Collective Excitations in Nanostructures: Towards Spatially-Resolved EELS from First Principles

Soutenance de Thèse

Ralf Hambach

19/11/2010, Ecole Polytechnique

Outline

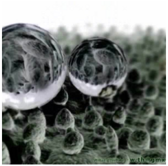
Outline

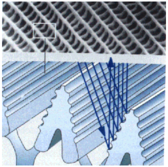
Material Physics

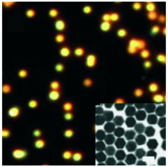
Dream of the Materials Physicist: Understand macroscopic properties from microscopic structure + design new materials.

macro

micro







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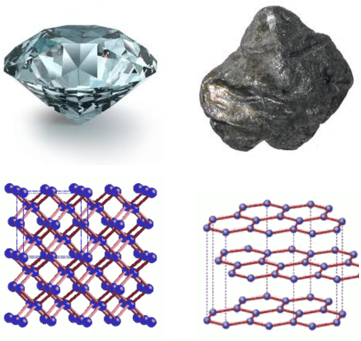

How can we obtain information about nanostructures?

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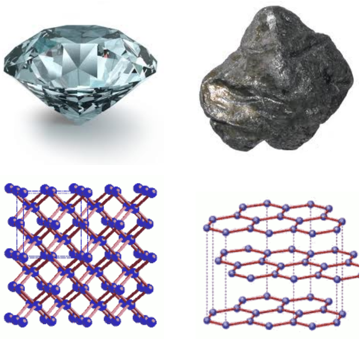

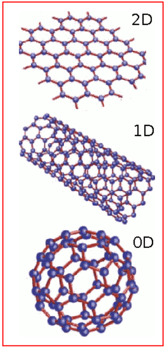

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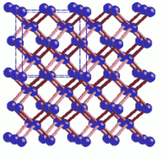
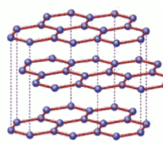
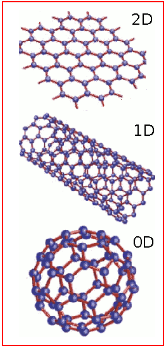


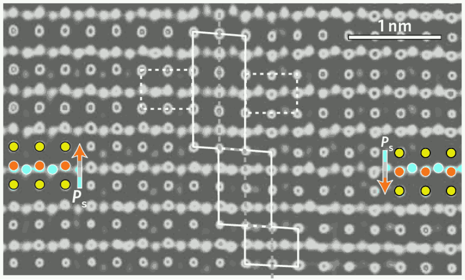




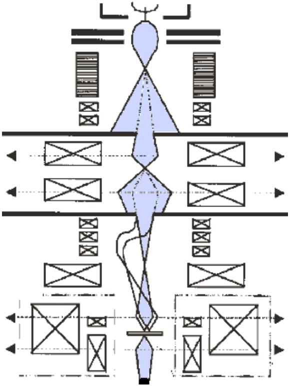
How can we obtain information about nanostructures?

Microscopy

- optical microscopy: $\lambda \approx 0.5\ \mu\mathrm{m}$
- electron microscopy: $\lambda \ll 0.1\ \text{Å}$



Polarisation domain wall in ferroelectric PZT

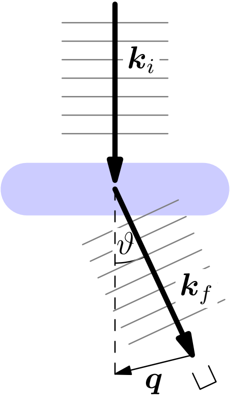


[K. Urban: Nat. Mater. **8**, 260 (2009), I. Arslan *et al.*: MRT **69**, 330 (2006)]

Spectroscopy

- optical absorption
- electron scattering, EELS

Perturbation Excitation Response



[P. E. Batson: Micron **39**, 648 (2008)]

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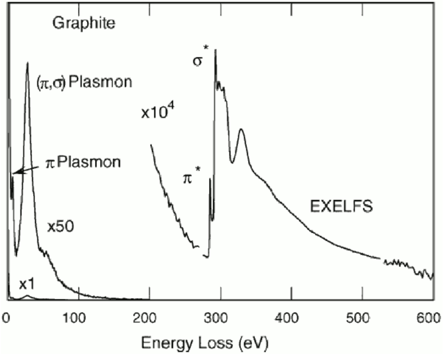

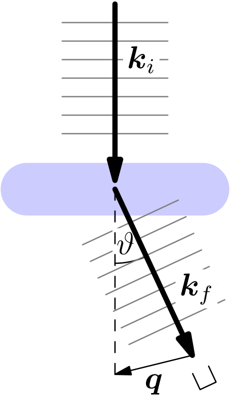

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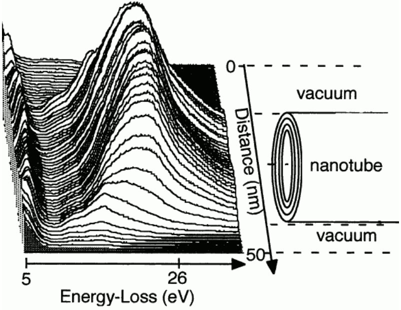
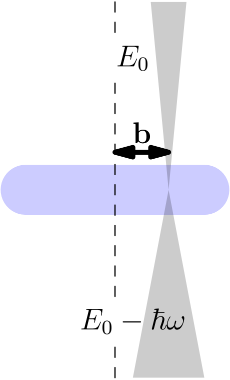
Microscopy + Spectroscopy

- near-field scanning optical microscopy
- spatially-resolved EELS





[O. Stéphan *et al.*, JESRP **114**, 209 (2001)]

Max Born (Symbol und Wirklichkeit, 1964):

"*Was man in einem Mikroskop bei hoher Vergrößerung sieht, was Teleskope, Spektroskope und die mannigfachen Vergrößerungsapparate der Elektronik enthüllen, ist nicht ohne Theorie verständlich, es muss gedeutet werden.*"

How can we describe the scattering process ?

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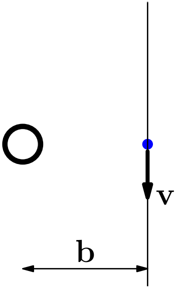
How can we describe the scattering process ?

EELS: Classical Perturbation



1. electron flying along straight line

$$\rho^{ext}(\boldsymbol{r}, t) = -e\delta\big(\boldsymbol{r} - (\boldsymbol{b} + \boldsymbol{v}t)\big)$$

2. external potential (no retardation)

$$\Delta\varphi^{ext} = -\rho^{ext}/\varepsilon_0$$

3. linear response of the medium

$$\varphi^{ind} = (\epsilon^{-1} - 1)\varphi^{ext}$$

4. energy loss of the electron

$$\langle \frac{dW}{dt} \rangle_t = \int d\boldsymbol{r} \, \langle \varphi^{ind}(\boldsymbol{r}, t) \, \rho^{ext}(\boldsymbol{r}, t) \rangle_t$$

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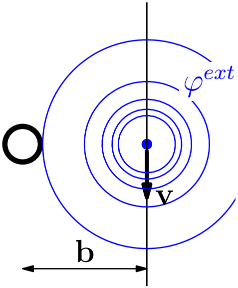

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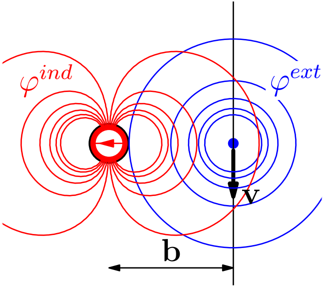

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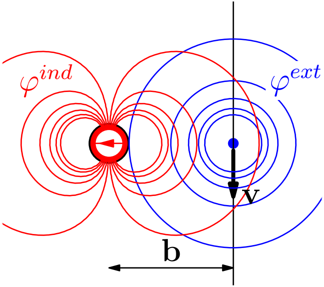

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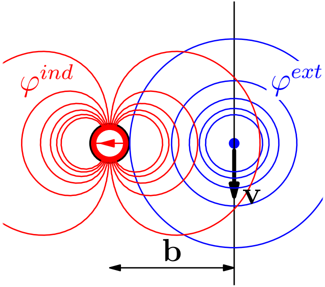

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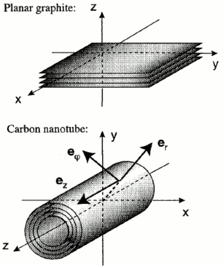
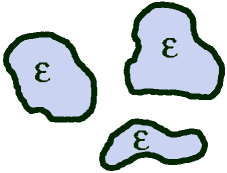
$\Rightarrow$ energy loss probability $S(\boldsymbol{b},\omega)$

Dielectric Response

mesoscopic scale

- solve Maxwell equations for homogeneous dielectric with sharp boundaries (BEM,DDA)
- include anisotropy $\epsilon^{\alpha\beta}(\omega)$
- include spatial dispersion $\epsilon(\boldsymbol{q},\omega) \longleftrightarrow \epsilon(\boldsymbol{r}-\boldsymbol{r}',\omega)$





atomic scale

- atomic resolution
- atomic defects
- monolayer systems

[Abajo: RMP **82**, 209 (2010), Stöckli *et al.*: Phil. Mag. B **79**, 1531 (1999)]

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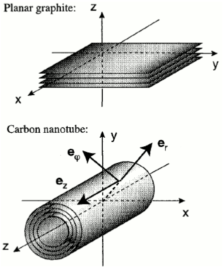

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Microscopic Dielectric Function

local dielectric function:

$$\epsilon(\omega) = 1 - v\chi^0(\omega) \qquad \epsilon(\omega)$$

including nonlocal effects:

$$\epsilon(\boldsymbol{q}, \omega) = 1 - v(\boldsymbol{q})\chi^0(\boldsymbol{q}, \omega) \qquad \epsilon(\boldsymbol{r} - \boldsymbol{r}', \omega)$$

microscopic dielectric function:

$$\epsilon(\boldsymbol{q}, \boldsymbol{q}', \omega) = \delta(\boldsymbol{q} - \boldsymbol{q}') - v(\boldsymbol{q})\chi^0(\boldsymbol{q}, \boldsymbol{q}', \omega) \qquad \epsilon(\boldsymbol{r}, \boldsymbol{r}', \omega)$$

$\Longrightarrow$ density-response function from perturbation theory

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Density-Functional Theory

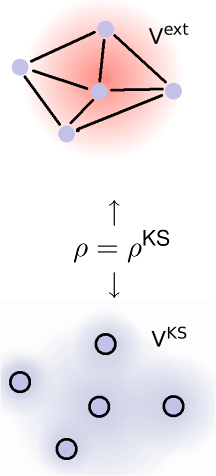
Aim: calculate ground-state for interacting particles in crystal potential V^{ext}

Density Functionals

- use $\rho(\boldsymbol{r})$ instead of $\psi(\boldsymbol{r}_1, ...\boldsymbol{r}_N)$
- minimise energy functional $E[\rho]$

Kohn-Sham Particles

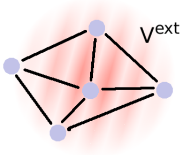
- map to non-interacting particles in V^{KS} with same ground-state density ρ
  $V^{\text{KS}}[\rho] = V^{ext} + V_H[\rho] + V_{\text{XC}}[\rho]$
- solve single-particle problem: $\epsilon_\lambda, \varphi_\lambda(\boldsymbol{r})$



[Hohenberg, Kohn: PR **136**, 864 (1964), Kohn, Sham: PR **140**, 1133 (1965)]

Time-Dependent Density-Functional Theory

Aim: calculate linear response of interacting particles to small perturbation δV^{ext}



Full Polaris. / Susceptibility $\chi = \delta\rho/\delta V^{ext}$

density response of interacting particles

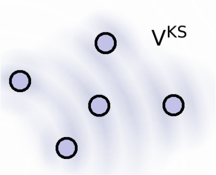
$$\chi = \chi^0 + \chi^0\left(\frac{\delta V_H}{\delta\rho} + \frac{\delta V_{XC}}{\delta\rho}\right)\chi = \chi^0 + \chi^0\left(v + f_{XC}\right)\chi$$

$$\uparrow \quad \rho = \rho^{KS} \quad \downarrow$$

Kohn-Sham Polarisability $\chi^0 = \delta\rho/\delta V^{KS}$

density response of non-interacting particles

$$\chi^0(\boldsymbol{r},\boldsymbol{r}',\omega) \propto \sum_{vc} \frac{\varphi_v^*(\boldsymbol{r})\varphi_c(\boldsymbol{r})\varphi_c^*(\boldsymbol{r}')\varphi_v(\boldsymbol{r}')}{\hbar\omega + i\eta - (\epsilon_c - \epsilon_v)} - \text{a.r.}$$

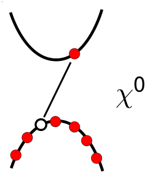


[Gross & Kohn: PRL **55**, 2850 (1985), Zangwill & Soven: PRA **21**, 1561 (1980)]

Ab-Initio Calculations

ab initio calculations (DFT, RPA)

1. ground-state calculation gives $\epsilon_\lambda^{\mathrm{KS}}, \varphi_\lambda^{\mathrm{KS}}$
2. Kohn-Sham polarisability χ^0
3. susceptibility $\chi = \chi^0 + \chi^0 v \chi$
4. dielectric function $\epsilon^{-1} = 1 + v\chi$



microscopic dielectric response

$$\delta\rho(\boldsymbol{r}, t) = \int d\boldsymbol{r}' dt' \; \chi(\boldsymbol{r}, \boldsymbol{r}'; t - t') \delta V^{ext}(\boldsymbol{r}', t')$$

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

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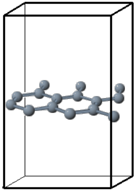

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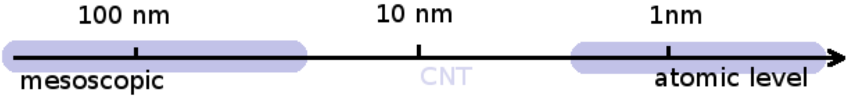

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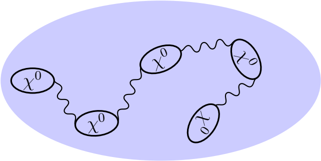
Polarisability vs Susceptibility

polarisability χ^0 is restricted to sheets and local

$$\chi^0(\boldsymbol{r}, \boldsymbol{r}') \propto \sum_{vc} \frac{\varphi_v^*(\boldsymbol{r})\varphi_c(\boldsymbol{r})\varphi_c^*(\boldsymbol{r}')\varphi_v(\boldsymbol{r}')}{\hbar\omega + i\eta - (\epsilon_c - \epsilon_v)} - \text{a.r.}$$

susceptibility χ is restricted to sheets, but nonlocal

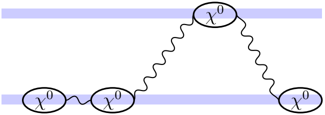
$$\chi(\boldsymbol{r}, \boldsymbol{r}') = \chi^0 + \chi^0 v \chi^0 + \chi^0 v \chi^0 v \chi^0 + \dots$$

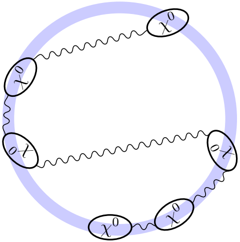


Building-Block Approach

Calculate the response of complex systems from the polarisability of a single sheet:

- assembly of several layers
- new geometries





Summary

Dielectric Theory

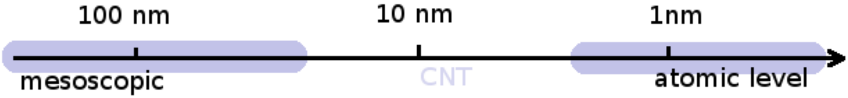
$\epsilon(\omega)$ + boundary

TDDFT

$\epsilon(\boldsymbol{r}, \boldsymbol{r}', \omega) = 1 - v\chi^0$

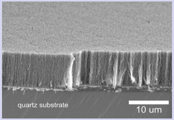
Building-Block Approach

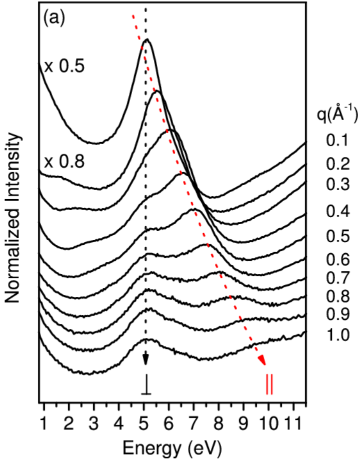
use transferability of $\chi^0(\boldsymbol{r}, \boldsymbol{r}', \omega)$ to calculate complex systems



Outline

EELS on SWCNTs

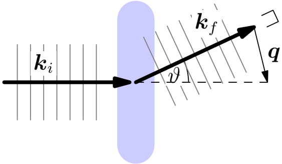




specimen

- oriented SWCNT
- diameter: 2 nm
- nearly isolated

spectroscopy



[C. Kramberger, R. H., Ch. Giorgetti, *et.al.*: PRL **101**, 266406 (2008)]

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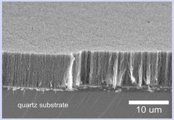

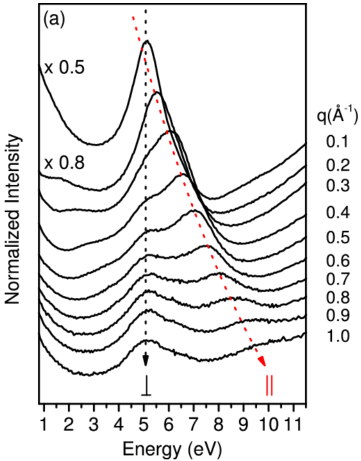

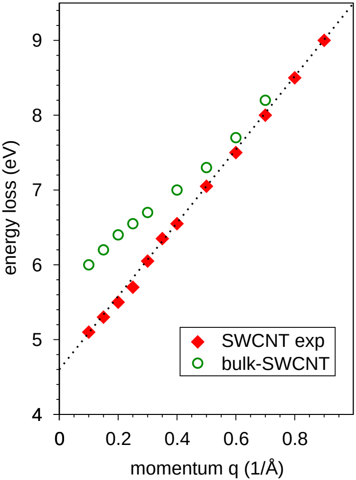

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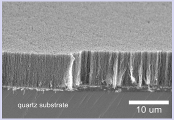

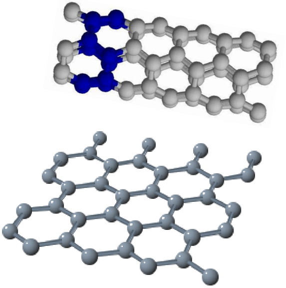

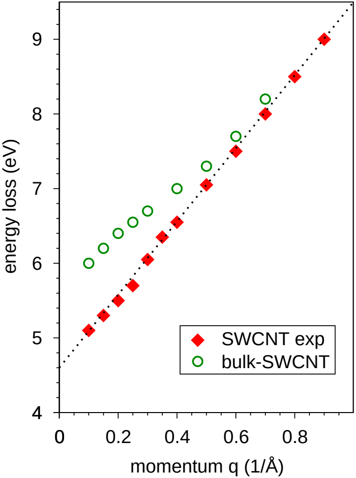

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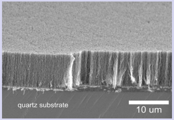
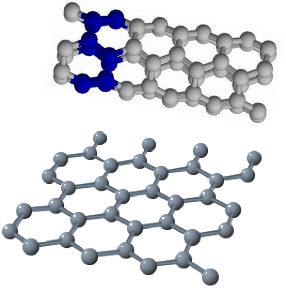
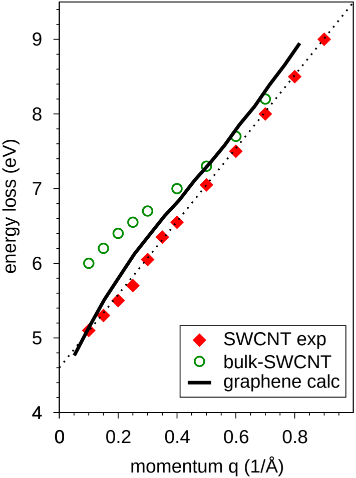


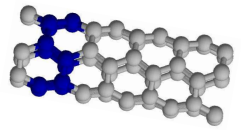




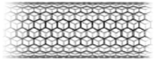
[C. Kramberger, R. H., Ch. Giorgetti, *et.al.*: PRL **101**, 266406 (2008)]

Questions

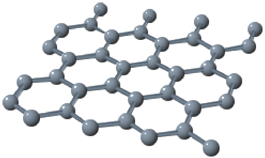
- How to calculate the response for perpendicular $\boldsymbol{q}$?
- Can we formulate a relation between excitations in graphene and SWCNTs?



Building-Block Approach for SWCNT

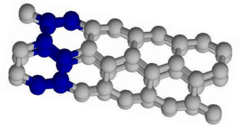


full *ab-initio* for periodic graphene ribbon



1. ground-state calculation gives ϕ_i^{KS}
2. independent-particle polarisability χ^0_{sheet}

zone-folding model for χ^0



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5. energy-loss $S = -\frac{1}{\pi} \operatorname{Im} \chi(\boldsymbol{qq}, \omega)$

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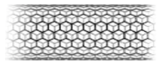

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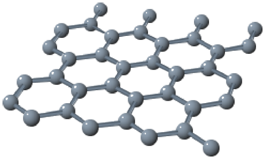

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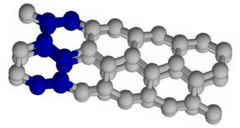

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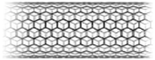
Zone-Folding for Polarisability



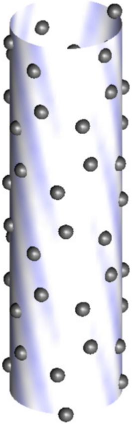
real space: cylinder coordinates $(\varrho, \varphi, \mathfrak{z})$

$$\chi^0(\boldsymbol{\varrho}, \boldsymbol{\varrho}') \cdot \rho' \approx \chi^0_{\text{sheet}}\big(\boldsymbol{r}(\boldsymbol{\varrho}), \boldsymbol{r}(\boldsymbol{\varrho}')\big) \cdot R$$

reciprocal space: helical momentum (m, p)

$$\chi^0(mm'pp'; \varrho\varrho', \omega) \cdot \varrho' \approx \chi^0_{\text{sheet}}(q_x q_x', q_y q_y'; zz', \omega)$$

$m/R \leftrightarrow q_x$	azimuthal momentum
$p \leftrightarrow q_y$	on-axis momentum
$\varrho - R \leftrightarrow z$	radial position



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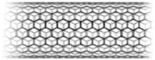

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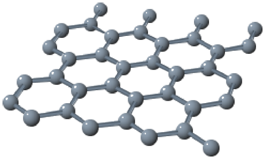

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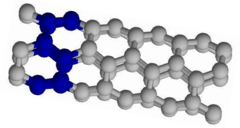

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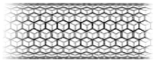
Dyson Equation in Cylindrical Coordinates



real space:

$$\chi(\varrho, \varrho') = \chi^0(\varrho, \varrho') + \iint d\varrho_1 d\varrho_2 \, \varrho_1 \varrho_2 \, \chi^0(\varrho, \varrho_1) v(\varrho_1, \varrho_2) \chi(\varrho_2, \varrho')$$

$$v(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2) = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\boldsymbol{r}(\boldsymbol{\rho}_1) - \boldsymbol{r}(\boldsymbol{\rho}_2)|}$$

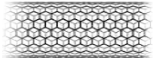
reciprocal space: helical momentum (m, p) [J. D. Jackson]

$$v(m_1 m_2, p_1 p_2; \varrho_1 \varrho_2) = \frac{e^2}{\varepsilon_0} I_{m_1}(|p_1|\rho_<) \, K_{m_1}(|p_1|\rho_>) \delta_{m_1 m_2} \delta(p_1 - p_2)$$

with the modified Bessel-functions of first kind I_m and K_m

$\Longrightarrow$ cylinder susceptibility $\chi(mm', pp', \varrho\varrho')$

Building-Block Approach for SWCNT



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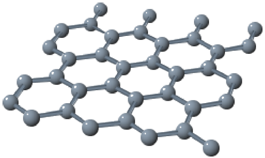

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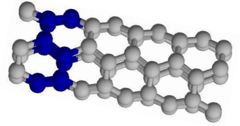

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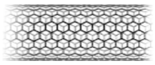
AR-EELS for a SWCNT



- expand external pert. in cylinder waves, $\boldsymbol{q} = (\boldsymbol{q}_\perp, p)$:

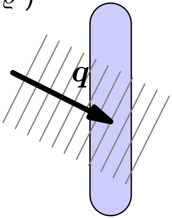
$$e^{i\boldsymbol{q}\boldsymbol{r}} = e^{iq_\perp \varrho \cos\varphi} e^{ipz} = \sum_m i^m J_m(|\boldsymbol{q}_\perp|\varrho)\ e^{im\varphi} e^{ipz}$$

- susceptibility in Cartesian coord.

$$\chi(\boldsymbol{q}\boldsymbol{q}) \approx \frac{2\pi}{L^2} \sum_{m,m'} \iint d\varrho d\varrho'\ \varrho\varrho' (-i)^{m-m'} \cdot$$
$$\cdot J_m(|\boldsymbol{q}_\perp|\varrho) J_{m'}(|\boldsymbol{q}_\perp|\varrho') \chi(mm', pp, \varrho\varrho')$$

- energy-loss function

$$S(\boldsymbol{q}, \omega) = -\frac{1}{\pi} \operatorname{Im} \chi(\boldsymbol{q}\boldsymbol{q}, \omega)$$



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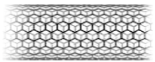

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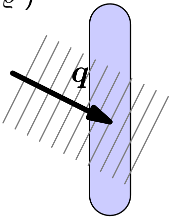
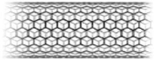
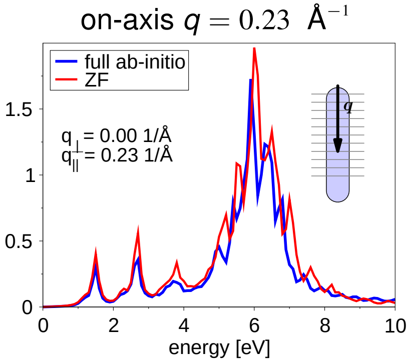
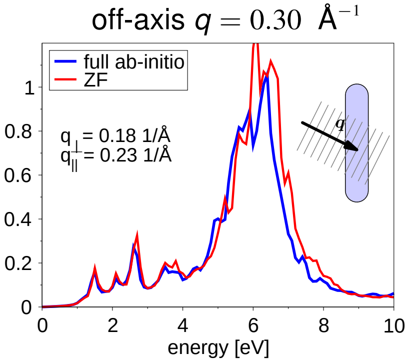


$\Longrightarrow$ numerical test for CNT(9,9), [$\varnothing$1.2nm]

Ab-Initio vs. Zone-Folding: CNT(9,9)







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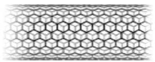

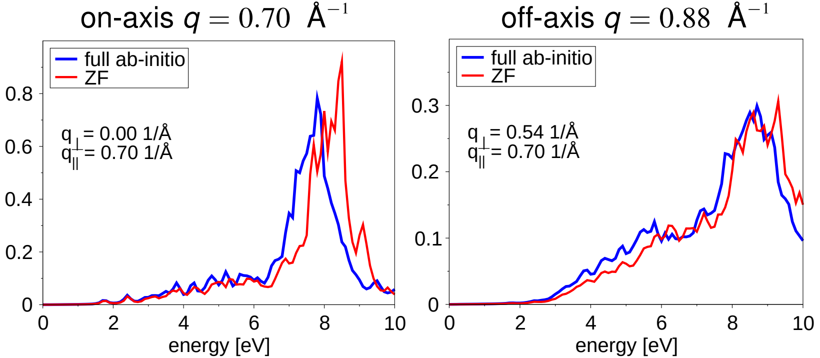

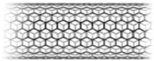

Summary: Building-Block Approach

- applied building-block approach to SWCNTs
- computational effort reduced (two-atom unit cell)
- zone-folding: graphene $\rightarrow$ SWCNT

Perspective:

- fill gap: larger tubes, different chiralities, varying $\boldsymbol{q}$
- apply building-block approach to different geometries

[Chang, Bussi, Ruini & Molinari: PRL **92**, 196401 (2004)]

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⇒ still missing: physical understanding

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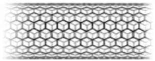
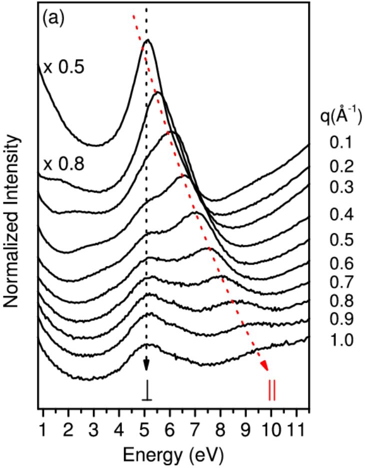


Experiment: oriented SWCNTs
($|\boldsymbol{q}| = 0.65$ Å^{-1}, $\oslash \approx 2$ nm)



Questions

- Is the decomposition of the spectra in perpendicular and parallel contribution valid?
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$\Longrightarrow$ we need a simplified model!

[C. Kramberger, manuscript in preparation]

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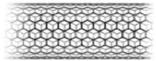

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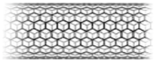
Local-Response Approximation



Dyson equation: coordinates (m, p, ϱ), no in-plane LFE

$$\chi(\varrho, \varrho') = \chi^0(\varrho, \varrho') + \iint d\varrho_1 d\varrho_2\, \varrho_1 \varrho_2\, \chi^0(\varrho, \varrho_1) v(\varrho_1, \varrho_2) \chi(\varrho_2, \varrho')$$

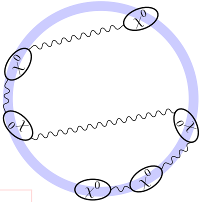
$$v(m, p; \varrho_1 \varrho_2) = \frac{e^2}{\varepsilon_0} I_m(|p|\rho_<)\, K_m(|p|\rho_>)$$

integrated cylinder response functions

$$\bar{\chi}^0(m, p) \equiv \iint d\rho_1 d\rho_2\, \rho_1 \rho_2\, \chi^0(mm, pp; \rho_1 \rho_2)$$

scalar Dyson equation

$$\bar{\chi}(m, p) \approx \bar{\chi}^0(m, p) + \bar{\chi}^0(m, p)\, v_{\mathrm{cnt}}(m, p)\, \bar{\chi}(m, p)$$



[M. F. Lin, *et al.*: PRB, 53, 15493 (1996).]

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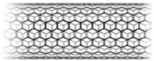

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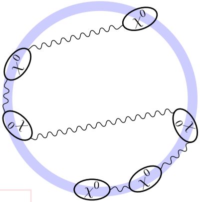

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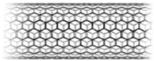

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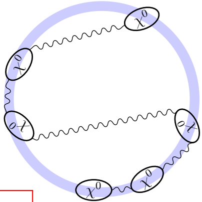

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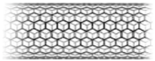

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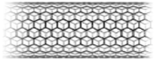

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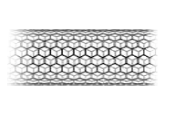
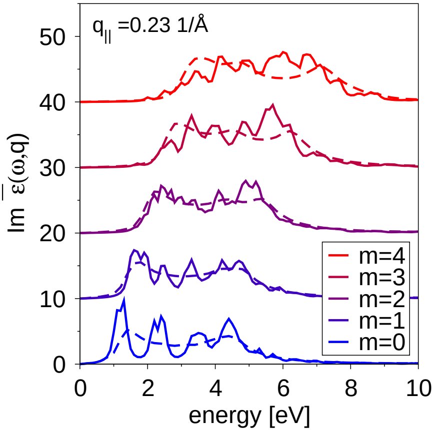
Cylinder Response for CNT(9,9)



cylinder pol. Im $\bar{\chi}^0_{\mathrm{cnt}}(m,p)$



cylinder polarisability

$$\bar{\chi}^0_{\mathrm{cnt}}(m,p) = R \cdot \chi^0_{\mathrm{sheet}}(q_x, q_y)$$

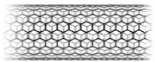
cylinder susceptibility

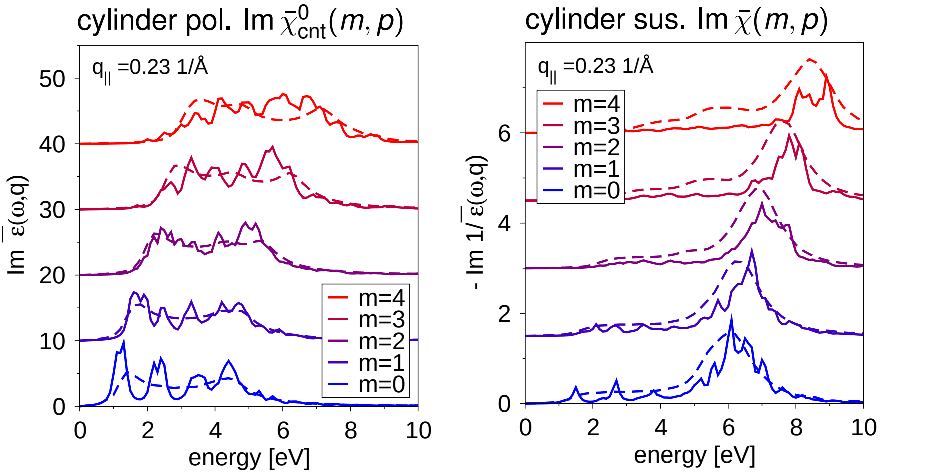
$$\bar{\chi}_{\mathrm{cnt}} \approx \bar{\chi}^0_{\mathrm{cnt}} + \bar{\chi}^0_{\mathrm{cnt}} v_{\mathrm{cnt}} \bar{\chi}$$

dashed: graphene

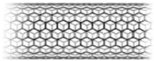
solid: graphene ribbon

Cylinder Response for CNT(9,9)





Local-Response Approximation



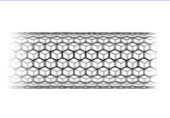
full *ab-initio* for periodic graphene ribbon

1. ground-state calculation gives ϕ_i^{KS}
2. independent-particle polarisability χ^0_{sheet}

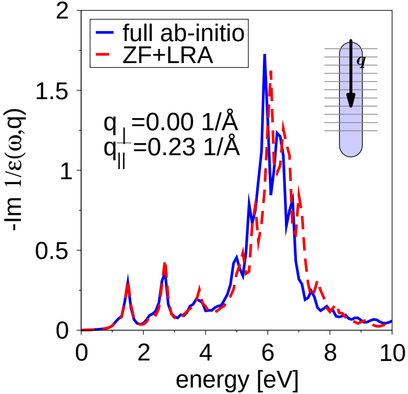
zone-folding model for χ^0

3. polarisability of tube $\chi^0_{\mathrm{sheet}} \to \bar{\chi}^0_{\mathrm{cnt}}$
4. cylinder susceptibility $\bar{\chi} \approx \bar{\chi}^0_{\mathrm{cnt}} + \bar{\chi}^0_{\mathrm{cnt}} v_{\mathrm{cnt}} \bar{\chi}$
5. energy-loss
   $S(\boldsymbol{q}, \omega) \approx -\frac{2}{L^2} \sum_m J_m^2(|\boldsymbol{q}_\perp| R)\ \mathrm{Im}\, \bar{\chi}(m, p)$

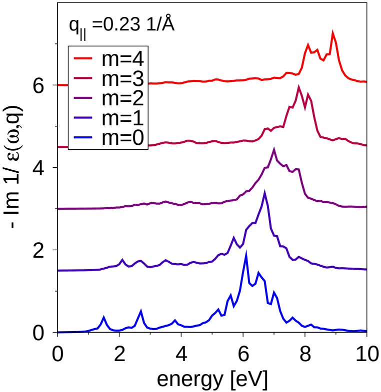
AR-EELS for CNT(9,9)



on-axis $q = 0.23\ \text{Å}^{-1}$



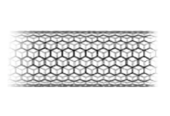
cylinder sus. $\mathrm{Im}\,\bar{\chi}(m,p)$



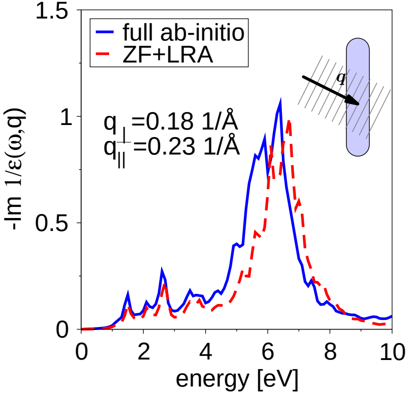
$$\sum_m J_m^2(|\boldsymbol{q}_\perp|R)\ \mathrm{Im}\,\bar{\chi}(m,p)$$

m	0	±1	±2	±3
J_m^2	1	0	0	0

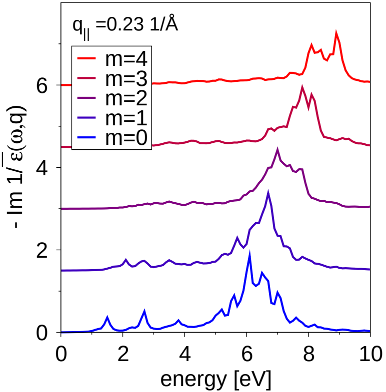
AR-EELS for CNT(9,9)



off-axis $q = 0.30$ Å^{-1}



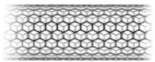
cylinder sus. Im $\bar{\chi}(m, p)$



$$\sum_m J_m^2(|\boldsymbol{q}_\perp| R) \;\; \text{Im}\, \bar{\chi}(m, p)$$

m	0	± 1	± 2	± 3
J_m^2	0.5	0.2	0	0

AR-EELS for CNT(9,9)



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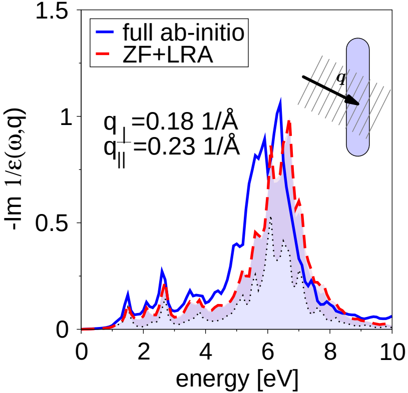

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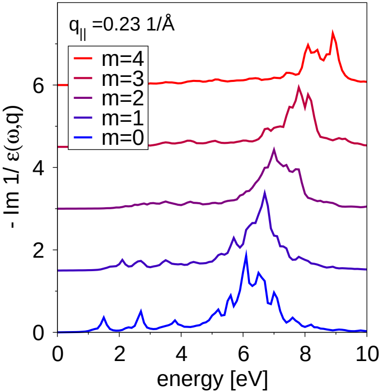

$$\sum_m J_m^2(|\boldsymbol{q}_\perp|R)\ \mathrm{Im}\,\bar{\chi}(m,p)$$

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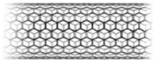
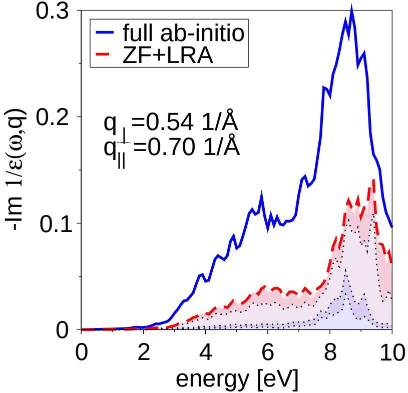
J_m^2	0.5	0.2	0	0

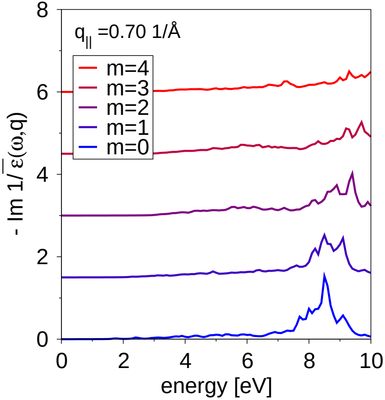
AR-EELS for CNT(9,9)



large off-axis $q = 0.88$ Å^{-1}



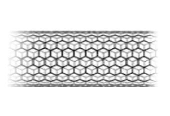
cylinder sus. Im $\bar{\chi}(m, p)$



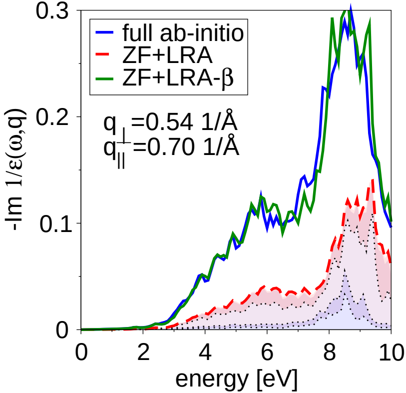
$$\sum_m J_m^2(|\boldsymbol{q}_\perp| R) \;\; \mathrm{Im}\,\bar{\chi}(m, p)$$

m	0	± 1	± 2	± 3
J_m^2	0.1	0.05	0.2	0.1

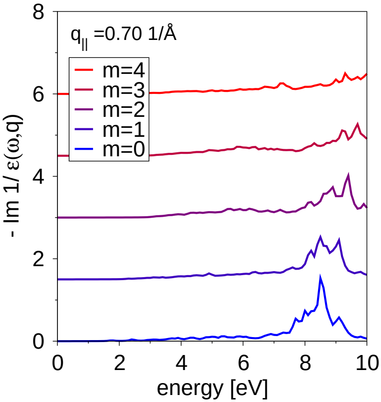
AR-EELS for CNT(9,9)



large off-axis $q = 0.88$ Å^{-1}



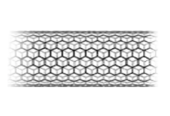
cylinder sus. Im $\bar{\chi}(m, p)$



$\sum_m J_m^2(|\boldsymbol{q}_\perp| R)$ Im $\bar{\chi}(m, p)$

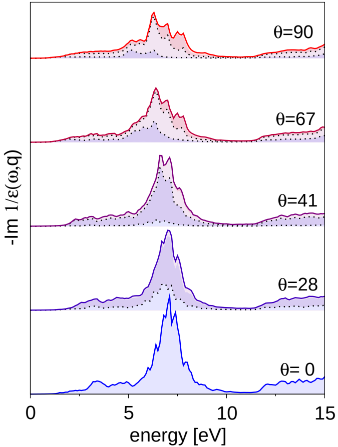
m	0	± 1	± 2	± 3
J_m^2	0.1	0.05	0.2	0.1

AR-EELS on SWCNTs



Experiment: oriented SWCNTs
($|\boldsymbol{q}| = 0.65$ Å^{-1}, $\oslash \approx 2$ nm)

Calculation: (9,9) SWCNT
($|\boldsymbol{q}| = 0.47$ Å^{-1}, $\oslash \approx 1.2$ nm)



[C. Kramberger, manuscript in preparation]

Summary: Local-Response Approximation

- simple connection between graphene and SWCNTs
- AR-EELS in terms of normal-mode excitations
- explained the dispersion of the spectral features
- explained dependence upon orientation of $\boldsymbol{q}$

Perspective:

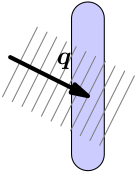
- consider AR-EELS for large tubes
- study exchange-correlation effects for $\boldsymbol{q} \to 0$
- different perturbation: spatially-resolved EELS

Outline

SR-EELS for SWCNTs

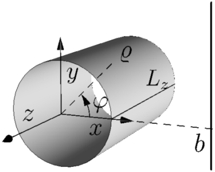
plane-wave perturbation

$$S(\boldsymbol{q},\omega) \approx -\frac{2}{L^2}\sum_m J_m^2(|\boldsymbol{q}_\perp|R)\ \mathrm{Im}\,\bar{\chi}(m,p)$$



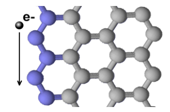
delta-like perturbation

$$S(b,\omega) \propto \sum_m \int dp\, \tilde{C}_b^2(m,p,\omega)\ \mathrm{Im}\,\bar{\chi}(m,p)$$



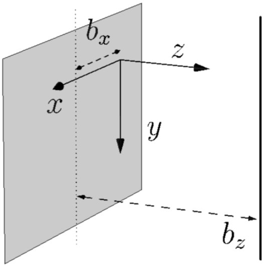
[G.F. Bertsch *et al.*: PRB (**58**) 14031 (1998)], metal wires
[D. Taverna *et al.*: PRB (**66**) 235419 (2002)], MWCNTs from $\epsilon^{\alpha\beta}(\omega)$
[D.J. Mowbray *et al.*: PRB (**82**) 035405 (2010)], SWCNTs from $\epsilon_{\mathrm{hyd}}(\boldsymbol{q},\omega)$

SR-EELS for Graphene

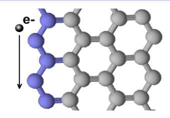


Electron Parallel to Graphene Sheet

- What is the response of an atomically thin layer?
- How delocalised is the response?
- Are non-local effects important?
- Can we resolve single atoms?



Dielectric Response



1. full microscopic response: $\epsilon(\boldsymbol{q}, \boldsymbol{q}', \omega)$

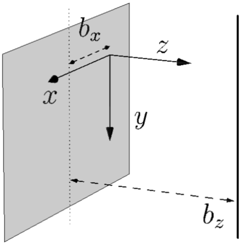
   $$S(b_x, b_z, \omega) \propto \text{Im} \int d\boldsymbol{q}\, d\boldsymbol{q}'\, [\varphi_{\boldsymbol{b}}^{ext}(\boldsymbol{q}, \omega)]^* \chi(\boldsymbol{q}, \boldsymbol{q}', \omega) \varphi_{\boldsymbol{b}}^{ext}(\boldsymbol{q}', \omega)$$

2. local-response approximation: $\epsilon(\bar{\boldsymbol{q}}, \omega)$

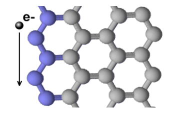
   $$S(b_z, \omega) \propto \int dq_x\; C(b_z; q_x, \omega)\; \text{Im}\, \bar{\chi}(\bar{\boldsymbol{q}}, \omega)$$

3. non-dispersive dielectric function: $\epsilon(\omega)$

   $$\bar{\epsilon}_{\text{local}}(\omega) \equiv \bar{\epsilon}(\bar{\boldsymbol{q}} \to 0, \omega)$$



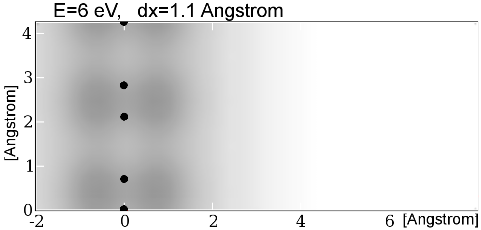
Full Microscopic Response $\chi(\boldsymbol{q}, \boldsymbol{q}', \omega)$

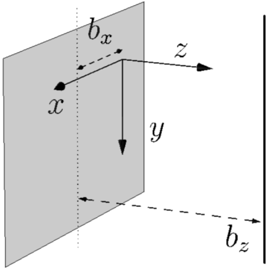


Spatially-Resolved EELS for:

$$S(\boldsymbol{b}_\perp, \omega) \propto \mathrm{Im} \int d\boldsymbol{q}_\perp d\boldsymbol{q}'_\perp \, \frac{\chi(\boldsymbol{q}, \boldsymbol{q}', \omega)}{|\boldsymbol{q}|^2 |\boldsymbol{q}'|^2} \, e^{i(\boldsymbol{q}_\perp - \boldsymbol{q}'_\perp)\boldsymbol{b}_\perp}, \qquad \boldsymbol{q} = \boldsymbol{q}_\perp + \frac{\omega}{v} \boldsymbol{e}_y$$

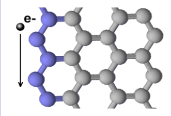
Test calculation excluding $|\boldsymbol{q}_\perp^{(\prime)}| < q_0$:





H. Kohl, H. Rose: AEEP **65**, 173 (1985)

Dielectric Response

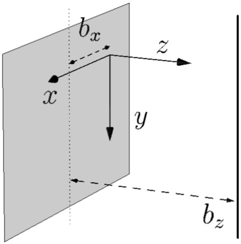


1. full microscopic response: $\epsilon(\boldsymbol{q}, \boldsymbol{q}', \omega)$

   $$S(b_x, b_z, \omega) \propto \operatorname{Im} \int d\boldsymbol{q}\, d\boldsymbol{q}' \, [\varphi_{\boldsymbol{b}}^{ext}(\boldsymbol{q}, \omega)]^* \chi(\boldsymbol{q}, \boldsymbol{q}', \omega) \varphi_{\boldsymbol{b}}^{ext}(\boldsymbol{q}', \omega)$$

2. local-response approximation: $\epsilon(\bar{\boldsymbol{q}}, \omega)$

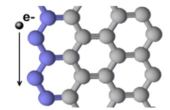
   $$S(b_z, \omega) \propto \int dq_x \; C(b_z; q_x, \omega) \; \operatorname{Im} \bar{\chi}(\bar{\boldsymbol{q}}, \omega)$$



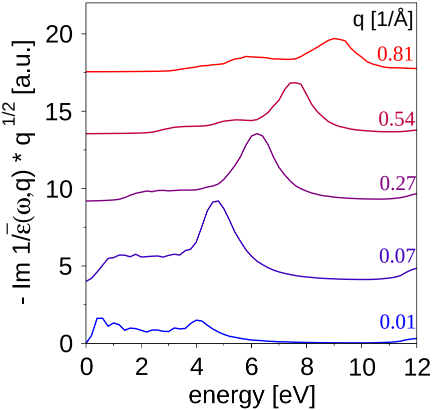
3. non-dispersive dielectric function: $\epsilon(\omega)$

   $$\bar{\epsilon}_{\text{local}}(\omega) \equiv \bar{\epsilon}(\bar{\boldsymbol{q}} \rightarrow 0, \omega)$$

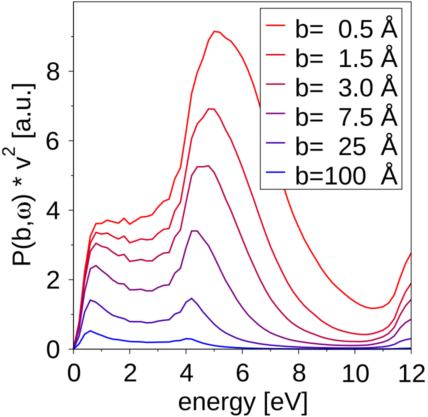
Local-Response Approximation: $\epsilon(\bar{\boldsymbol{q}}, \omega)$



AR-EELS Im $\bar{\chi}(\bar{\boldsymbol{q}}, \omega)$

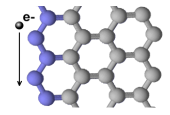


SR-EELS $S(b_z, \omega)$



$$S(b_z, \omega) \propto \int dq_x \; C(b_z; q_x, \omega) \; \text{Im}\, \bar{\chi}(\bar{\boldsymbol{q}}, \omega) \qquad C = \frac{e^{-2b_z\sqrt{q_x^2+(\omega/v)^2}}}{q_x^2+(\omega/v)^2}$$

Dielectric Response



1. full microscopic response: $\epsilon(\boldsymbol{q}, \boldsymbol{q}', \omega)$

   $$S(b_x, b_z, \omega) \propto \operatorname{Im} \int d\boldsymbol{q}\, d\boldsymbol{q}'\, [\varphi_{\boldsymbol{b}}^{ext}(\boldsymbol{q}, \omega)]^* \chi(\boldsymbol{q}, \boldsymbol{q}', \omega) \varphi_{\boldsymbol{b}}^{ext}(\boldsymbol{q}', \omega)$$

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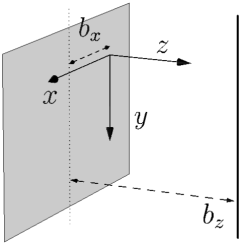
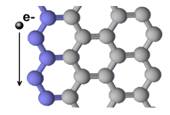
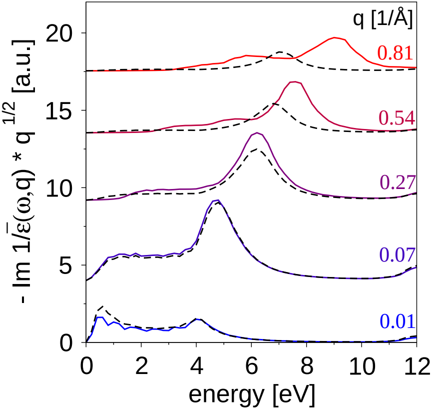


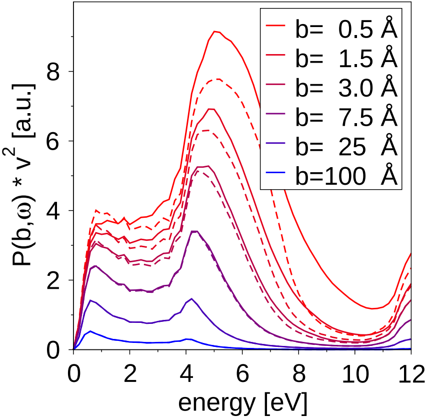
Non-Dispersive Dielectric Function: $\epsilon(\omega)$



AR-EELS $\mathrm{Im}\,\bar{\chi}(\bar{\boldsymbol{q}},\omega)$

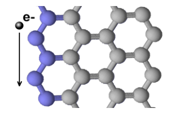


SR-EELS $S(b_z,\omega)$



$$\bar{\chi}^0_{\mathrm{local}}(\bar{\boldsymbol{q}},\omega) \approx \bar{\boldsymbol{q}}^2\Pi(\omega), \qquad \Pi(\omega) \equiv \lim_{\bar{\boldsymbol{q}}\to 0} \frac{1}{\bar{\boldsymbol{q}}^2}\bar{\chi}^0(\bar{\boldsymbol{q}},\omega)$$

Dielectric Response



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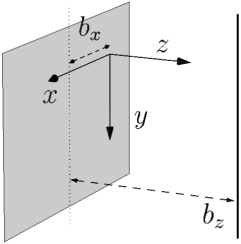
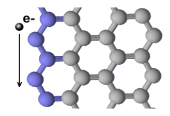


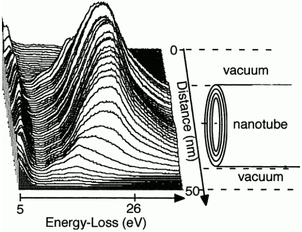


Summary

- ab-initio calculation for SR-EELS on graphene
- non-local corrections only for small distance
- route towards atomic resolution in SR-EELS

Outlook

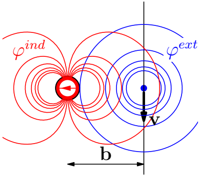
- SR-EELS for a SWCNT
- atomically-resolved valence EELS



Results of Thesis

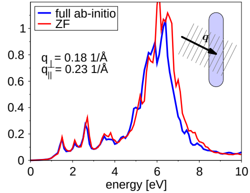
Theory of EELS

1. semi-classical approach
2. quantum-mechanical scattering theory



Angular-Resolved EELS

3. Graphite: discontinuity of $S(\boldsymbol{q}, \boldsymbol{q}')$ at $\boldsymbol{G}$
4. Graphene: local-response approx.
5. SWCNTs: building-block approach



Spatially-Resolved EELS

6. Graphene: including spatial dispersion
7. microscopic charge oscillations

Results of Thesis

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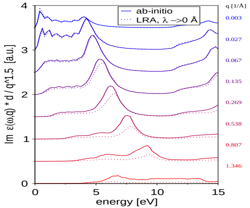

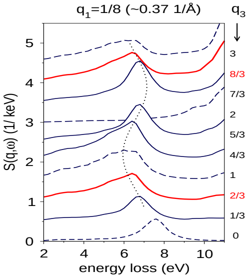

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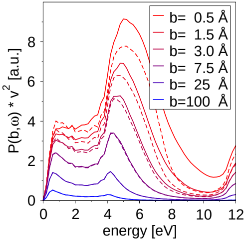
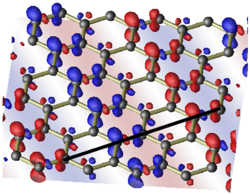
6. Graphene: including spatial dispersion
7. microscopic charge oscillations





Collaborations

Theory

Theory group of the LSI + ETSF Network

Experiments

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Thank you for your attention.