u^{(1,2)}=\left[\frac{1}{2}\left(1+\frac{1\mp\sqrt{1+X^2/\delta^2}}{1+X^2/\delta^2\mp\sqrt{1+X^2/\delta^2}}\right)\right]^{1/2},$$



$$|C_u^{(1,2)}|^2+\int_0^\infty d\omega\int d\mathbf{R}\,|C_l^{(1,2)}(\mathbf{R},\omega)|^2=1$$

$$\varepsilon_0=-\frac{\tilde{x}_A}{2},\quad \varepsilon_{1,2}=\frac{1}{2}\left(x_p\mp\sqrt{\delta^2+X^2}-i\Delta x_p\right),\quad \varepsilon_3=\frac{\tilde{x}_A}{2}+x_p-i\Delta x_p$$

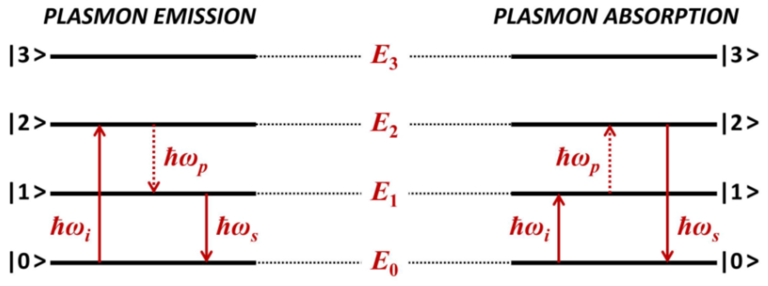
$$\varepsilon_i=E_i/2\gamma_0\ (i=0,1,2,3),\ \gamma_0=2.7\,\text{eV},\ (\tilde{x}_A,x_p,\Delta x_p)=\hbar(\tilde{\omega}_A,\omega_p,\Delta\omega_p)/2\gamma_0$$

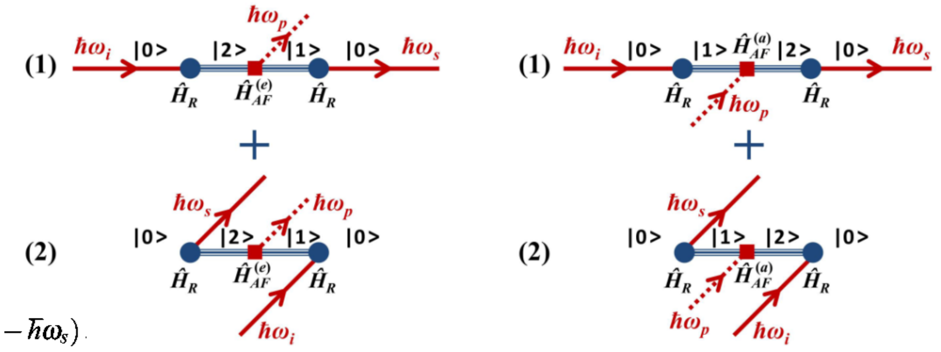
$$\delta=\tilde{x}_A-x_p,\ X=(\hbar/2\gamma_0)[2\Delta\omega_0\Gamma_0(\omega_p)(1+\omega_A^2/\omega_p^2)\xi(\mathbf{r}_A,\omega_p)]^{1/2}$$

Fermi Golden Rule scattering probability

$$\left(\frac{2\pi}{\hbar}\right)\left|\frac{\langle 0|\hat{H}_R(\omega_s)|1\rangle\langle 1|\hat{H}_{AF}^{(e)}|2\rangle\langle 2|\hat{H}_R(\omega_i)|0\rangle}{[\hbar\omega_i-\hbar\omega_p-(E_1-E_0)][\hbar\omega_i-(E_2-E_0)]}+\frac{\langle 0|\hat{H}_R(\omega_i)|1\rangle\langle 1|\hat{H}_{AF}^{(e)}|2\rangle\langle 2|\hat{H}_R(\omega_s)|0\rangle}{[-\hbar\omega_s-\hbar\omega_p-(E_1-E_0)][-\hbar\omega_s-(E_2-E_0)]}\right|^2\delta(\hbar\omega_i-\hbar\omega_p-\hbar\omega_s)$$

$$+\left|\frac{\langle 0|\hat{H}_R(\omega_s)|2\rangle\langle 2|\hat{H}_{AF}^{(a)}|1\rangle\langle 1|\hat{H}_R(\omega_i)|0\rangle}{[\hbar\omega_i+\hbar\omega_p-(E_2-E_0)][\hbar\omega_i-(E_1-E_0)]}+\frac{\langle 0|\hat{H}_R(\omega_i)|2\rangle\langle 2|\hat{H}_{AF}^{(a)}|1\rangle\langle 1|\hat{H}_R(\omega_s)|0\rangle}{[-\hbar\omega_s+\hbar\omega_p-(E_2-E_0)][-\hbar\omega_s-(E_1-E_0)]}\right|^2\delta(\hbar\omega_i+\hbar\omega_p-\hbar\omega_s)$$



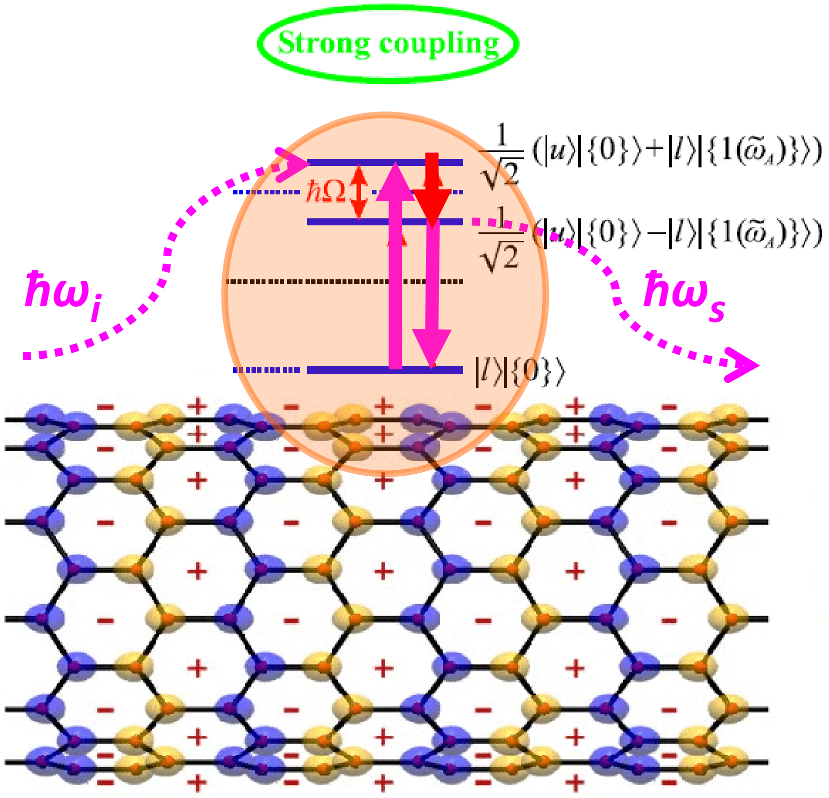


FOUR-LEVEL SYSTEM OF A TWO-LEVEL ATOM COUPLED TO AN INTERBAND PLASMON RESONANCE

Schematic illustration

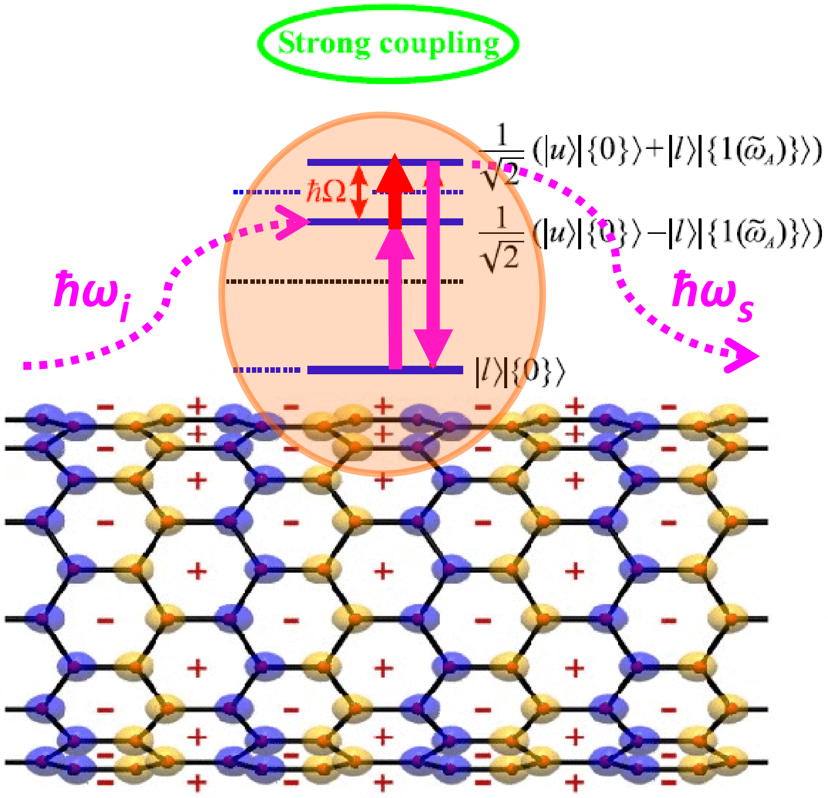
Plasmon Emission

$\hbar\omega_s = \hbar\omega_i - \hbar\omega_p$



Plasmon Absorption

$\hbar\omega_s = \hbar\omega_i + \hbar\omega_p$



$$d_zE_z^{(loc)}(\mathbf{r}_A)\sim X\propto\left[\Gamma_0(\omega_p)\xi(\mathbf{r}_A,\omega_p)\right]^{1/2}$$

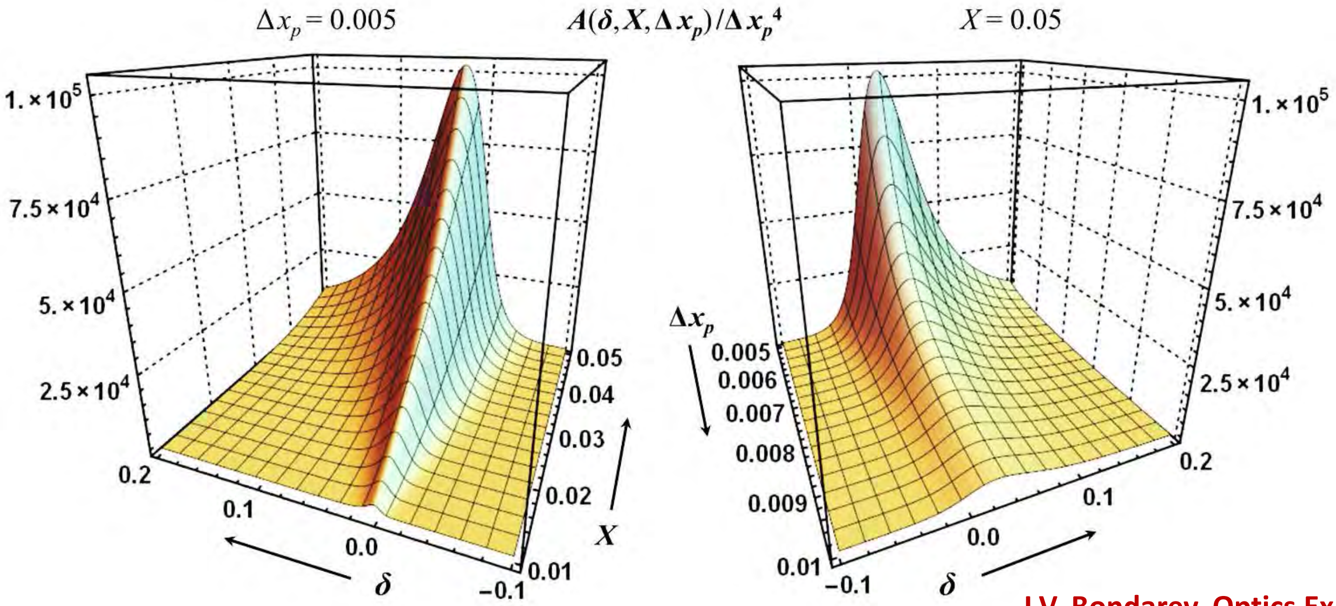
FOUR-LEVEL SYSTEM OF A TWO-LEVEL ATOM COUPLED TO AN INTERBAND PLASMON RESONANCE

Raman scattering cross-section. Enhancement factor

$$\frac{d\sigma}{d\Omega_s}=\frac{(2\gamma_0)^2|d_z|^4}{\hbar^4c^4}\cos^2\vartheta_i\cos^2\vartheta_s\,P(x_i,x_s)\,,\quad x_{i,s}=\hbar\omega_{i,s}/2\gamma_0,\quad \cos\theta_{i,s}=\mathbf{e}_{i,s}\cdot\mathbf{e}_z$$

$$P(x_i,x_s)=x_ix_s^3A(\delta,X,\Delta x_p)\left\{\frac{1}{[(x_i-x_p-\delta_+/2)^2+\Delta x_p^2][(x_s-x_p-\delta_-/2)^2+\Delta x_p^2]}+\frac{1}{[(x_i-x_p-\delta_-/2)^2+\Delta x_p^2][(x_s-x_p-\delta_+/2)^2+\Delta x_p^2]}\right\},\qquad \delta_\pm=\delta\pm\sqrt{\delta^2+X^2}$$

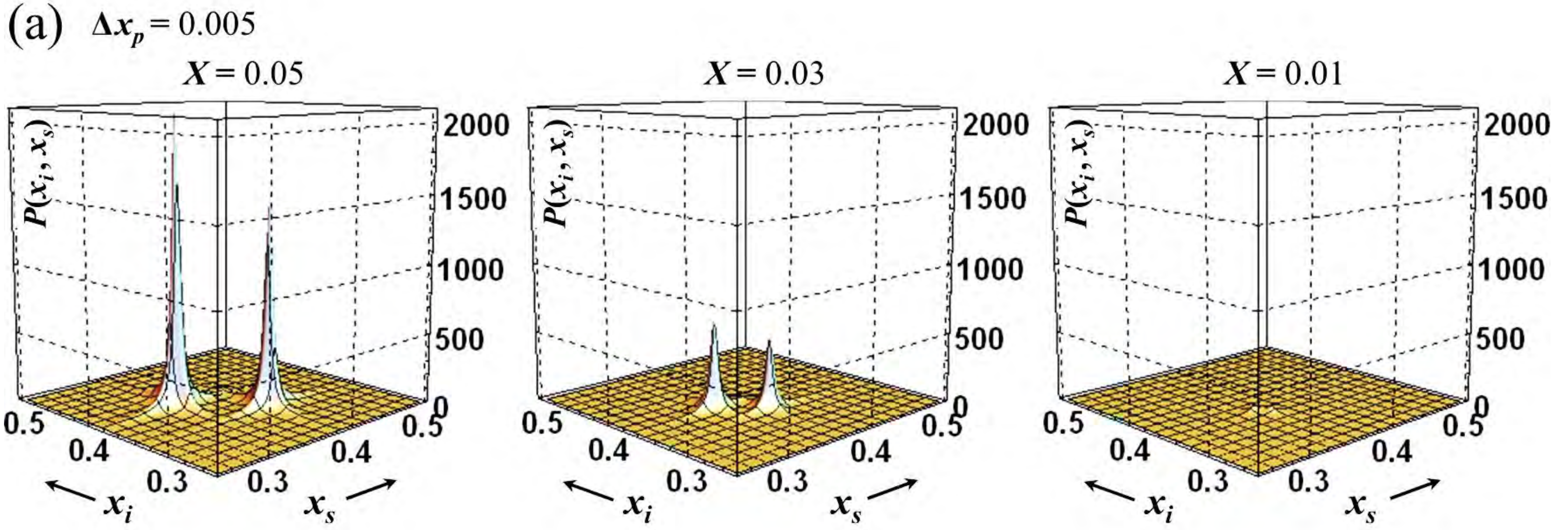
$$A(\delta,X,\Delta x_p)=\frac{X^8}{2^6(\delta^2+X^2)^2(\delta_-^2+\Delta x_p^2)}\sim[d_zE_z^{(loc)}(\mathbf{r}_A)]^4\propto\xi^2(\mathbf{r}_A,\omega_p)$$



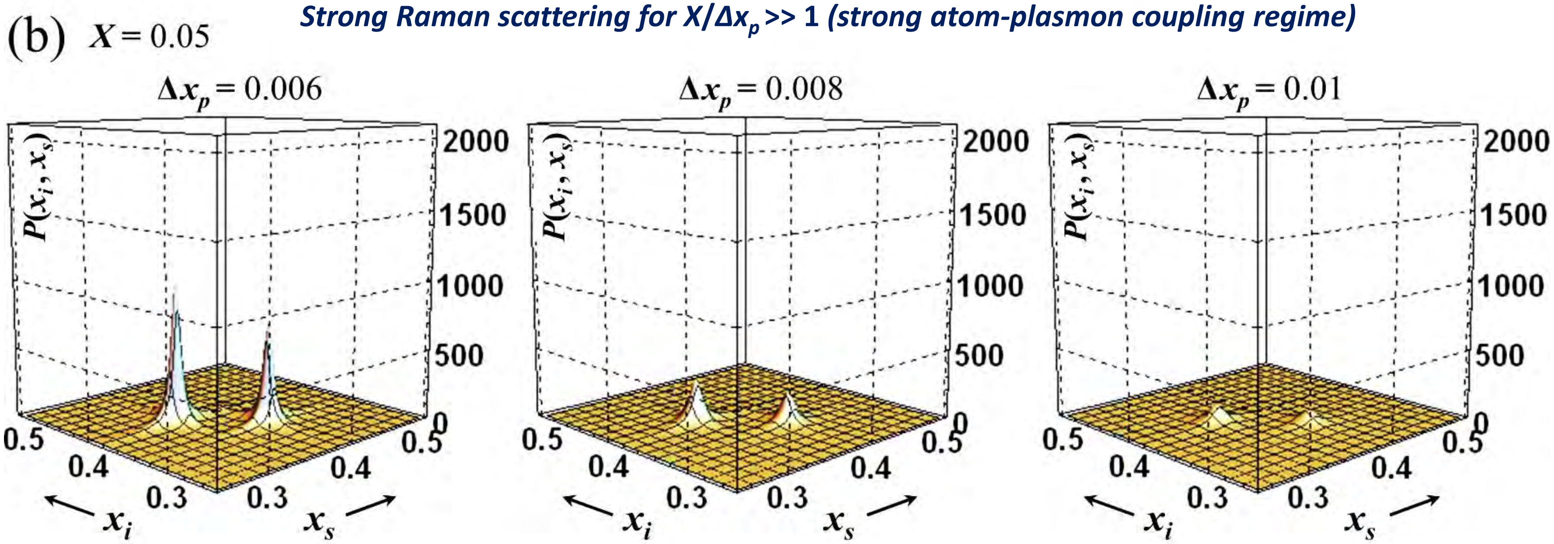
I.V. Bondarev, Optics Express 23, 3971 (2015)

FOUR-LEVEL SYSTEM OF A TWO-LEVEL ATOM COUPLED TO AN INTERBAND PLASMON RESONANCE

Raman scattering probability



Strong Raman scattering for $X/\Delta x_p >> 1$ (strong atom-plasmon coupling regime)



I.V. Bondarev, Optics Express 23, 3971 (2015)

OUTLINE

- Introduction:

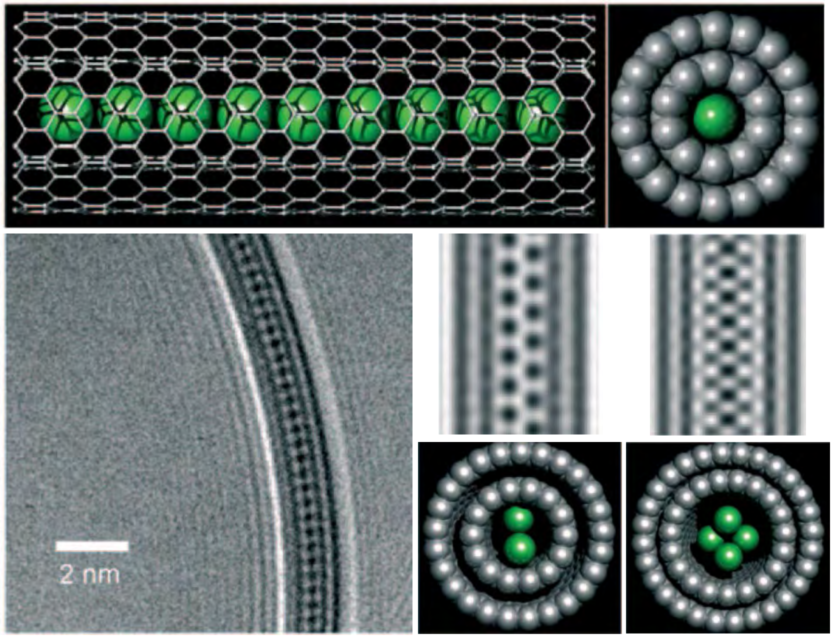
  Interband Plasmons in Individual Single-Wall Carbon Nanotubes

- Hybrid Carbon Nanotube Systems:

  (a.) *Quantum Theory of the Plasmon Enhanced Raman Scattering*
  (b.) *Electron Transport in Metal-Semiconductor Hybrid Systems*

- Summary

HYBRID NANOSTRUCTURES OF CARBON NANOTUBES ENCAPSULATING METALLIC NANOWIRES

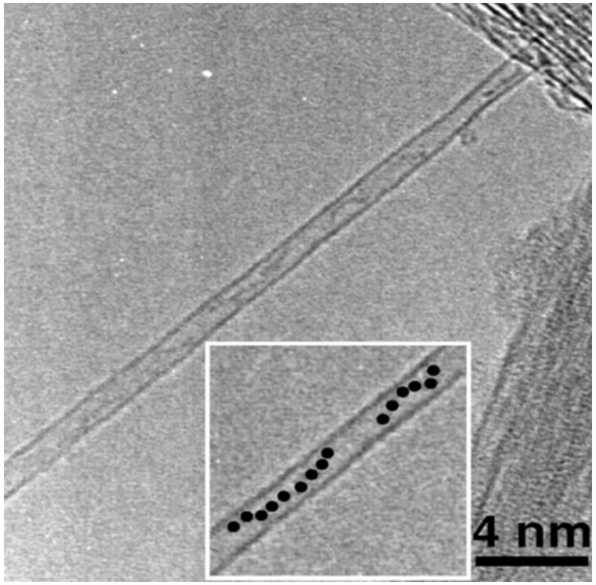


*H.SHINOHARA group,
JAPAN, Nagoya
University-Chemistry:*

*R.Kitaura, et al.,
Angew. Chem. Int. Ed.
48, 8298 (2009)*

*R.Nakanishi, et al.,
Phys. Rev. B 86,
115445 (2012)*

Carbon nanotubes can encapsulate various sorts of atomic chains provided that the size of the atom does not exceed the diameter of the nanotube. Cr, Fe, Co, Ni, Cu, Eu, Gd, Cs, Mo, Na, etc.



Single-walled CN filled with cesium atoms.
Jeong e.al. PRB68, 075410 (2003)

SEMICONDUCTING

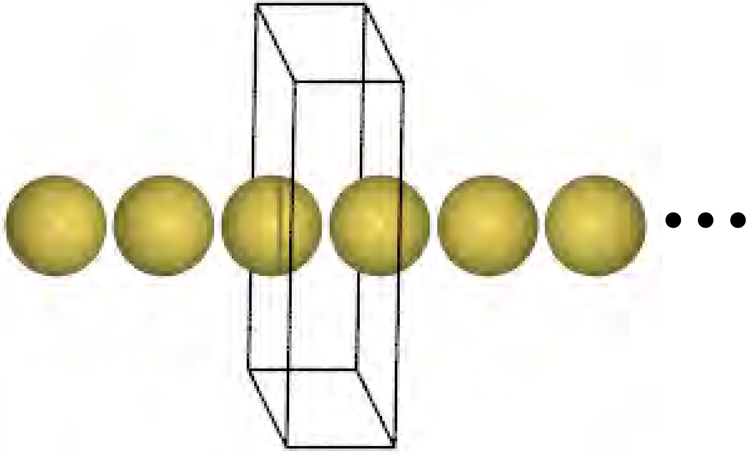
CARBON NANOTUBES

&

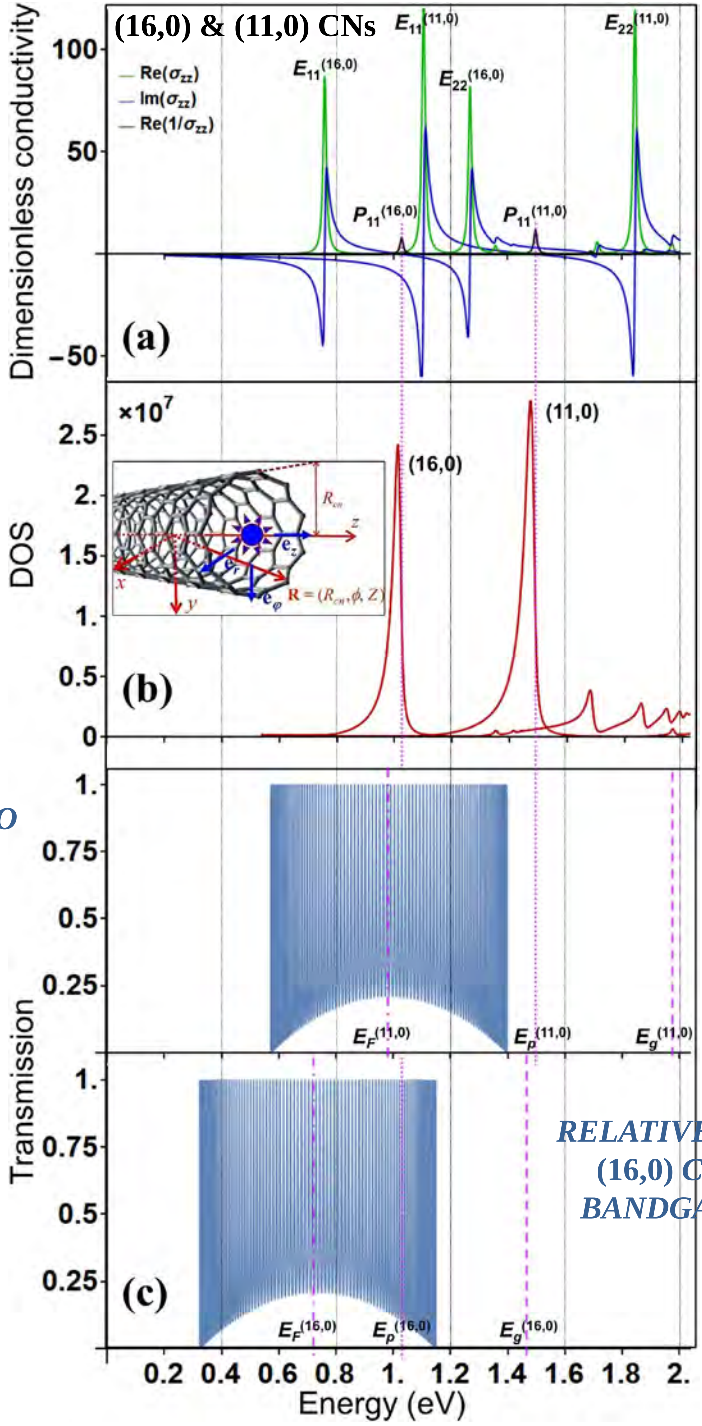
METALLIC NANOWIRES

(noninteracting)

TRANSMISSION BAND
OF THE *FREE* SODIUM ATOMIC WIRE
(100 atoms)

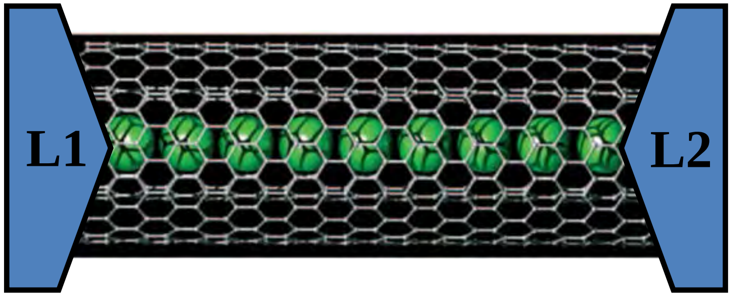


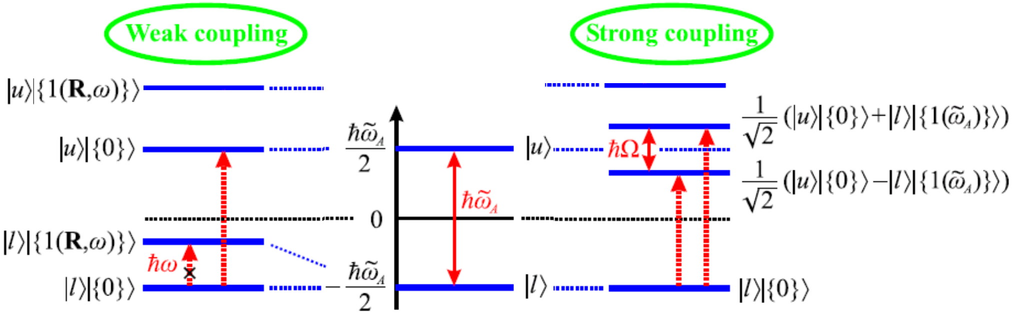
RELATIVE TO
(11,0) CN
BANDGAP



RELATIVE TO
(16,0) CN
BANDGAP

HYBRID METAL-SEMICONDUCTOR CARBON NANOTUBE SYSTEM: THE MODEL





$$T(E) = 4\Delta_1(E)\Delta_N(E)|G_{1N}(E)|^2$$

Mujica, Kemp, & Ratner, J. Chem. Phys. 101, 6849, 6856 (1994)
[Scattering matrix formalism for molecular wires of finite length]

$$\mathbf{G}(E) = [E - \mathbf{H} - \mathbf{\Sigma}(E)]^{-1},\ \Sigma_{NN}(E) = \Lambda_N - i\Delta_N,\ \ \Sigma_{11}(E) = \Lambda_1 - i\Delta_1$$

$$\hat{H} = \hat{H}_{\mathrm{AW}} + \hat{H}_{\mathrm{CN}} + \hat{H}_{\mathrm{int}}$$

Gelin & Bondarev,
PRB93, 115422 (2016)

$$\hat{H}_{\mathrm{AW}} = E_0 \sum_{k=1}^{N} B_k^\dagger B_k + V \sum_{k=1}^{N-1} (B_k^\dagger B_{k+1} + B_{k+1}^\dagger B_k)$$

$$\hat{H}_{\mathrm{CN}} = \sum_{\mathbf{n}} \int_0^\infty d\omega \hbar\omega \hat{f}^\dagger(\mathbf{n},\omega)\hat{f}(\mathbf{n},\omega) \approx E_p \hat{f}^\dagger \hat{f}$$

$$\hat{H}_{\mathrm{int}} = \sum_{k=1}^{N} \mu_k (B_k \hat{f}^\dagger + B_k^\dagger \hat{f}),\ \ \mu_k = \mu \lesssim \boxed{\hbar g} = \sqrt{\frac{2\pi \boxed{d_z^2} \hbar\tilde{\omega}_A}{\tilde{V}}} \approx \sqrt{\frac{2\alpha^3}{\pi}\frac{\hbar c}{R_{\mathrm{CN}}}}$$

Bondarev, Optics Express 23, 3971 (2015) [and Refs. therein]

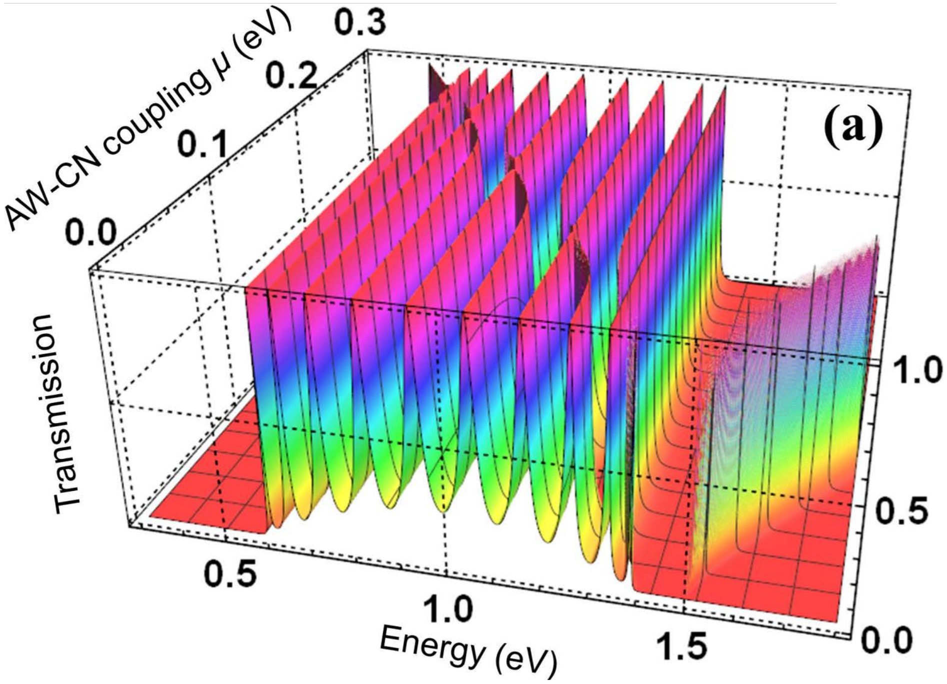
$$\{B_k^\dagger|0\rangle\}_{k=1,\ldots,N}, \hat{f}^\dagger|0\rangle$$

$$\mathbf{H} = \begin{bmatrix} E_0 & V & 0 & \ldots & 0 & 0 & \mu \\ V & E_0 & V & \ldots & 0 & 0 & \mu \\ 0 & V & E_0 & \ldots & 0 & 0 & \mu \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \ldots & E_0 & V & \mu \\ 0 & 0 & 0 & \ldots & V & E_0 & \mu \\ \mu & \mu & \mu & \ldots & \mu & \mu & E_p \end{bmatrix} \updownarrow \boldsymbol{N+1}$$

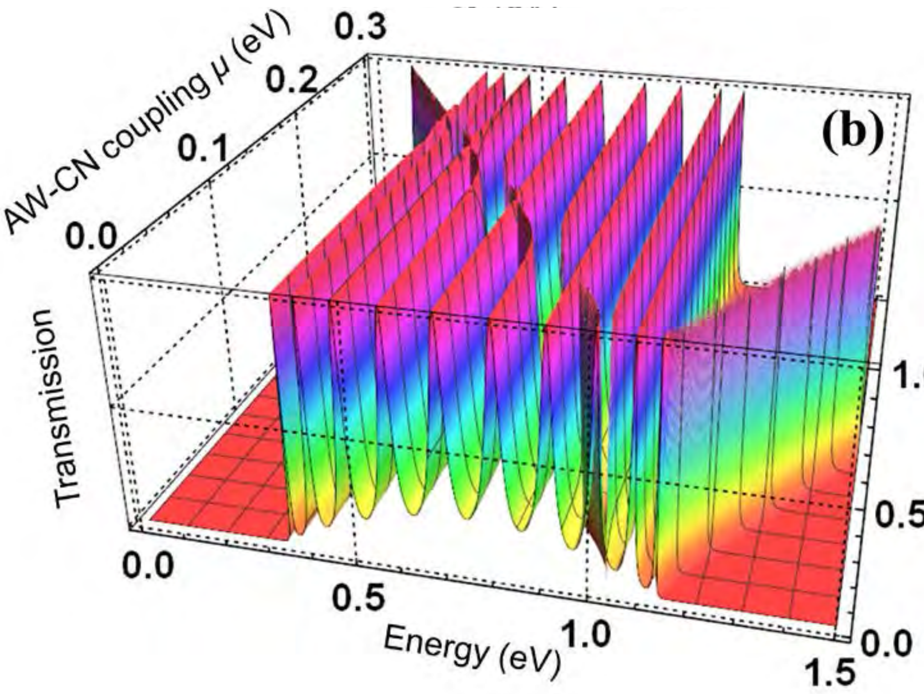
$$\longleftarrow \boldsymbol{N+1} \longrightarrow$$

TRANSMISSION VERSUS ENERGY AND WIRE-CN COUPLING

sodium wire of N=10 atoms long; wire-lead coupling Δ = 0.05 eV



(11,0) CN



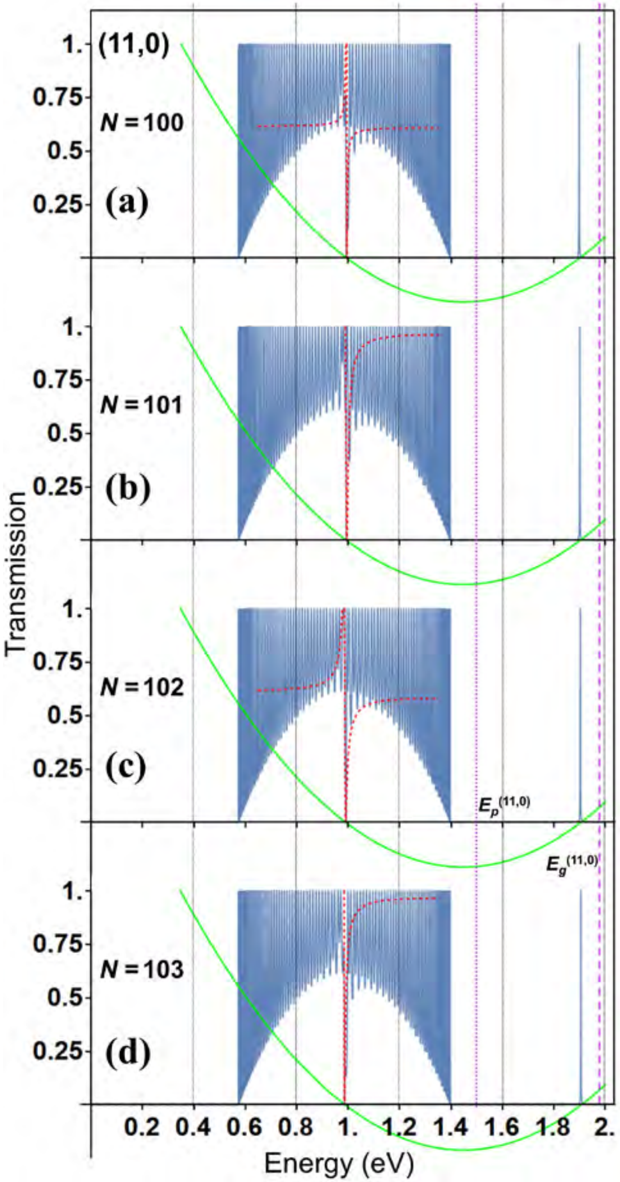
(16,0) CN

$$(E_p - E)(E_0 - E + 2V) = N\mu^2$$

$$E_{1,2} = \frac{1}{2}[E_0 + 2V + E_p \pm \sqrt{(E_0 + 2V - E_p)^2 + 4N\mu^2}]$$

Gelin & Bondarev, PRB93, 115422 (2016)

TRANSMISSION VERSUS ENERGY
sodium wire of N=100-103 atoms
μ = 0.045 eV, Δ = 0.1 eV

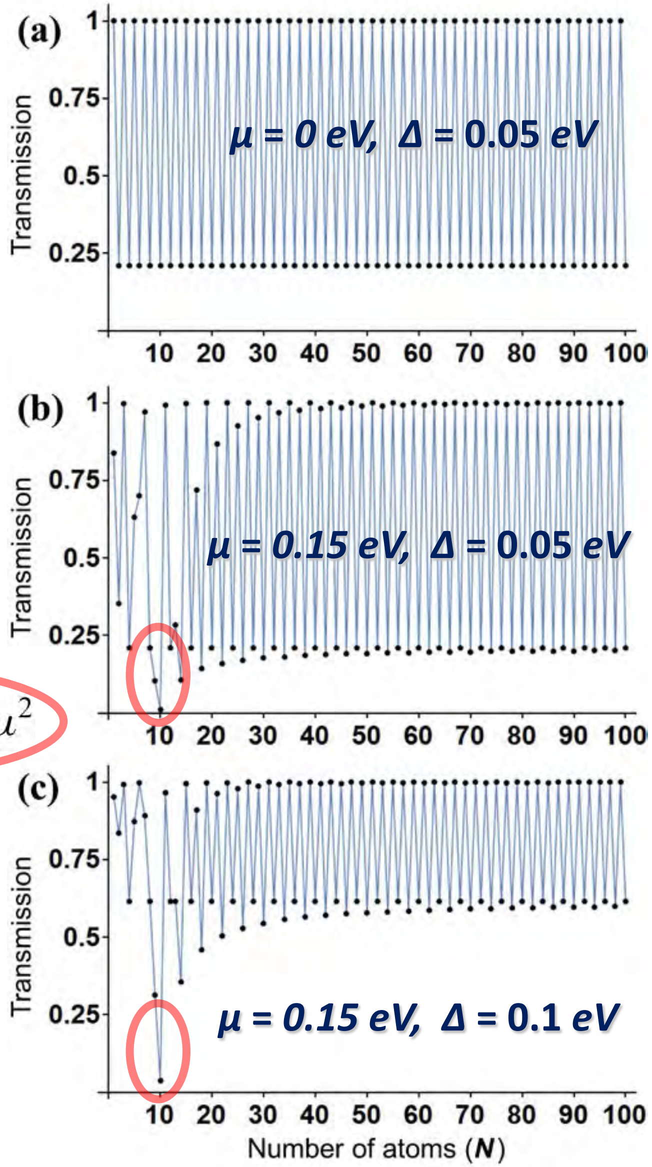


TRANSMISSION VERSUS WIRE LENGTH AT *E*=*E*$_0$=*E*$_F$
sodium wire inside (11,0) *CN*

$$(E_p - E)(E_0 - E + 2V) = N\mu^2$$

$$\Gamma \approx \frac{\mu^2 \kappa(\xi, N)}{|E_0 - 2V - E_p|}, \ \xi = \Delta / V$$

$$\boxed{2V(E_p - E_F) = N\mu^2}$$



Gelin & Bondarev,
PRB93, 115422 (2016)

SUMMARY – I

Scientific Achievement

Quantum theory is developed to show that carbon nanotubes (CNs) can enhance Raman scattering by atom type species nearby

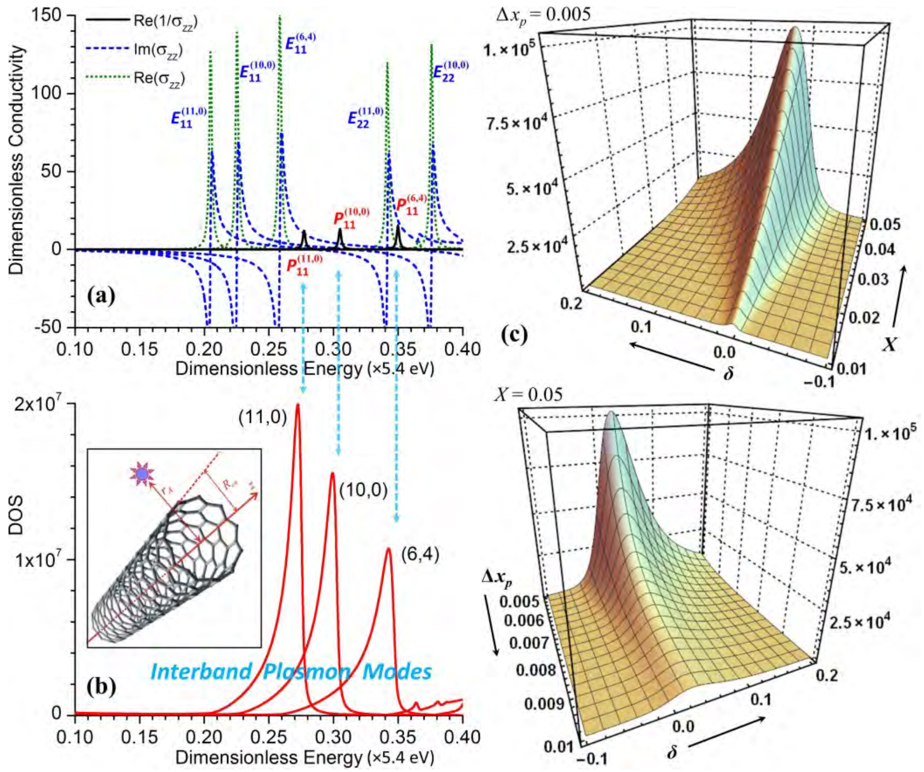
Significance and Impact

Opens paths for new design concepts of CN based nanophotonics platforms with varied characteristics on-demand, for single atom detection, sensing, control and manipulation

Research Details

- Most of the applications of CNs to enhance Raman scattering have been to decorate them with metallic nanoparticles, to use metal plasmons as spectroscopic enhancers with CNs serving as their supporters
- In this work, individual CNs are shown to be able to provide a strong resonance Raman enhancement effect due to their intrinsic (interband) plasmon modes
- Raman scattering signal raises dramatically for atom type species *physisorbed* on the CN surface when coupled strongly to the interband plasmon resonance of the CN

I.V. Bondarev, Optics Express 23, 3971-3984 (2015)



(a) : Axial surface conductivities σ_{zz} (divided by $e^2/2\pi\hbar$) for the (6,4), (10,0) and (11,0) CNs. Peaks of Re(σ_{zz}) represent excitons (E_{11}, ...); peaks of Re($1/\sigma_{zz}$) indicate interband plasmons (P_{11}, ...).

(b) : Photonic density-of-states for the two-level atomic system (TLS) placed 2.84 Å away from the surface of the CNs in (a).

(c), upper & lower : Raman scattering enhancement factor for the P_{11}(6,4) resonance in (a) with typical X, Δx_p and δ to stand for TLS Rabi splitting, plasmon resonance width and TLS detuning from the plasmon resonance (in units of the double C-C overlap integral, 5.4 eV). **The enhancement factor increases dramatically for $X/\Delta x_p$ >>1 (strong TLS-plasmon coupling regime).**

SUMMARY – II

Scientific Achievement

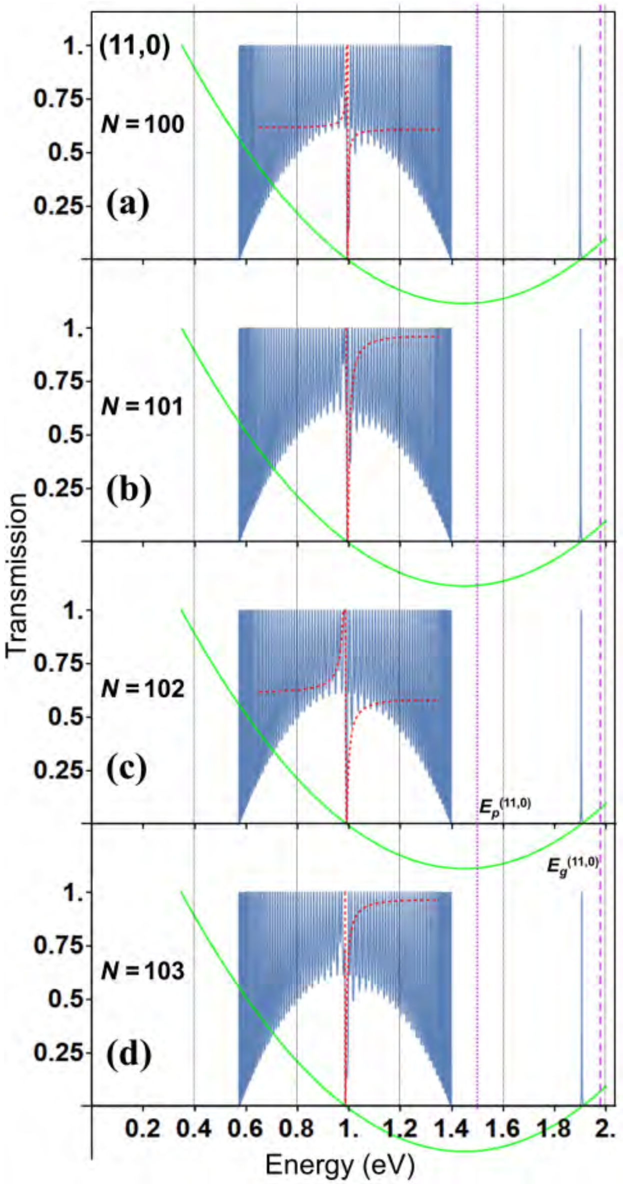
Electron transport theory has been developed for the hybrid system of a semiconducting CN that encapsulates a one-atom-thick metallic wire (AW).

Significance and Impact

The theory predicts Fano resonances in electron transport through the system, whereby CN plasmon generated near-field blocks some of the AW transmission band channels to open up a new coherent channel in the CN bandgap outside the AW transmission band. This makes the entire hybrid system transparent in the energy domain where neither AW nor CN is individually transparent.

Research Details

- Scattering matrix formalism is used for molecular wires of finite length with the near-field electron-plasmon interaction included. Exact analytical solution is obtained for the transmission coefficient
- The condition for the conductance $g = T(E \sim E_F)$ of the hybrid metal-semiconductor CN structure to be affected significantly by the AW-CN plasmon coupling is $2V\,(E_p - E_F) = N\mu^2$



M.F.Gelin and I.V.Bondarev, Physical Review B 93, 115422 (2016)

MORE ON INTERBAND PLASMONS IN CNs

(1) Controlled absorption due to plasmon generation by optically excited excitons in individual CNs

I.V.Bondarev, Physical Review B 85, 035448 (2012)
I.V.Bondarev, L.M.Woods, and K.Tatur, Physical Review B 80, 085407 (2009)

(2) Quasi-1D exciton BEC in individual semiconducting CNs due to the exciton-plasmon coupling controlled by a perpendicular electrostatic field applied

I.V.Bondarev and A.V.Meliksetyan, Physical Review B 89, 045414 (2014)

(3) Spontaneous emission, absorption, and scattering near CNs

I.V.Bondarev and Ph.Lambin, Physical Review B 70, 035407 (2004)
I.V.Bondarev and B.Vlahovic, Physical Review B 74, 073401 (2006)
I.V.Bondarev, Optics Express 23, 3971 (2015)

(4) Distant two-qubit entanglement of two dipole emitters coupled to the same plasmon resonance, schemes for its non-linear optical monitoring

M.F.Gelin, I.V.Bondarev, and A.Meliksetyan, J. Chem. Phys. 140, 064301 (2014)
M.F.Gelin, I.V.Bondarev, and A.Meliksetyan, Chem. Phys. 413, 123 (2013)

(5) Casimir-van der Waals interactions in single/double-wall CNs

A.Popescu, L.M.Woods, and I.V.Bondarev, Physical Review B 83, 081406(R) (2011)
I.V.Bondarev and Ph.Lambin, Physical Review B 72, 035451 (2005)

……. *More to come: Planar periodic CN arrays, Exciton BEC in double wall CNs …………*

COLLABORATORS:

USF
UNIVERSITY OF SOUTH FLORIDA
COLLEGE OF ARTS & SCIENCES

Lilia Woods group

Wolfgang Domcke group