Ab Initio calculations of electronic excitations

Carbon Nanotubes and Graphene layer systems

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Ecole Polytechnique, Palaiseau - France
European Theoretical Spectroscopy Facility (ETSF)

Strasbourg, 27 August 2008

Outline

1. Introduction
2. Electron Energy Loss Spectroscopy
   - Linear response within DFT
3. Applications: Nanotubes and Graphene
4. Perspectives

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Introduction

- Theoretical Spectroscopy Group (ETSF)
- Results on Nanotubes and Graphene:

  Coordinator: Christine Giorgetti
  Ralf Hambach
  Xochitl Lopéz
  Federico Iori
  V.Olevano, A. Marinopoulos, L. Reining, F. Sottile
  Experiments: Thomas Pichler group (Dresden)

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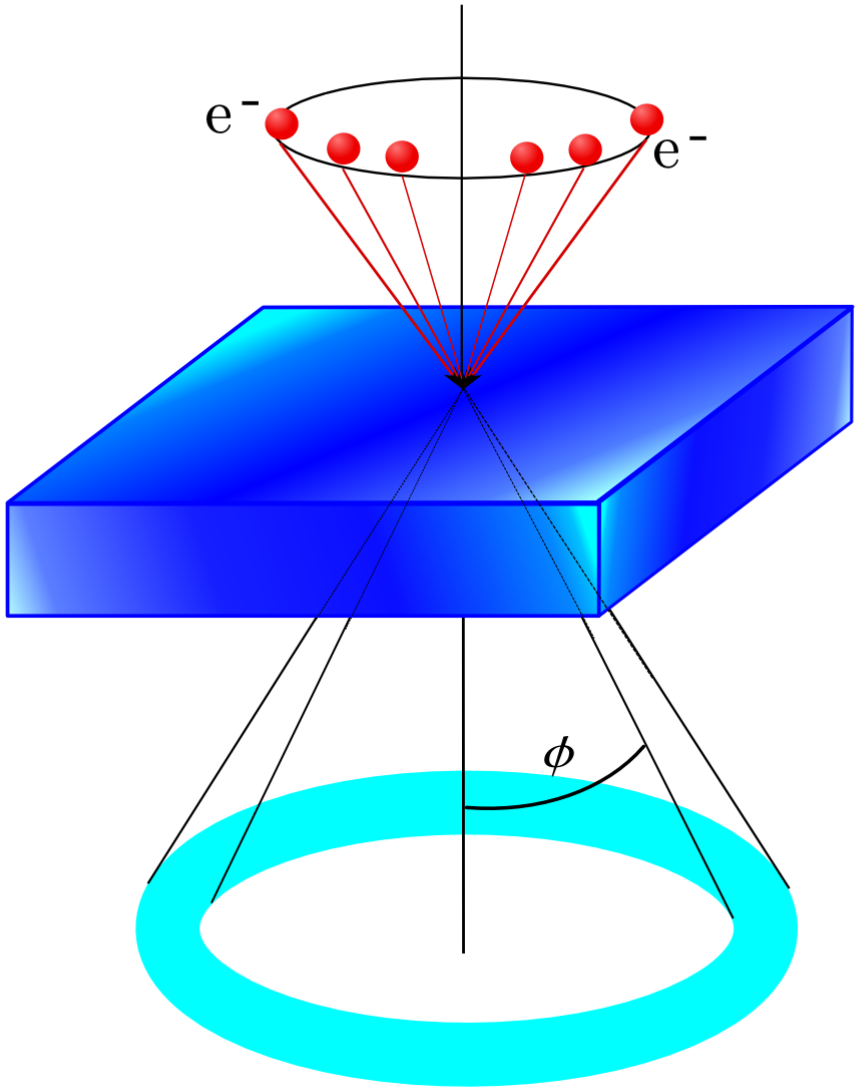
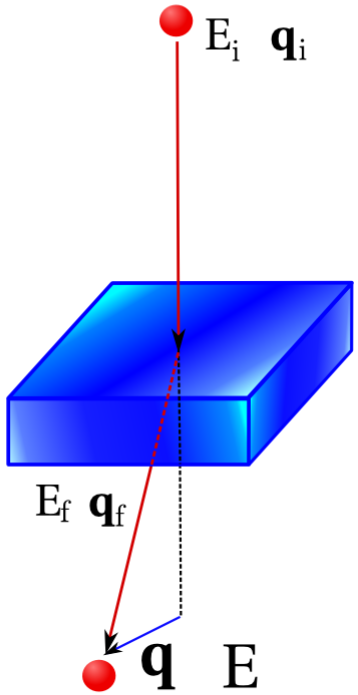
Spectroscopy: Electron Scattering



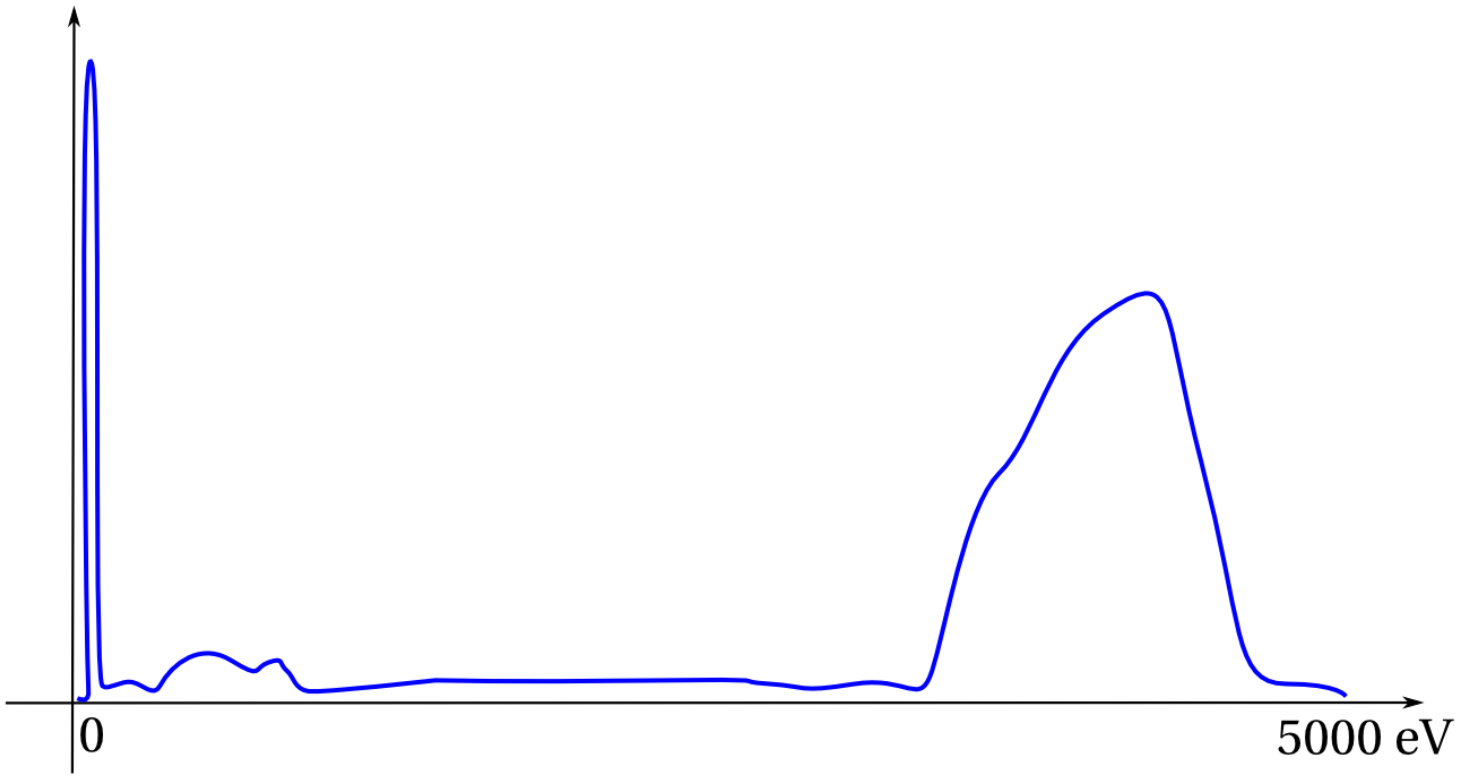


Spectroscopy: Electron Scattering

Energy Loss Function

$$\frac{d^2\sigma}{d\Omega dE} \propto \mathrm{Im}\left\{\varepsilon^{-1}\right\}$$

Spectroscopy: Electron Scattering



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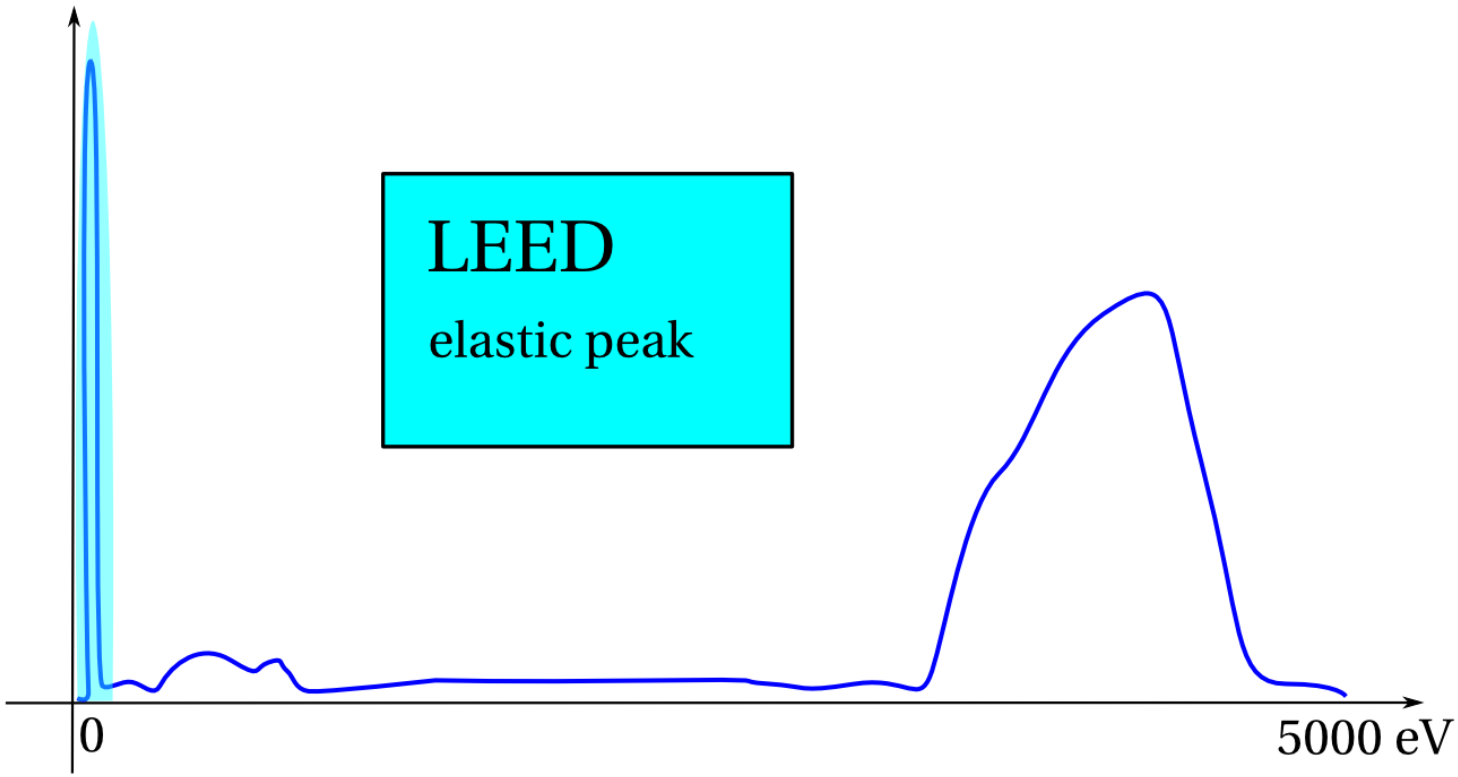

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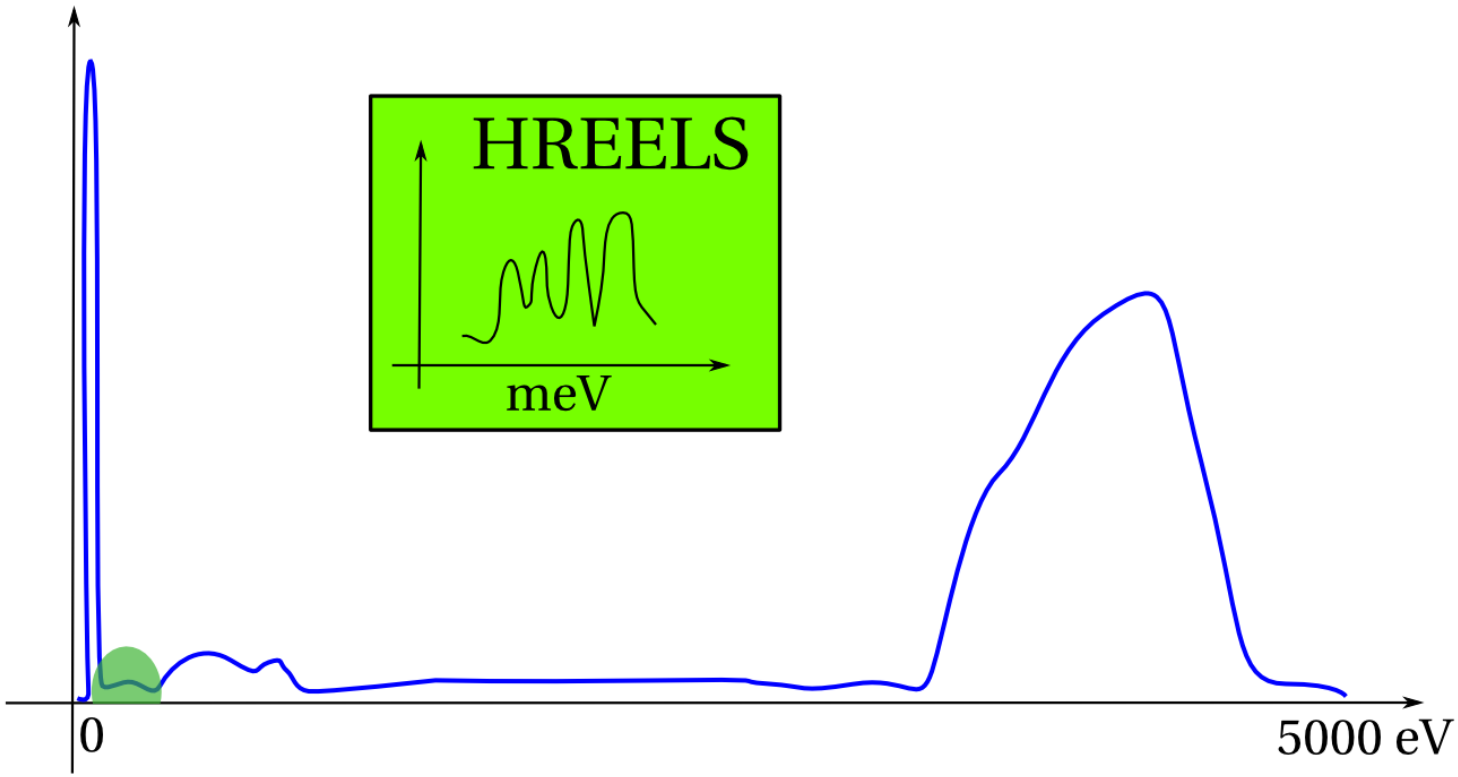

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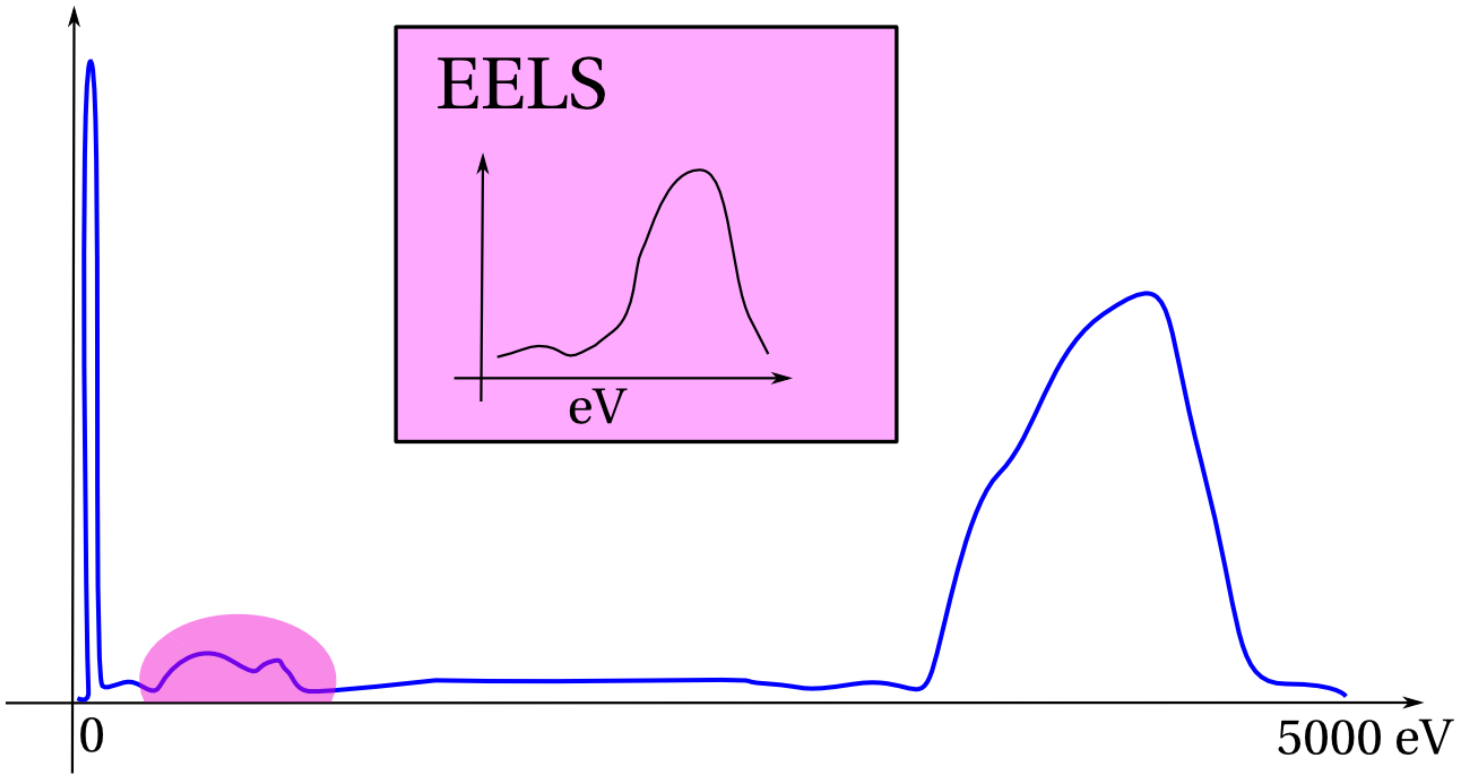

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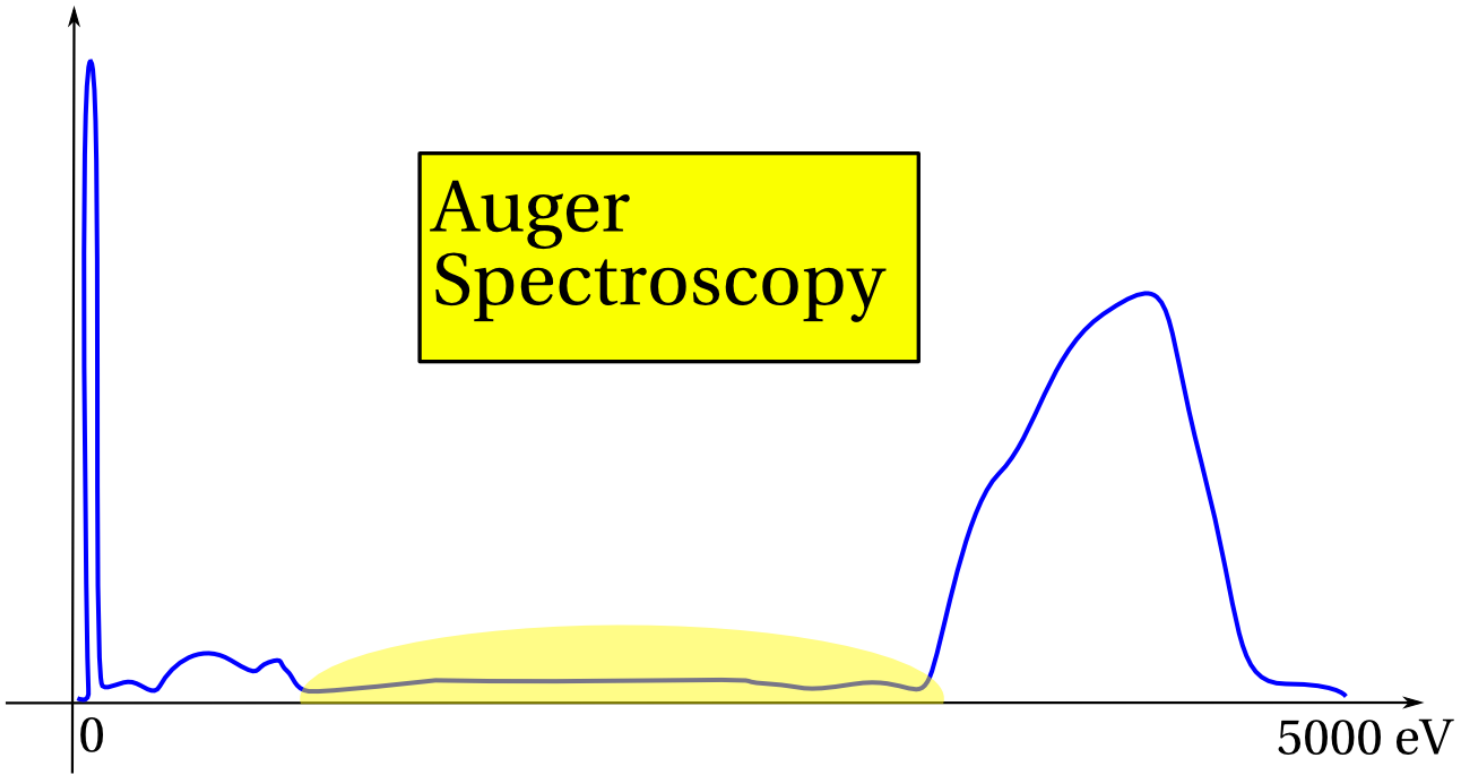

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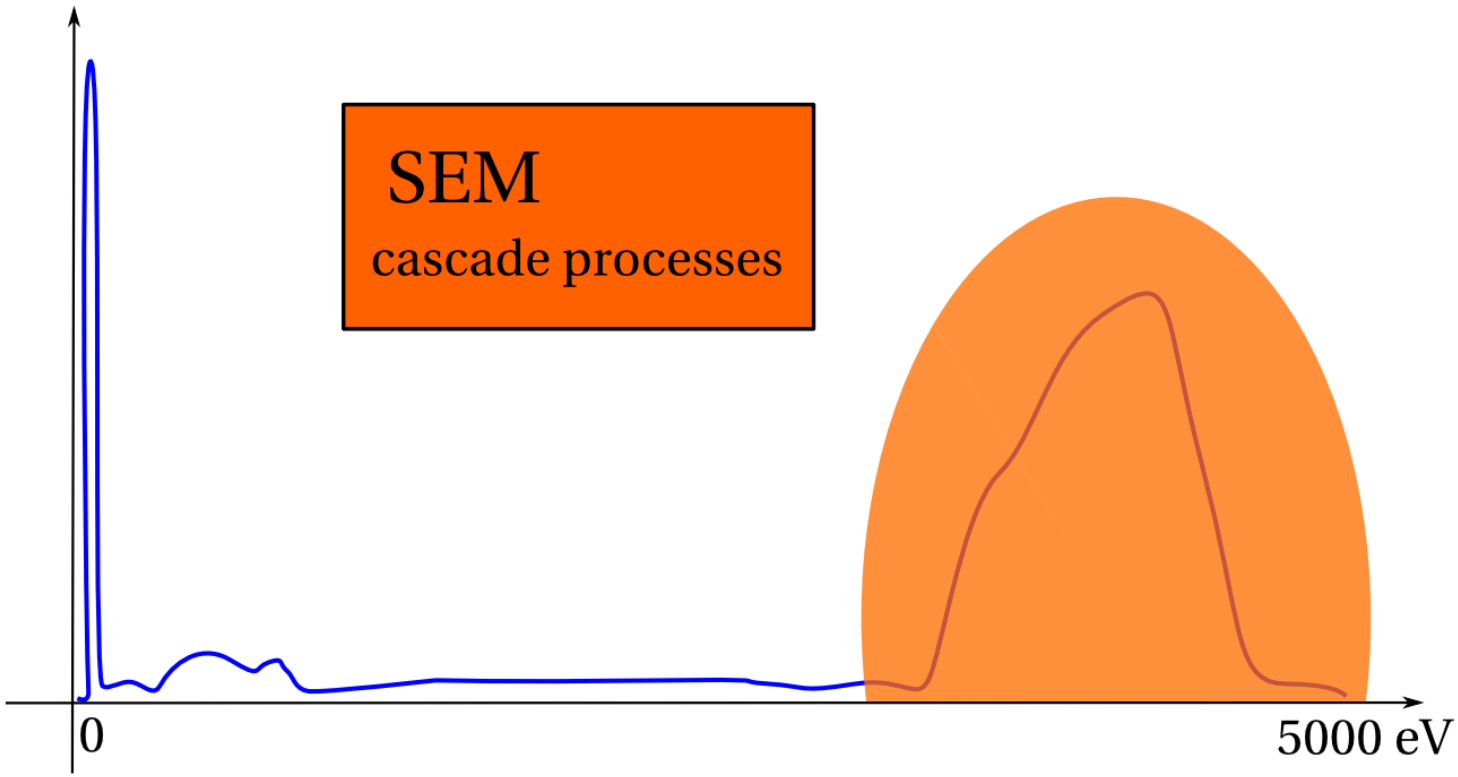

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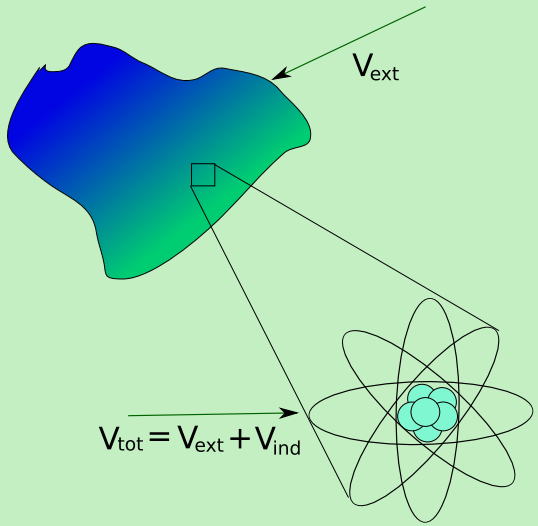
Linear Response Approach

System submitted to an external perturbation



$$V_{tot} = \varepsilon^{-1} V_{ext}$$

$$V_{tot} = V_{ext} + V_{ind}$$

$$\mathbf{E} = \varepsilon^{-1} \mathbf{D}$$

Linear Response Approach

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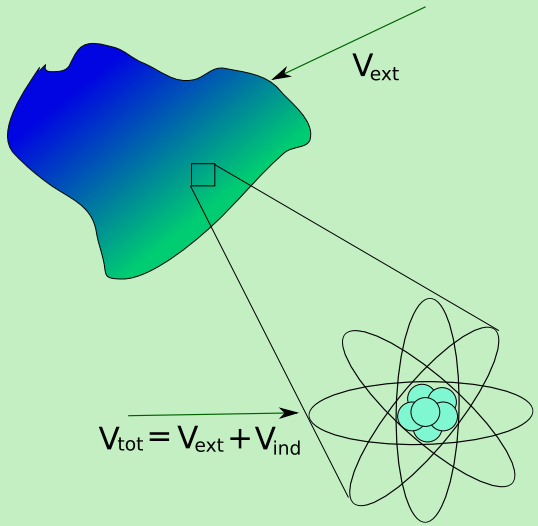

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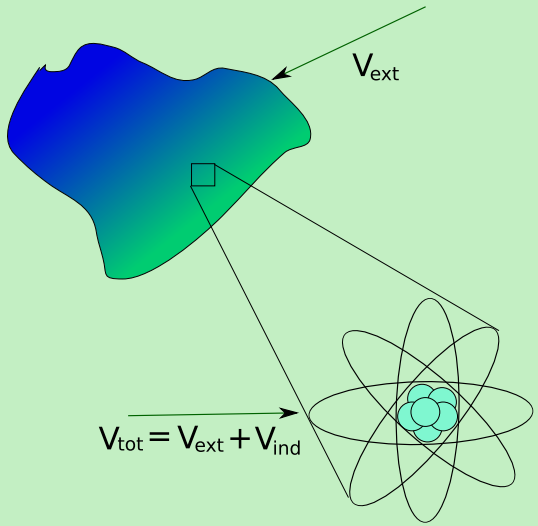

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Linear Response Approach

Definition of polarizability

$$\text{not polarizable} \Rightarrow V_{tot} = V_{ext} \Rightarrow \varepsilon^{-1} = 1$$
$$\text{polarizable} \Rightarrow V_{tot} \neq V_{ext} \Rightarrow \varepsilon^{-1} \neq 1$$
$$\varepsilon^{-1} = 1 + v\chi$$

χ is the polarizability of the system

Linear Response Approach

Definition of polarizability

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Linear Response Approach

Polarizability

$$\text{interacting system} \quad \delta n = \chi \delta V_{ext}$$

$$\text{non-interacting system} \quad \delta n_{n-i} = \chi^0 \delta V_{tot}$$

Linear Response Approach

Polarizability

interacting system $\delta n = \chi \delta V_{ext}$

non-interacting system $\delta n_{n-i} = \chi^0 \delta V_{tot}$

Single-particle polarizability

$$\chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega - (\epsilon_i - \epsilon_j)}$$

hartree, hartree-fock, dft, etc.

G.D. Mahan *Many Particle Physics* (Plenum, New York, 1990)

Linear Response Approach

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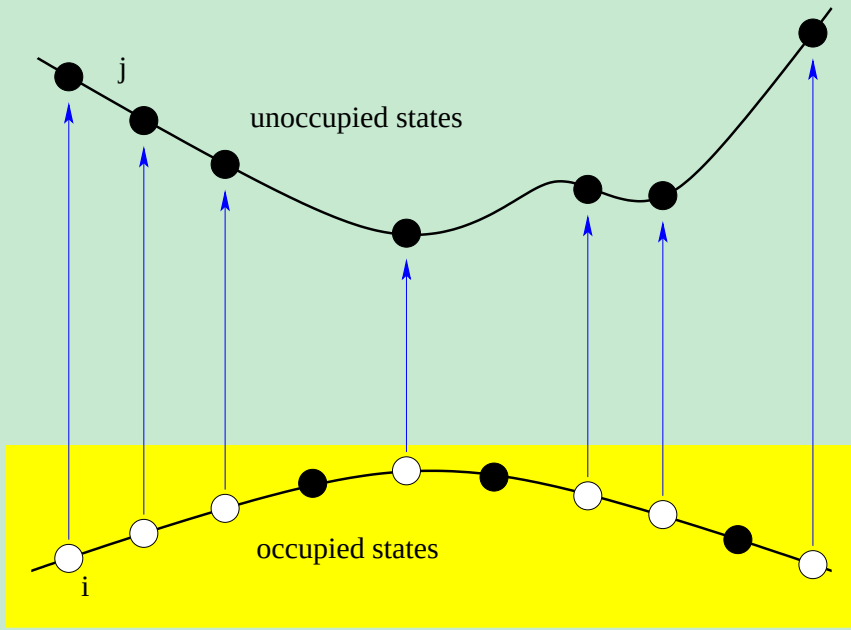

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Polarizability

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non-interacting system $\delta n_{n-i} = \chi^0 \delta V_{tot}$

$\Updownarrow$

Density Functional Formalism

$$\delta n = \delta n_{n-i}$$

$$\delta V_{tot} = \delta V_{ext} + \delta V_H + \delta V_{xc}$$

Linear Response Approach

Polarizability

$$\chi \delta V_{ext} = \chi^0 \left(\delta V_{ext} + \delta V_H + \delta V_{xc} \right)$$

$$\chi = \chi^0 \left(1 + \frac{\delta V_H}{\delta V_{ext}} + \frac{\delta V_{xc}}{\delta V_{ext}} \right)$$

$$\frac{\delta V_H}{\delta V_{ext}} = \frac{\delta V_H}{\delta n} \frac{\delta n}{\delta V_{ext}} = v\chi$$

$$\frac{\delta V_{xc}}{\delta V_{ext}} = \frac{\delta V_{xc}}{\delta n} \frac{\delta n}{\delta V_{ext}} = f_{xc}\chi$$

with f_{xc} = **exchange-correlation kernel**

Linear Response Approach

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Linear Response Approach

Polarizability χ in TDDFT

1. DFT ground-state calc. $\longrightarrow$ ϕ_i, ϵ_i $[V_{xc}]$
2. $\phi_i, \epsilon_i \longrightarrow \chi^0 = \sum_{ij} \frac{\phi_i(\mathbf{r})\phi_j^*(\mathbf{r})\phi_i^*(\mathbf{r}')\phi_j(\mathbf{r}')}{\omega-(\epsilon_i-\epsilon_j)}$
3. $\left.\begin{array}{l} \frac{\delta V_H}{\delta n} = v \\ \frac{\delta V_{xc}}{\delta n} = f_{xc} \end{array}\right\}$ variation of the potentials
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Linear Response Approach

RPA and other approximations

- $f_{xc} = \begin{cases} \frac{\delta V_{xc}}{\delta n} \\ \text{“any” other function} \end{cases}$ $\quad f_{xc} = 0 \mapsto \text{RPA}$

Local field effects

$$\chi = \left(1 - \chi^0 v\right)^{-1} \chi^0 \quad ; \quad \chi^0_{\mathbf{G}\mathbf{G}'}$$

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Actual work at the Theoretical Spectroscopy Group

- EELS of semiconductors
- IXS and CIXS of semiconductors and metals
- EELS of nanotubes and graphene layers
- EELS and IXS of strongly correlated systems (Hf, V oxydes)
- RIXS spectroscopy

User projects

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User projects

EELS of nanotubes: plasmon dispersion

Questions

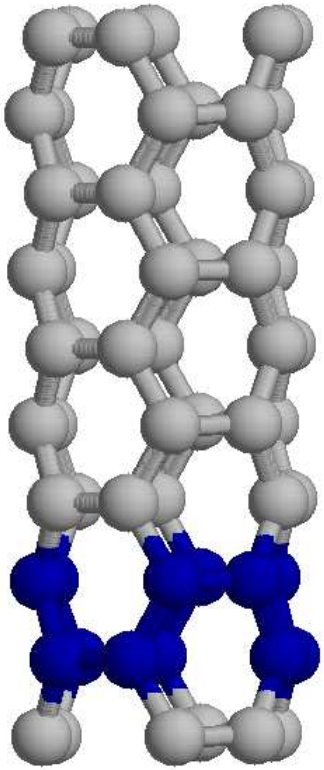
- theoretical understanding of electronic excitations of SWNT **plasmon dispersion**
- SWNT and graphene. Strong **connection and analysis**

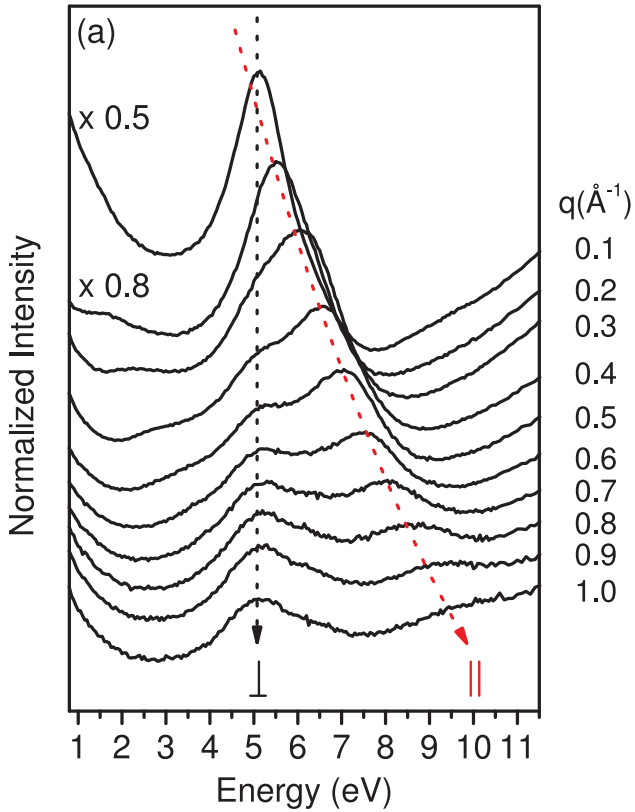
EELS of nanotubes: plasmon dispersion

VA-SWCNT

diameter: 2nm

nearly isolated





Kramberger, Hambach, Giorgetti, Rümmeli, Knupfer, Fink, Büchner, Reining, Einsarsson, Maruyama, Sottile, Hannewald, Olevano, Marinopoulos, Pichler, Phys. Rev. Lett. **100**, 196803 (2008)

EELS of nanotubes: plasmon dispersion

2nm is big!!

linear dispersion reminds us the *Dirac cone*

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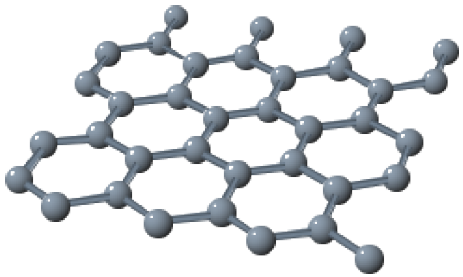
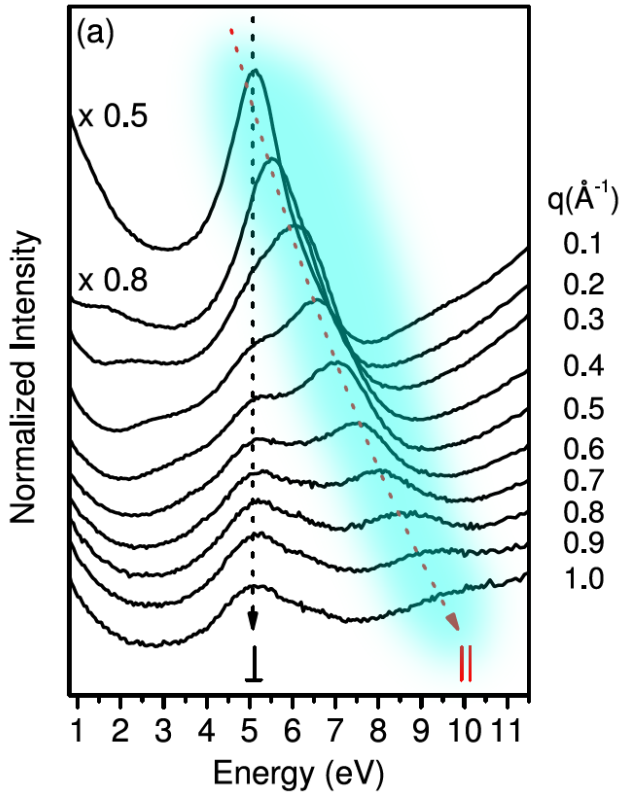
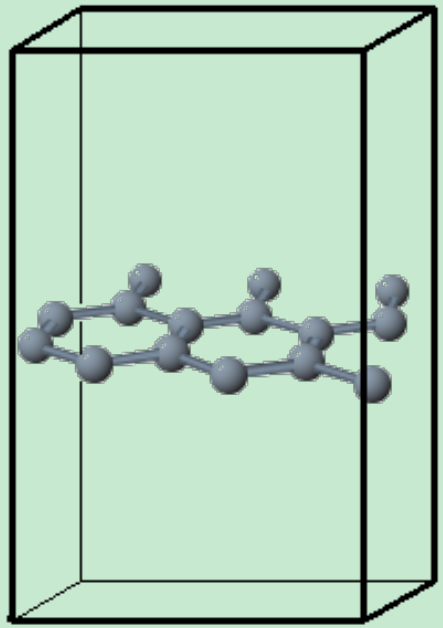




Numerical simulations

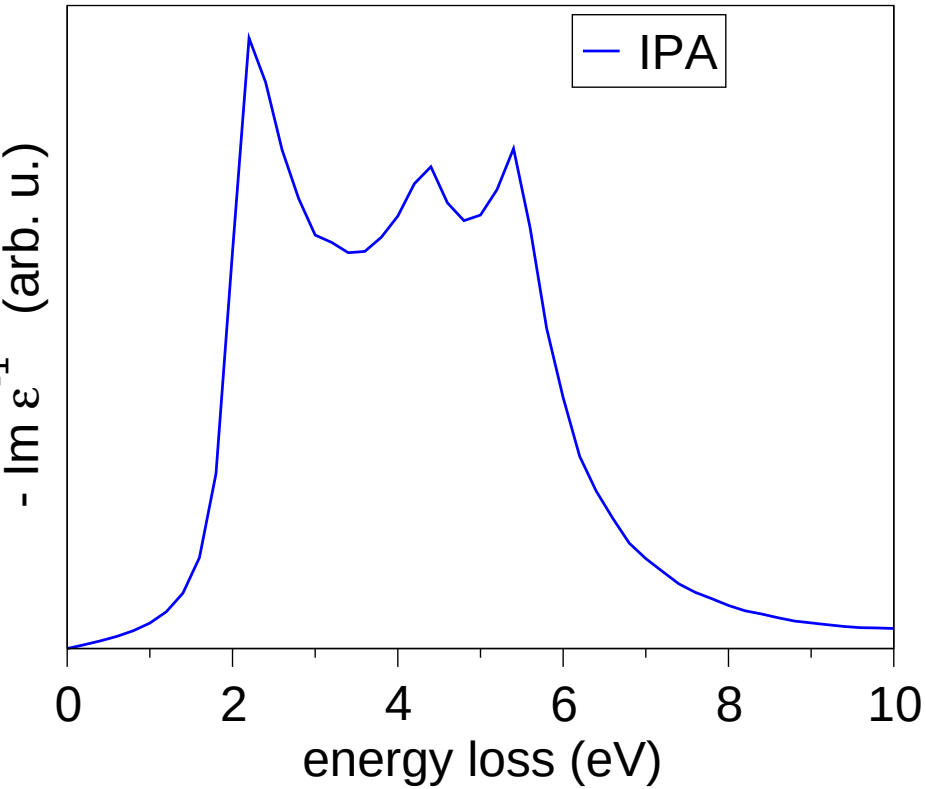
ab-initio calculations

- DFT ground-state calculations (LDA)
- Independant Particles polarizability: χ^0
- RPA Full polarisability: $\chi = \left[1 - \chi^0 v\right]^{-1} \chi^0$
- Dielectric function $\varepsilon^{-1} = 1 + v\chi$
- energy loss function $-\mathrm{Im}\{\varepsilon^{-1}(\mathbf{q}, \omega)\}$

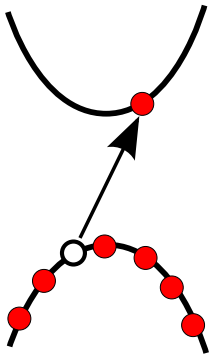


Independent particle picture

energy loss in graphene
(in-plane, $q = 0.41$Å)



$\Longrightarrow$ given by χ^0:
interpretation in terms of
band-transitions



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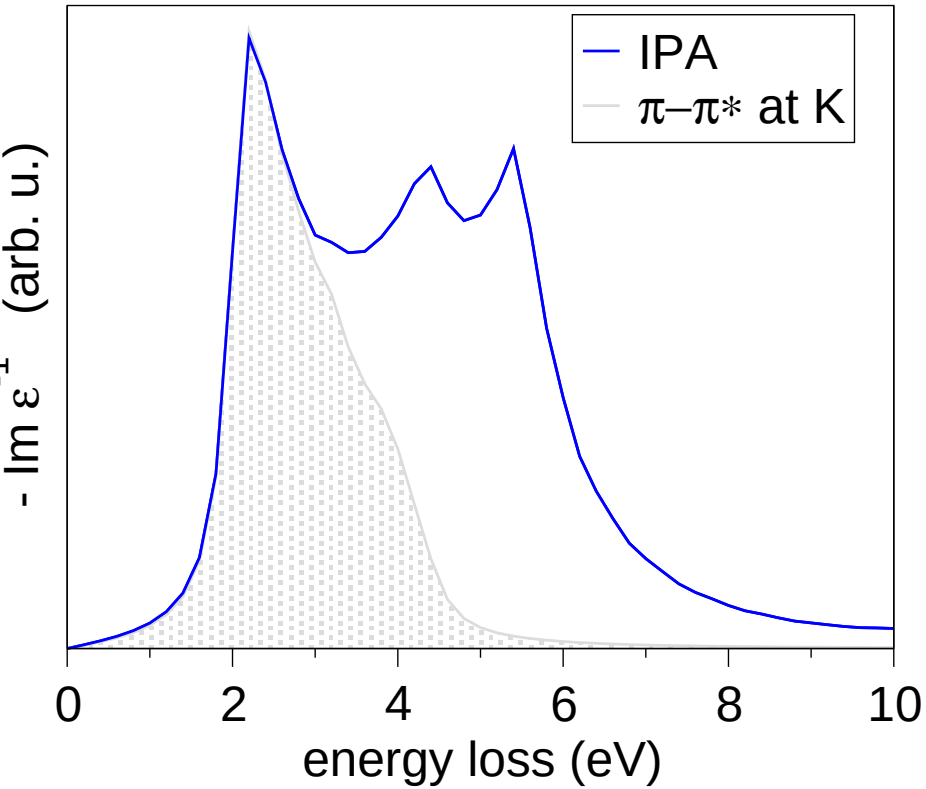
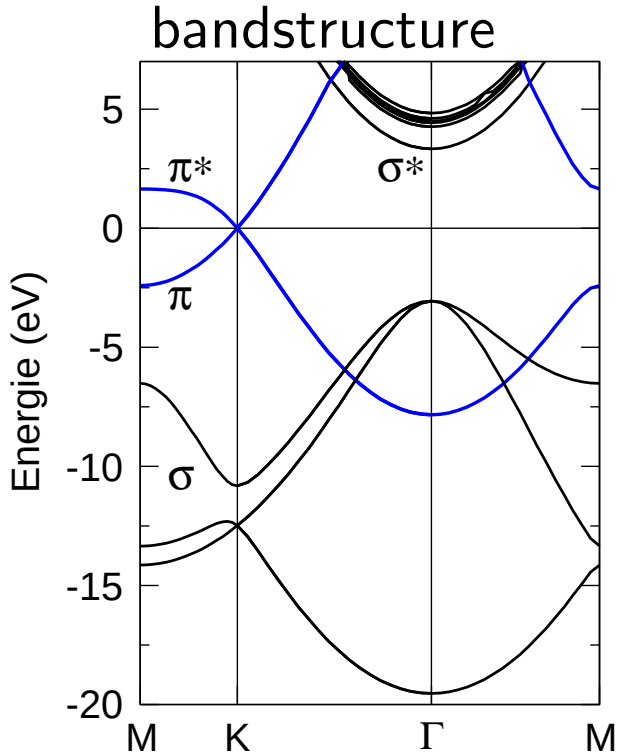
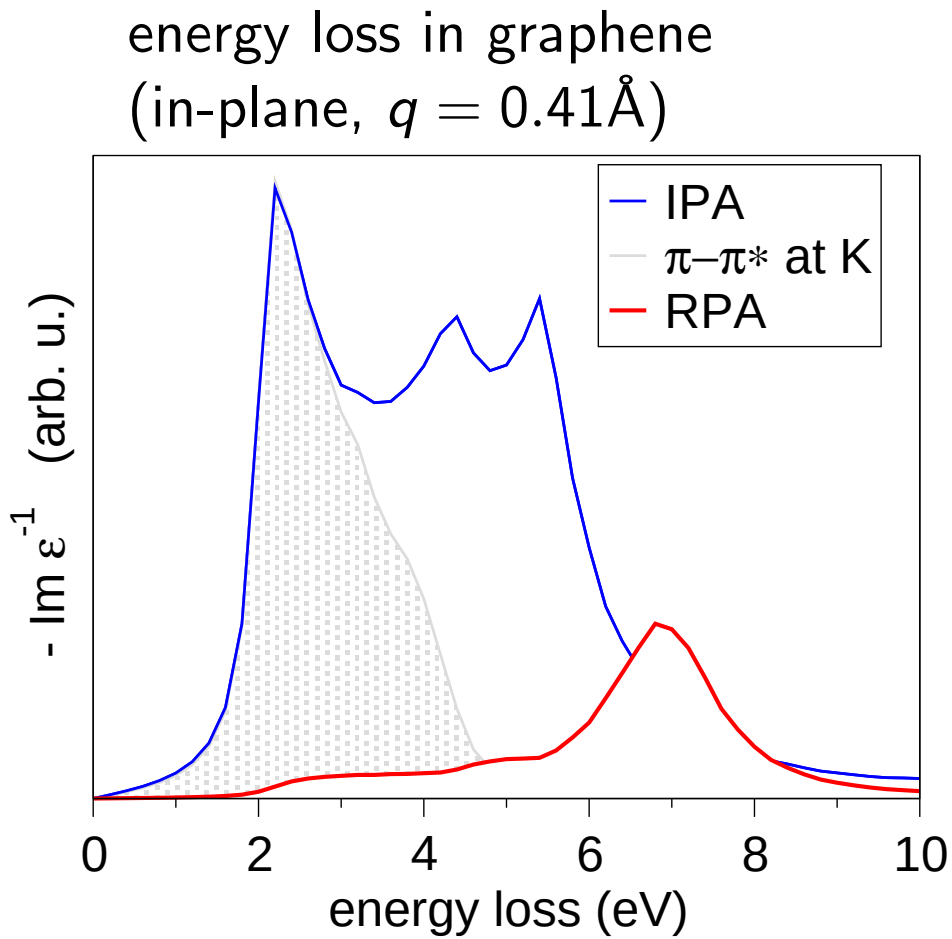




RPA: random phase approx.



- given by χ:
  no interpretation by band-transitions
- contributions from K
- mixing of transitions

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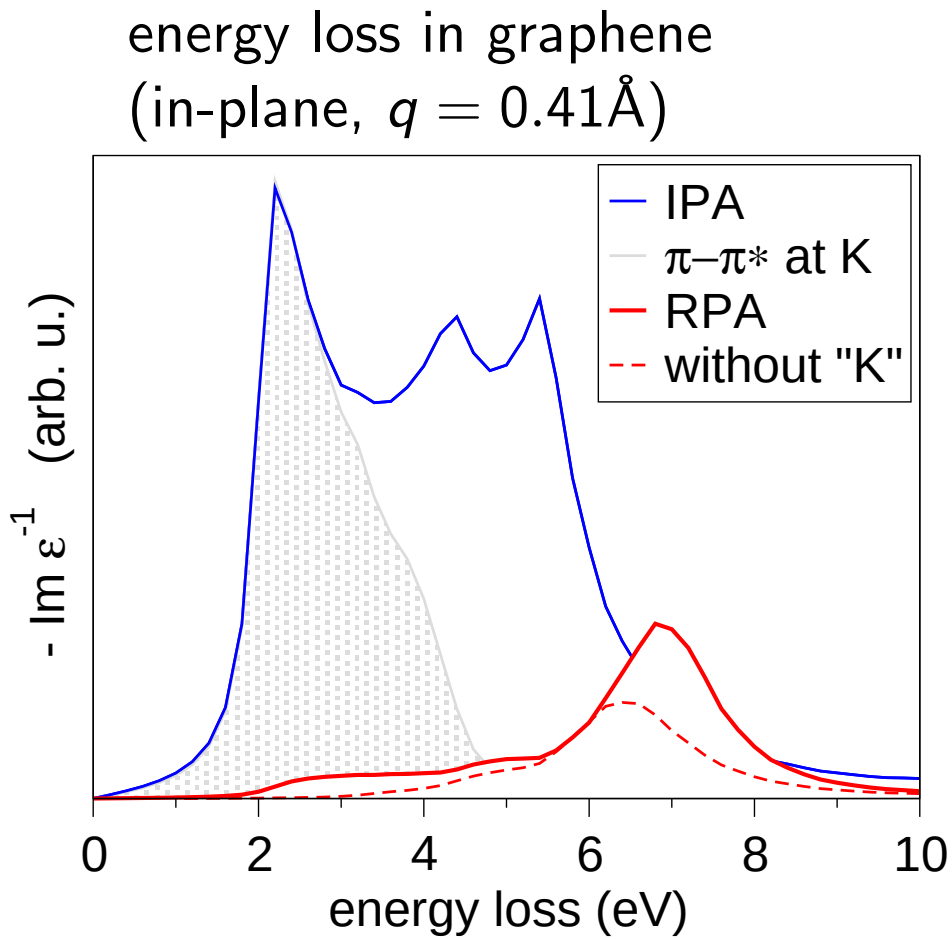

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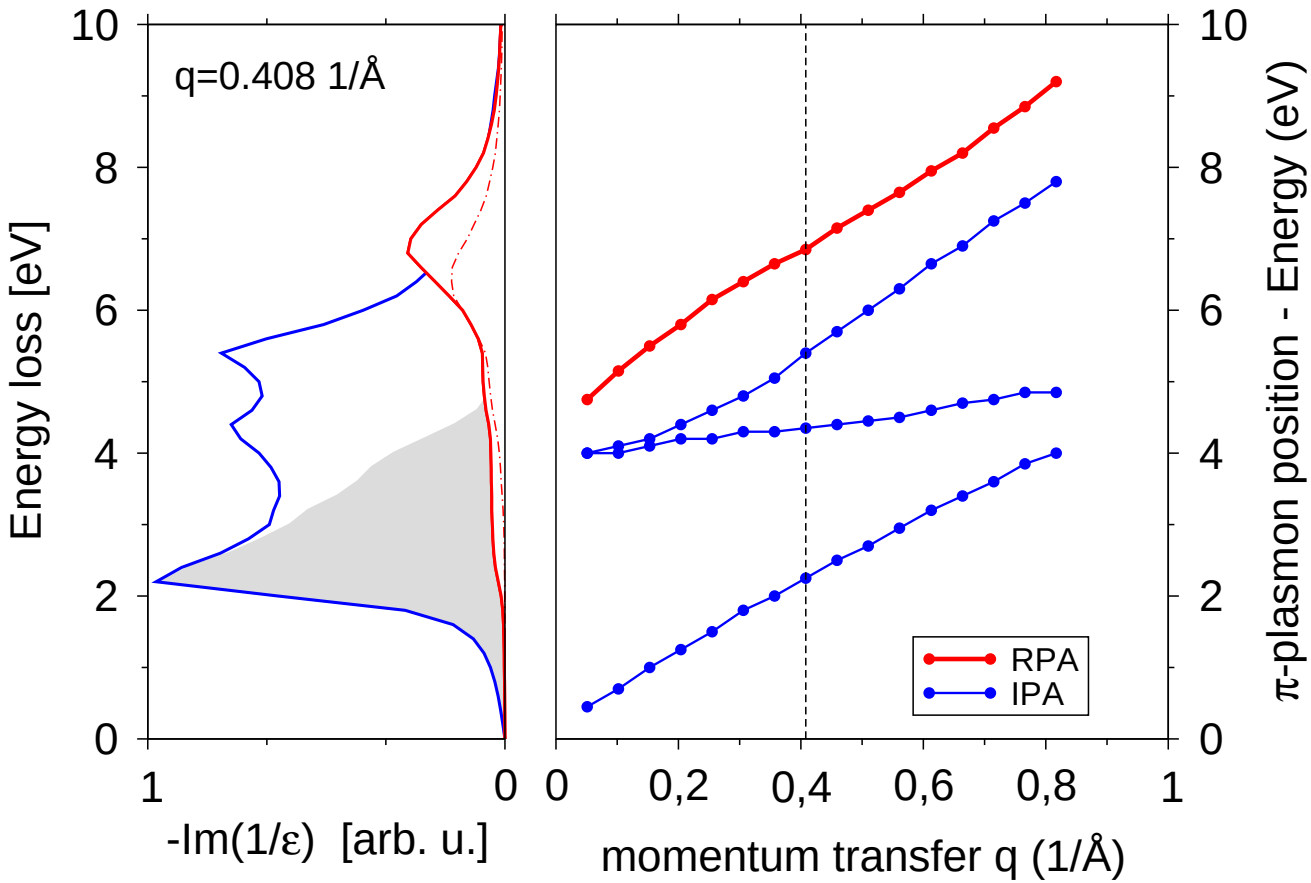
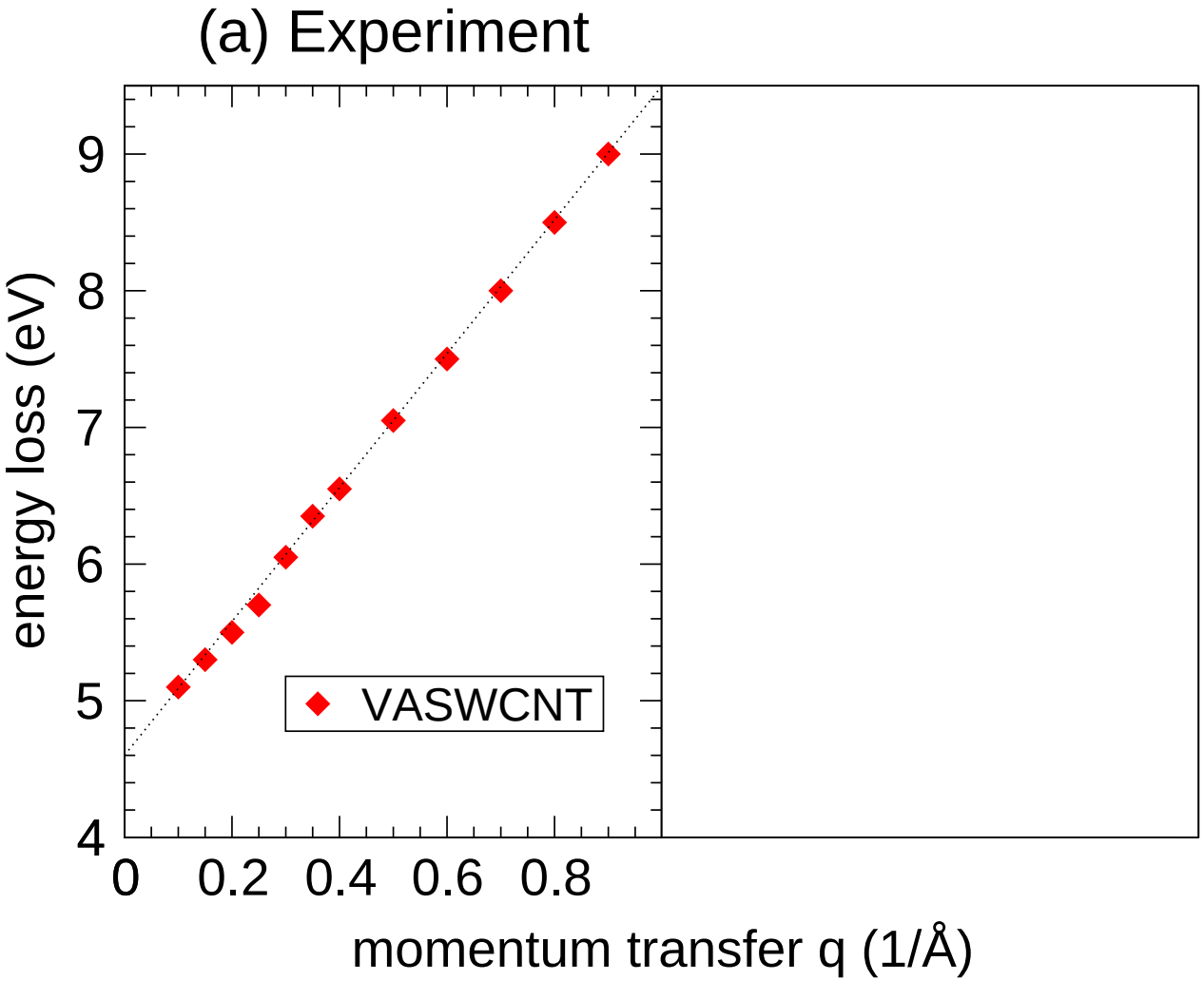
Plasmon dispersion



SWCNT vs. Graphene



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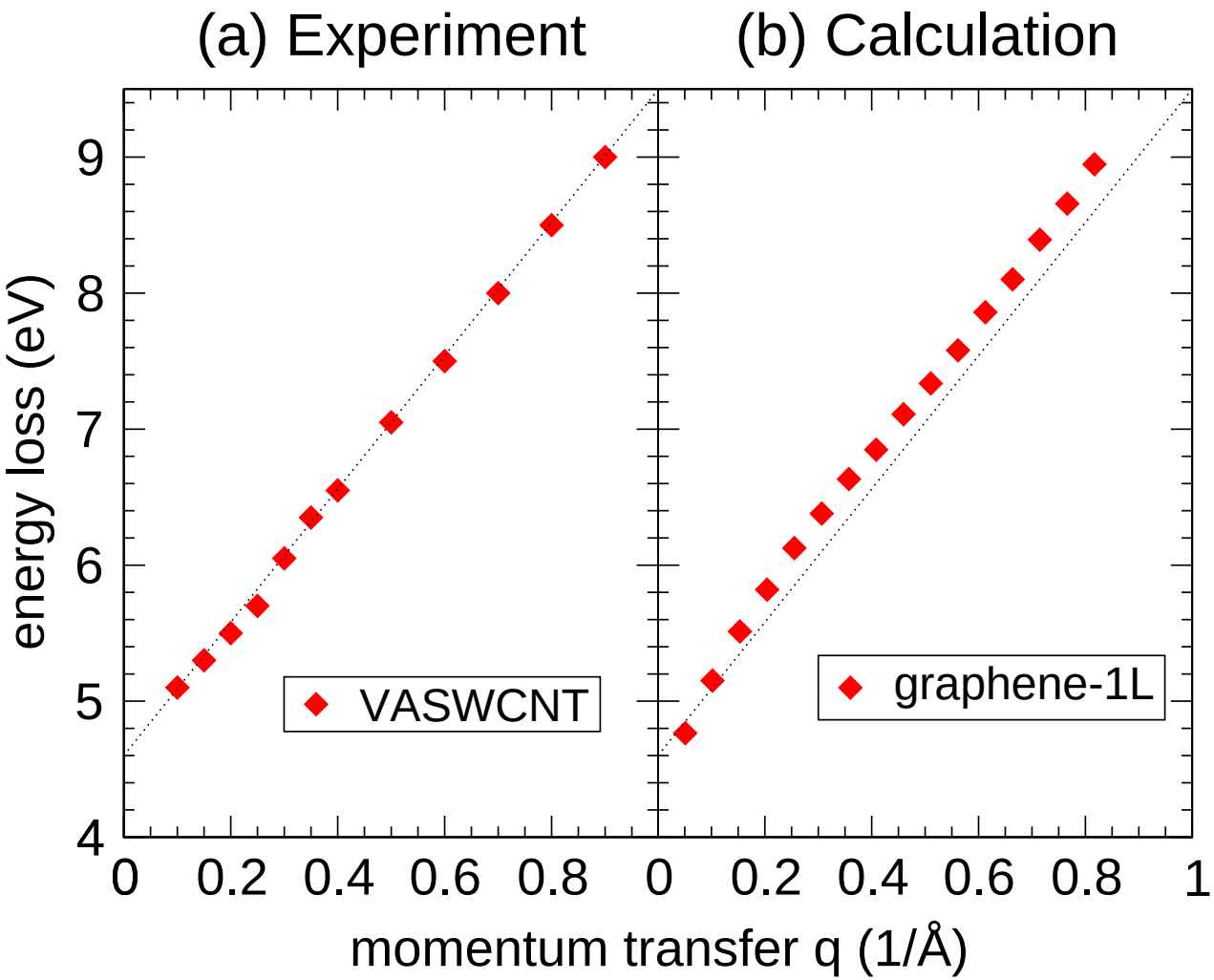
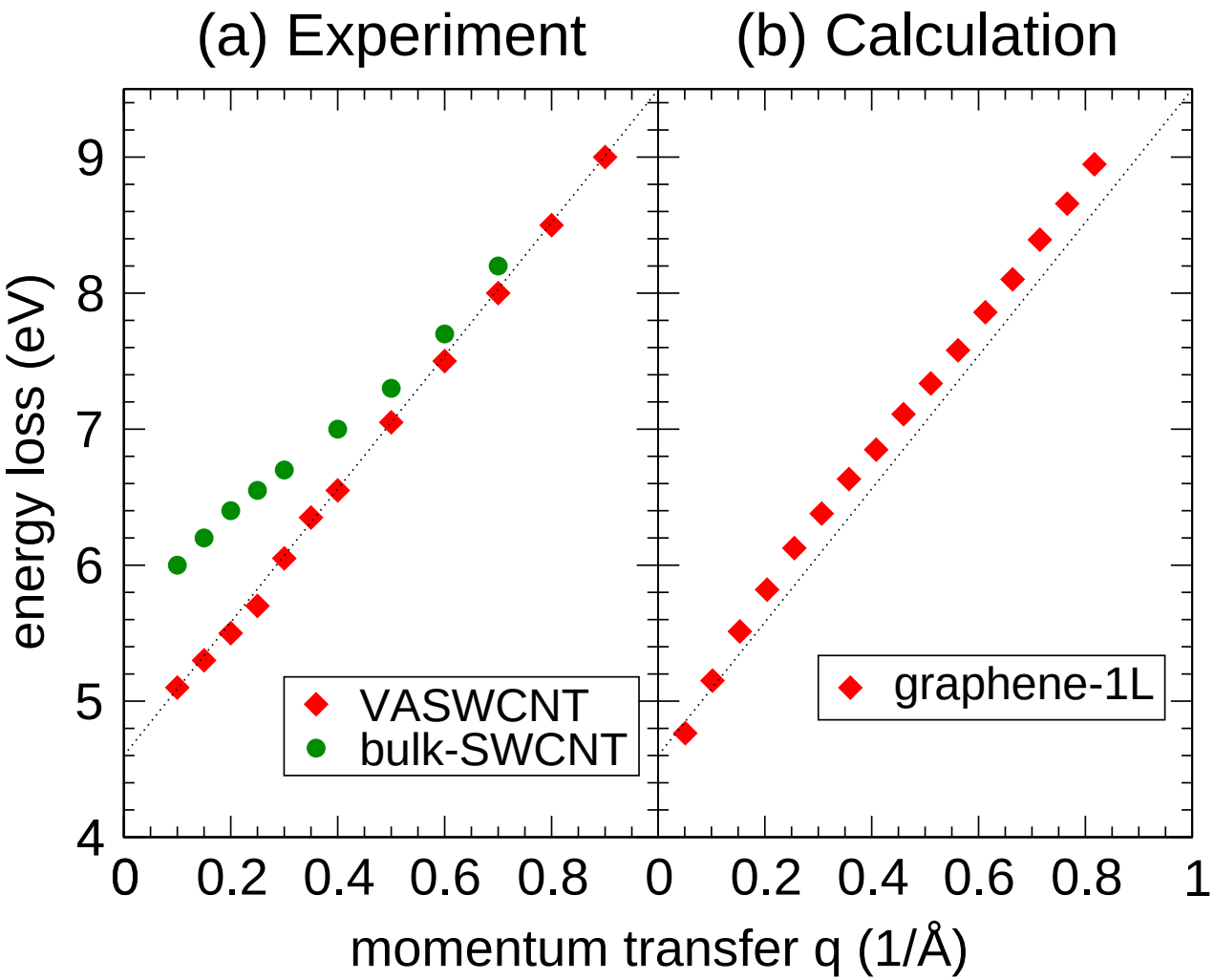
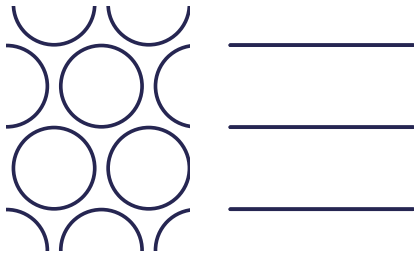


SWCNT vs. Graphene





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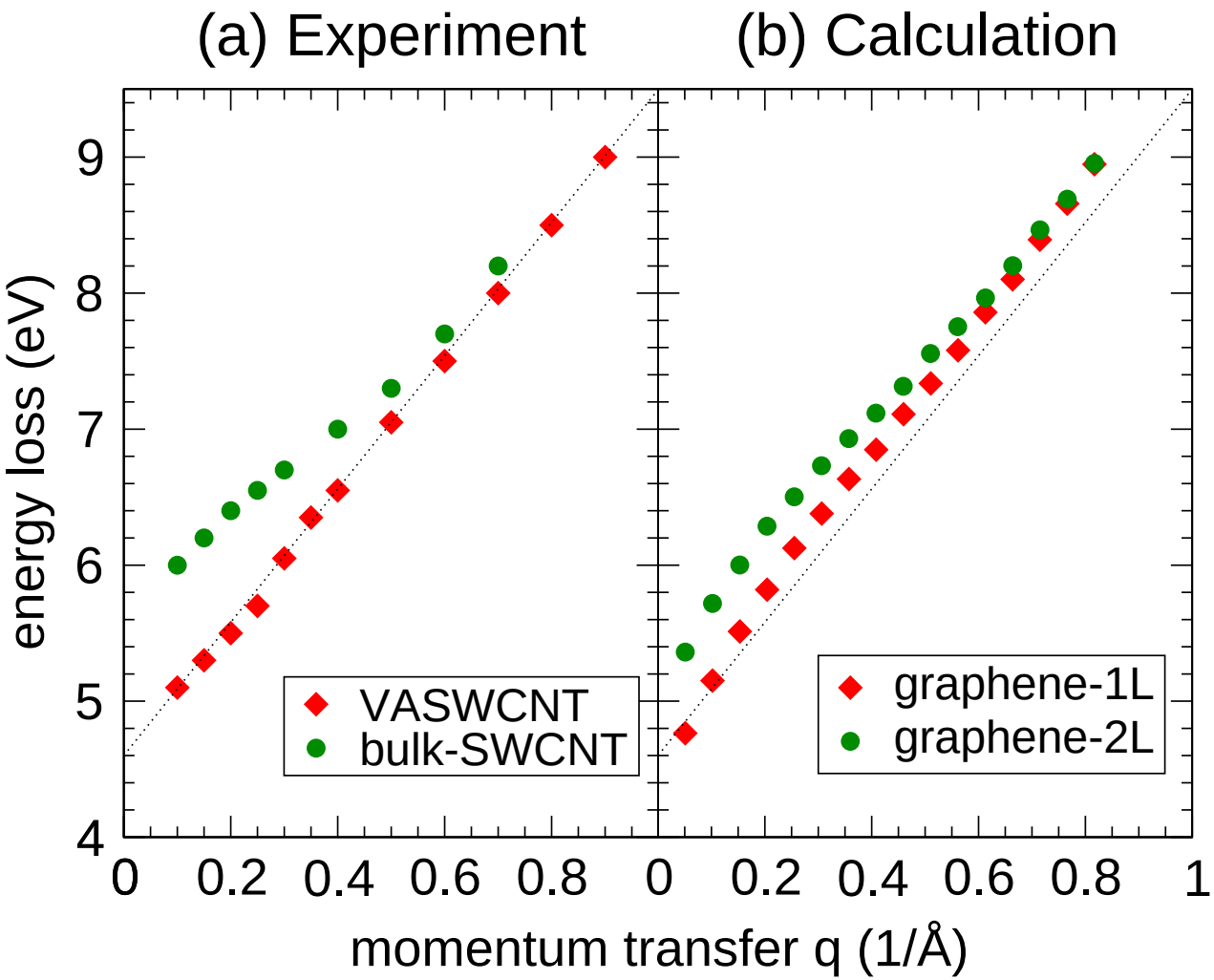

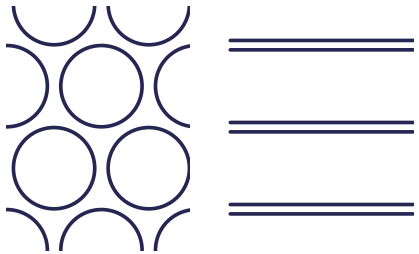

SWCNT vs. Graphene: Conclusions

- Graphene can be studied to get quantitative information about VA-SWNT
- Vice-versa is also true!
- Bulk (bundled) nanotubes can be studied using double layer graphene
- High q measurements are applicable to probe intrinsic properties of individual objects within bulk arrays.

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Outline

1. Introduction
2. Electron Energy Loss Spectroscopy
   - Linear response within DFT
3. Applications: Nanotubes and Graphene
4. Perspectives

Ab initio simulation of electronic excitations

Advantages and limits

- √ reliable
- √ predictive
- × cumbersome

Actual developments in the group

- multiwall nanotubes - stacking of graphene layers (1 postdoc)
- towards more complex systems - strongly correlated (2 postdocs)
- different spectroscopies (X-ray ?) (1 postdoc)
- spatial resolution EELS (PhD thesis)

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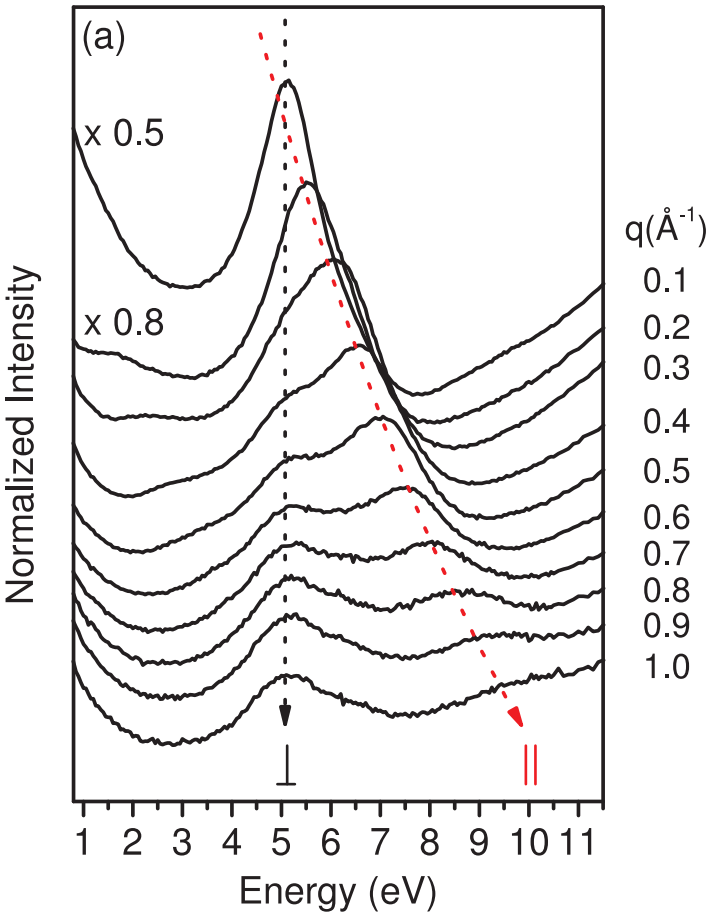
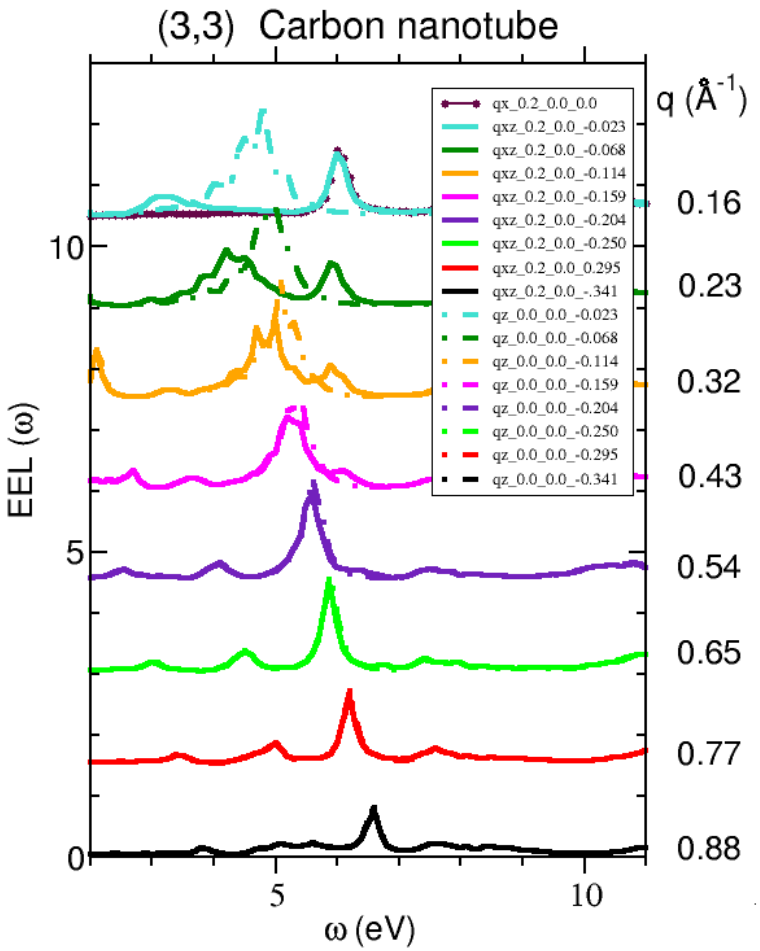
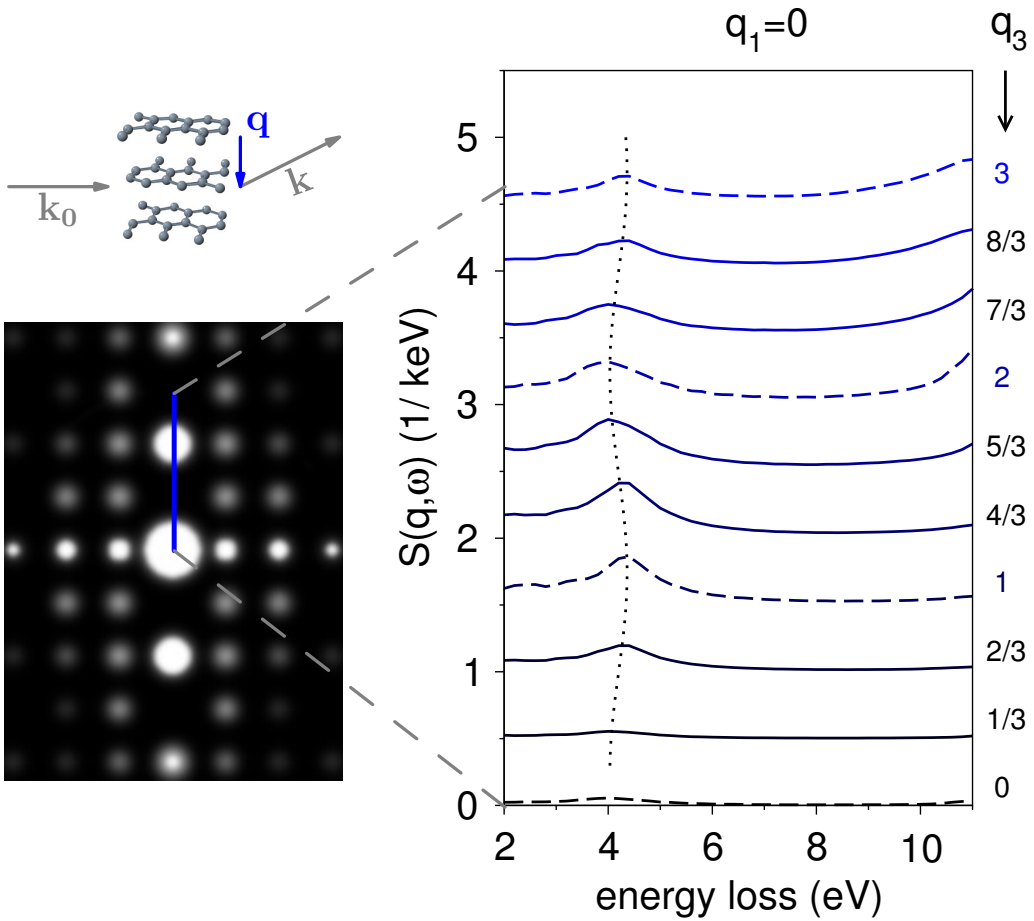

(a)
x 0.5
x 0.8
Normalized Intensity
q(Å^{-1})
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1 2 3 4 5 6 7 8 9 10 11
Energy (eV)


(3,3) Carbon nanotube
q (Å^{-1})
qx_0.2_0.0_0.0
qxz_0.2_0.0_-0.023
qxz_0.2_0.0_-0.068
qxz_0.2_0.0_-0.114
qxz_0.2_0.0_-0.159
qxz_0.2_0.0_-0.204
qxz_0.2_0.0_-0.250
qxz_0.2_0.0_0.295
qxz_0.2_0.0_-.341
qz_0.0_0.0_-0.023
qz_0.0_0.0_-0.068
qz_0.0_0.0_-0.114
qz_0.0_0.0_-0.159
qz_0.0_0.0_-0.204
qz_0.0_0.0_-0.250
qz_0.0_0.0_-0.295
qz_0.0_0.0_-0.341
0.16
0.23
0.32
0.43
0.54
0.65
0.77
0.88
EEL (ω)
10
5
0
5
10
ω (eV)

Discontinuity of the loss function



elastic

inelastic

- energy loss $S(\mathbf{q}, \omega)$ in graphite (AB)
- $\mathbf{q}$ along c-axis
- for multiple Brillouin zones
- **discontinuity:**
  → dispersion
  → peak vanishes

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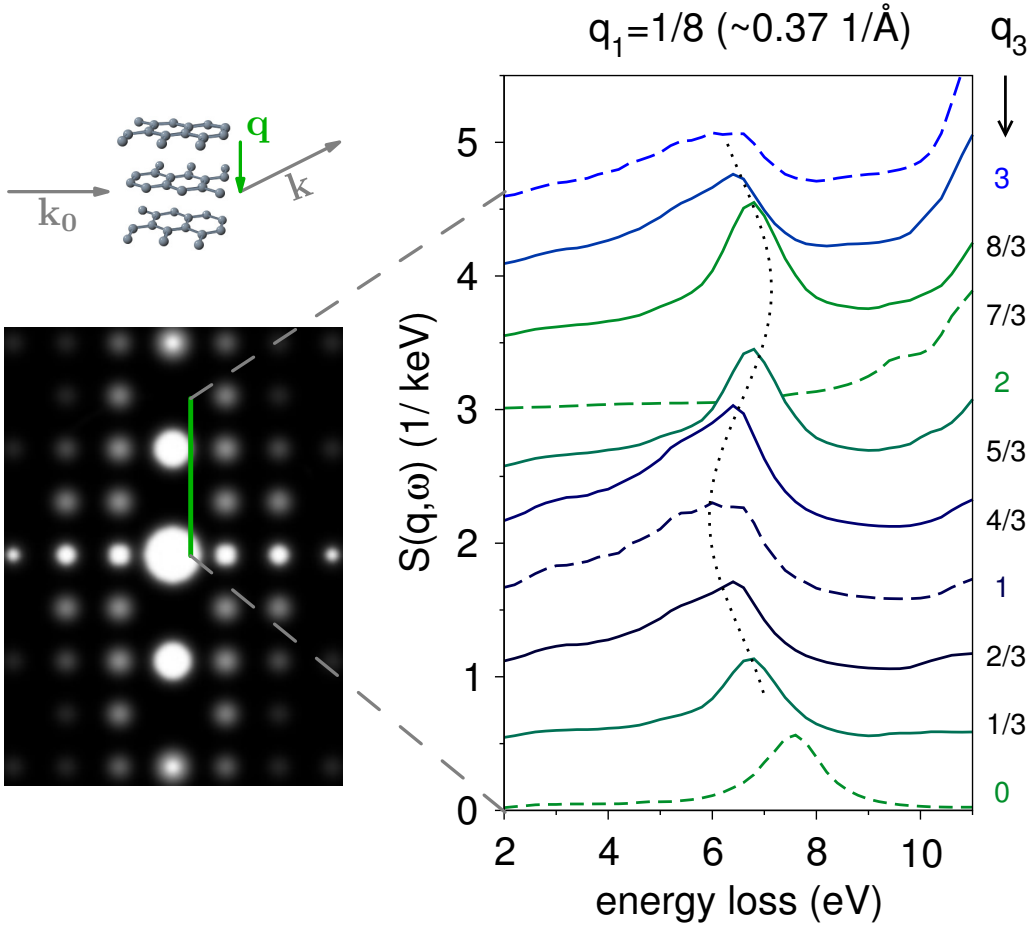

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