Towards electronic properties of complex systems

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Toulouse 17-19/ 11./ 2010
Theory Days on Quantum Wires and Dots

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

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ETSF European Theoretical Spectroscopy Facility

NanoSciences ILE-DE-FRANCE

Interest in

- Photovoltaic
- Conductance

within *ab initio* framework

- size of the systems limited but predicative
- can include many-body effects

Objectives

- extend the range of ab initio calculations
- understand interactions
  - longe range Coulomb interation
    $\Rightarrow$ Local Field effects
  - exchange-correlation effects

Outline

- Background
- Illustrations
  - Anisotropy in Graphite
    Ralf Hambach
  - Plasmon in Graphene and SWCNT
    Ralf Hambach
  - (3,3) Carbon nanotube
    Xochitl Lopez-Lozano
  - Many-Body Effects in Graphene
    Paolo E. Trevisanutto
- Summary

conductance G^{4P} and conductivity σ

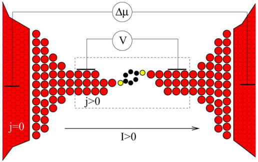


FIG. 1. (Color online) Measurement of the voltage between the macroscopic electrodes, where the current density is zero, gives the two-point conductance $G^{2P}=I/(\Delta\mu/e)$. Measuring the voltage drop inside the simulation box (supercell), where the current density is nonzero, gives the four-point conductance $G^{4P}=I/V$. Increasing the supercell the two quantities approach each other (see Sec. V).

$$G^{4P} = \frac{\mathcal{F}^{\sigma}[\sigma^{irr,e}]}{\mathcal{F}^{\sigma}[\sigma^{irr,e}] - \mathcal{F}^{\sigma}[\sigma^{irr}]} \mathcal{G}^{\sigma}[\sigma^{irr}]$$

with:

$$\mathcal{G}^{\sigma}[\sigma] = \lim_{\alpha \to 0^+} \iint \frac{dqdq'}{2\pi} \sigma(q, q', i\alpha)$$

$$\mathcal{F}^{\sigma}[\sigma] = -\lim_{\alpha \to 0^+} \int dq \sigma(q, q' = 0, i\alpha)$$

[1] P. Bokes, J. Jung, and R. W. Godby, PRB **76**, 125433 (2007)

conductivity σ and response function χ in TDDFT

$$\boldsymbol{j}^{\text{ind}}(\boldsymbol{r},t) = \int d\boldsymbol{r}' dt' \sigma^{irr}(\boldsymbol{r},\boldsymbol{r}',t-t')\boldsymbol{E}^{\text{tot}}(\boldsymbol{r}',t')$$

For bulk materials:

$$\varepsilon(\boldsymbol{q},\boldsymbol{q}',\omega) = \delta(\boldsymbol{q}-\boldsymbol{q}') + i\frac{4\pi}{\omega}\sigma^{irr}(\boldsymbol{q},\boldsymbol{q}',\omega)$$

$$\varepsilon(\boldsymbol{q},\boldsymbol{q}',\omega) = \delta(\boldsymbol{q}-\boldsymbol{q}') - \upsilon(\boldsymbol{q},\boldsymbol{q}')\chi^{irr}(\boldsymbol{q},\boldsymbol{q}',\omega)$$

$$\Longrightarrow \sigma^{irr}(\boldsymbol{q},\omega) = \frac{i\omega}{q^2}\chi^{irr}(\boldsymbol{q},\omega)$$

For a nanojunction:

$$\sigma^{irr}(q,q',i\alpha) = -\frac{\alpha}{qq'}\chi^{irr}(q,q',i\alpha)$$

The key quantity is: χ^{irr}

[2] P. Bokes, and R. W. Godby, PRB **69**, 245420 (2004)

Time Dependent Density Functional Theory

Many-body problem:

$$\partial_t \Psi = H \Psi$$

$$H = T + U + V_{ext}$$

(TD)DFT : Kohn-Sham
fictitious single-particle problem:
independant particles
in an effective, local, potential V_{KS}

$$\partial_t \psi = H \psi$$

$$H = T_{KS} + V_{KS}$$

$$V_{KS} = V_{ext} + V_H + V_{xc}$$

V_H: Hartree potential
V_{xc}: Exchange-Correlation potential

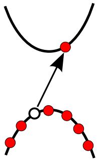
Ab initio response functions

$$n^{\text{ind}}(\boldsymbol{r},t) = \int d\boldsymbol{r}' dt' \chi^{??}(\boldsymbol{r},\boldsymbol{r}',t-t') V_{??}(\boldsymbol{r}',t')$$

$$n^{\text{ind}} = \chi^0 V_{KS} \Longleftrightarrow \chi^0 \text{ : independent particles}$$

$$\chi^0_{\boldsymbol{G},\boldsymbol{G}'}(\boldsymbol{q}_r,\omega) = 2\sum_{v,c,k} \frac{\tilde{\rho}_{vck}(\boldsymbol{q}_r,\boldsymbol{G})\tilde{\rho}^*_{vck}(\boldsymbol{q}_r,\boldsymbol{G}')}{E_{v,k}-E_{c,k+q}+\omega+i\eta}$$

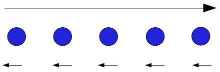
$$\tilde{\rho}_{vck}(\boldsymbol{q}_r,\boldsymbol{G}) = <\varphi_{v,k}|e^{-i(\boldsymbol{G}+\boldsymbol{q})\cdot\boldsymbol{r}}|\varphi_{c,k+q}>$$



$$n^{\text{ind}} = \chi V^{\text{ext}} \Longleftrightarrow \chi = \chi^0 + \chi^0(v+f_{xc})\chi$$

- self-consistent response
- exchange-correlation effects
- Mixing of the matrix elements
- $\Rightarrow$ Mixing of the transitions

Local Field effects:
microscopic response
to a macroscopic excitation



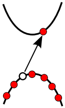
$$\chi = \chi^0 + \chi^0(v+f_{xc})\chi \Leftrightarrow \chi = \chi^{irr} + \chi^{irr} v \chi \Rightarrow n^{\text{ind}} = \chi^{irr} V^{\text{tot}}$$

$$\chi^{irr} = \chi^0 + \chi^0 f_{xc} \chi^{irr}$$

Illustration of these effects

ab-initio calculations

- DFT ground-state calculations (LDA)
- RPA:
  - $f_{xc} = 0$
  - dielectric function: $\epsilon = 1 - v\chi^0$



dielectric function in crystals

- ϵ is a matrix: $\epsilon(\boldsymbol{q}, \boldsymbol{q}'; \omega) = \left(\epsilon_{\boldsymbol{G},\boldsymbol{G}'}(\boldsymbol{q}_r, \omega)\right)$
- energy loss function (EELS, IXS)
  $S(\boldsymbol{q}, \omega) \propto -\Im\{\epsilon^{-1}_{\boldsymbol{GG}}(\boldsymbol{q}_r, \omega)\}, \quad \boldsymbol{q} = \boldsymbol{q}_r + \boldsymbol{G}$

$\Rightarrow$ mixing of all transitions in χ^0
$\Rightarrow$ crystal local field effects (LFE)

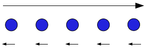


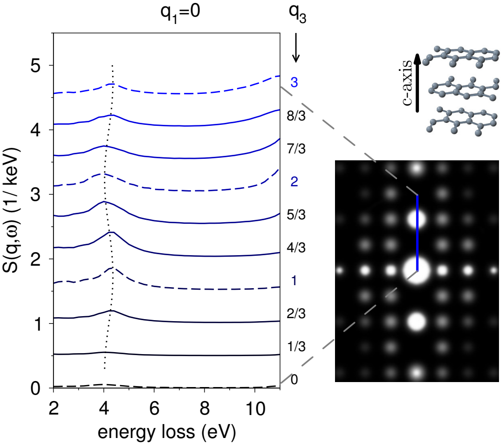
Illustration of these effects

- Anisotropy in graphite
- Plasmon dispersion in graphene

Illustration of these effects

- Anisotropy in graphite

Anisotropy in Graphite



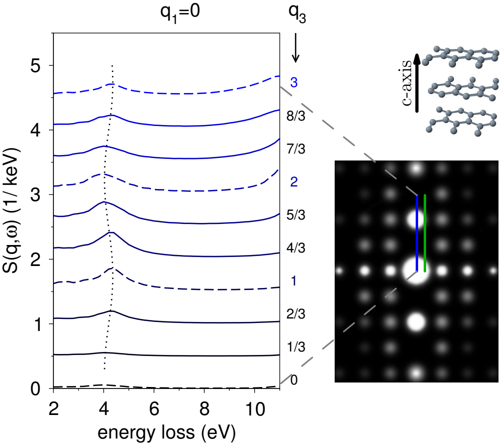
- energy loss $S(\boldsymbol{q}, \omega)$ in graphite (AB)
- $\boldsymbol{q}$ along c-axis
- weak dispersion[1]
- and off-axis?

inelastic

elastic

[3]Y. Q. Cai *et. al.*, Phys. Rev. Lett. **97**, 176402 (2006)

Anisotropy in Graphite



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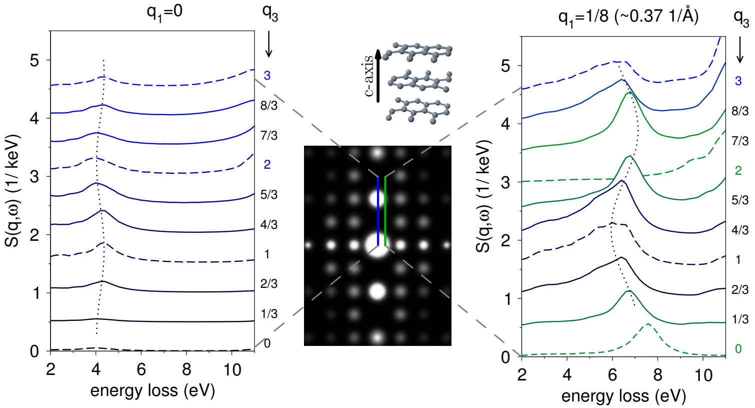


inelastic | elastic | inelastic

⇒ Due to crystal local field effects!

Physical picture of LFE: Dipoles

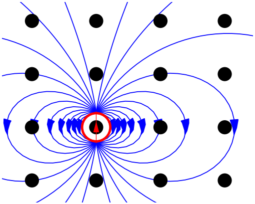
Two ways of understanding crystal local field effects:

dipole picture

perturbation induced dipoles

$$\varphi^{t} \underset{\leftarrow\cdots\cdots}{\xrightarrow{\text{sc}}} \varphi^{i}$$

- induced local fields
- crystal structure important



Physical picture of LFE: Coupled modes

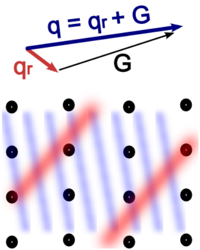
plane wave picture

perturbing mode — induced mode

$$e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \overset{\text{sc}}{\rightleftarrows} e^{i(\boldsymbol{q}+\boldsymbol{G})\cdot\boldsymbol{r}}$$

- Bragg-reflection inside the crystal
- couples modes with same $\boldsymbol{q}_r$
- $\epsilon_{\boldsymbol{G}\boldsymbol{G}'}(\boldsymbol{q}_r)$ describes coupling $\frac{\delta\varphi^{\mathrm{i}}(\boldsymbol{G})}{\delta\varphi^{\mathrm{t}}(\boldsymbol{G}')}$

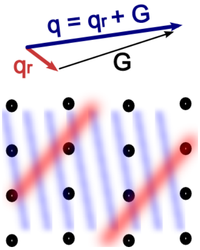
$\Rightarrow$ *key for understanding the discontinuity*



Simple 2×2 model for LFE

- dominant coupling between the two modes **0** and $\boldsymbol{G} = (0, 0, 2)$

$$\begin{pmatrix} \epsilon_{\mathbf{00}} & \cdots & \epsilon_{\mathbf{0G}} & \cdots \\ \vdots & & \vdots & \\ \epsilon_{\mathbf{G0}} & \cdots & \epsilon_{\mathbf{GG}} & \cdots \\ \vdots & & \vdots & \end{pmatrix} \longrightarrow \begin{pmatrix} \epsilon_{\mathbf{00}} & \epsilon_{\mathbf{0G}} \\ \epsilon_{\mathbf{G0}} & \epsilon_{\mathbf{GG}} \end{pmatrix}$$

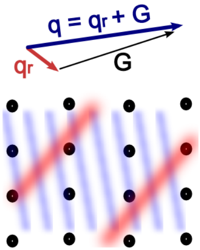


we introduce an effective 2×2-matrix $\tilde{\epsilon}$

- Remember: the loss function was

$$S(\boldsymbol{q}, \omega) \propto -\Im\{\epsilon^{-1}_{\mathbf{GG}}(\boldsymbol{q}_r, \omega)\}$$

Simple 2×2 model for LFE



- inverting the effective 2×2-matrix $\tilde{\epsilon}$

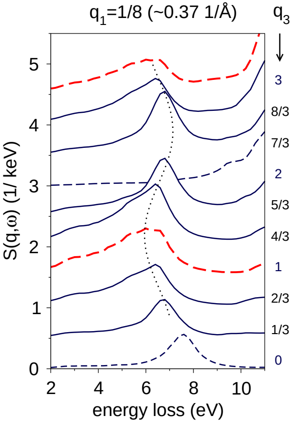
$$\epsilon^{-1}_{\boldsymbol{GG}}(\boldsymbol{q}_r,\omega) = \frac{1}{\tilde{\epsilon}_{\boldsymbol{GG}}} + \frac{\tilde{\epsilon}_{\boldsymbol{G0}}\tilde{\epsilon}_{\boldsymbol{0G}}}{(\tilde{\epsilon}_{\boldsymbol{GG}})^2}\ \epsilon^{-1}_{\boldsymbol{00}}(\boldsymbol{q}_r,\omega)$$

without LF   correction ...

(known as *two plasmon-band model*[4])

[4] L. E. Oliveira, K. Sturm, Phys. Rev. B **22**, 6283 (1980).

1. Recurring excitations



$$\epsilon^{-1}_{\boldsymbol{GG}}(\boldsymbol{q}_r,\omega) = \frac{1}{\tilde{\epsilon}_{\boldsymbol{GG}}} + \frac{\tilde{\epsilon}_{\boldsymbol{G0}}\tilde{\epsilon}_{\boldsymbol{0G}}}{(\tilde{\epsilon}_{\boldsymbol{GG}})^2}\ \epsilon^{-1}_{\boldsymbol{00}}(\boldsymbol{q}_r,\omega)$$

$$S(\boldsymbol{q}_r+\boldsymbol{G}) = S^{\mathrm{NLF}}(\boldsymbol{q}_r+\boldsymbol{G}) + f\cdot S(\boldsymbol{q}_r)$$

coupling of excitations of momentum

$\boldsymbol{q}_r$ 1. Brillouin zone

$\boldsymbol{q}_r+\boldsymbol{G}$ higher Brillouin zone

$\Rightarrow$ reappearance[5] of the anisotropic spectra from $\boldsymbol{q}\rightarrow\boldsymbol{0}$

[5] K. Sturm, W. Schülke, J. R. Schmitz, PRL **68**, 228 (1992).

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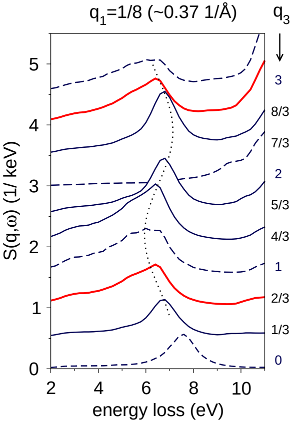

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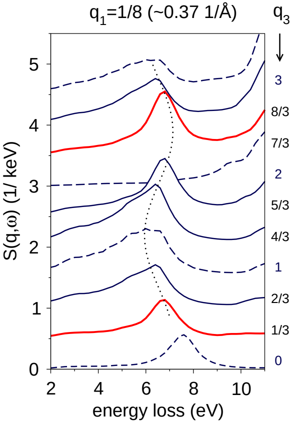

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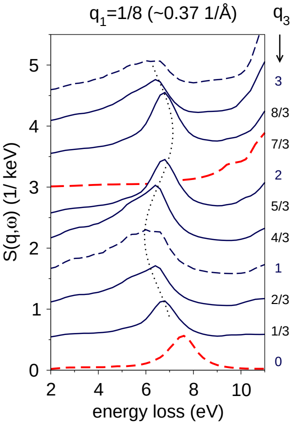
2. Strength of coupling

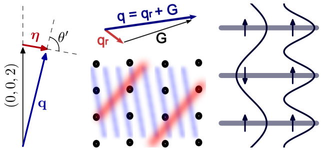


$$\epsilon^{-1}_{\boldsymbol{GG}}(\boldsymbol{q}_r,\omega) = \frac{1}{\tilde{\epsilon}_{\boldsymbol{GG}}} + \frac{\tilde{\epsilon}_{\boldsymbol{G0}}\tilde{\epsilon}_{\boldsymbol{0G}}}{(\tilde{\epsilon}_{\boldsymbol{GG}})^2}\ \epsilon^{-1}_{\boldsymbol{00}}(\boldsymbol{q}_r,\omega)$$

strength of coupling $\epsilon_{\boldsymbol{G0}}$ depends on:

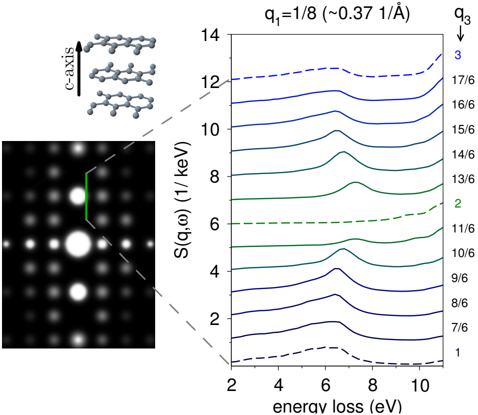
- angle $\angle(\boldsymbol{q}_r, \boldsymbol{q}_r + \boldsymbol{G})$ and
- structure factor $\propto$ density $n_{\boldsymbol{G}}$

$\Rightarrow$ enhances the angular anomaly



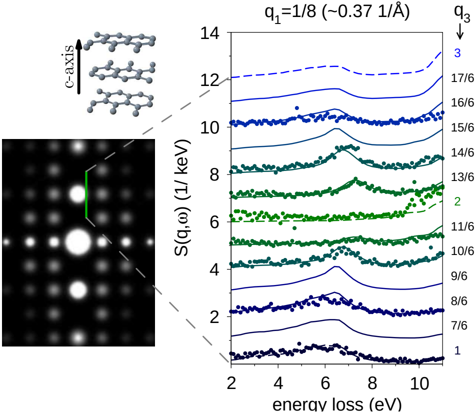
Experimental verification
by inelastic x-ray scattering

IXS experiments



- IXS experiments
  N. Hiraoka
  (Spring8, Taiwan)
- elastic tail removed
- uniform scaling

IXS experiments



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Anisotropy in Graphite: Conclusions

graphite

- angular anomaly close to Bragg reflections
- originates from local field effects (coupling to 1. BZ):
  1. spectrum from $\boldsymbol{q} \to 0$ reappears (direction of $\boldsymbol{q}_r$)
  2. coupling $\epsilon_{\boldsymbol{G}0}(\boldsymbol{q}_r)$ enforces anisotropy

other systems

- *all* systems with strong local field effects
  e. g. layered systems, 1D structures

$\Rightarrow$ caution with loss experiments close to Bragg reflections

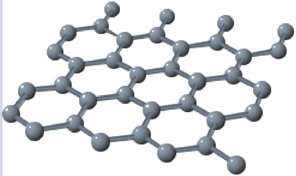
Illustration of these effects

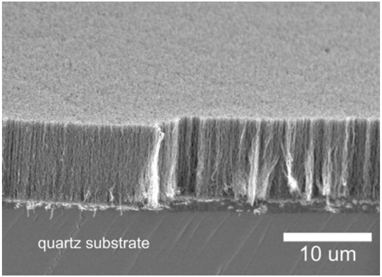
- Plasmon dispersion
  in graphene and SWCNT

Plasmon dispersion

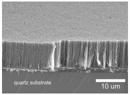
Graphene | Single-Wall CNT

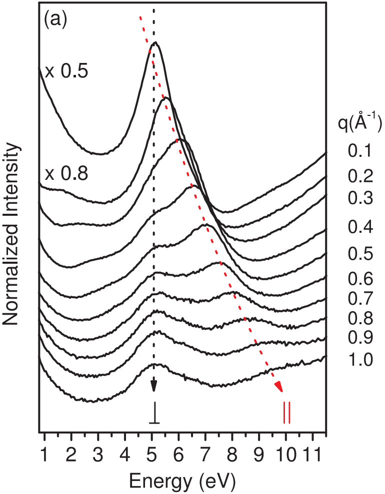
calculations | experiments





Vertically Aligned Single-Wall CNT





specimen

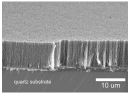
- oriented SWCNT
- diameter: 2 nm
- nearly isolated

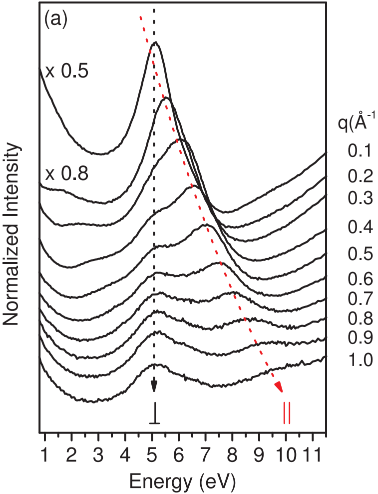
spectroscopy

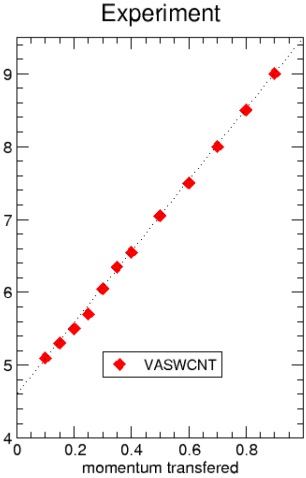
- angular-resolved EELS
- resolution:
  $\Delta E = 0.2\,\mathrm{eV}$
  $\Delta q = 0.05$ Å^{-1}

C. Kramberger, M.Rümmeli, M. Knupfer, J. Fink, B.Büchner, K. Hannewald,T. Pichler, IFW Dresden, Germany

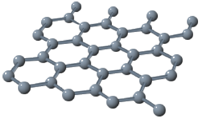
Vertically Aligned Single-Wall CNT



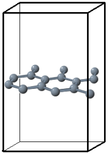




Calculation on Graphene

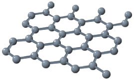


ab-initio calculations

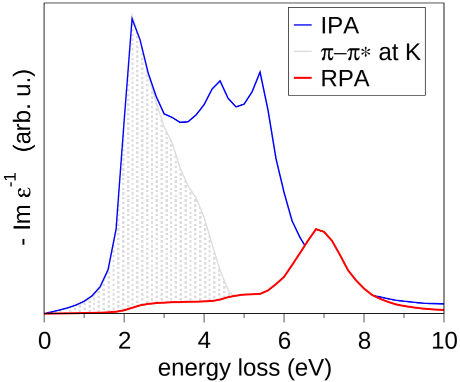


- DFT ground-state calculations (LDA)
- RPA dielectric function: $\epsilon(\boldsymbol{q},\omega) = 1 - v\chi^0$
- energy loss function $-\Im\{\epsilon^{-1}(\boldsymbol{q},\omega)\}$

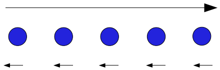
RPA: random phase approx.



energy loss in graphene
(in-plane, $q = 0.41$ Å^{-1})



- given by $\Im\{\chi\}$: no interpretation by ~~band-transitions~~



- contributions from K
- mixing of transitions

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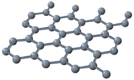

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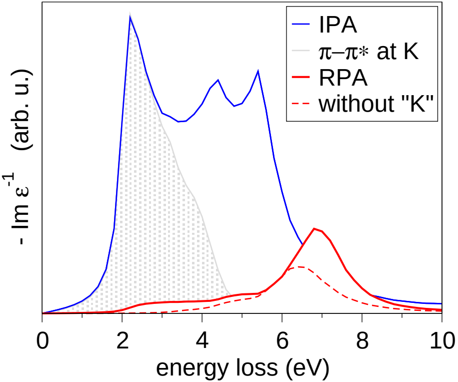

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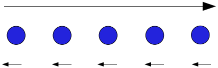

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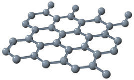
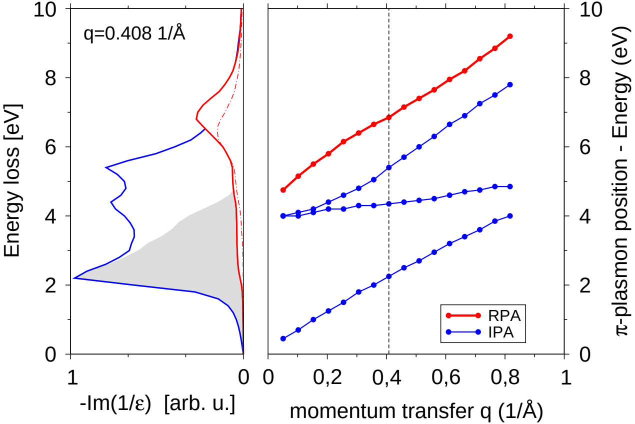
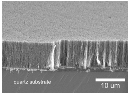
Plasmon dispersion

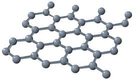


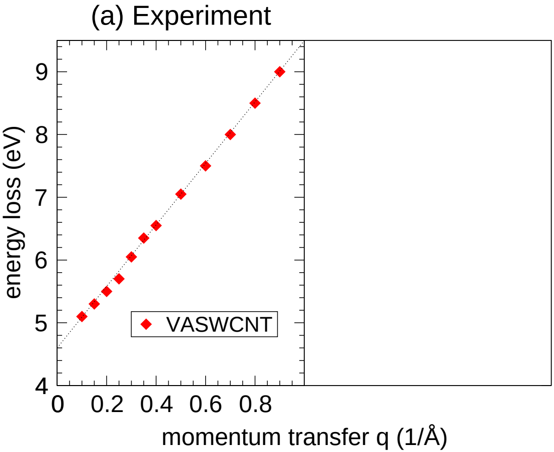


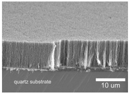
[6] P. Longe, and S. M. Bose, Phys. Rev. B **48**, 18239 (1993)
[7] F. L. Shyu and M. F. Lin, Phys. Rev. B **62**,8508 (2000)



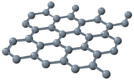
Plasmon dispersion

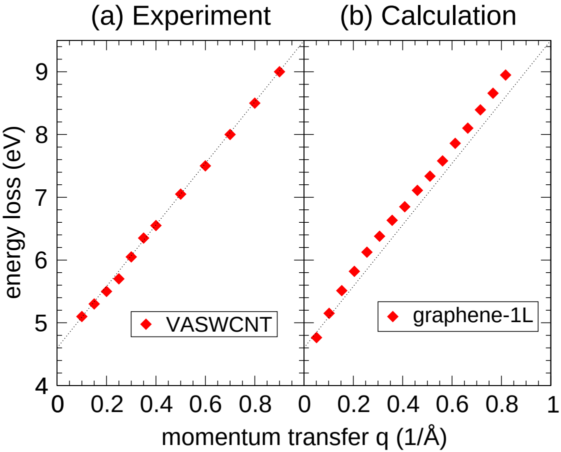


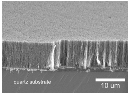




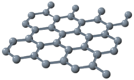
Plasmon dispersion

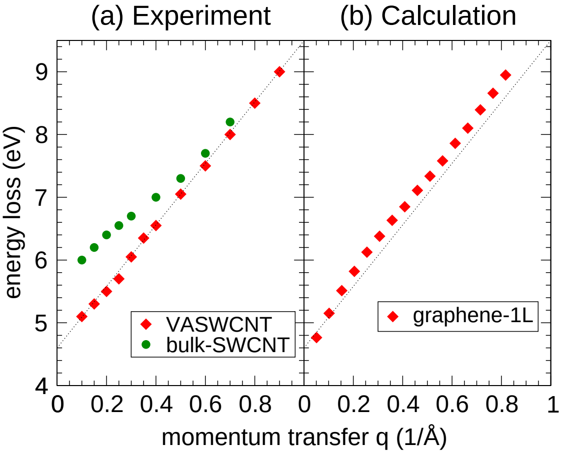


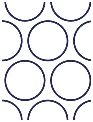


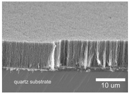


Plasmon dispersion

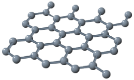


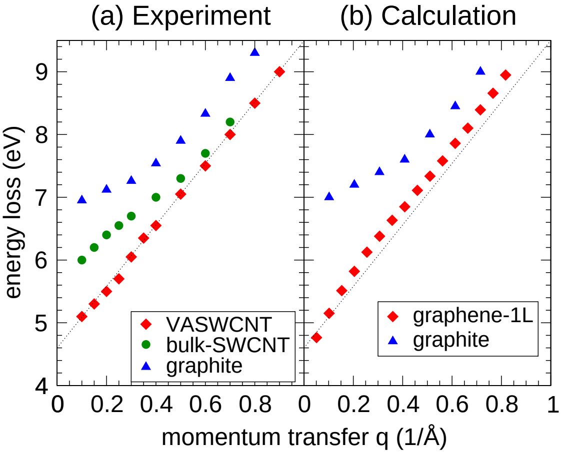


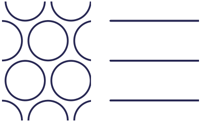


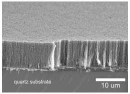


Plasmon dispersion

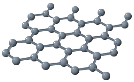


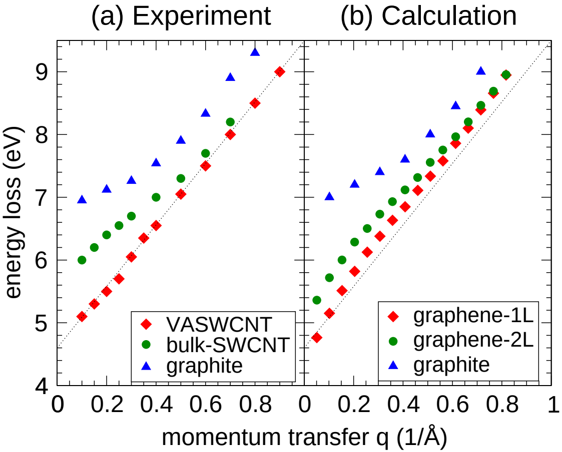


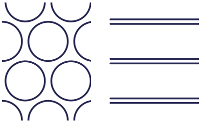




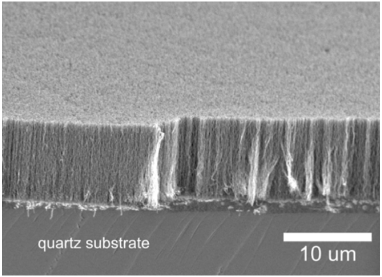
Plasmon dispersion

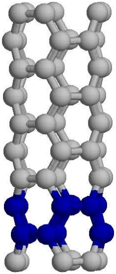




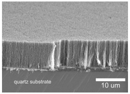


Carbon Nanotubes

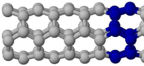


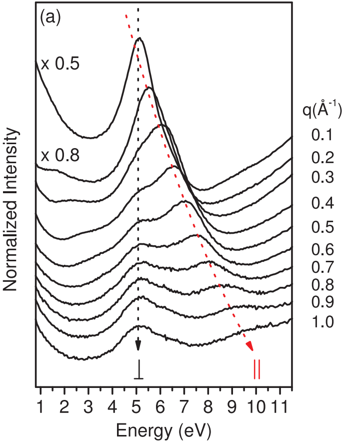


Xochitl Lopez-Lozano

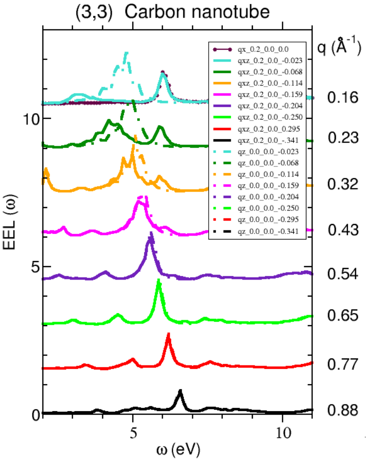


(3,3) Single Wall Carbon nanotubes





Experiment:
oriented SWCNT
Diameter 20 Å
nearly isolated

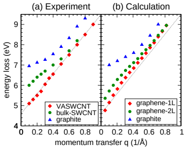


Calculation:
(3,3) SWCNT
Diameter 4 Å
low interaction

Plasmon dispersion: Conclusions

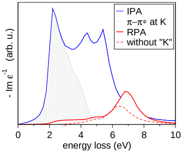
SWCNT $\Longleftrightarrow$ graphene

- isolated SWCNT $\Longleftrightarrow$ graphene-1L
- bundled SWCNT $\Longleftrightarrow$ graphene-2L



graphene

- induced Hartree potentials important
- ~~picture of independent transitions~~
- mixing of transitions/dispersions
  $\rightarrow$ leads to linear dispersion



Single Wall Carbon Nanotube

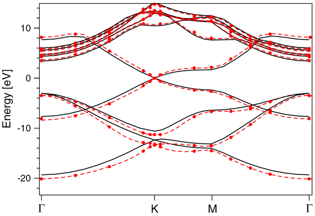
- Origin and behaviour of the π plasmon in progress

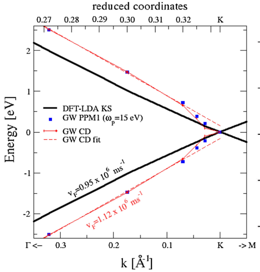
Many-Body Effects in Graphene

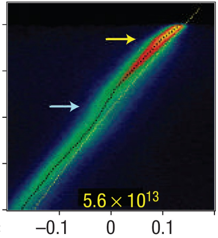
GW calculations of the bands structure

$$\Sigma^{GW}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i}{2\pi}\int d\omega' G(\boldsymbol{r},\boldsymbol{r}',\omega-\omega')W(\boldsymbol{r},\boldsymbol{r}',\omega')$$

$$E^{GW}_{nk} = E^{KS}_{nk} + Z\langle nk|\Sigma^{GW}(\omega = E^{KS}_{nk}) - v^{LDA}_{xc}|nk\rangle$$







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[8] P. E. Trevisanutto, C. Giorgetti, L. Reining, M. Ladisa, and V. Olevano, PRL **101**, 226405 (2008)

[9] A. Bostwick, T. Ohta, T. Seyller, K. Horn and E. Rotenberg, Nat. Phys. **3**, 36 (2007)

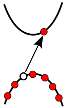
Summary

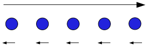
TDDFT: $n^{\text{ind}} = \chi V^{\text{ext}} \Longleftrightarrow \chi = \chi^{irr} + \chi^{irr} v \chi$

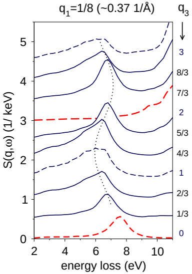
- self-consistent response
- exchange-correlation effects

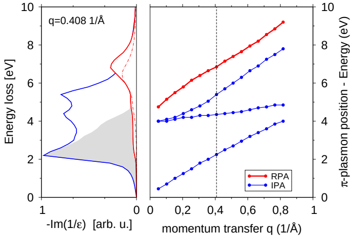
microscopic response
to a macroscopic excitation

Local Field Effects:









Many-Body Effects: GW $\Rightarrow \chi^{irr}$

Phys Rev Lett **101**, 266406 (2008)

Anomalous Angular Dependance of the Dynamic Structure Factor near Bragg Reflections: Graphite

R. Hambach, C. Giorgetti, N. Hiraoka, Y. Q. Cai,
F. Sottile, A. G. Marinopoulos, F. Bechstedt, and L. Reining

Phys Rev Lett **100**, 196803 (2008)

Linear plasmon dispersion in SWCNT and the collective excitation spectrum of graphene

C. Kramberger, R. Hambach, C. Giorgetti, M. Rümmeli, M. Knupfer, J. Fink, B. Büchner, L. Reining, E. Einarsson, S. Maruyama, F. Sottile, K. Hannewald, V. Olevano, A. G. Marinopoulos, T. Pichler

Phys Rev Lett **101**, 226405 (2008)

***Ab Initio GW* Many-Body Effects in Graphene**

P. E. Trevisanutto, C. Giorgetti, L. Reining, M. Ladisa, and V. Olevano

codes:

ABINIT: X. Gonze *et al.*, Comp. Mat. Sci. **25**, 478 (2002)
DP-code: `www.dp-code.org`; V. Olevano, *et al.*, unpublished.

LSI “Theoretical Spectroscopy” Group

Ralf Hambach Lucia Reining Andrea Cucca

+ V. Olevano, P. E/ Trevisanutto and A. G. Marinopoulos

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

ÉCOLE POLYTECHNIQUE

ETSF European Theoretical Spectroscopy Facility

NanoSciences ILE-DE-FRANCE