Ab initio description of exciton dispersion

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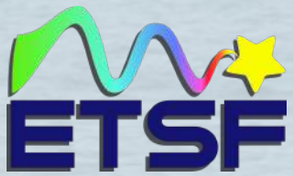
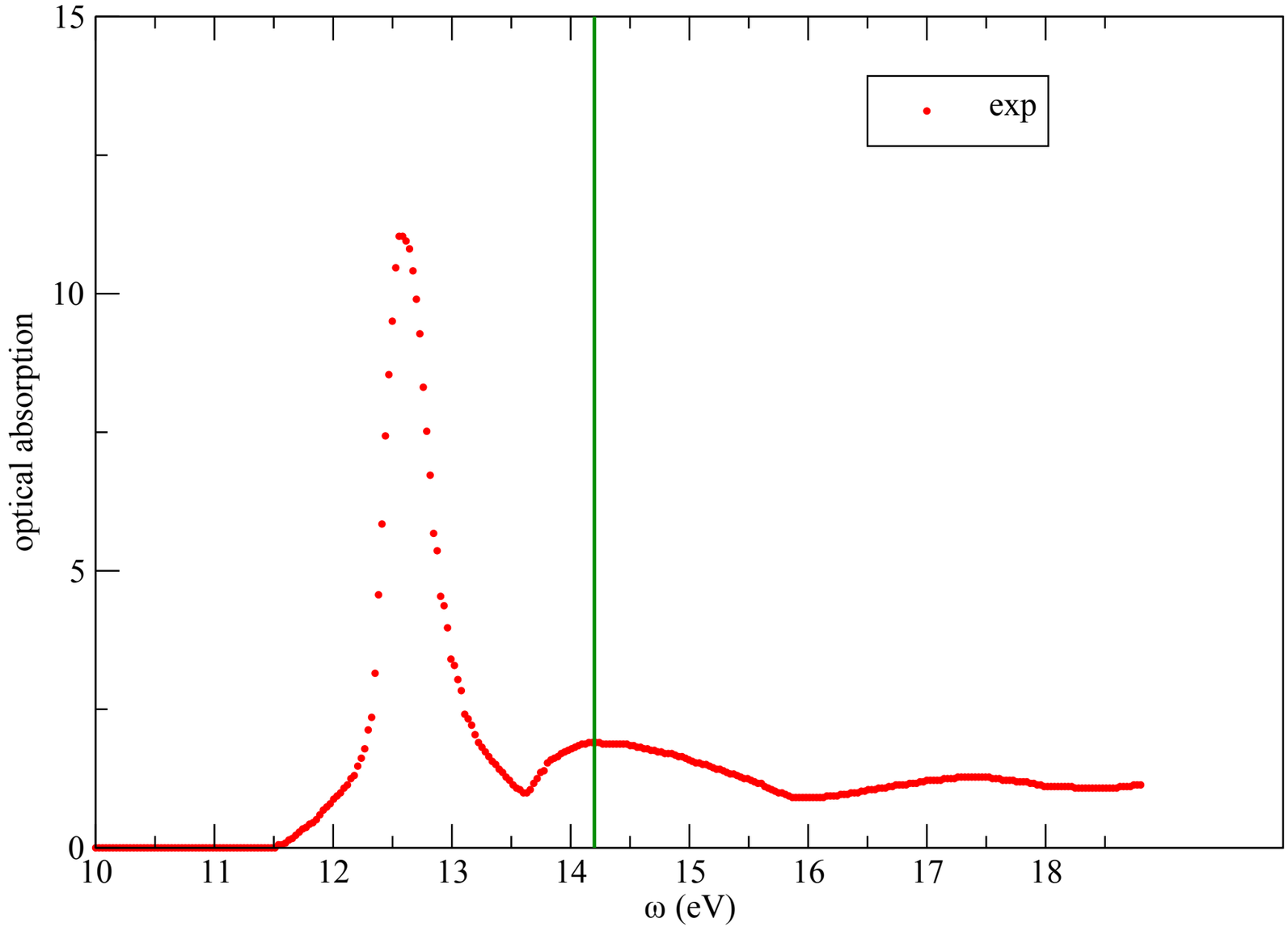
International Workshop on
Computational Physics and Materials Science:
Total Energy and Force Methods
15 January 2015



Outline

- Introduction and motivation
- Exciton dispersion in insulators
- Towards 2D systems
- Perspectives

Optical spectrum of LiF

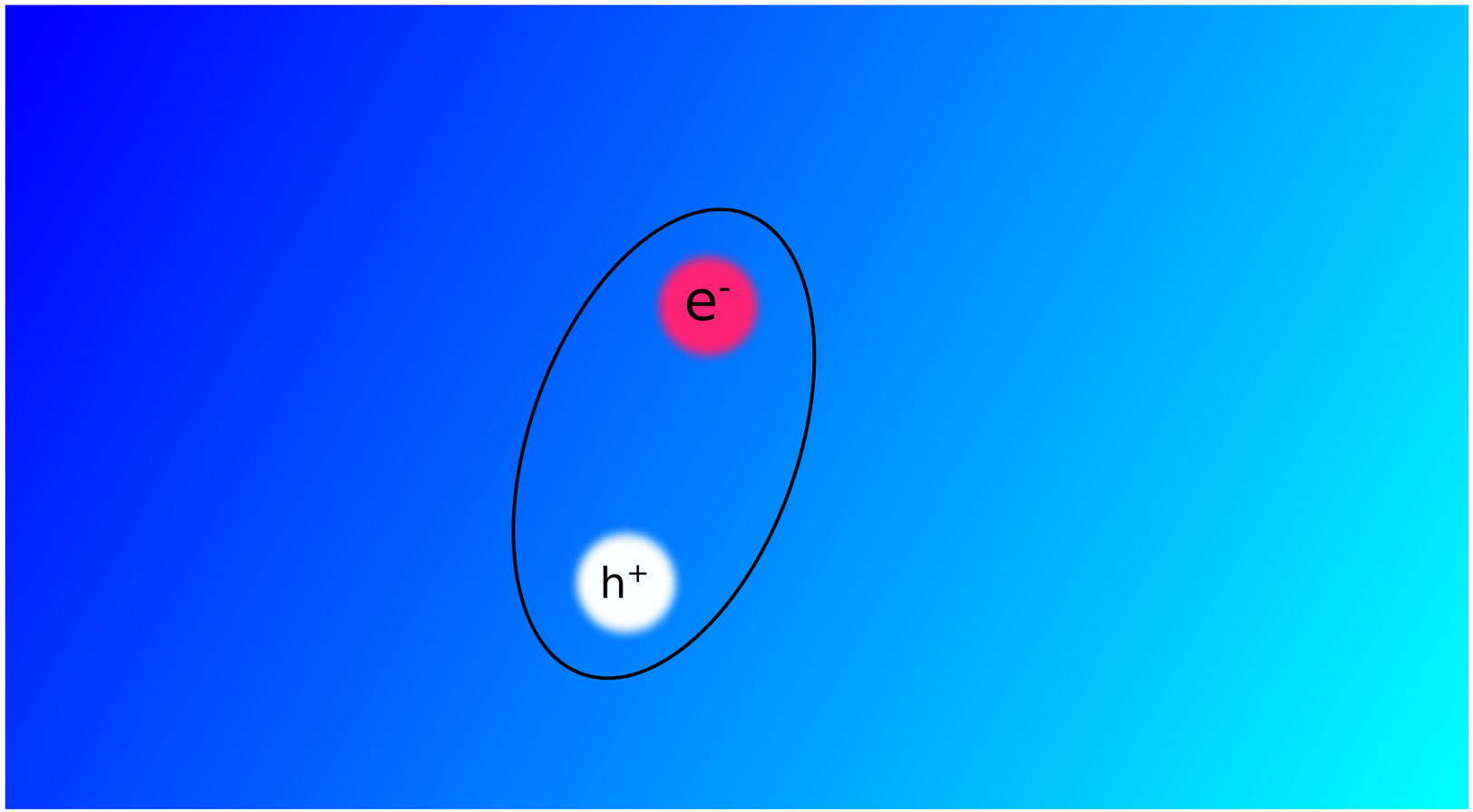


D. M. Roessler and W. C. Walker, J. Opt. Soc. Am. **57**, 835 (1967).

Optical Properties

- material characteristics (knowledge)
- photovoltaics, optoelectronics (exploit for application)
- photocatalysis, photo-therapy
  (actively using photo-conversion)

Theoretical Spectroscopy



Theoretical Spectroscopy

$$G^{(2)}\left(r_1^e, t_1; r_2^e, t_2; r_3^h, t_3; r_4^h, t_4\right) \quad \longleftrightarrow \quad \text{BSE}$$

Theoretical Spectroscopy

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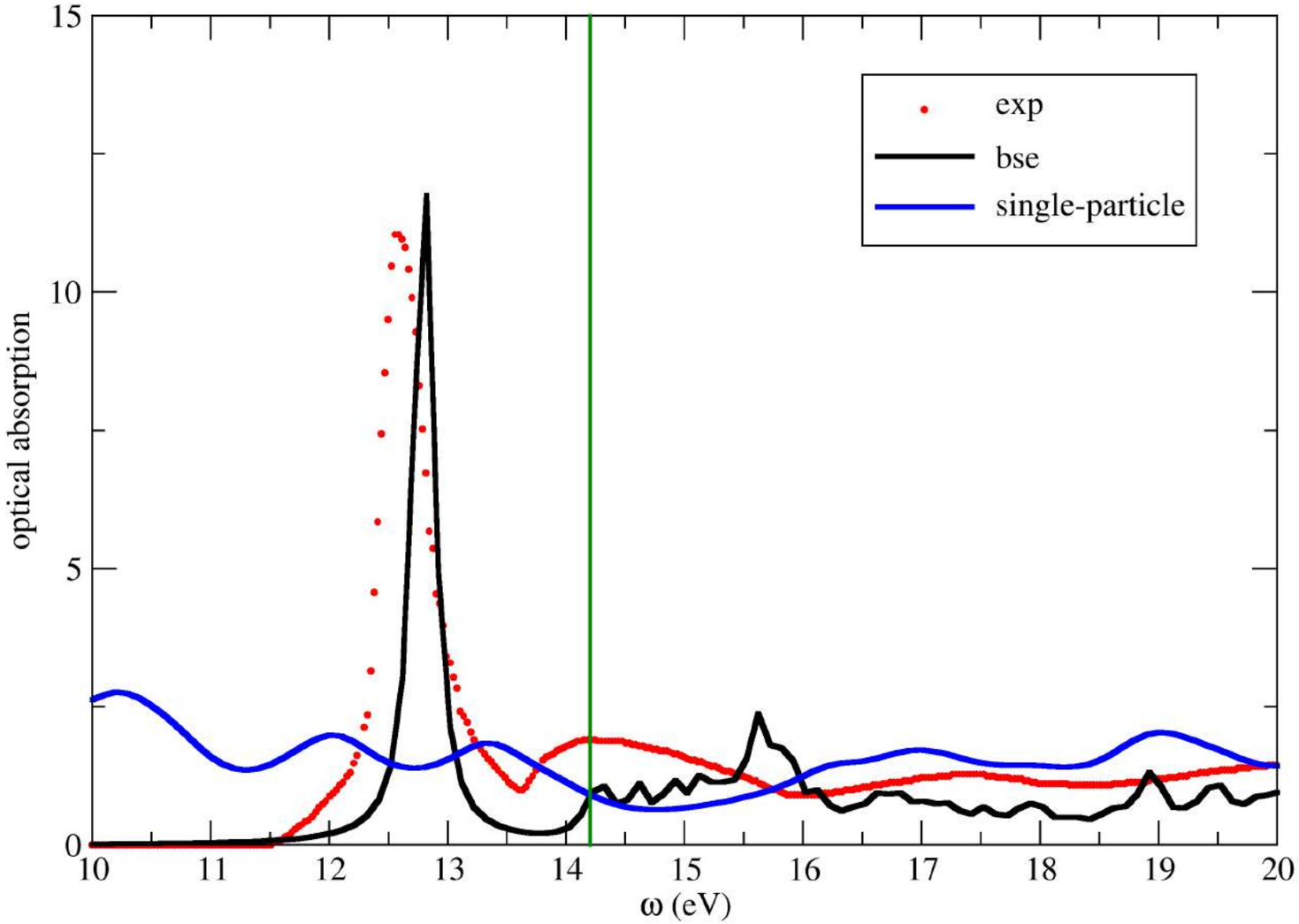


✓ accurate

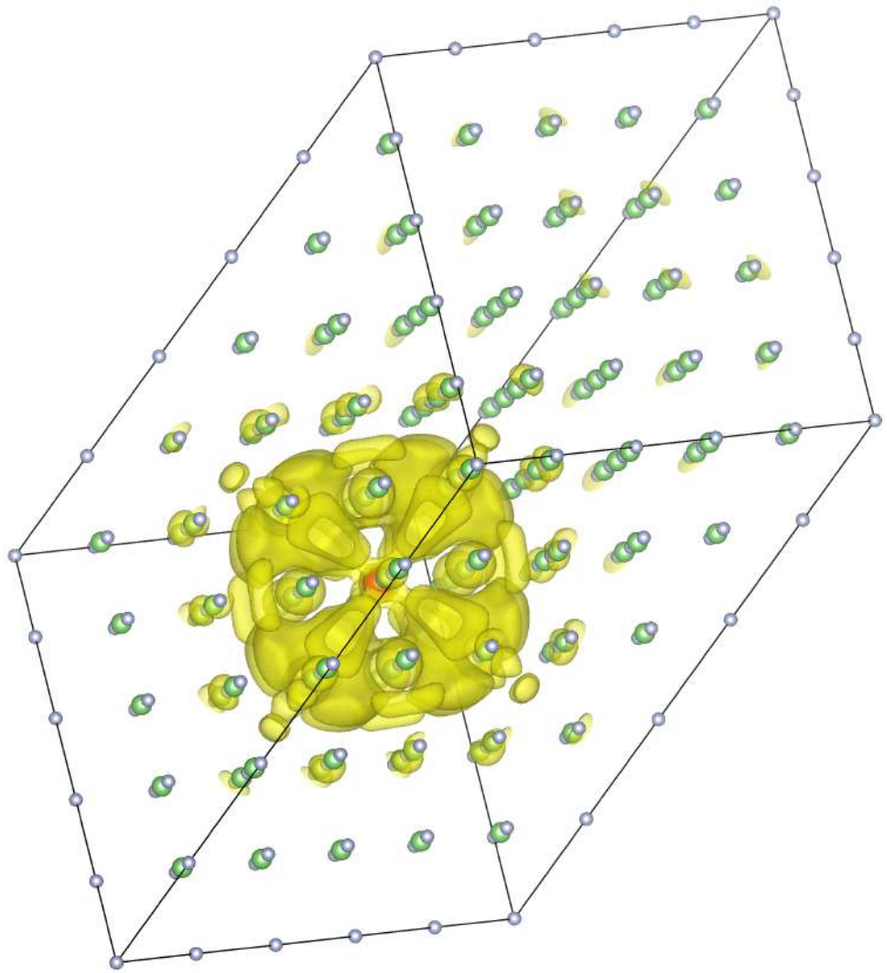
✗ cumbersome

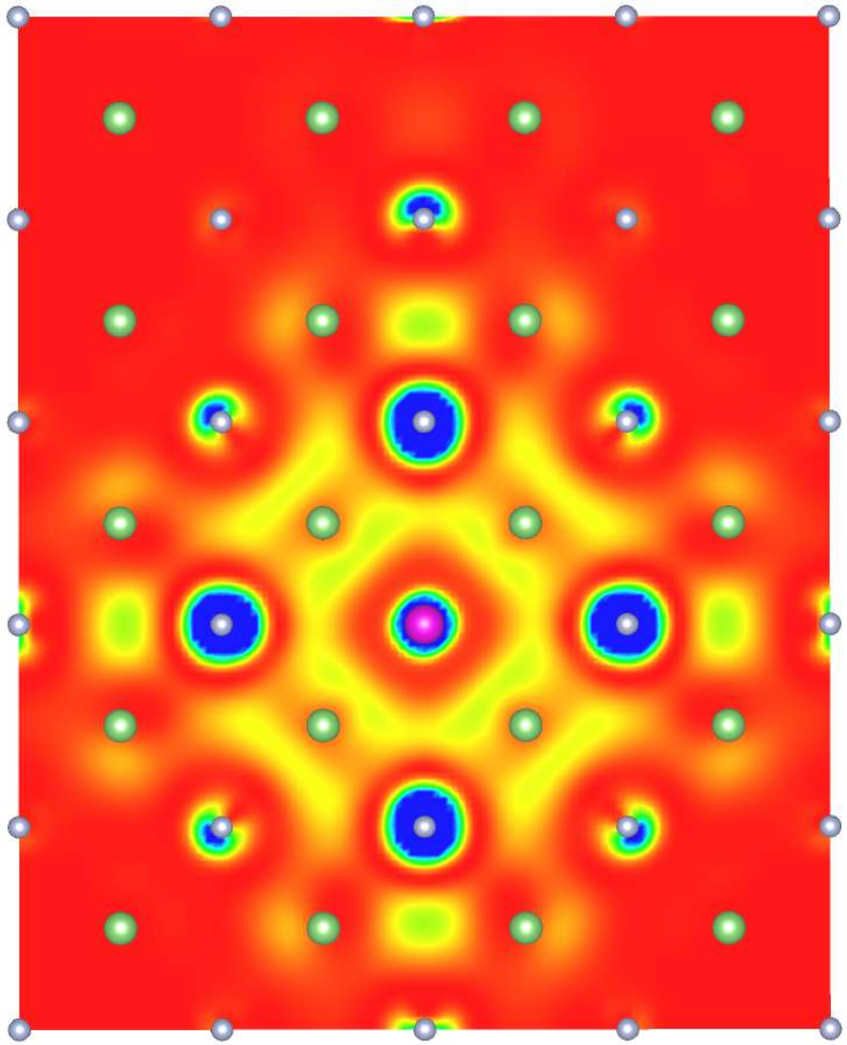
Theoretical Spectroscopy :: added values

Analysis

- where does it come from (bands, BZ region) ?
- spatial extension

Excitonic wavefunction (LiF)





Probability to find the electron for a fixed position of the hole (F atom)

Theoretical Spectroscopy :: added values

Analysis

- where does it come from (bands, BZ region) ?
- spatial extension

Prediction of features (*ab initio*)

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Exciton Dispersion (with momentum transfer)

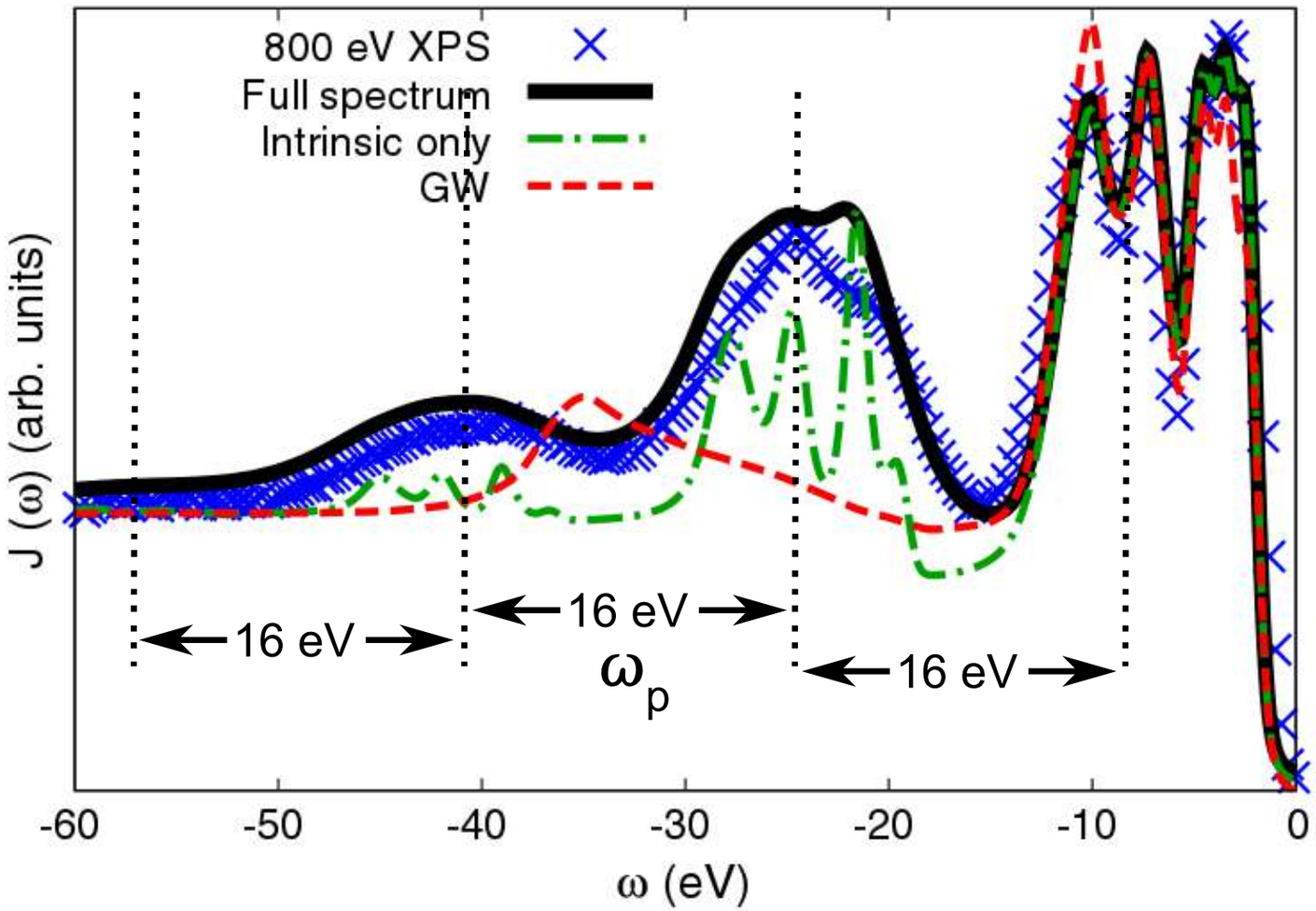
- other spectroscopies (Compton scattering, CIXS)
- effect on screening (photo-emission spectra, band-gap)
- first step towards exciton dynamics

Satellites in Photoemission

Silicon PES

Plasmon Satellites

Main ingredient ::
Loss function



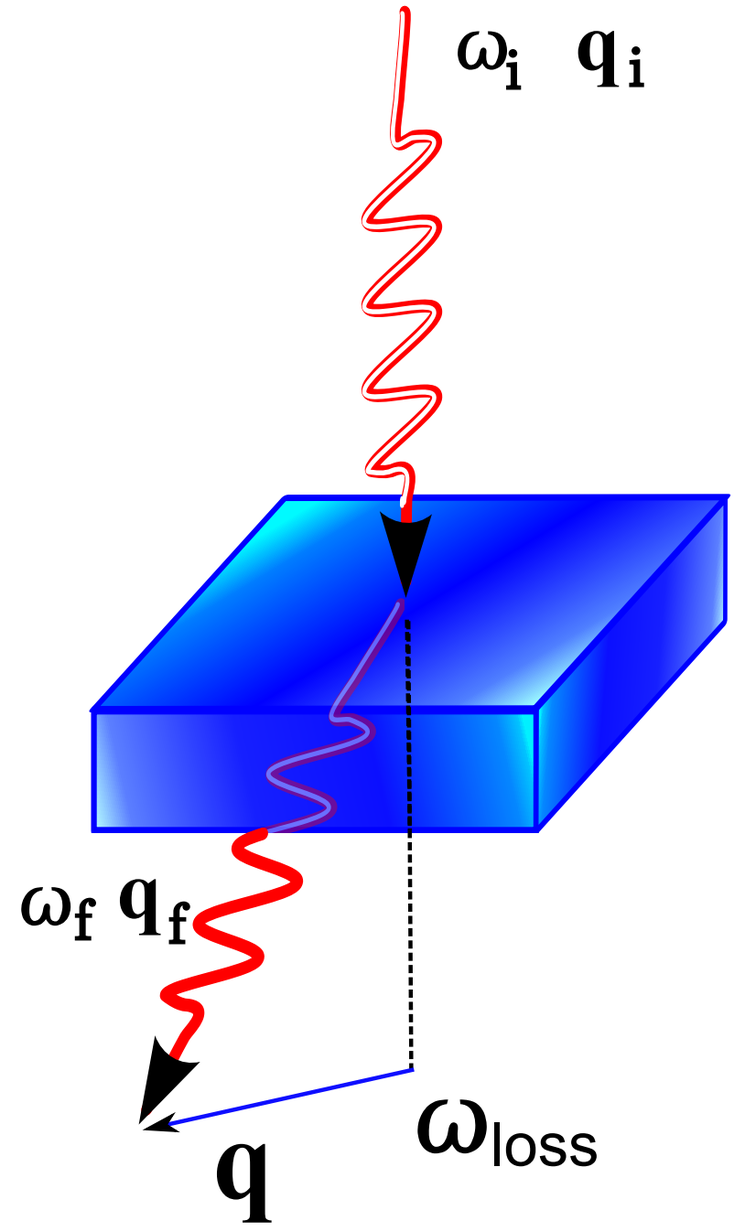
M. Guzzo et al. PRL **107**, 166401 (2011).

Exciton Dispersion (with momentum transfer)

E_λ (Optics)

$E_\lambda(\mathbf{q})$

IXS (big q)
EELS (small q)
~~Optics~~



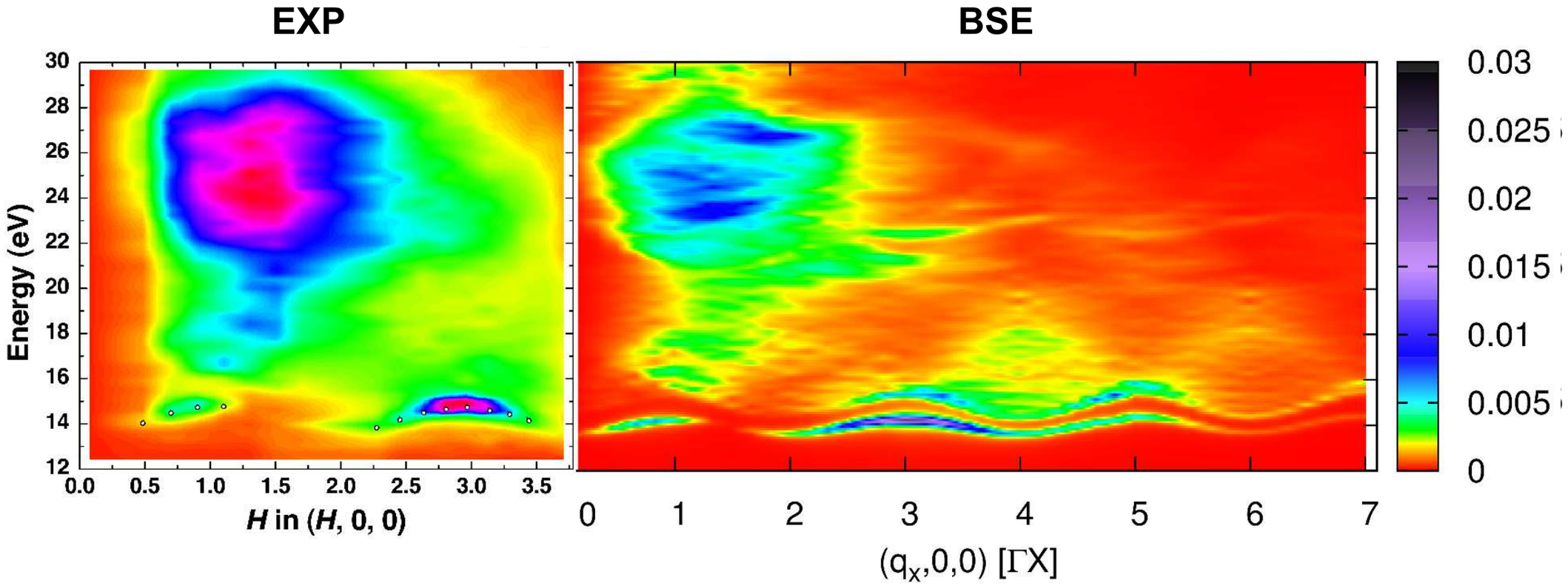
Bethe-Salpeter Equation extension (q)

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

- finite momentum transfer (beyond dipole)
- quasi-particle wavefunctions
- full coupling (beyond TDA)

EXC code www.bethe-salpeter.org/

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)

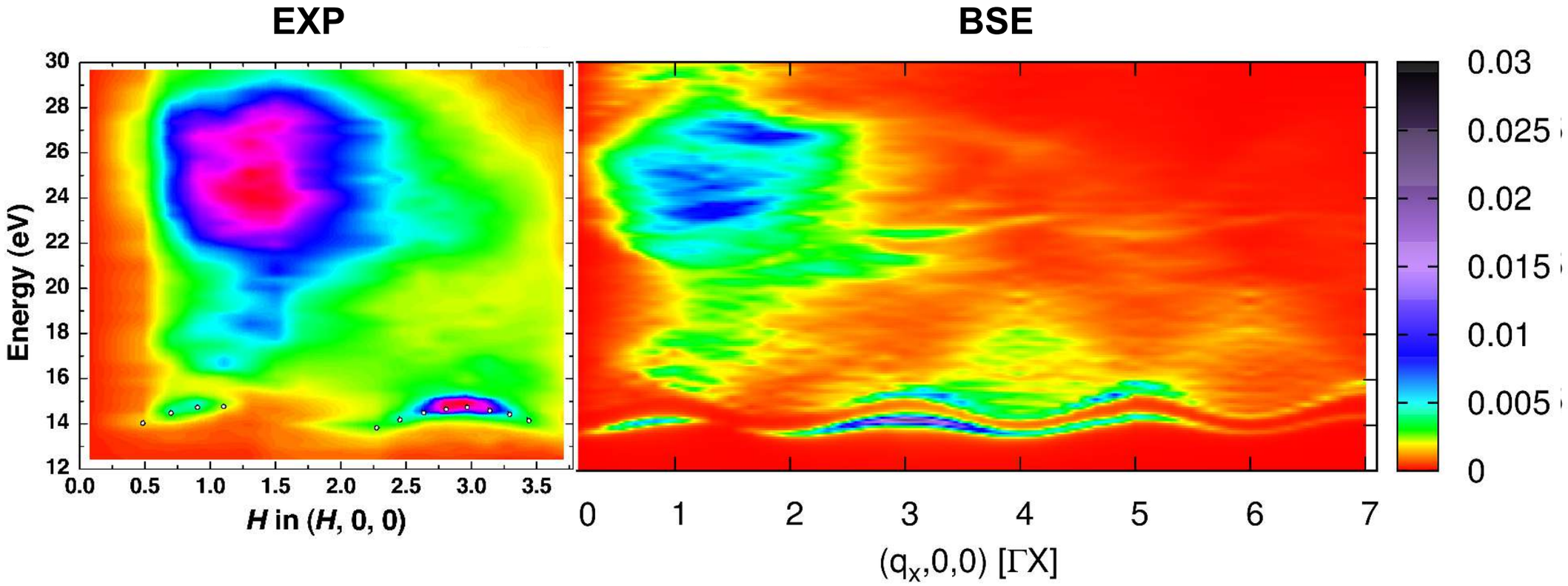
PRL 111, 157401 (2013) PHYSICAL REVIEW LETTERS week ending 11 OCTOBER 2013

First-Principles Method of Propagation of Tightly Bound Excitons: Verifying the Exciton Band Structure of LiF with Inelastic x-Ray Scattering

Chi-Cheng Lee (李啟正),[1,2,*] Xiaoqian M. Chen (陈小千),[3] Yu Gan (干禹),[3,4] Chen-Lin Yeh (葉承霖),[1,5] H. C. Hsueh (薛宏中),[5] Peter Abbamonte,[3,4,†] and Wei Ku (顧威)[1,‡]

Current state-of-the-art theoretical studies of excitons are based either on perturbation theory, via solution to the Bethe-Salpeter equation (BSE) [9–13], or on specially tuned approximations within the time-dependent density functional theory [13–16]. While providing great accuracy in some cases, the BSE method requires evaluation of four-point functions with both space and time indices, and are thus too computationally expensive to describe the full exciton kinetics or to address practical applications. Application of such methods have therefore been restricted to zero-momentum excitons only, and have not yet broached the issue of exciton propagation.

Dynamical Structure factor of LiF



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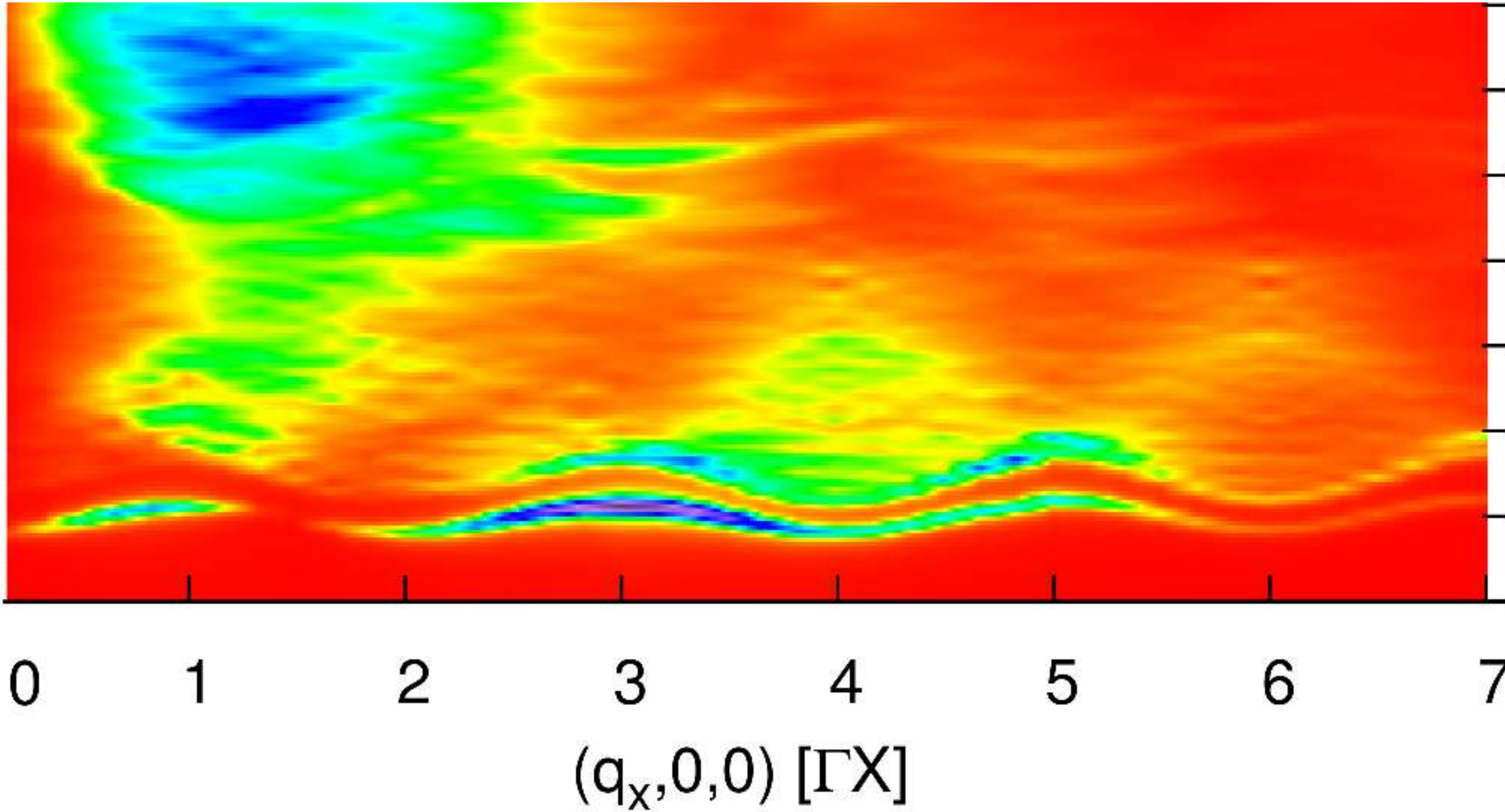
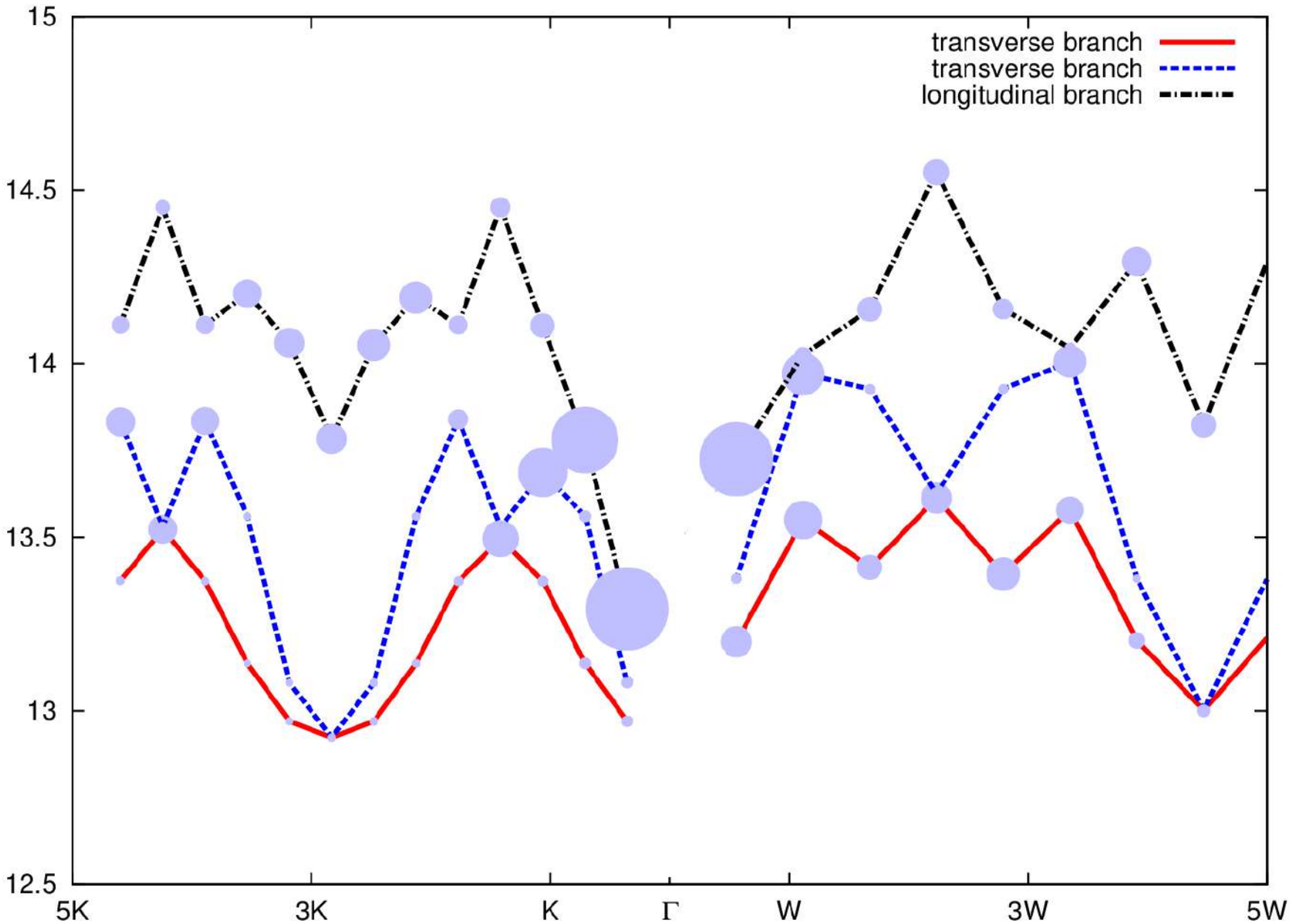
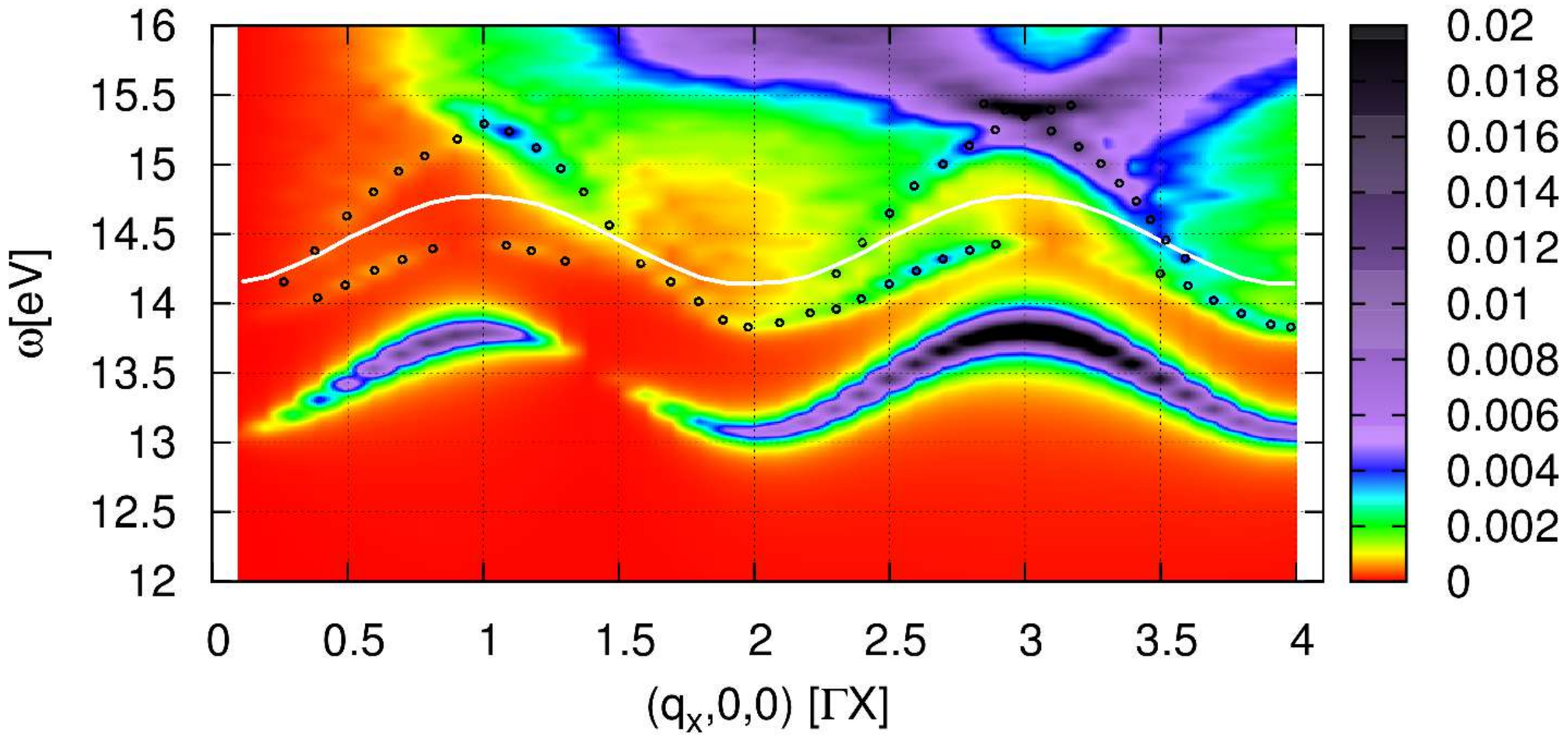

0
1
2
3
4
5
6
7
(q_x,0,0) [ΓX]

Excitonic bandstructure



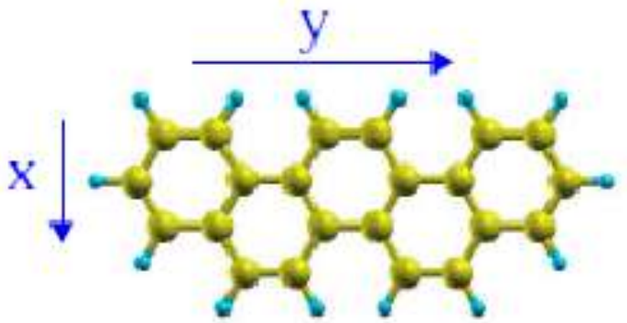
Predictions for Solid Argon



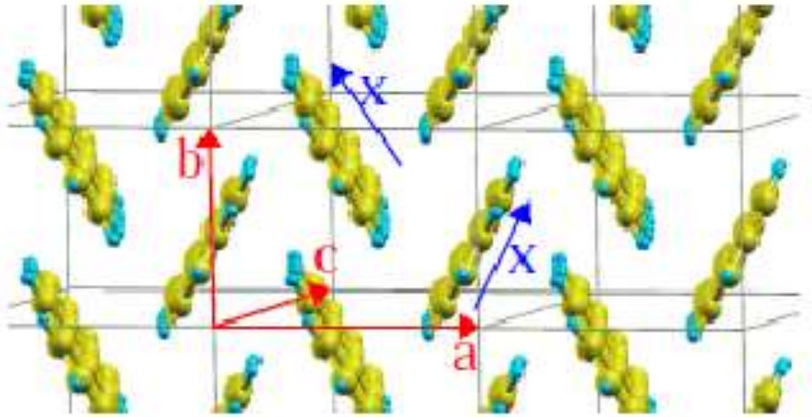
OK for big momentum transfer (with IXS)

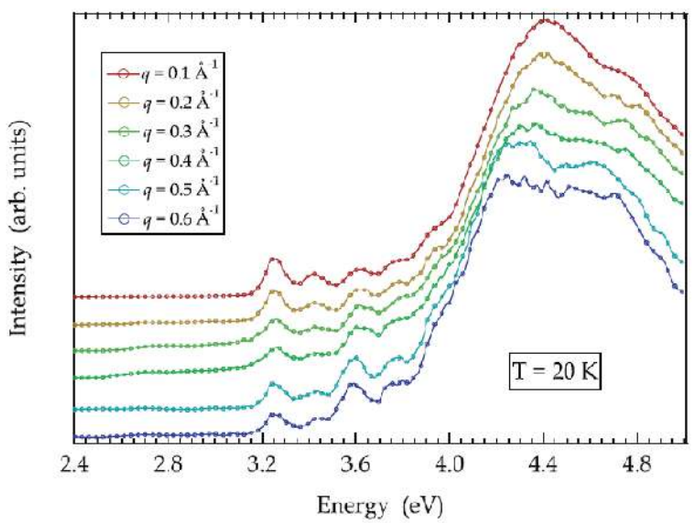
What about for small q ? EELS ?

The case of Molecular Solids

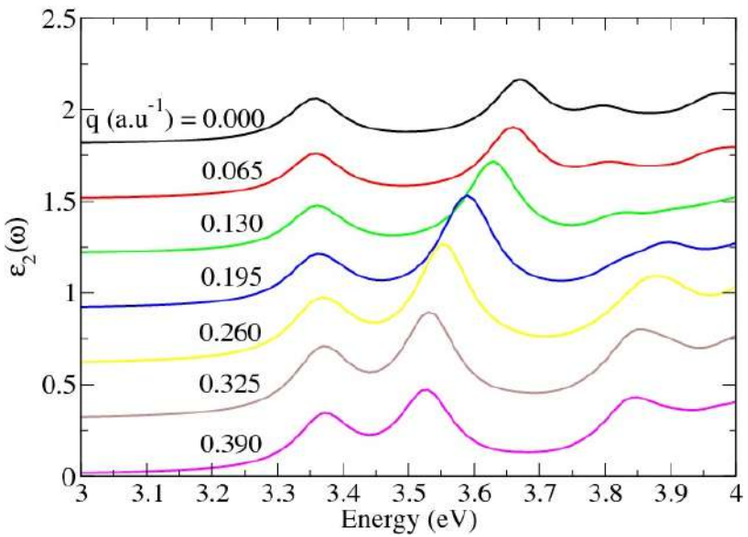


Picene





EELS

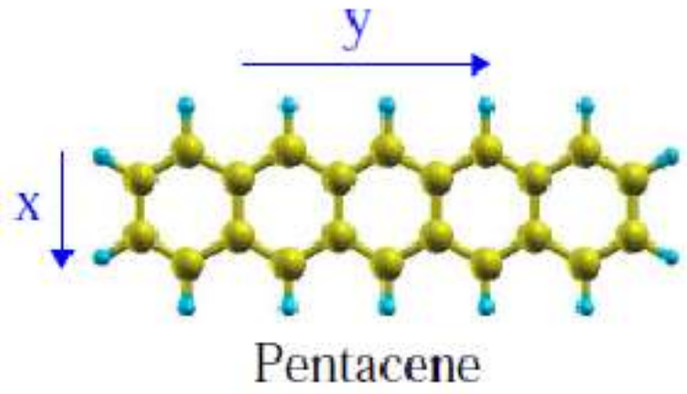


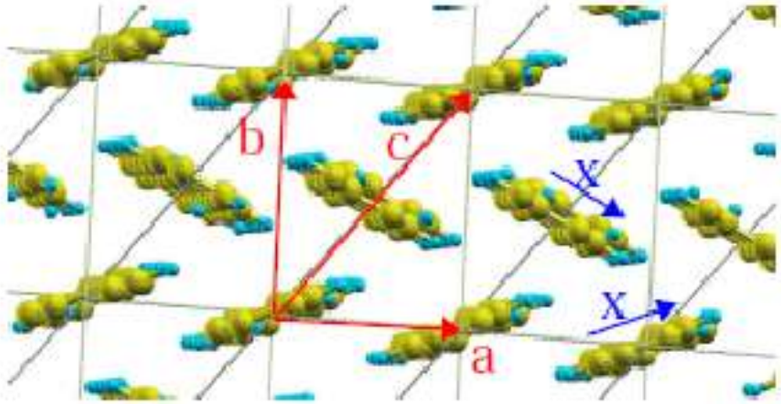
BSE

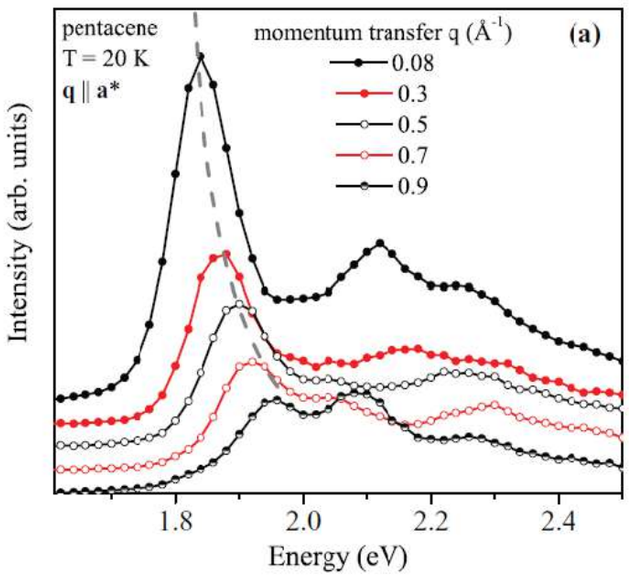
From F.Roth et al. PRB **83** (2011), JCP **136** (2012).

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

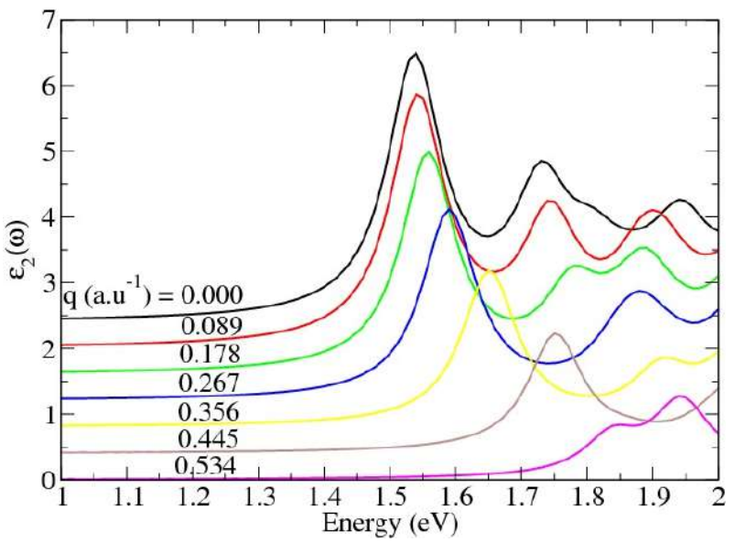
The case of Molecular Solids







EELS



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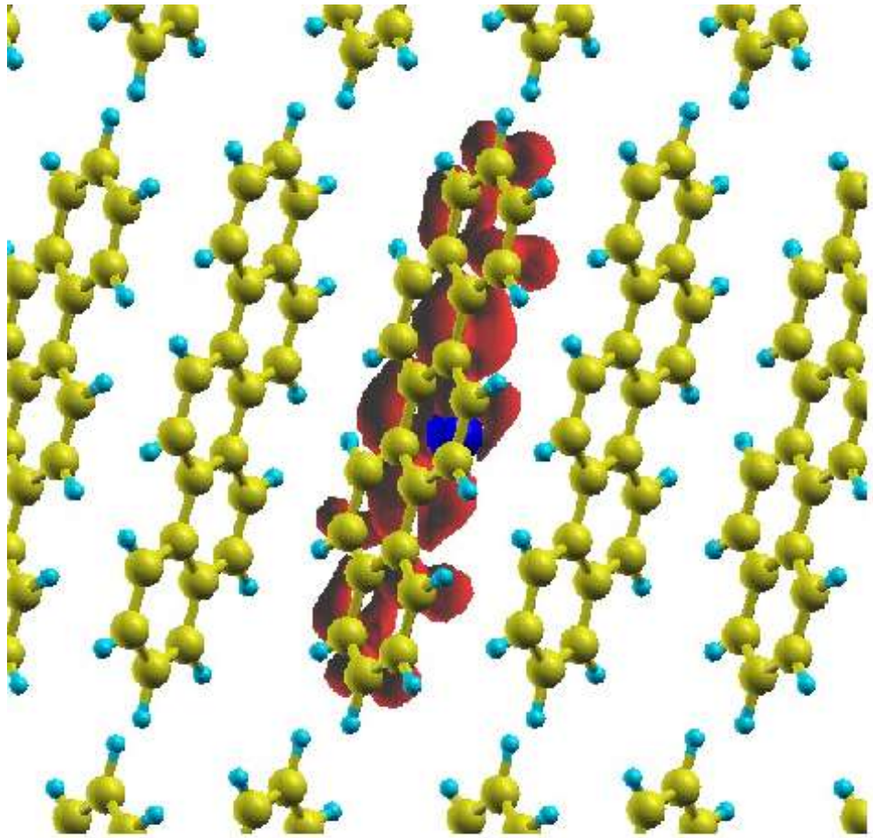
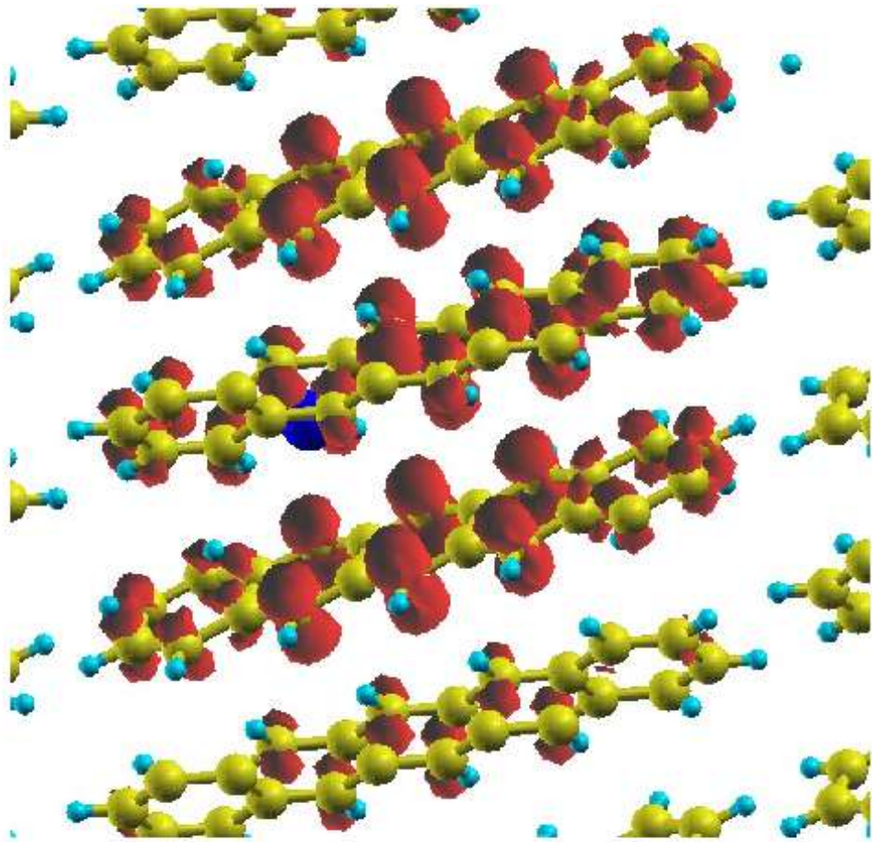


Picene



Pentacene

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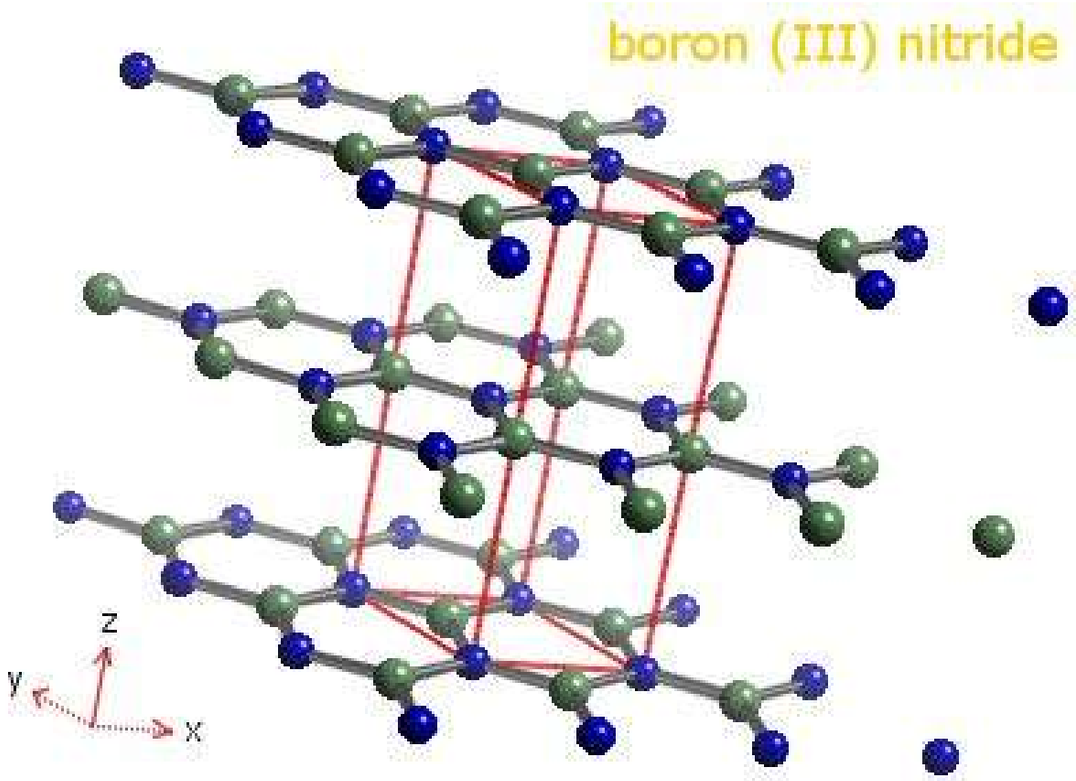
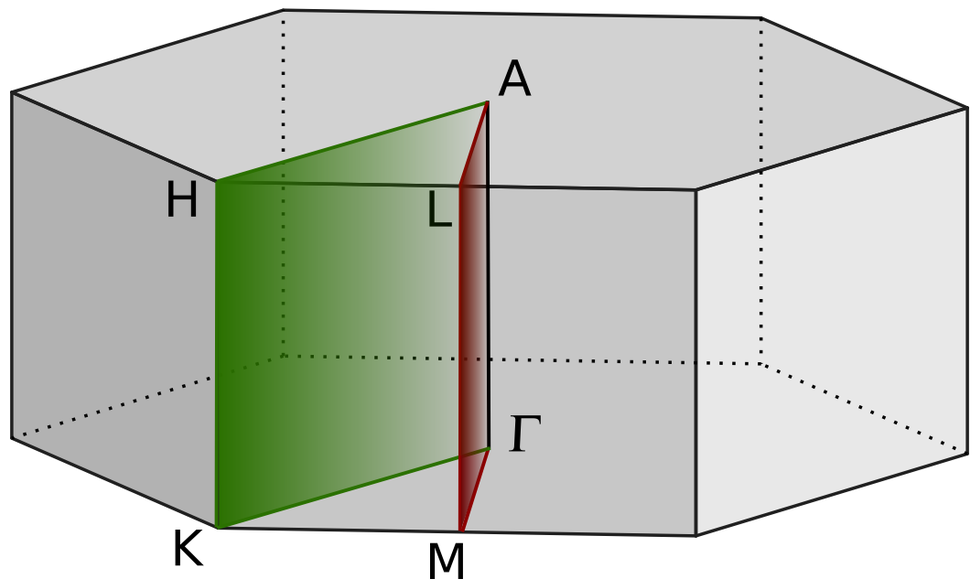
- **Towards 2D systems**
- Perspectives

hexagonal Boron Nitride

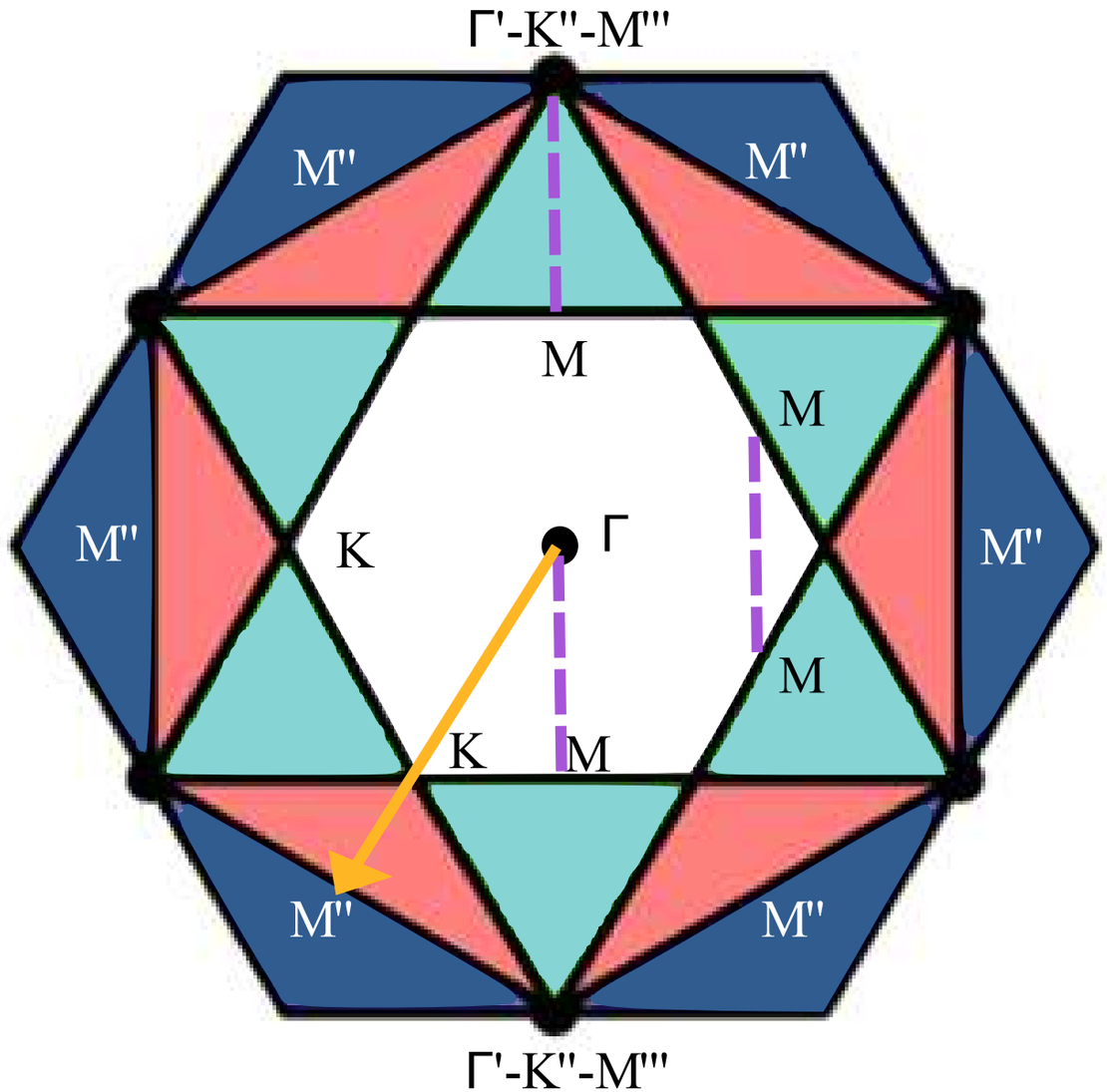
Giorgia Fugallo





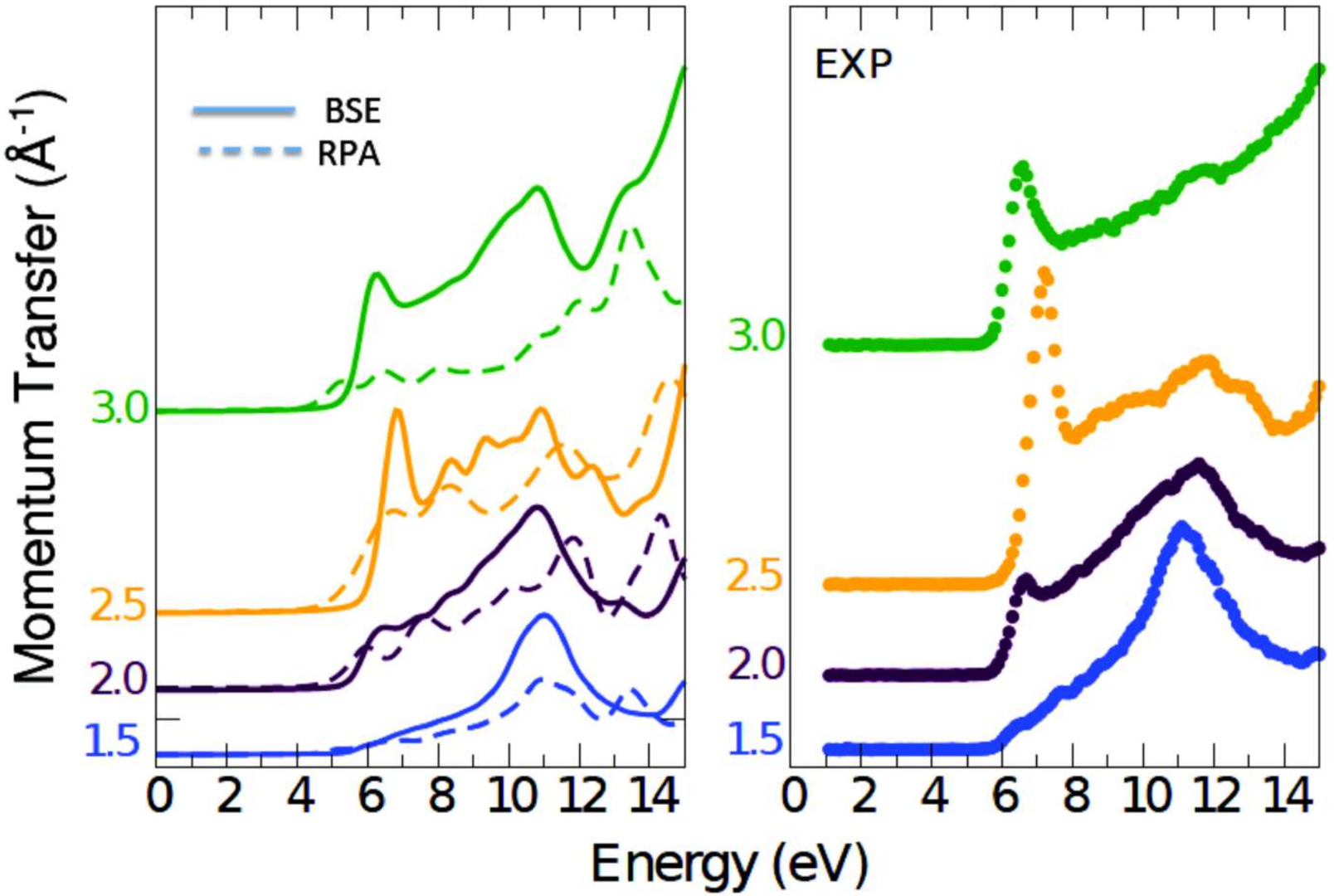
hexagonal Boron Nitride

Brillouin zones



hexagonal Boron Nitride

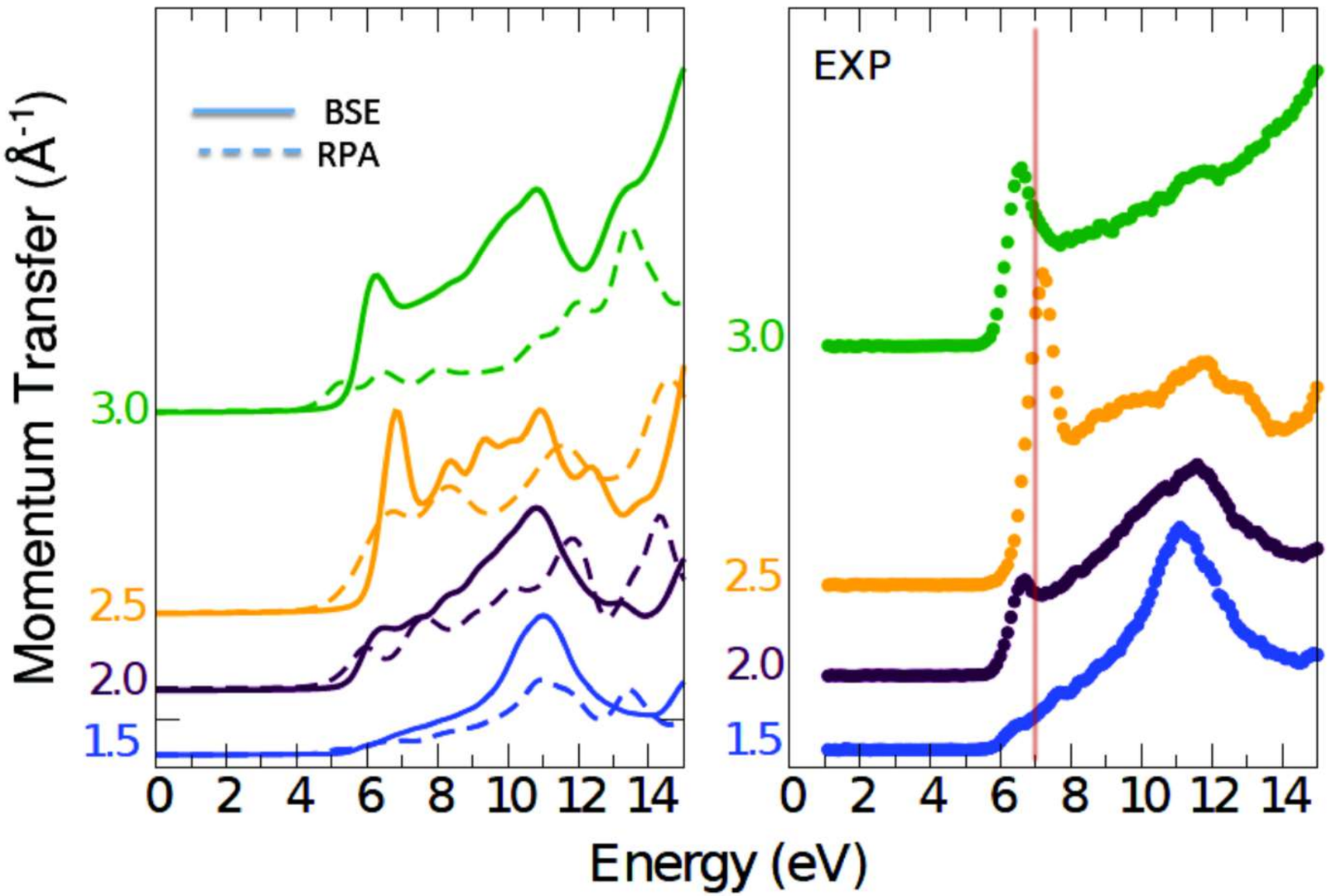
ΓK



Galambosi *et al.* Phys. Rev. B 83, 081413(R)

hexagonal Boron Nitride

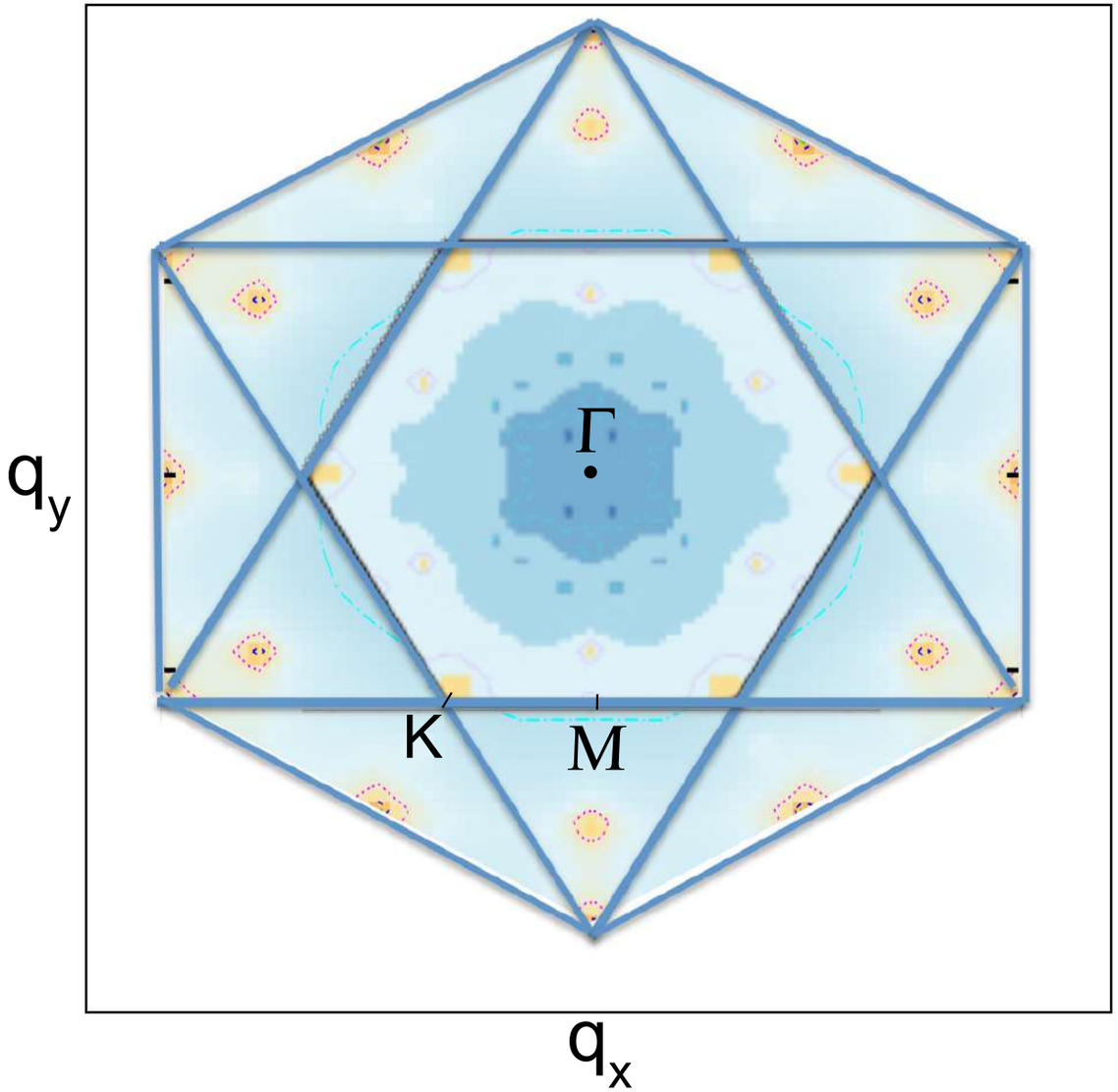
ΓK



Galambosi *et al.* Phys. Rev. B 83, 081413(R)

hexagonal Boron Nitride

$$S(q, \omega = 7eV)$$



hexagonal Boron Nitride

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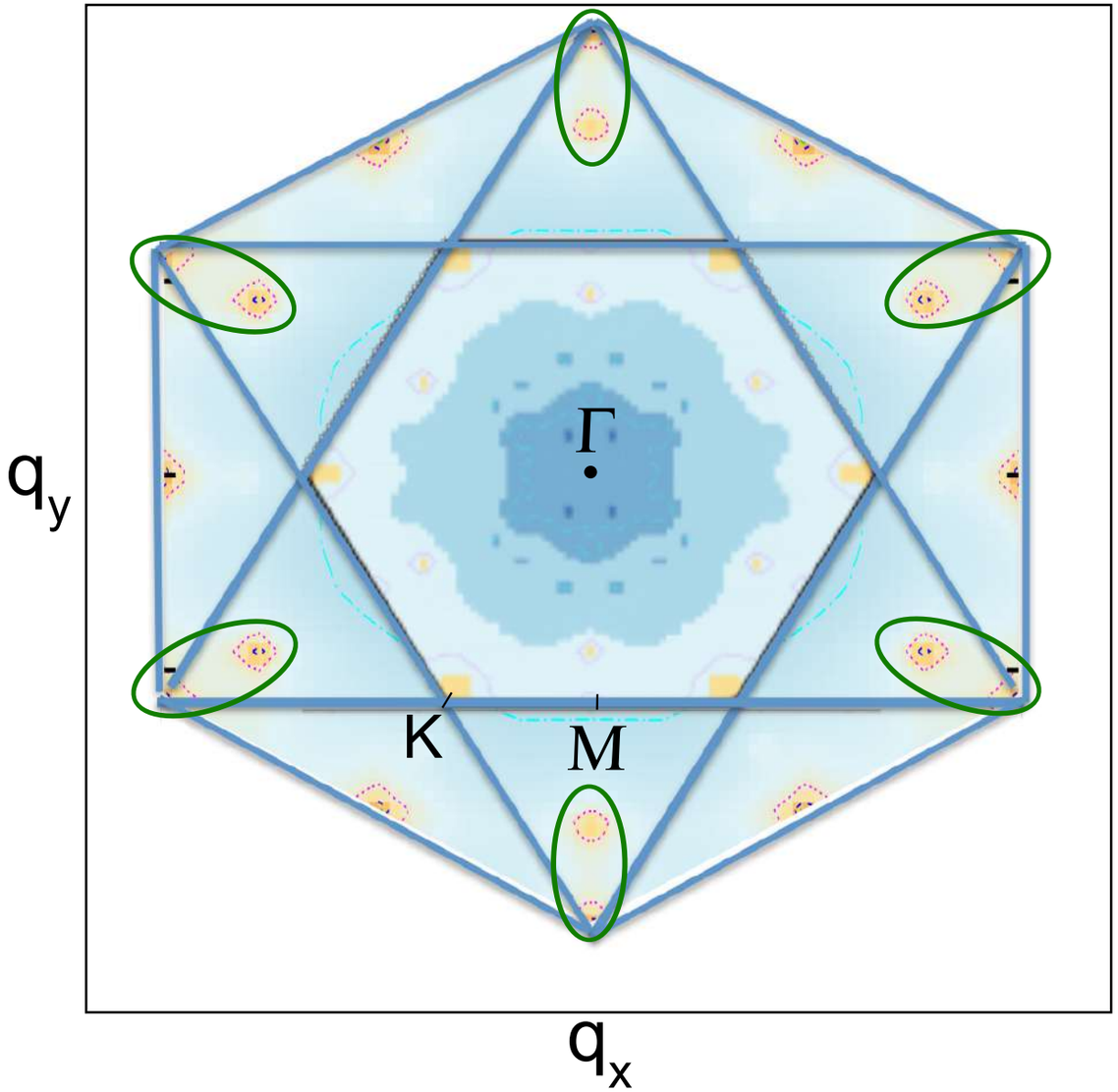
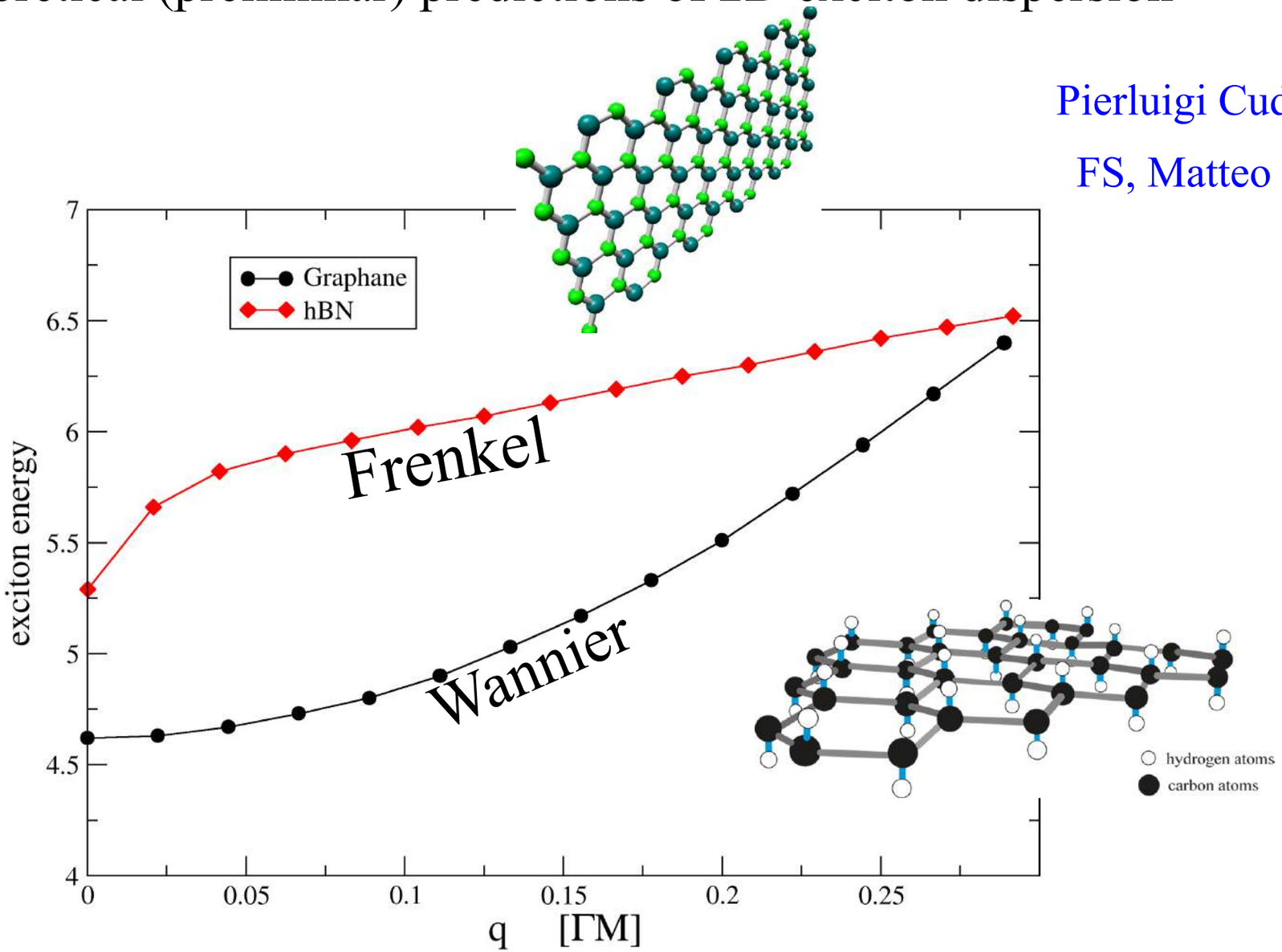


Beamtime obtained :: ESRF 2/2015

Theoretical (preliminar) predictions of 2D exciton dispersion

Pierluigi Cudazzo

FS, Matteo Gatti



C.A.Rozzi *et al.*, Phys. Rev. B 73, 205119 (2006).
S.Ismail-Beigi, Phys. Rev. B 73, 233103 (2006).

2D Cutoff

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Exciton dispersion :: Perspectives

- dispersion OK in 3D. ongoing in 2D and 1D
- excitonic effects in dielectric function (main ingredient in several spectroscopies) ?
- excitonic effects in CIXS and RIXS

People

Matteo Gatti *(exciton dispersion)*

Pierluigi Cudazzo *(molecular solids and 2D)*

Giorgia Fugallo *(hBN and MoS_2)*

Igor Reshetnyak *(non-diagonal response)*

Bernardo and Sean *(graphite and nanotubes)*