Exciton Dispersion from Theoretical Spectroscopy
Complementarity with EELS and IXS

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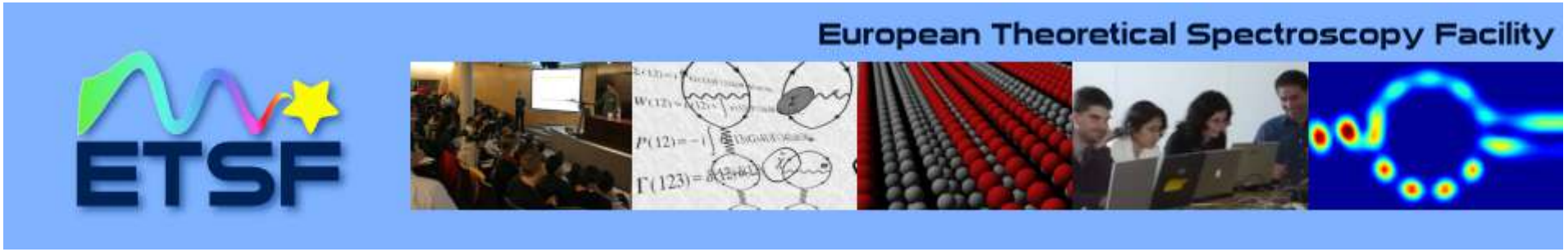
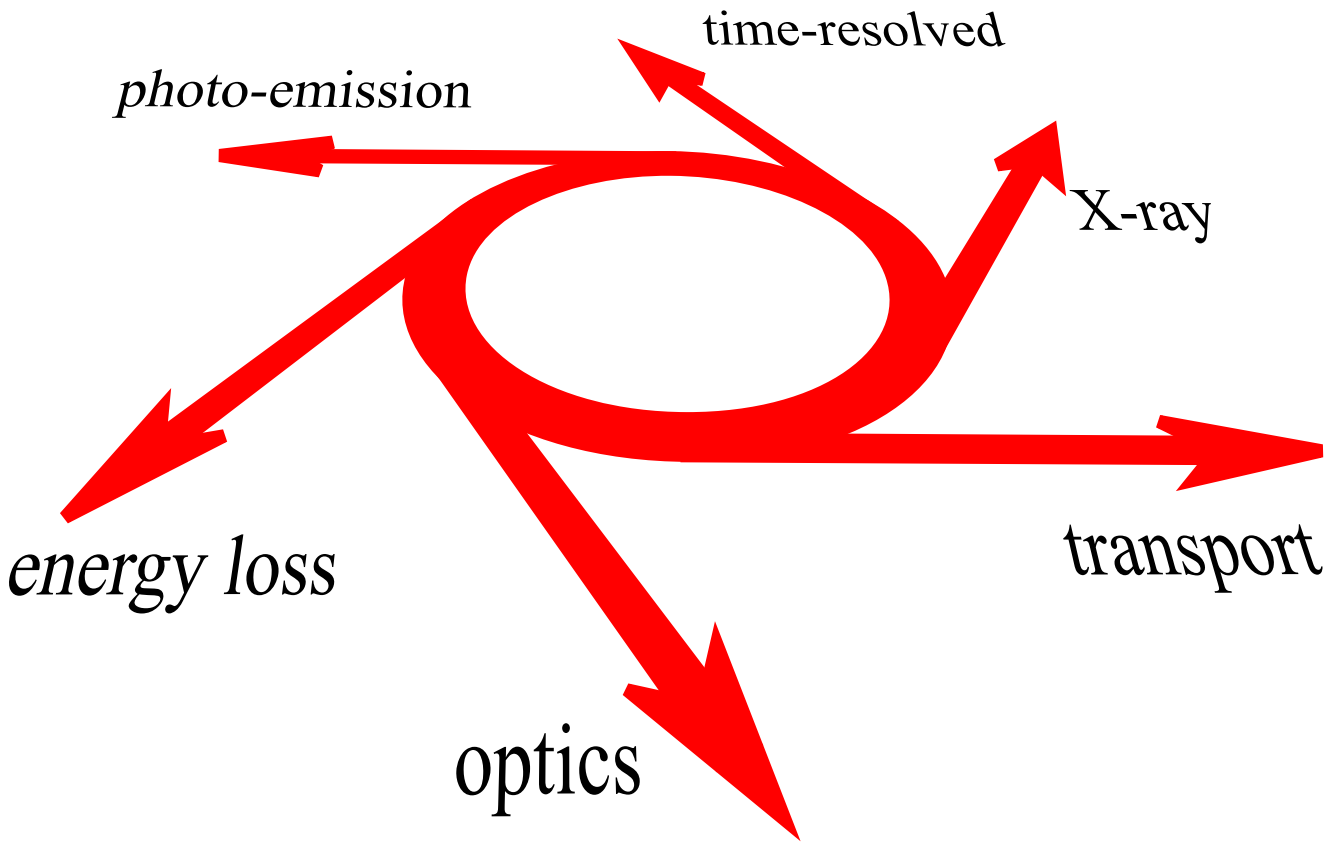
LSI, Ecole Polytechnique, Palaiseau

JEELS 2014
23-26 Juin 2014 Roscoff (France)



http://www.etsf.eu/



Outline

- **Exciton Dispersion** — Analysis and Predictions
- **Visualization of orbitals** — Visualization and Proposition
- **Nanotubes from Graphene** — Tools and Tricks
- **EELS for Photoemission** — Exp. Complementarity

Towards Exciton Dynamics

First step :: exciton dispersion (with momentum transfer)

E_λ { IXS, EELS, Optics } $\longrightarrow$ $E_\lambda(\mathbf{q})$ { IXS (big q), EELS (small q), ~~Optics~~ }

~~Wannier~~
~~Frenkel~~
~~Charge Transfer~~

Ab initio theory

Time Dependent Density Functional Theory

DFT + Linear response (q)

ground state

density fluctuations and local fields

ε {

IXS

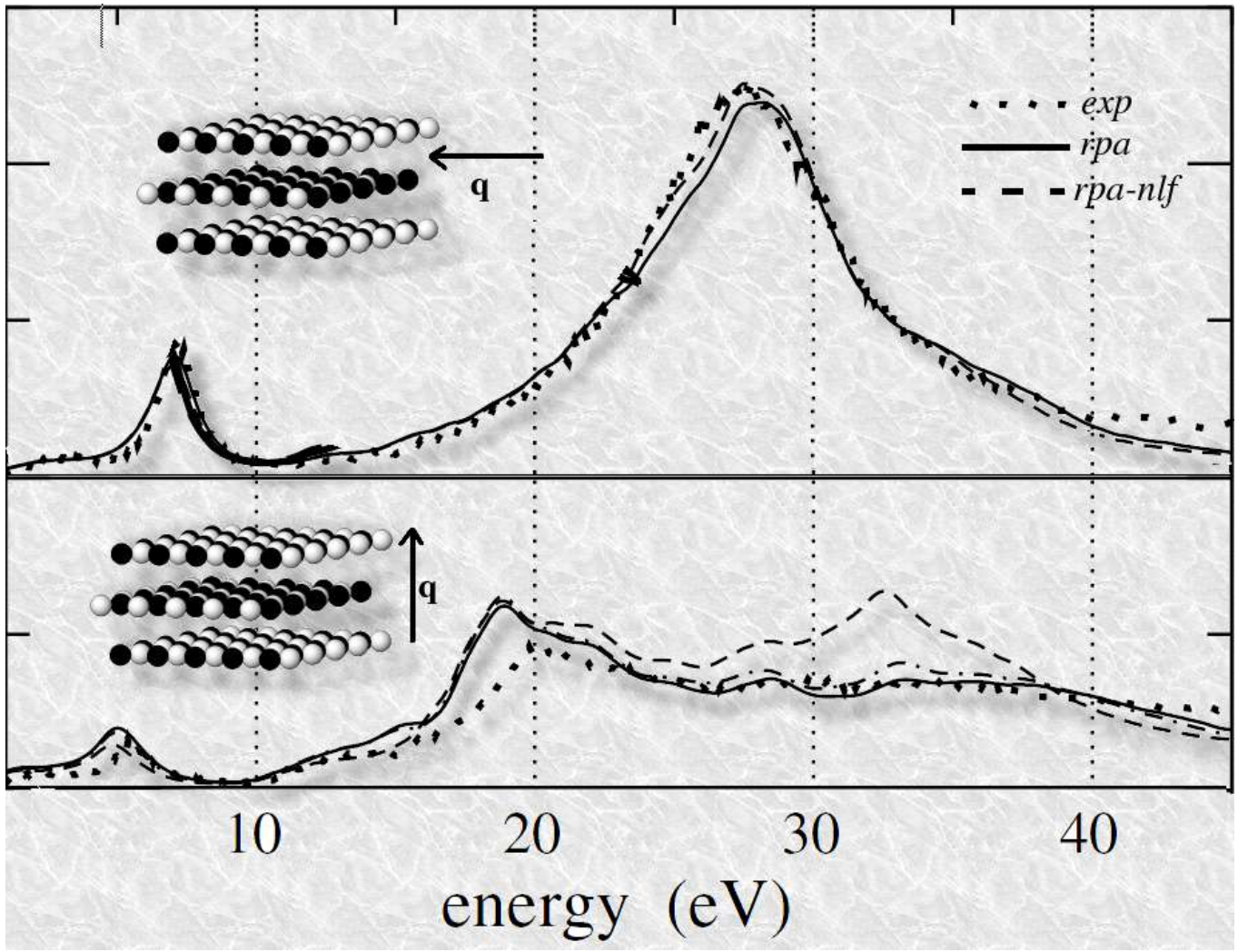
EELS

Optical Absorption

Refraction index

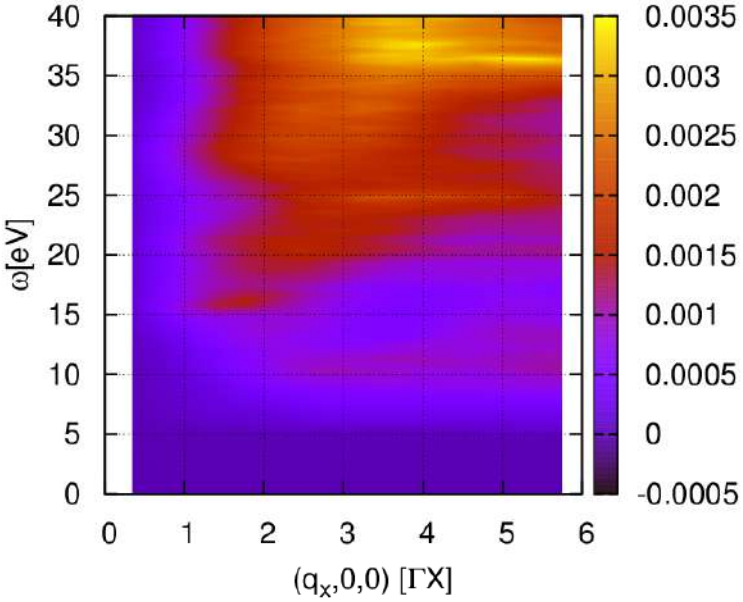
Photoemission spectroscopy

σ and π Plasmons of Graphite

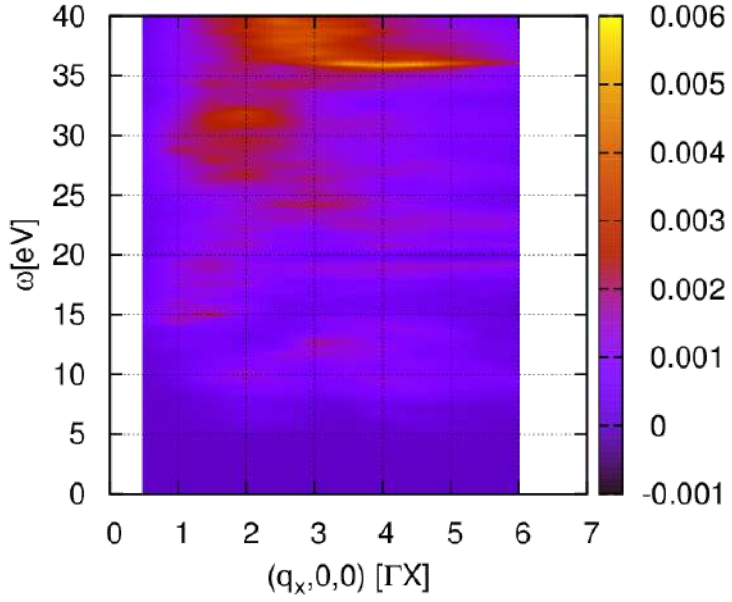


Plasmon Dispersion of Hafnia

monoclinic



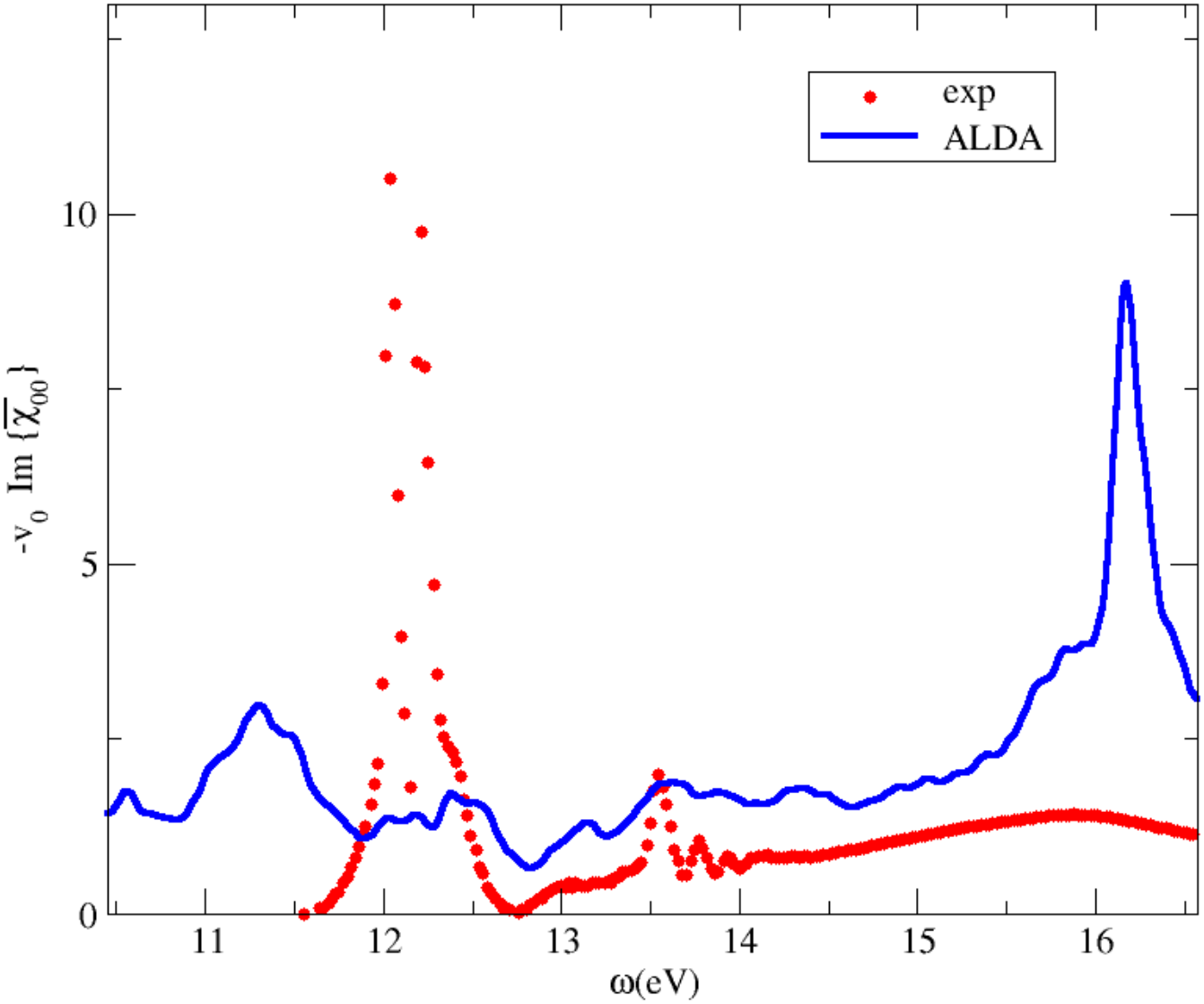
cubic



Collaboration with LETI-Grenoble

See Cyril Guedj's talk

Optical spectrum of Argon



Many Body Perturbation Theory

DFT + GW + BSE (q)

ground state

electronic band-structure

e-h (excitonic) interaction

ε {

IXS

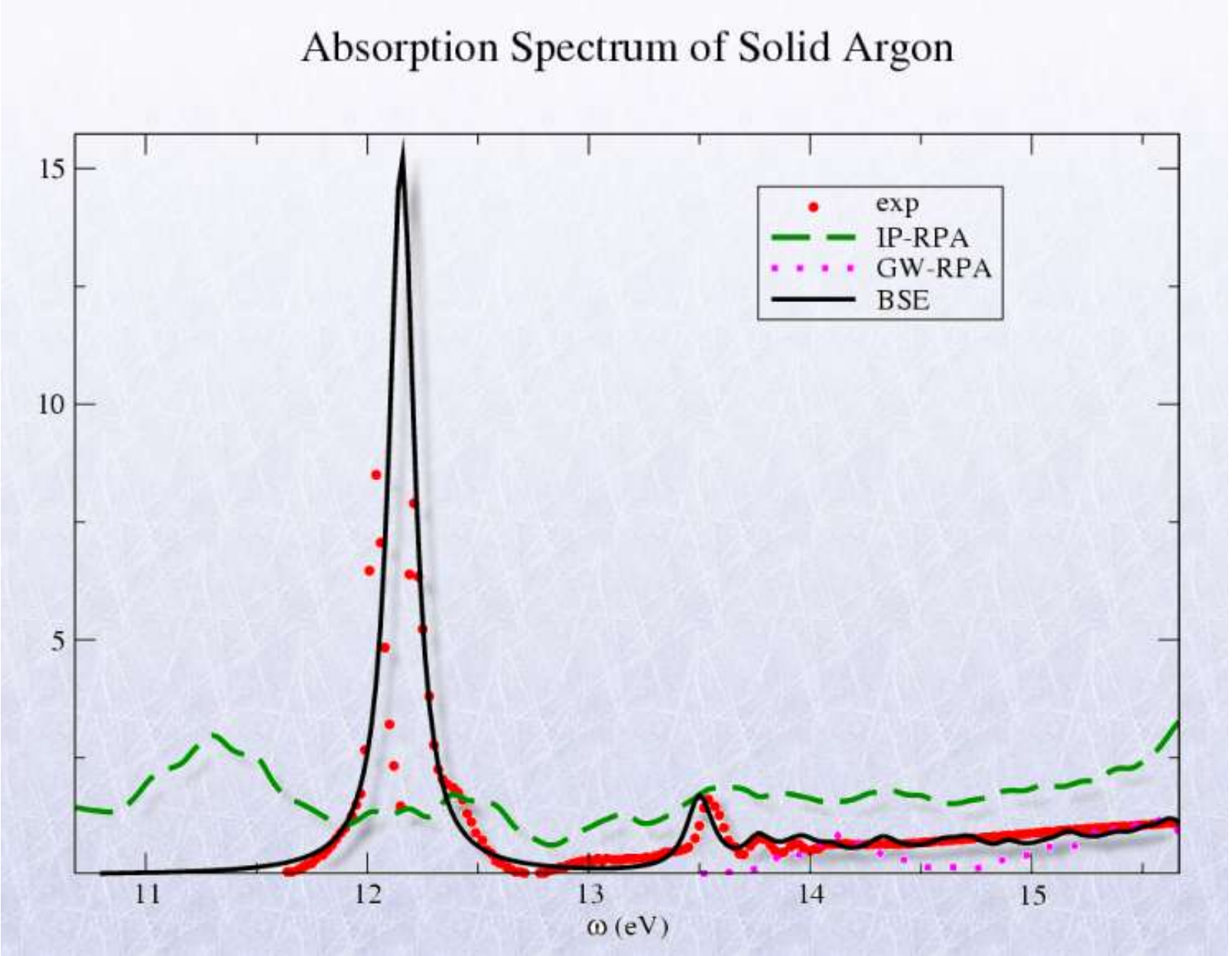
EELS

Optical Absorption

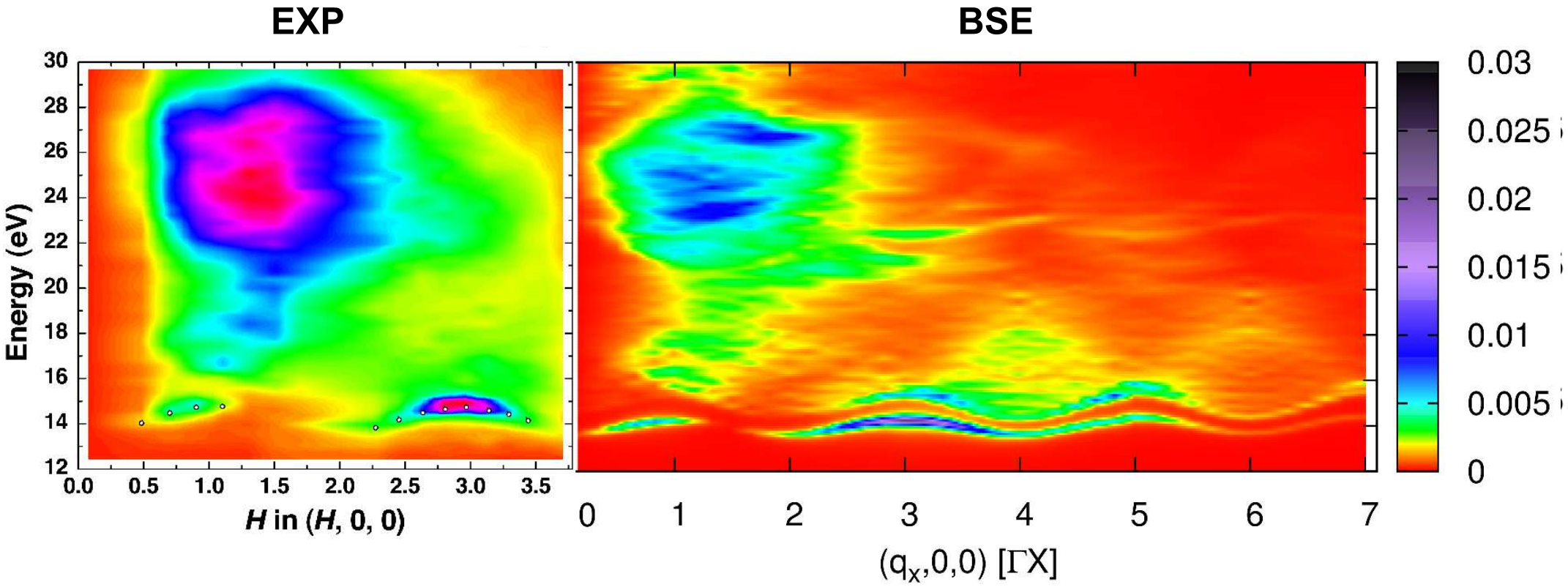
Refraction index

Photoemission spectroscopy

Optical spectrum of Argon

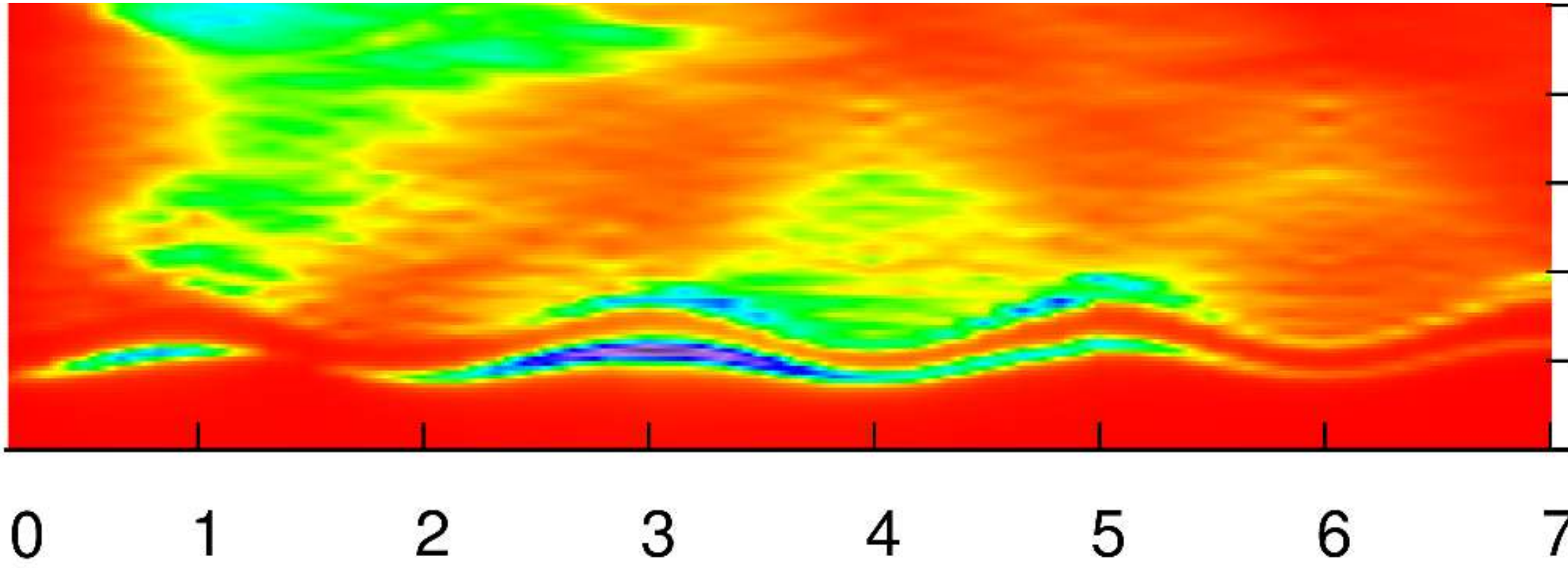


Dynamical Structure factor of LiF



P. Abbamonte et al. PNAS **105**, 12159 (2008);
Chi-Cheng Lee et al. PRL **111**, 157401 (2013)

M. Gatti and F. Sottile PRB **88**, 85425 (2013)


0
1
2
3
4
5
6
7
(q_x,0,0) [ΓX]

Analysis of the exciton dispersion

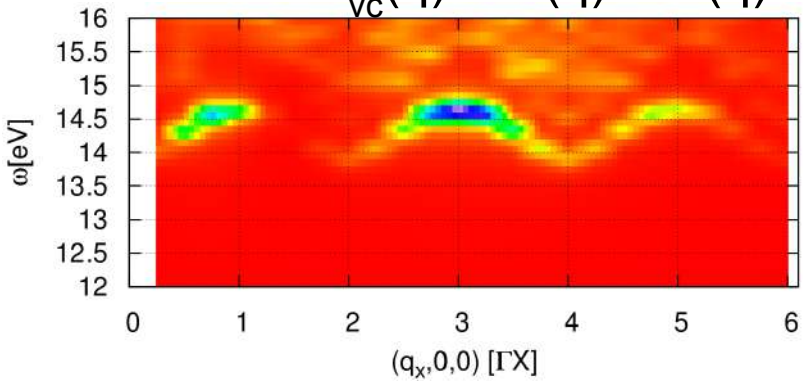
true bands

flat bands

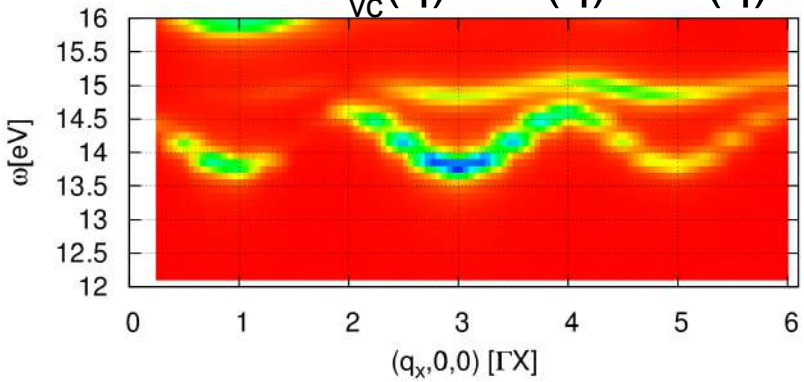
singlet

triplet

$H^{exc} = E_{vc}(q) + V(q) - W(q)$



$H^{exc} = \cancel{E_{vc}(q)} + V(q) - W(q)$



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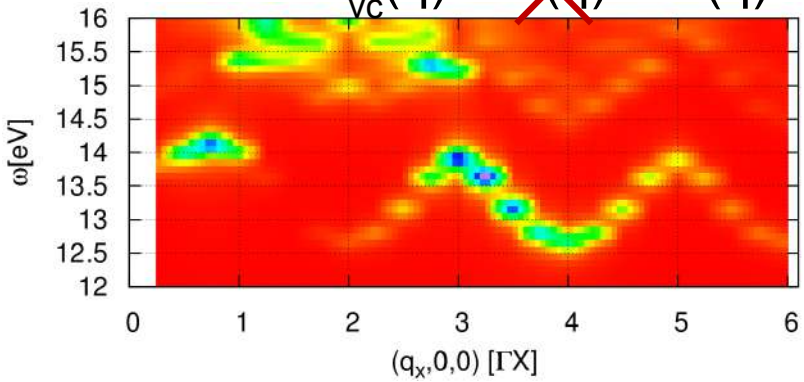

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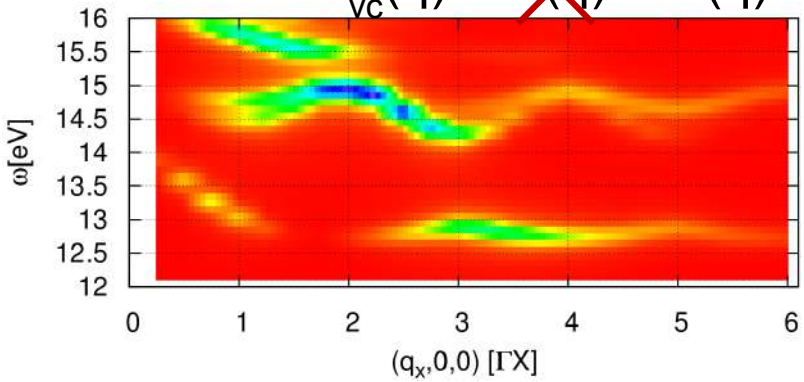

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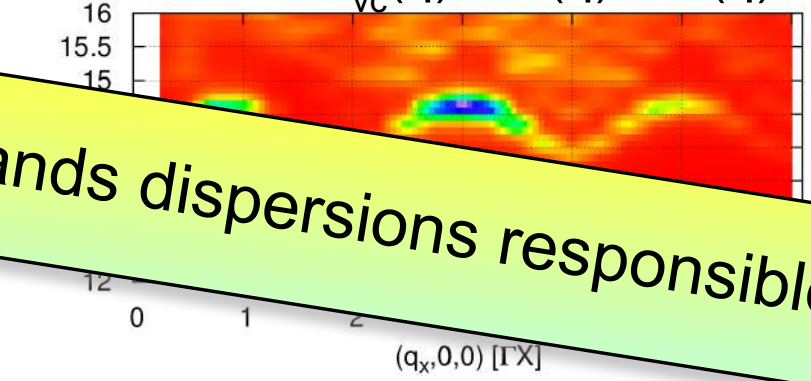

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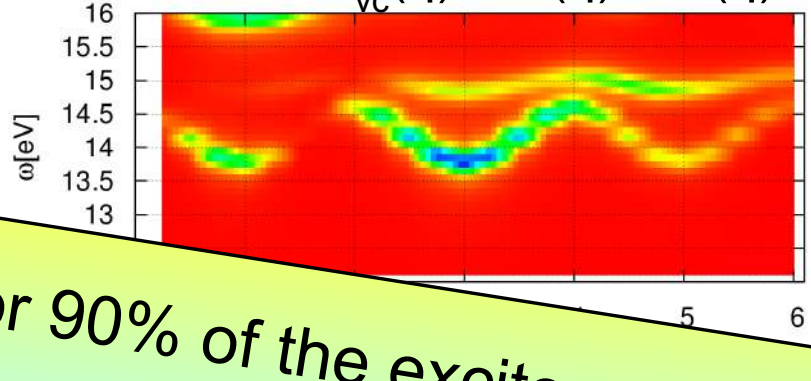

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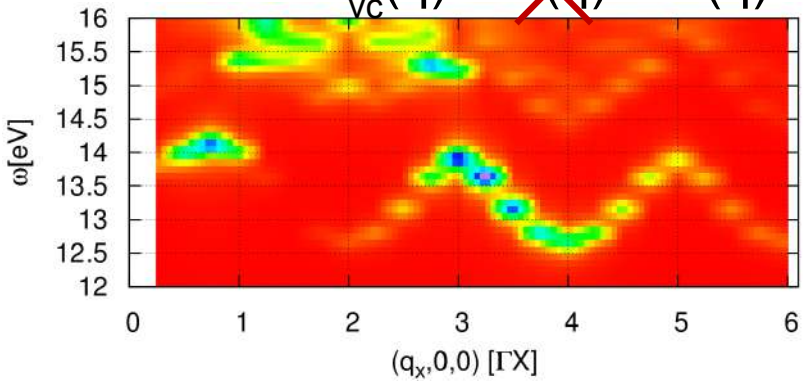
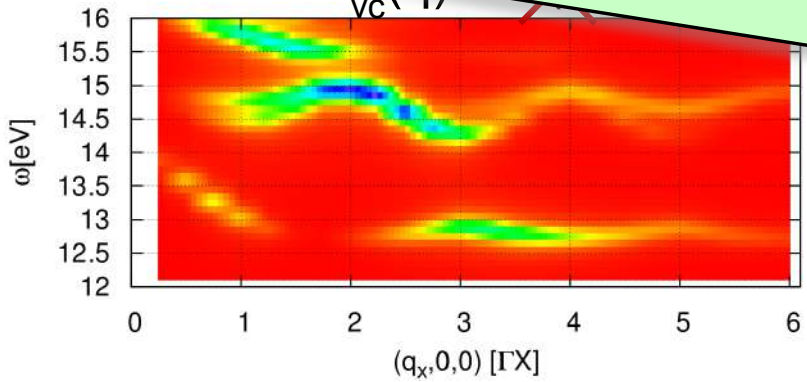
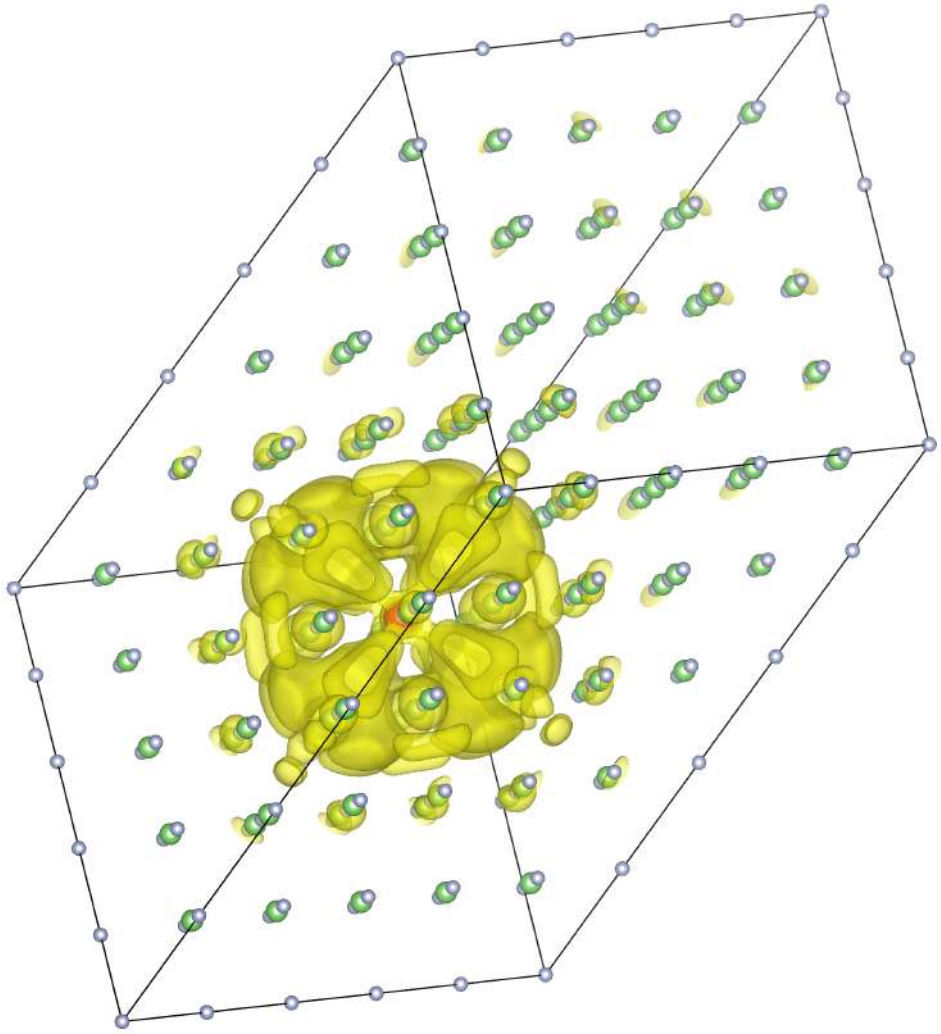


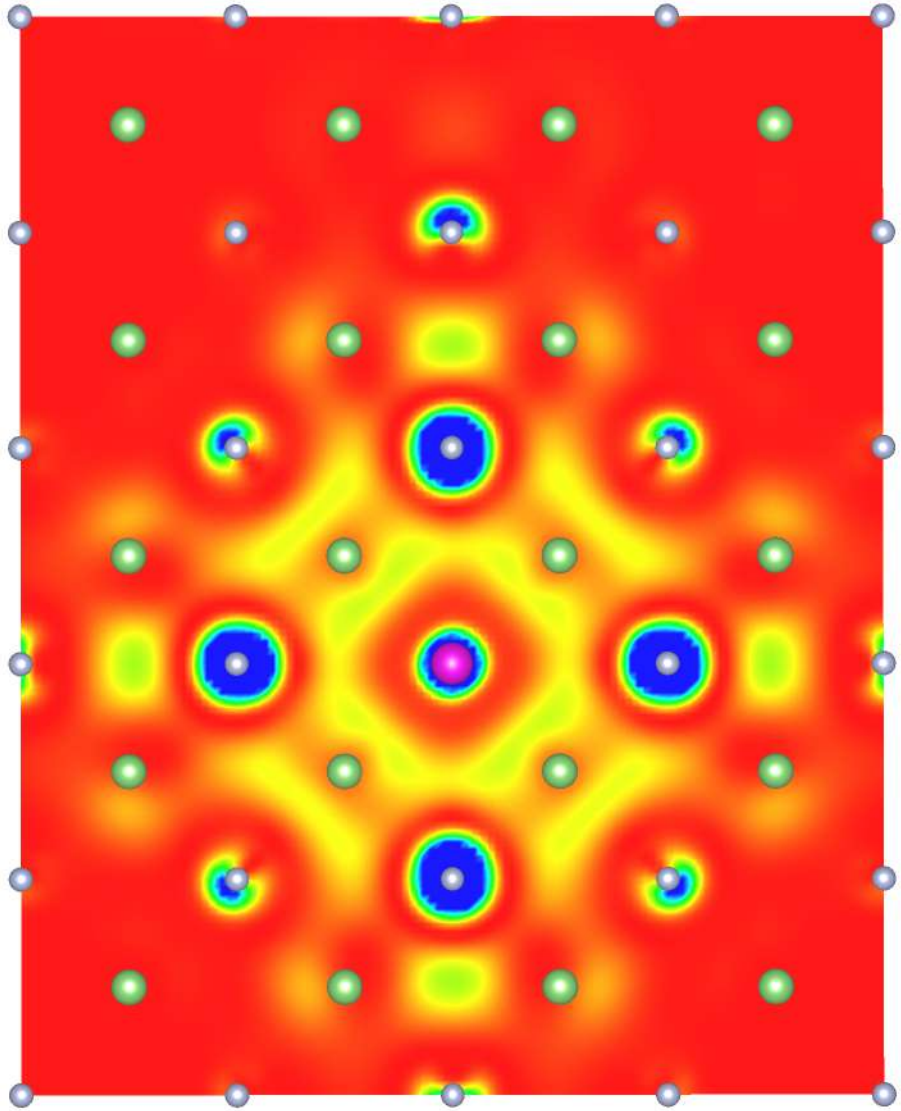
$H^{exc} = \cancel{E_{vc}(q)} \cancel{+ V(q)} - W(q)$



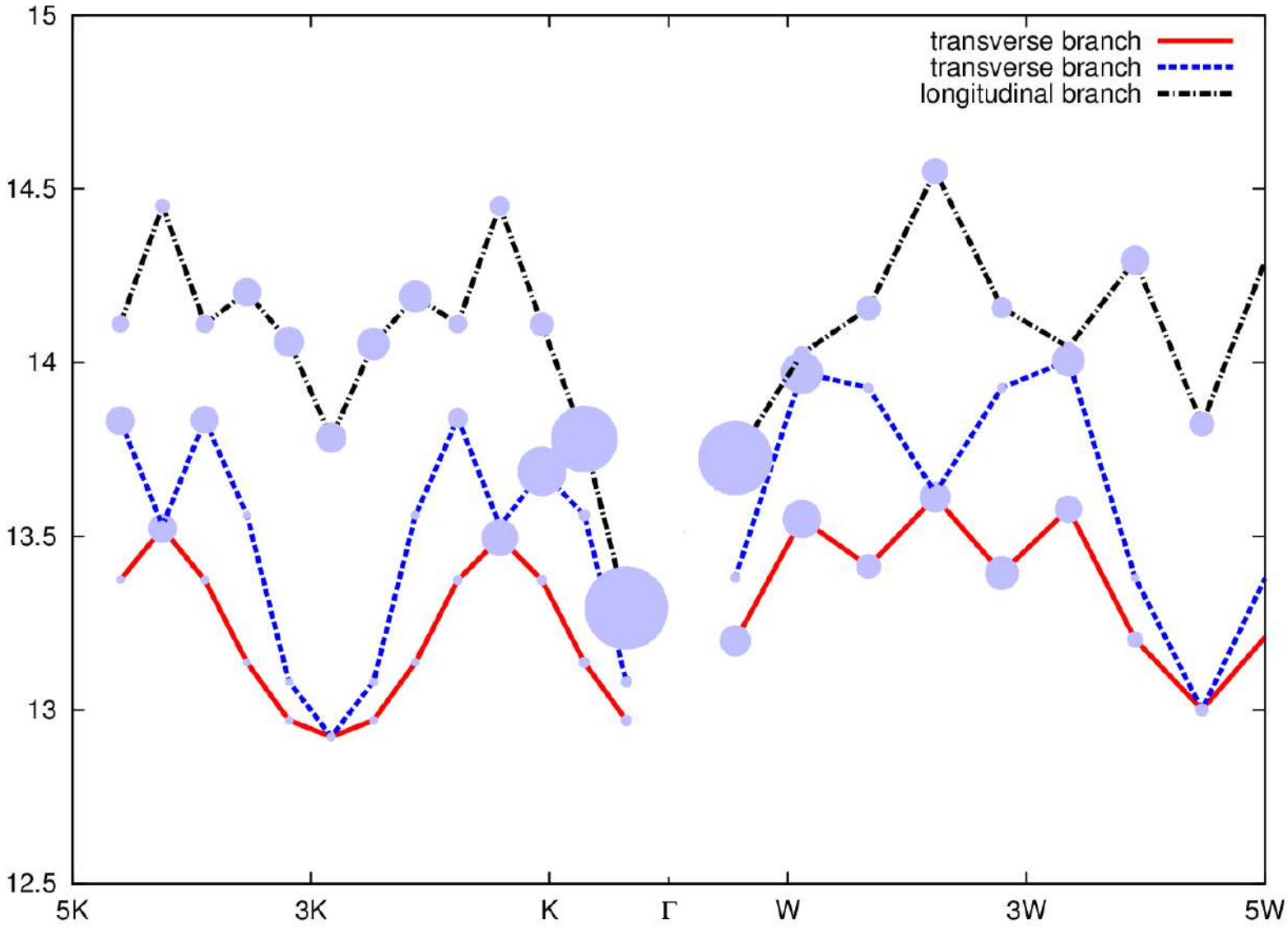
Bands dispersions responsible for 90% of the exciton dispersion

Excitonic wavefunction





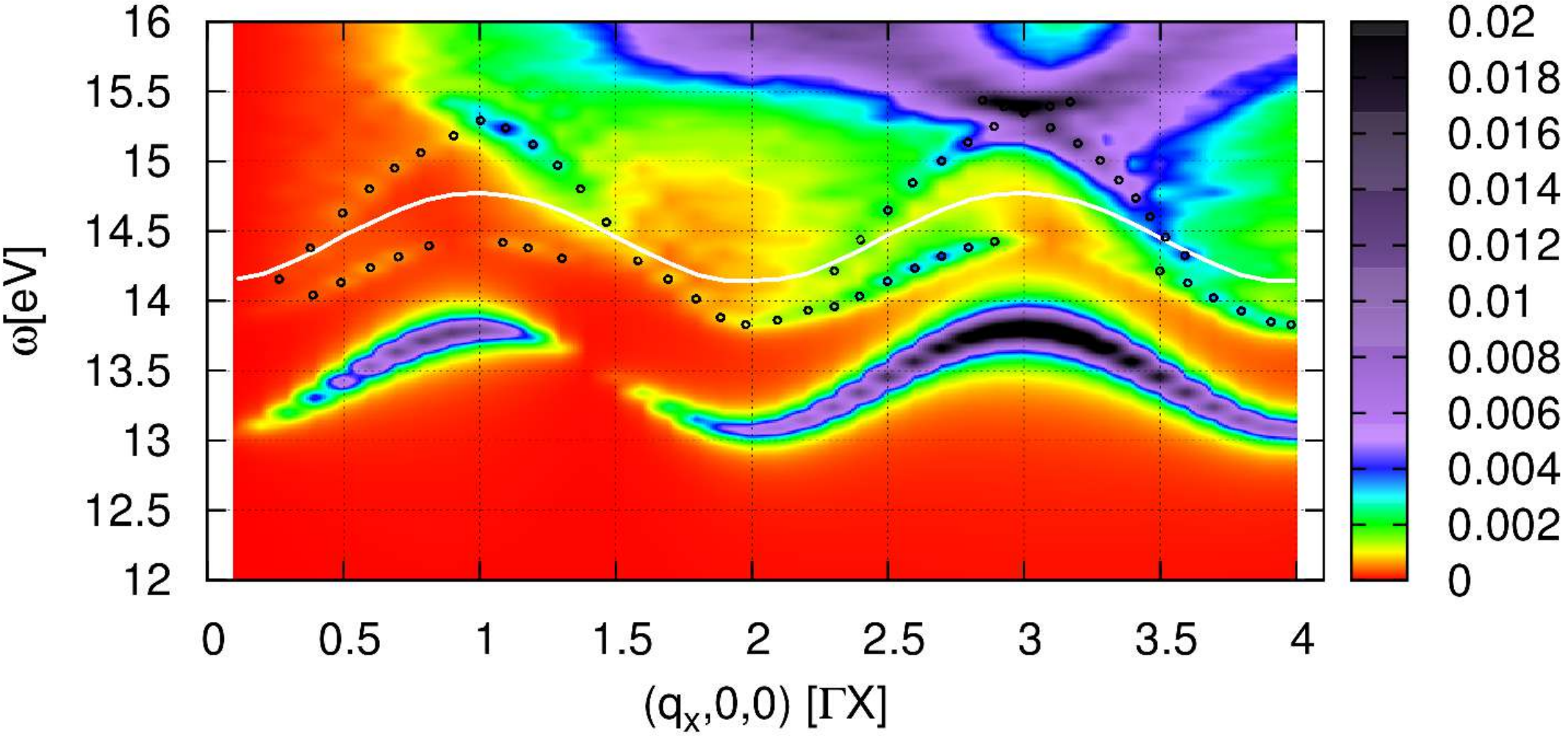
Excitonic bandstructure



Analysis ...

- mapping full momentum-energy dispersion
- analyse several features
  (localization, origin of the dispersion)
- full excitonic band-structure

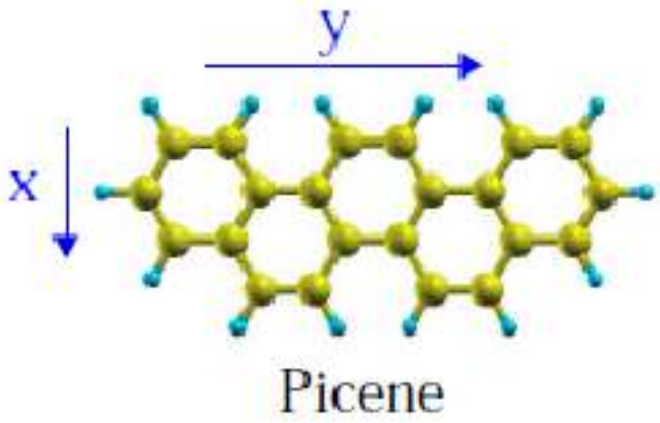
Predictions for Solid Argon

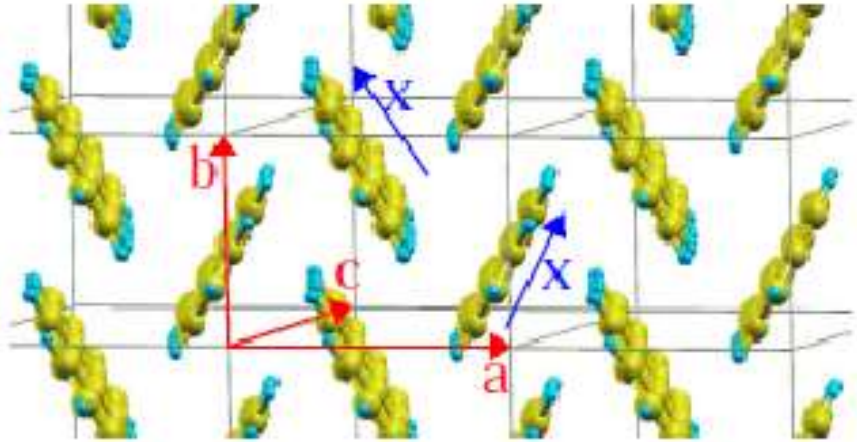


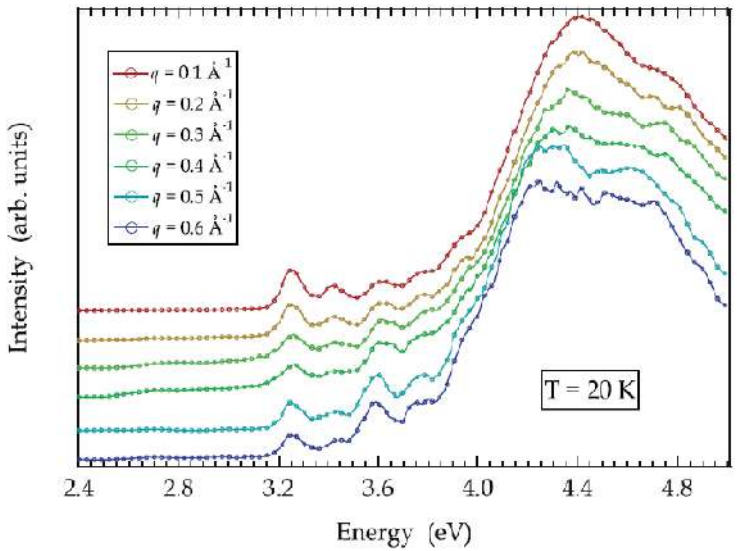
OK for big momentum transfer (with IXS)

What about for small q ? EELS ?

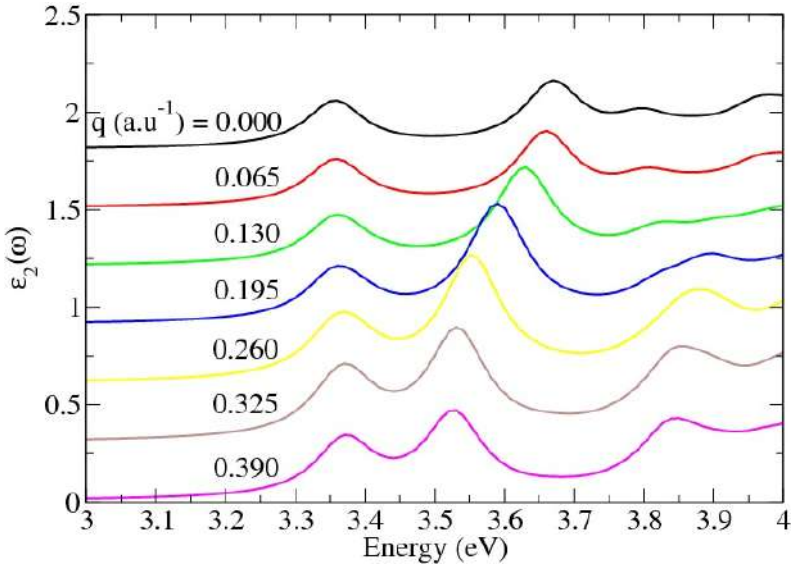
The case of Molecular Solids







EELS

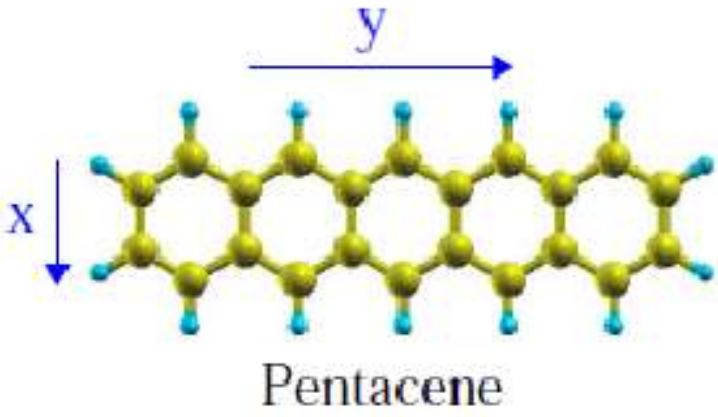


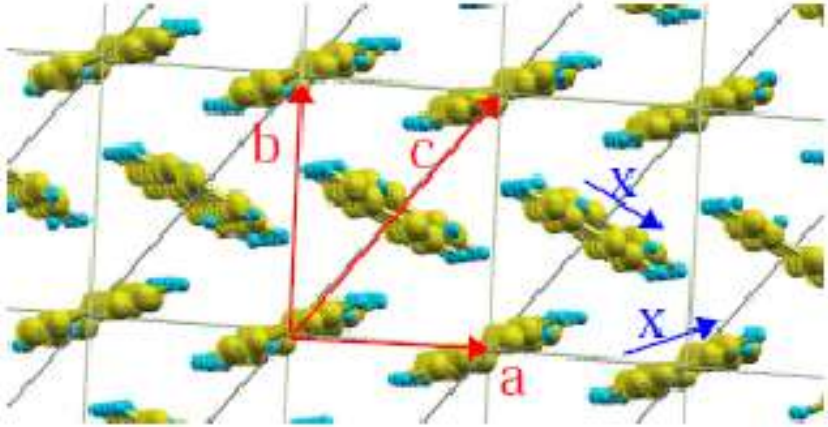
BSE

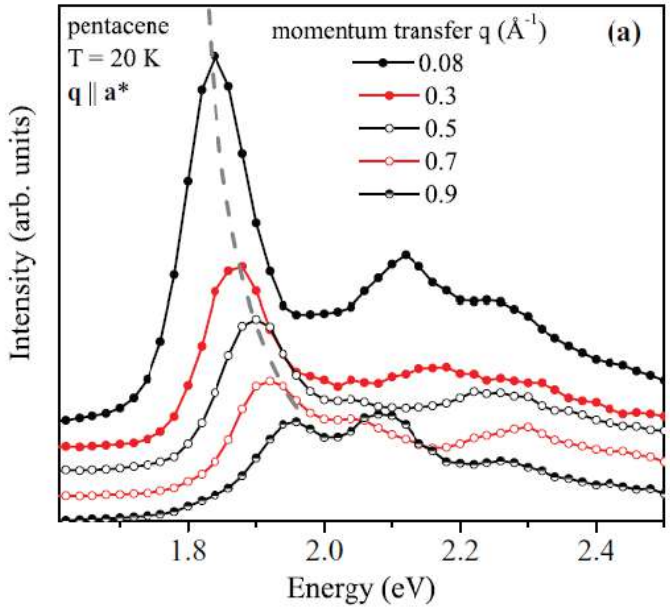
From F.Roth et al. PRB **83** (2011), JCP **136** (2012).

P. Cudazzo, M. Gatti, A. Rubio and F. Sottile, PRB **88**, 195152 (2013)

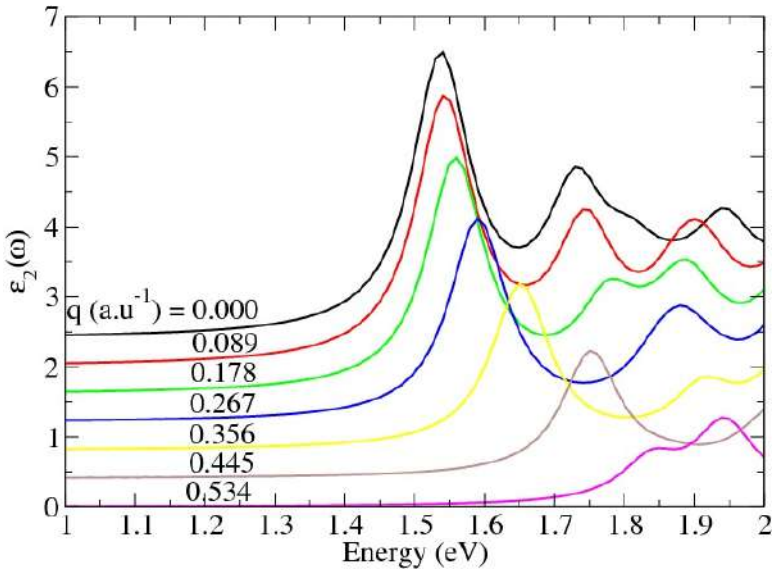
The case of Molecular Solids







EELS



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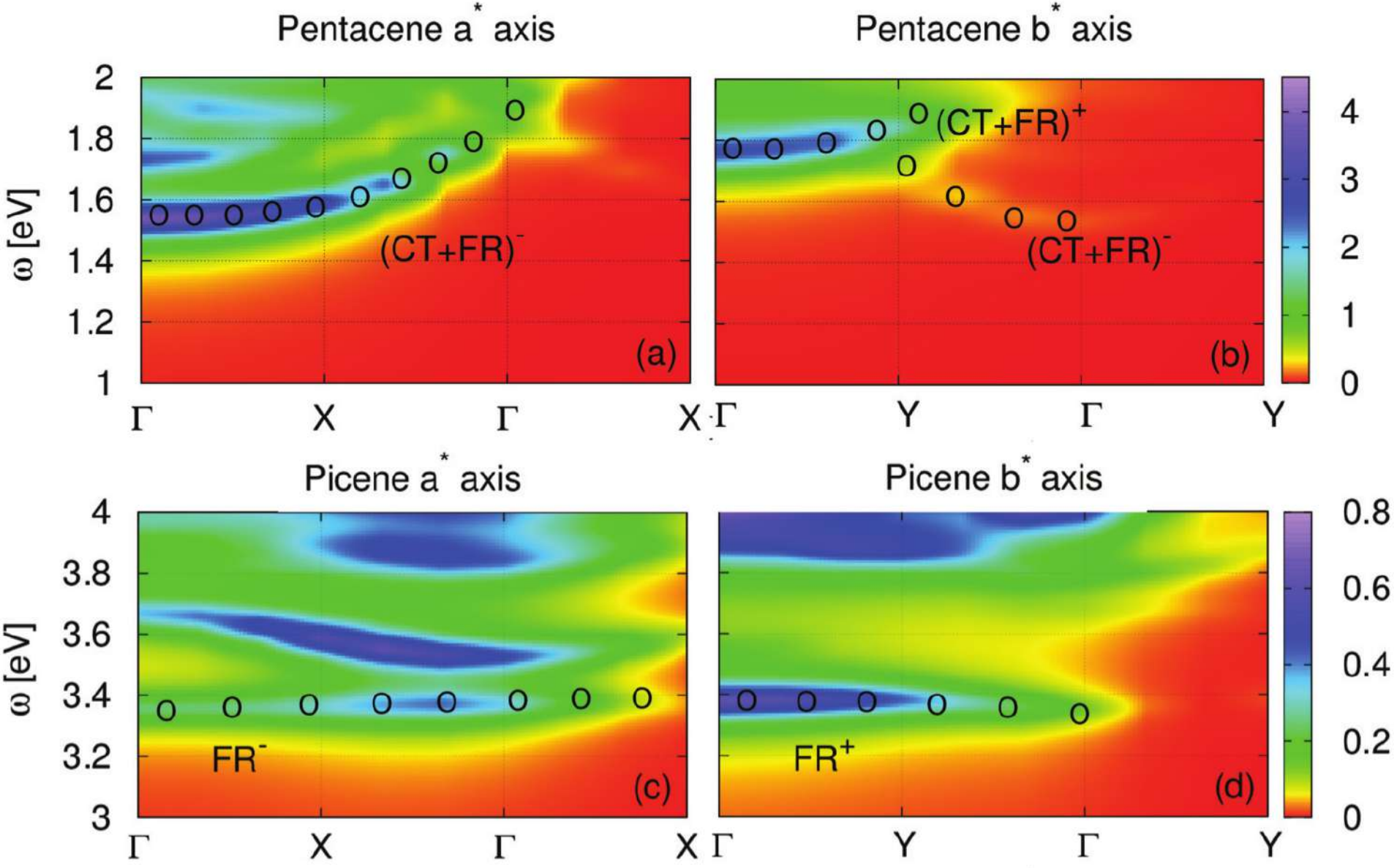
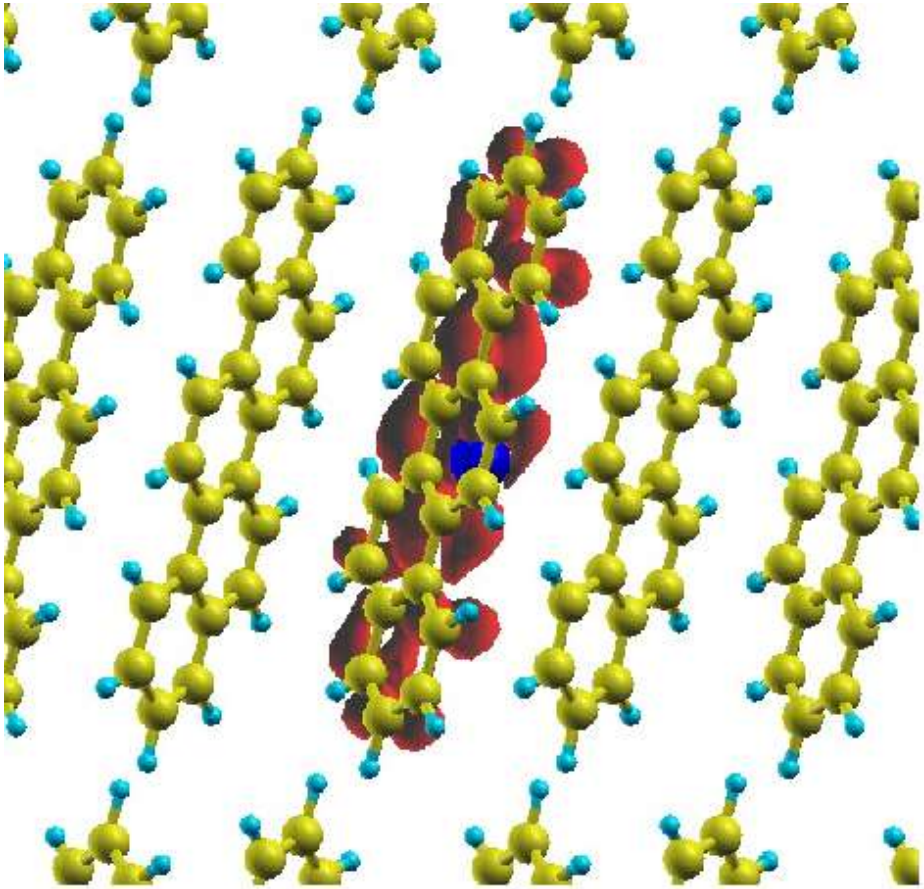
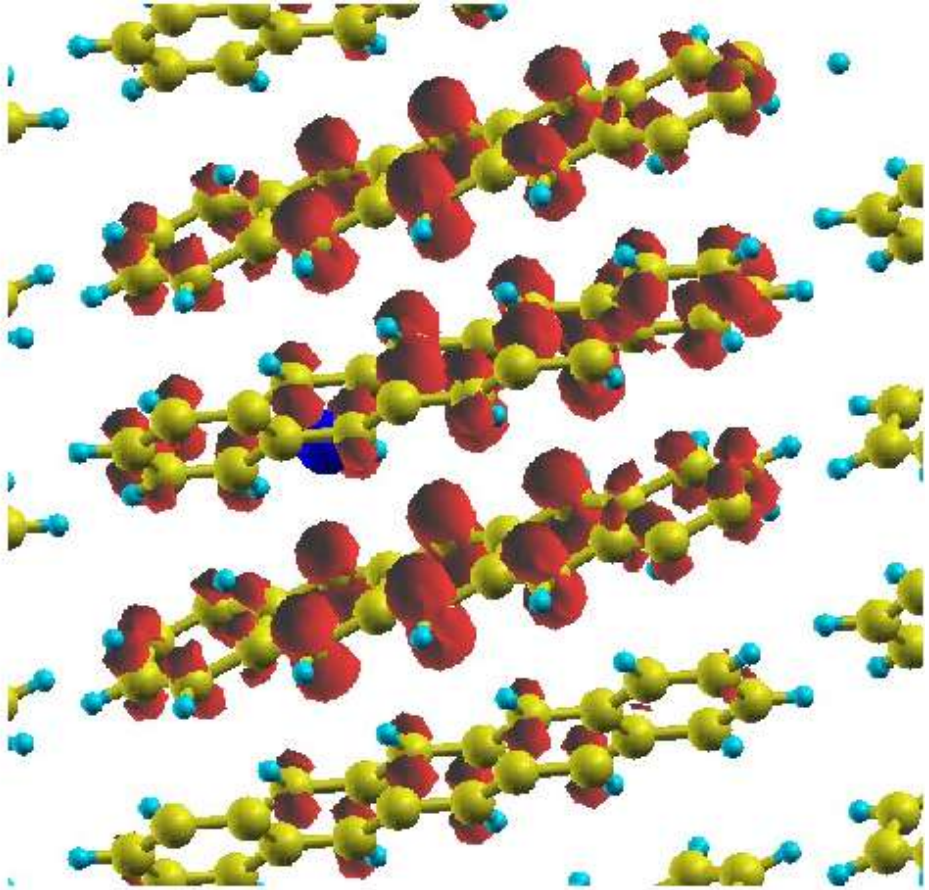


P. Cudazzo, M. Gatti, A. Rubio and F. Sottile, PRB **88**, 195152 (2013)

The case of Molecular Solids

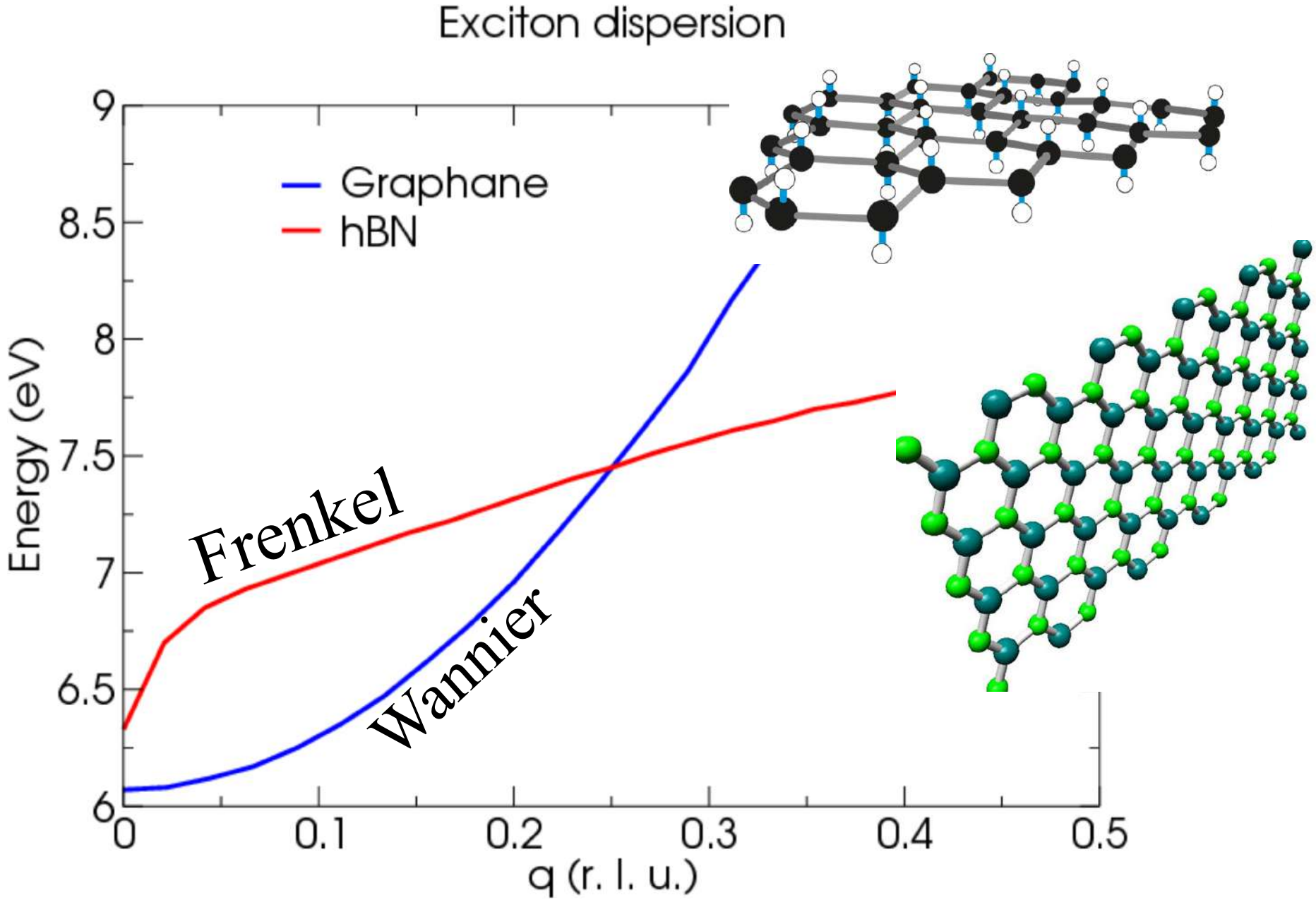


Picene



Pentacene

Theoretical (preliminar) predictions of 2D exciton dispersion



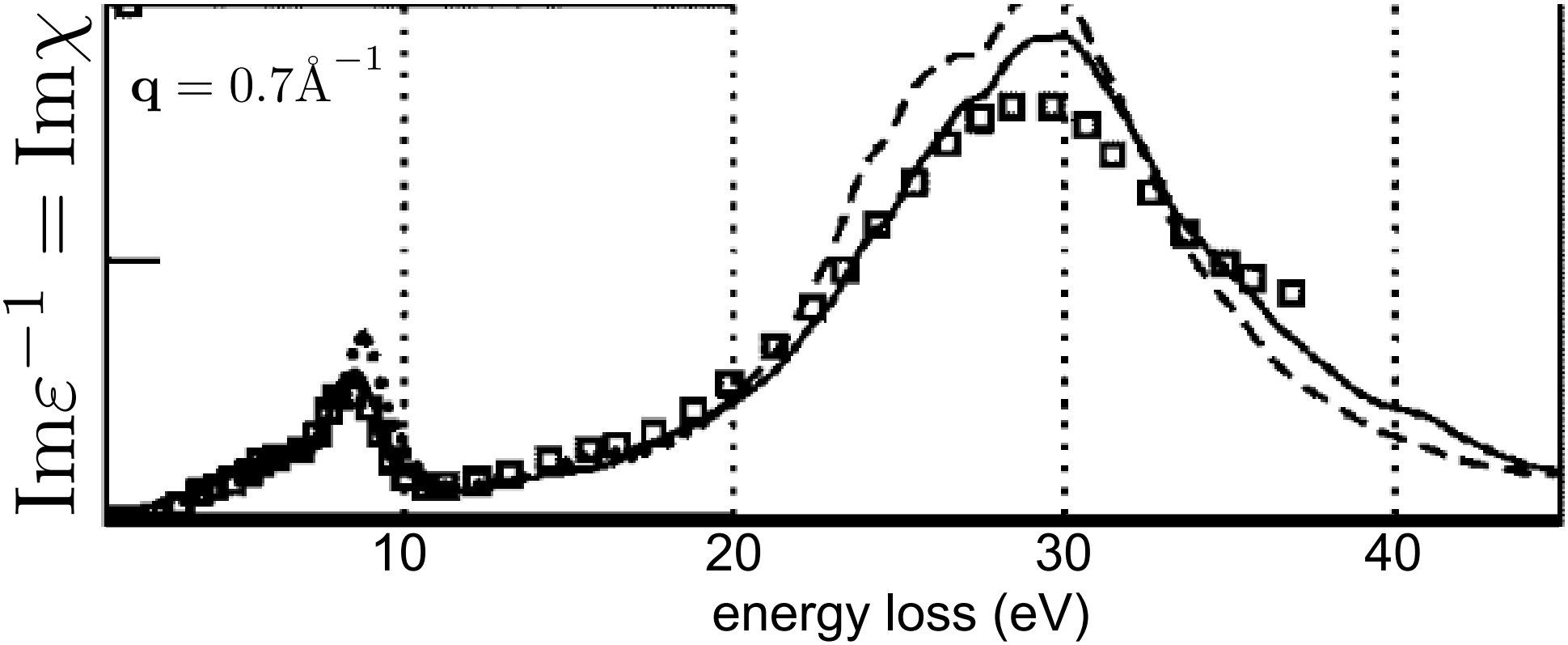
Ongoing with Giorgia Fugallo and Pierluigi Cudazzo

Outline

- Exciton Dispersion — Analysis and Predictions
- **Visualization of orbitals** — Visualization and Proposition
- Nanotubes from Graphene — Tools and Tricks
- EELS for Photoemission — Exp. Complementarity

Visualization of Plasmons

Graphite



U.Büchner, Phys. Status Solidi B 81, 227 (1977).

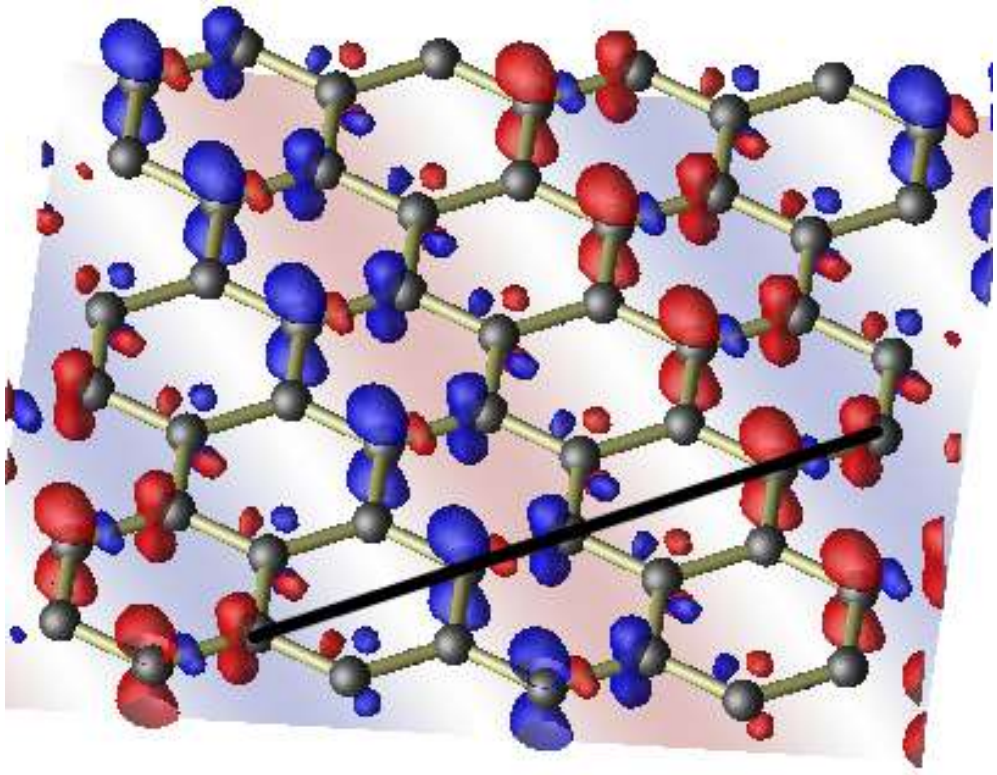
Visualization of Plasmons

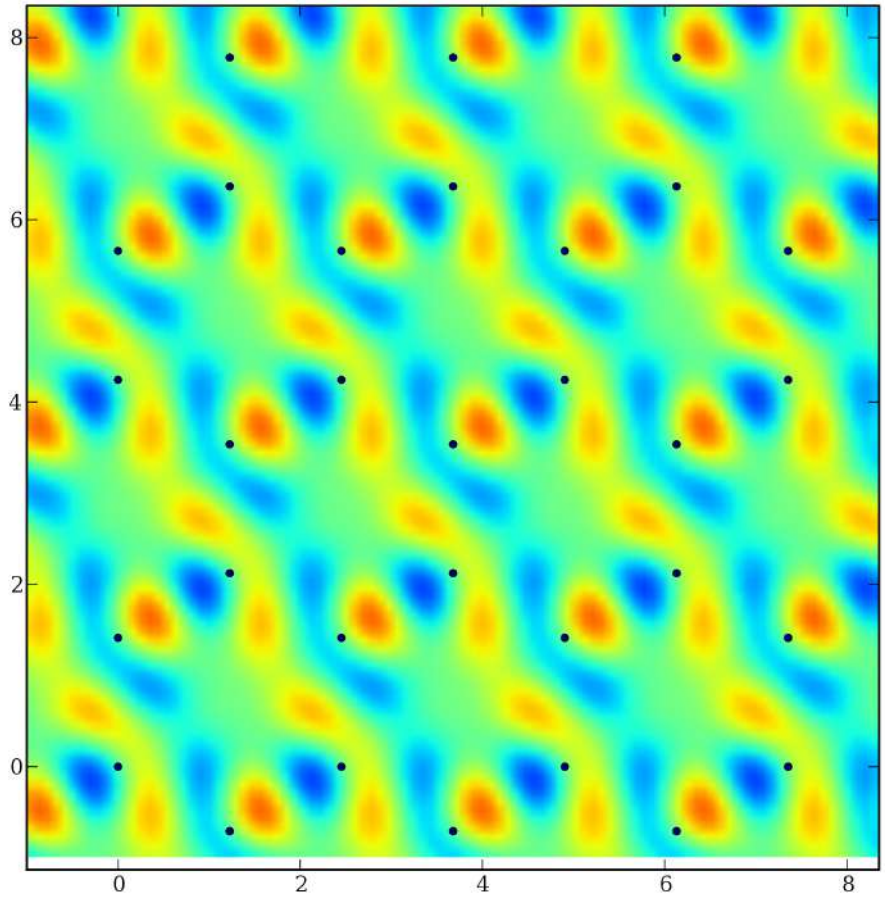
$$\rho_{\mathrm{ind}} = \chi V_{\mathrm{ext}}$$

$$V_{\mathrm{ext}} = e^{i(\mathbf{q}\cdot\mathbf{r} - \omega t)}$$

Visualization of Plasmons

π Plasmon



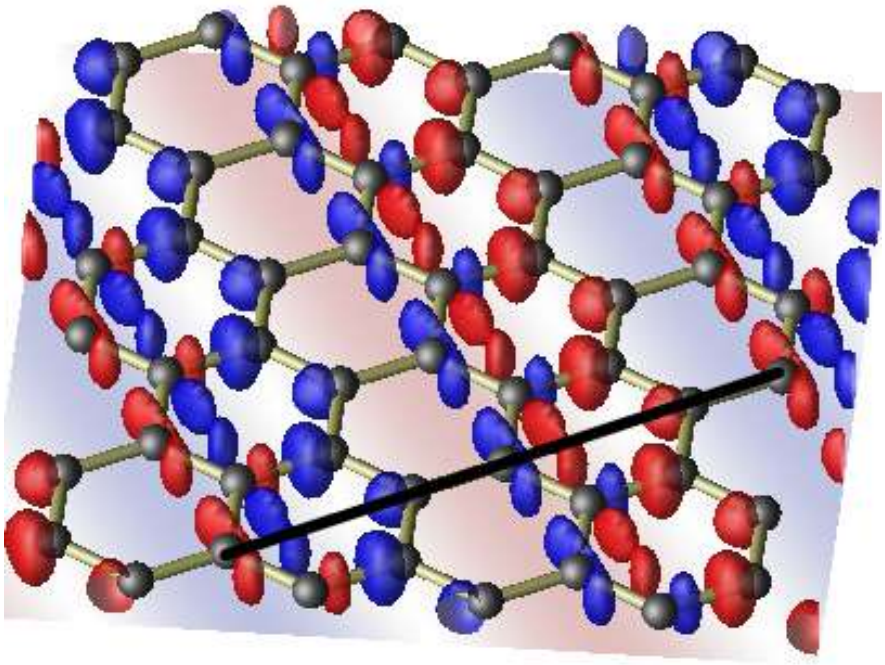


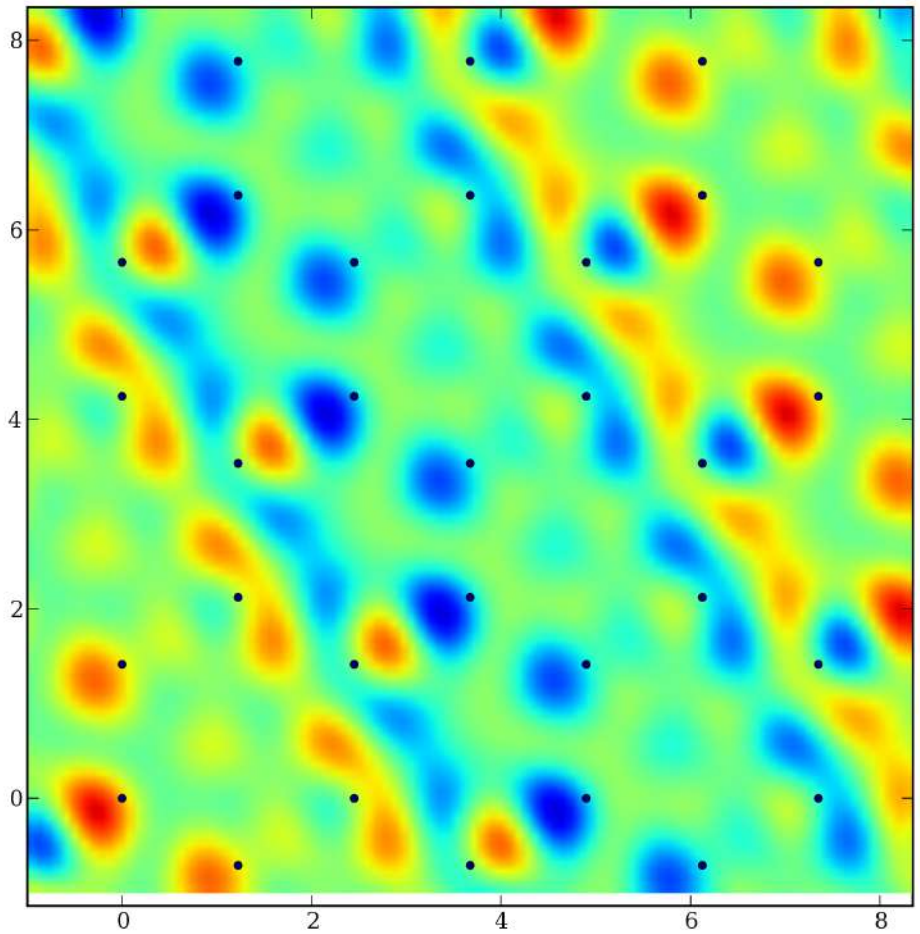
$\mathbf{q} = 0.7\text{Å}^{-1}$ ω = 9 eV

R. Hambach (PhD Thesis). G. Pegolotti (Master Thesis)

Visualization of Plasmons

π+σ Plasmon

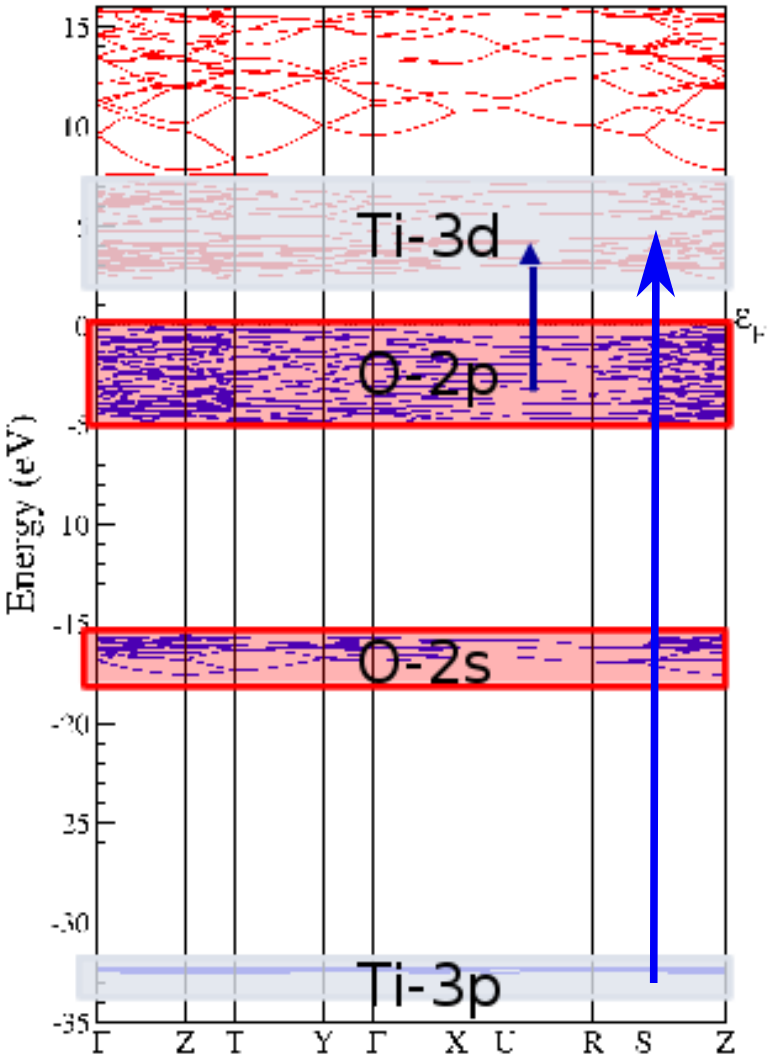




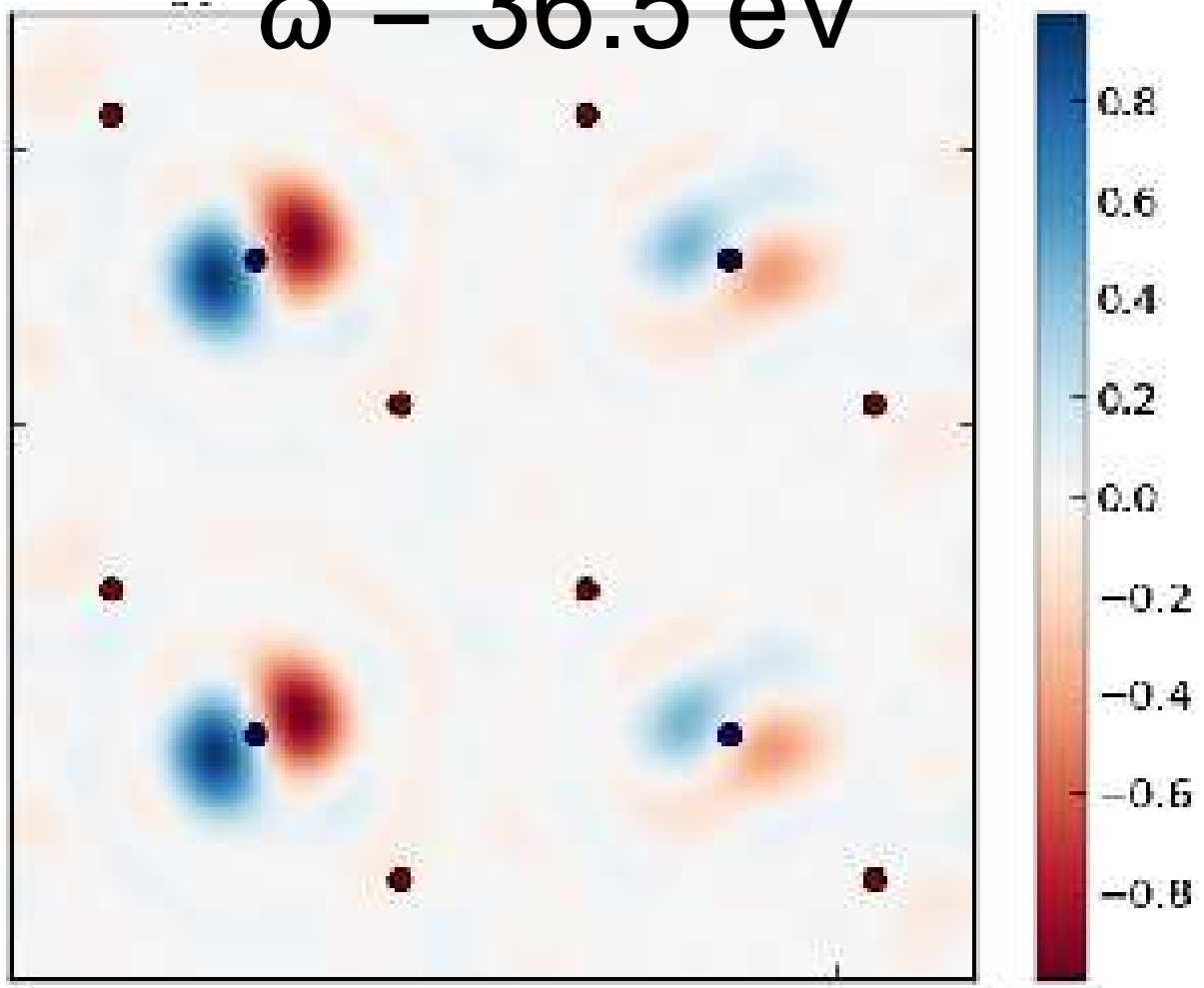
$\mathbf{q} = 0.7\text{Å}^{-1}$ ω = 30 eV

R. Hambach (PhD Thesis). G. Pegolotti (Master Thesis)

Visualization of Orbitals :: TiO_2



ω = 36.5 eV



L. Hung, C. Roedl, R. Hambach, L. Reining, FS (to be submitted)

Proposition :: non-diagonal Response

$$\rho^{\mathbf{q}}_{\mathrm{ind}}(\mathbf{r}) = \sum_{\mathbf{G}} \chi_{\mathbf{G}\mathbf{G_0}} e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$$

Interference of two plane-waves on the EELS detector, using Bragg diffraction, to measure $\varepsilon^{-1}(\mathbf{q}, \mathbf{q}+\mathbf{G})$

Ongoing :: non-diagonal response of Silicon in collaboration with G.Monaco and S. Huotari

Proposition :: non-diagonal Response

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Measuring Circular Dichroism using STEM

See Xiaoxiao's poster.

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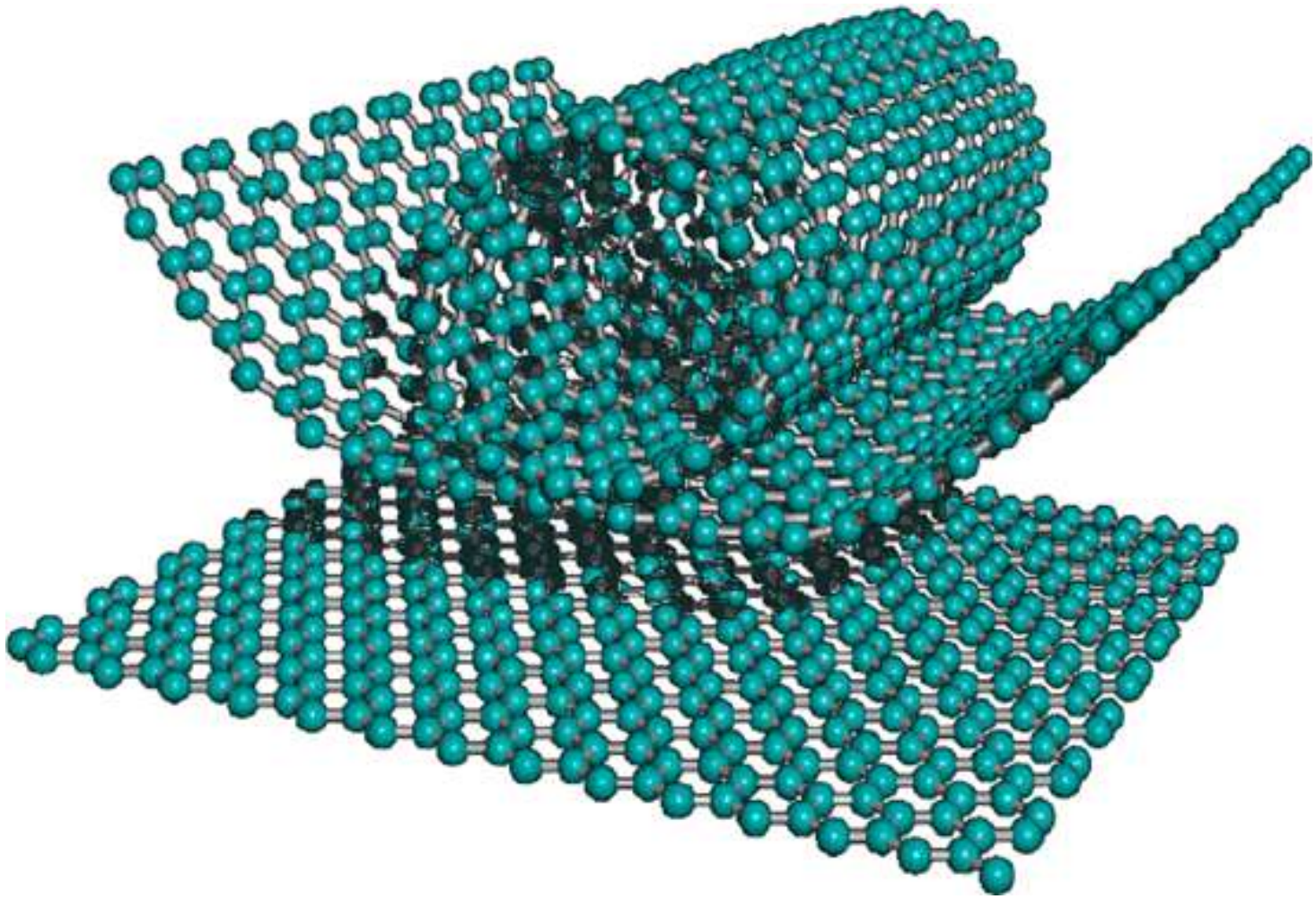
Nanotubes from Graphene

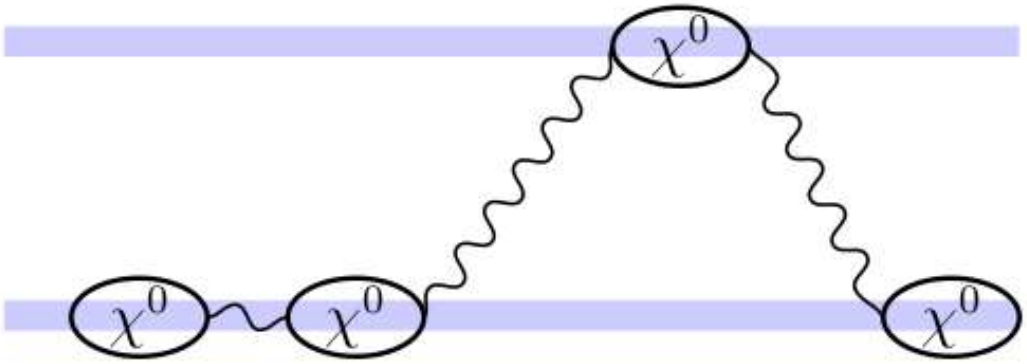


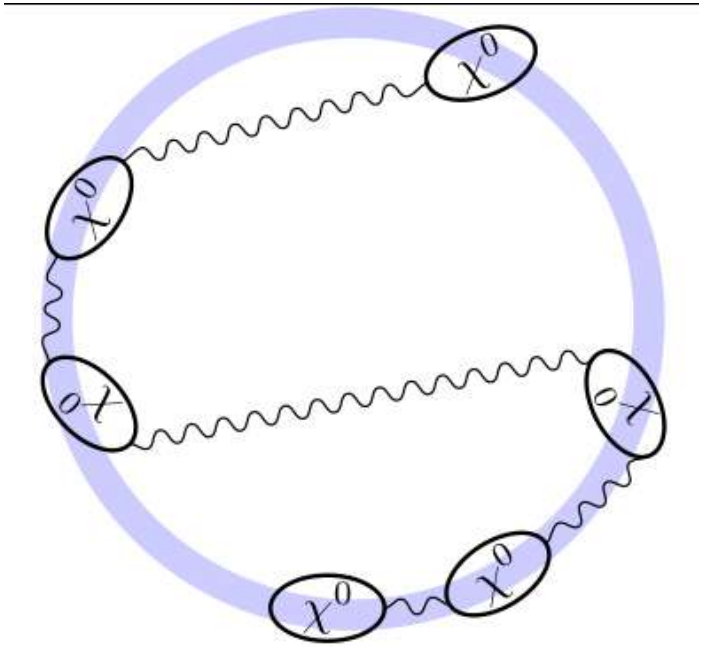
Can we *really* do that?

Nanotubes from Graphene

$$\varepsilon^{-1} = 1 + v\chi \qquad \chi = \chi^0 + \chi^0 v\chi$$

χ^0 { cumbersome calculation
local





Zone Folding Method

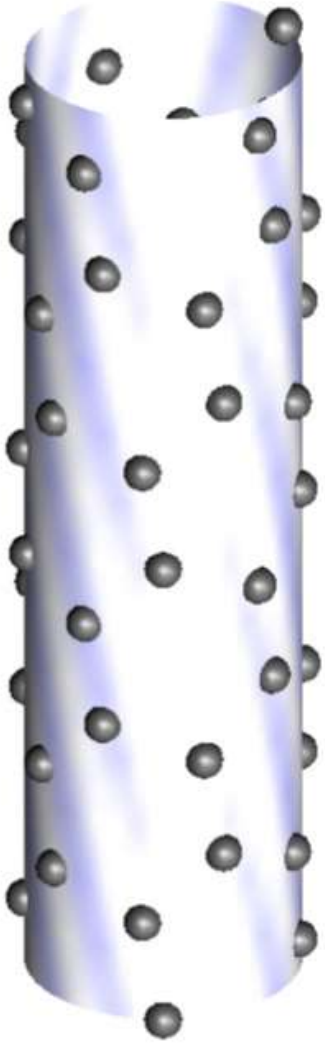
real space: cylinder coordinates (ϱ, φ, z)

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

reciprocal space: helical momentum (m, p)

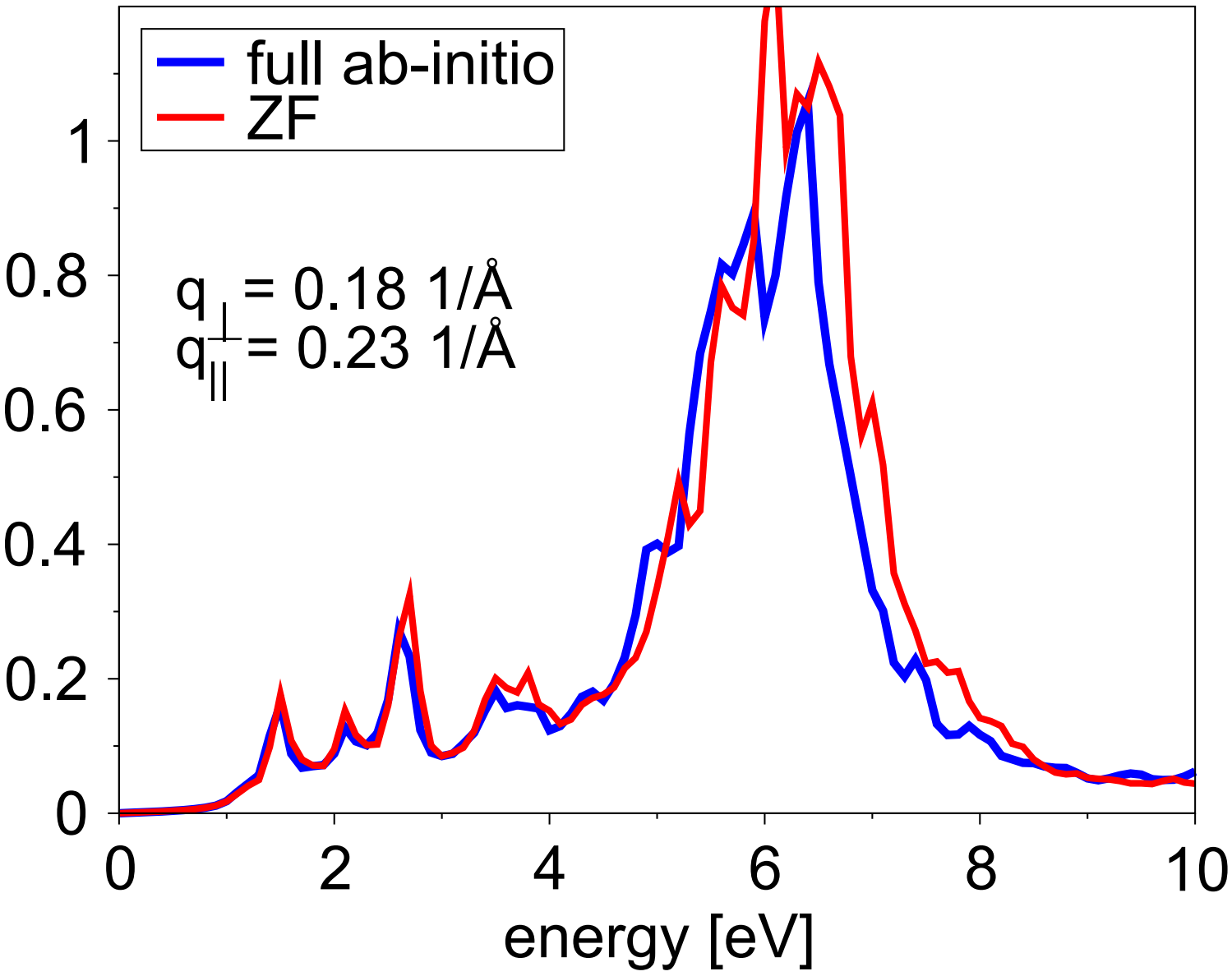
$$\chi^0(mm'pp'; \varrho\varrho', \omega) \cdot \varrho' \approx \chi^0_{\text{sheet}}(q_x q'_x, q_y q'_y; zz', \omega)$$

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



R. Hambach (PhD Thesis).

Zone Folding Method

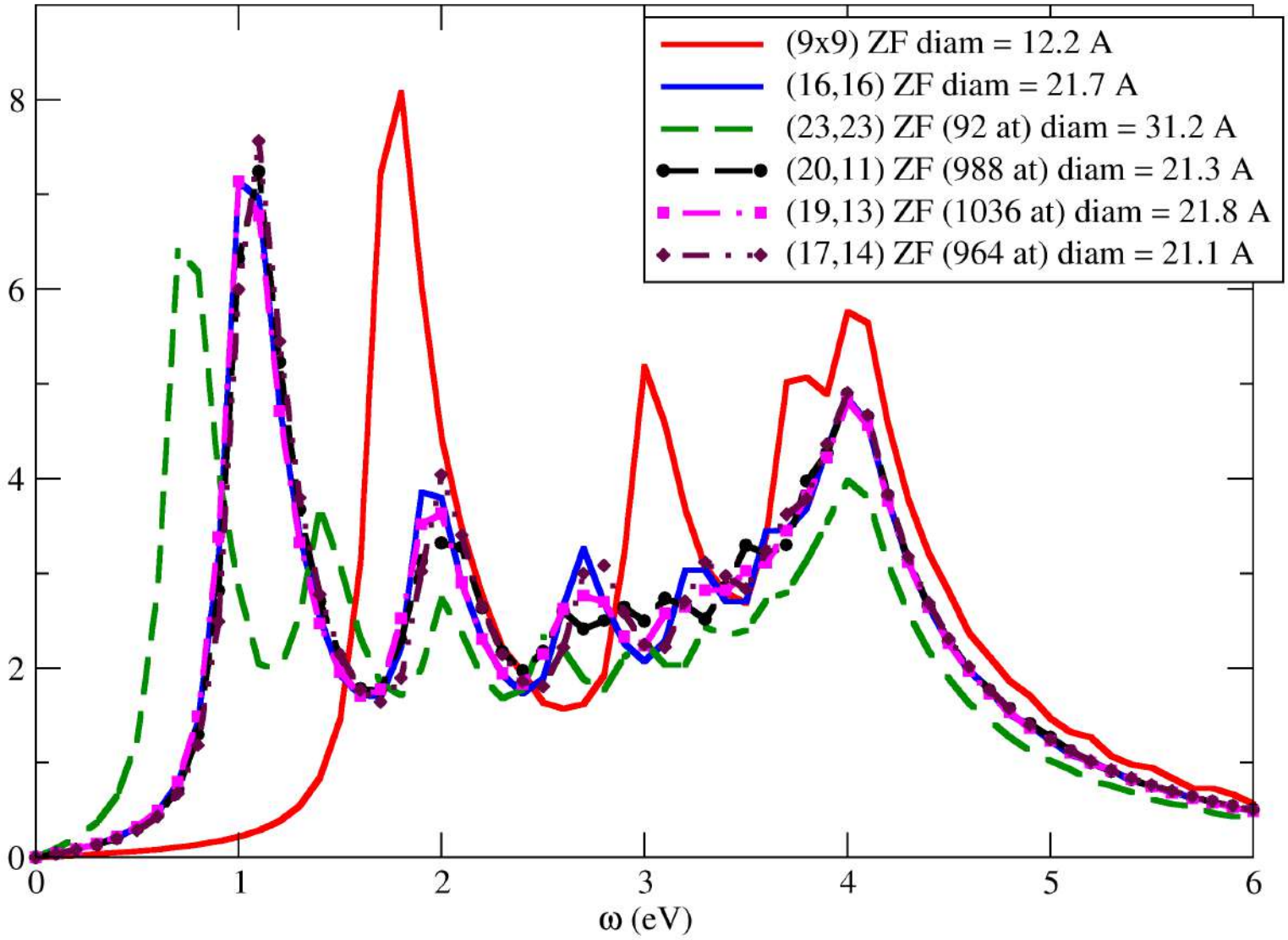


9x9

SWCNT

EELS

Zone Folding Method



Prediction for bigger tubes: size matters

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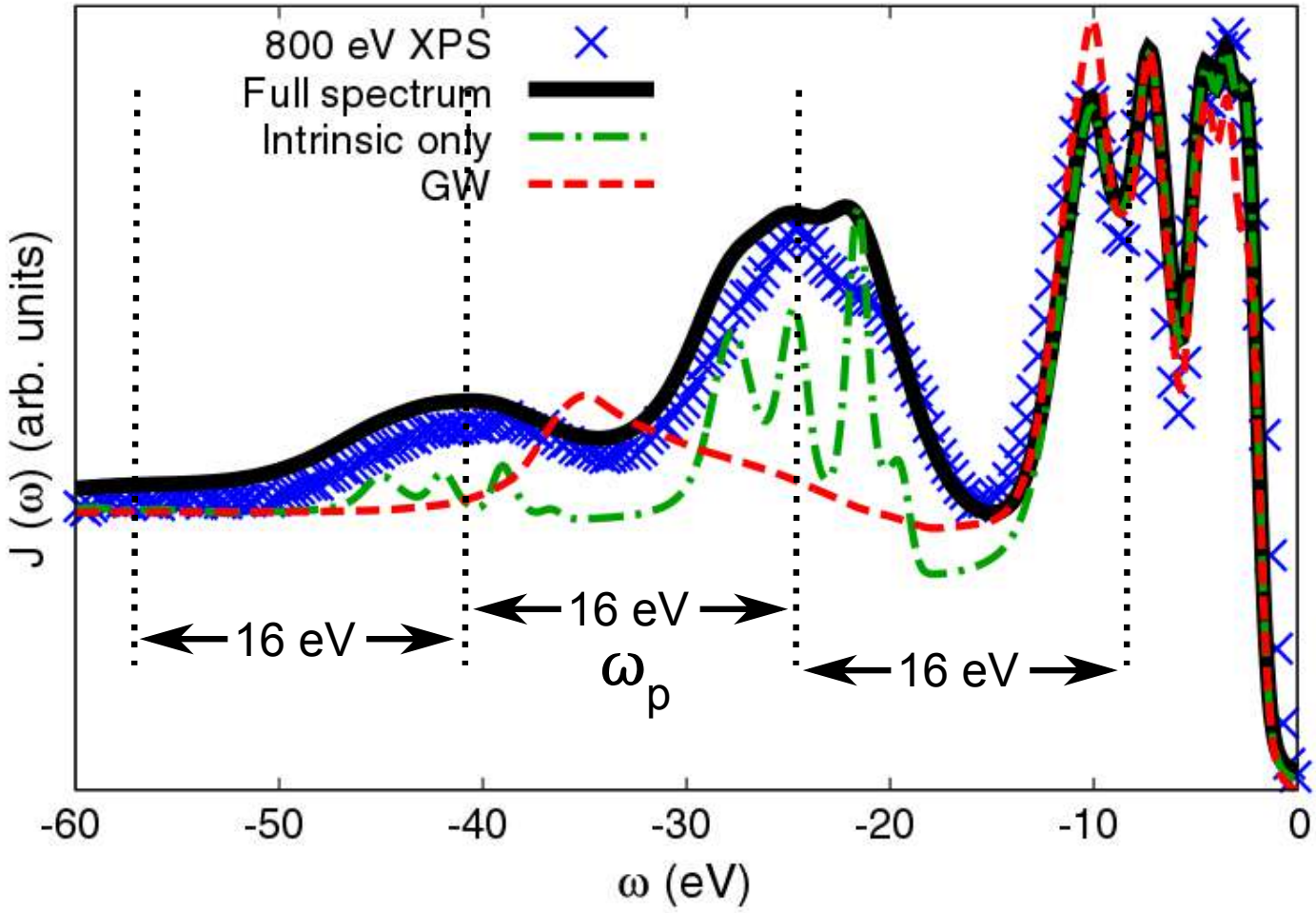
EELS for Photoemission

Silicon PES

Plasmon Satellites

Main ingredient ::
Loss function



M. Guzzo et al. PRL **107**, 166401 (2011).

Summary

- **Hérésie 1** — Richness of valence electron excitations
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- **Vérité fondamental** — Dans une conf de microscopie il faut faire semblant de supporter l'équipe de France pour avoir un verre de Champagne de plus

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