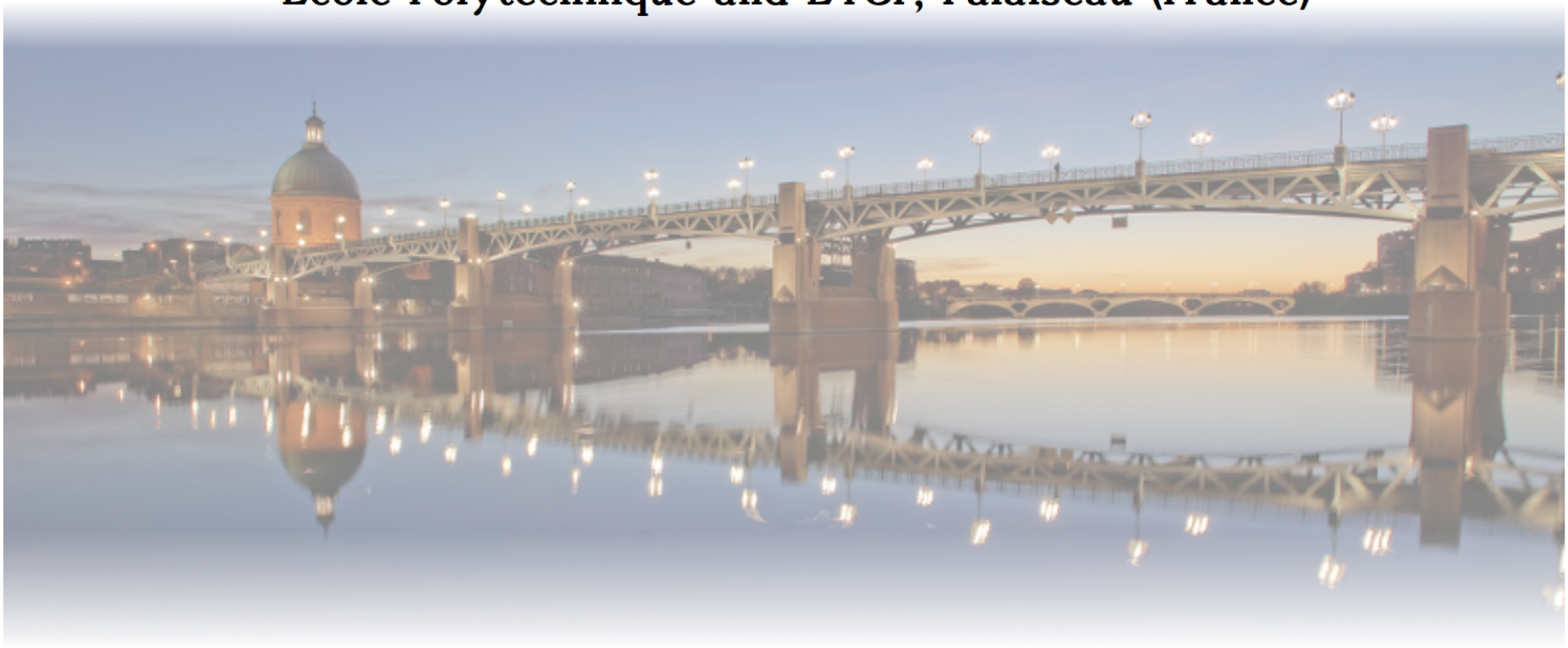
New frontiers for theoretical spectroscopy from the Bethe-Salpeter equation

Francesco Sottile
École Polytechnique and ETSF, Palaiseau (France)



Theoretical Chemistry for Extended Systems: systematically improvable electronic structure methods
Toulouse - 23 May 2017

ETSF
European Theoretical Spectroscopy Facility

ÉCOLE POLYTECHNIQUE
UNIVERSITÉ PARIS-SACLAY

Warning :: intruders

Warning :: intruders

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n)$$

$$\begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_n) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_n) \\ \dots & & \dots & \dots \\ \phi_n(\mathbf{r}_1) & \phi_n(\mathbf{r}_2) & \dots & \phi_n(\mathbf{r}_n) \end{vmatrix}$$

$$n(\mathbf{r}, t), G(\mathbf{r}, \mathbf{r}', \omega)$$

Warning :: intruders

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n)$$

$$\begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_n) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_n) \\ \dots & & \dots & \dots \\ \phi_n(\mathbf{r}_1) & \phi_n(\mathbf{r}_2) & \dots & \phi_n(\mathbf{r}_n) \end{vmatrix}$$

$$n(\mathbf{r}, t), G(\mathbf{r}, \mathbf{r}', \omega)$$

$$\langle ij|kl\rangle$$

$$\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, \omega)$$

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, .., \mathbf{r}_n)$$

$$\begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_n) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \dots & \phi_1(\mathbf{r}_n) \\ \dots & & \dots & \dots \\ \phi_n(\mathbf{r}_1) & \phi_n(\mathbf{r}_2) & \dots & \phi_n(\mathbf{r}_n) \end{vmatrix}$$

$$n(\mathbf{r}, t), G(\mathbf{r}, \mathbf{r}', \omega)$$

$$\langle ij|kl\rangle$$

$$\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q}, \omega)$$

cc-pVDZ
cc-pV5Z
aug-cc-pVTZ
cc-pCVDZ
:

$$\phi_{n\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n\mathbf{k}}^{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$$

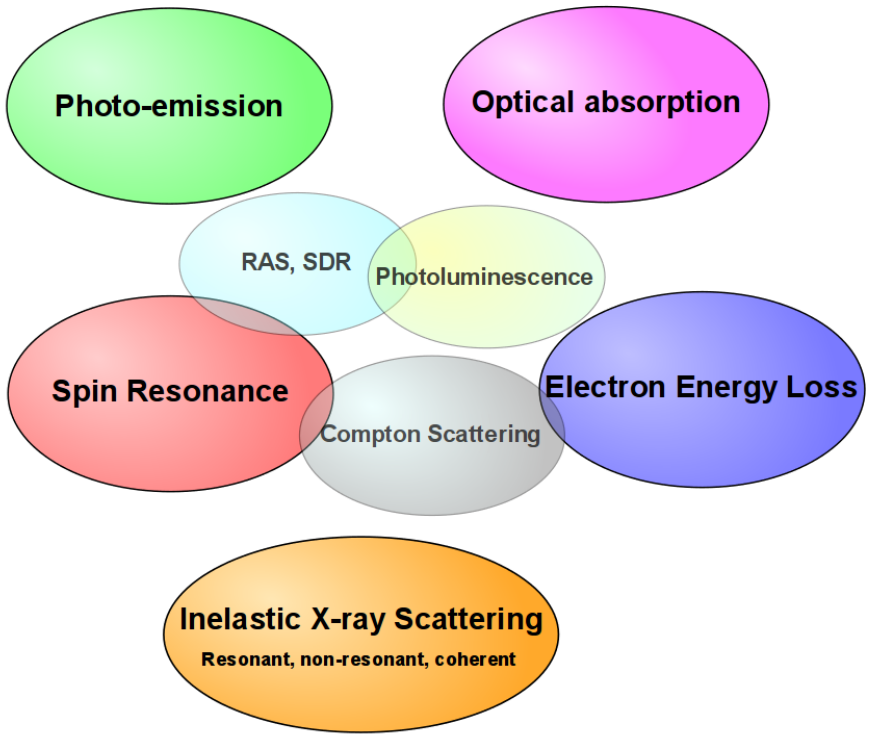
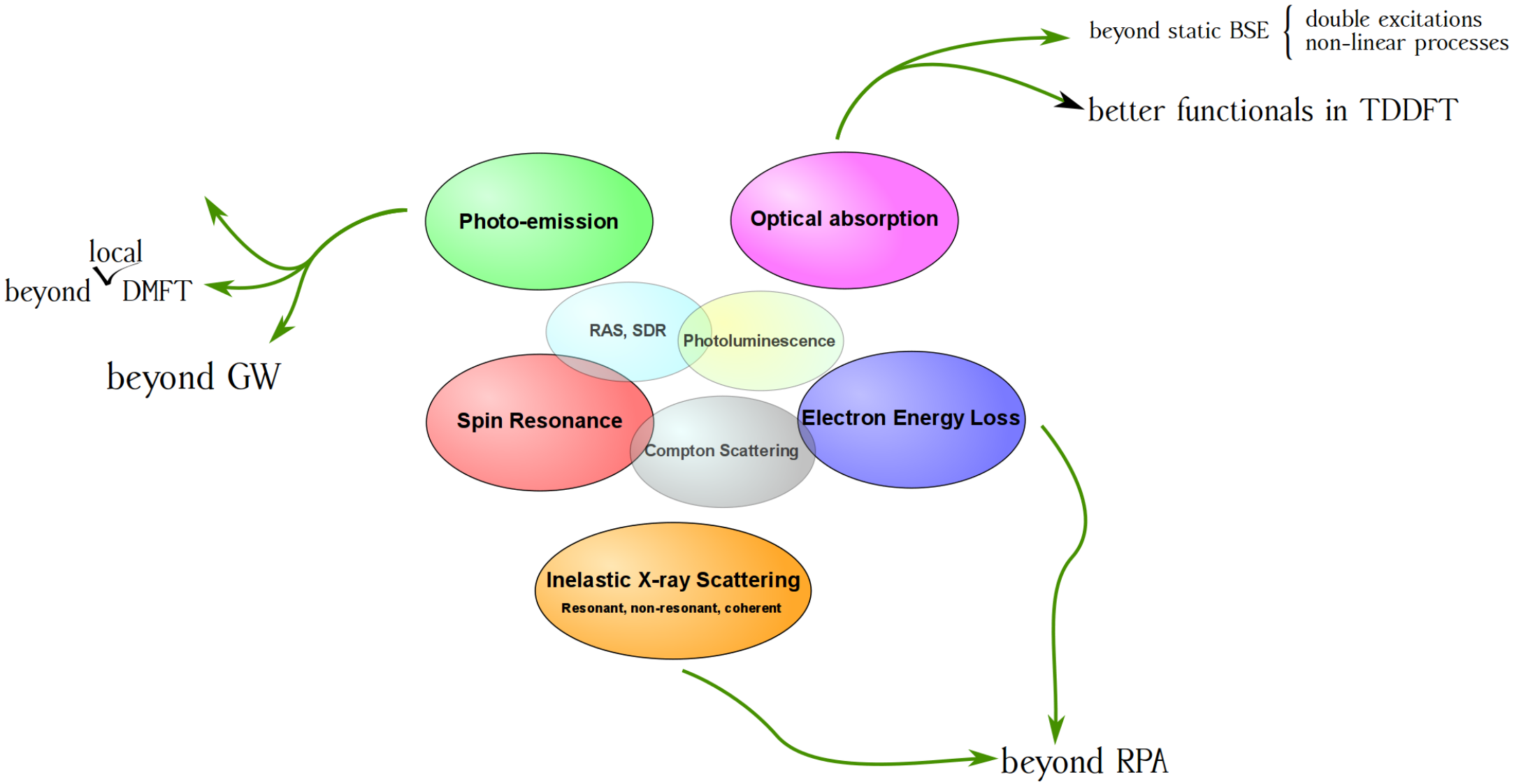
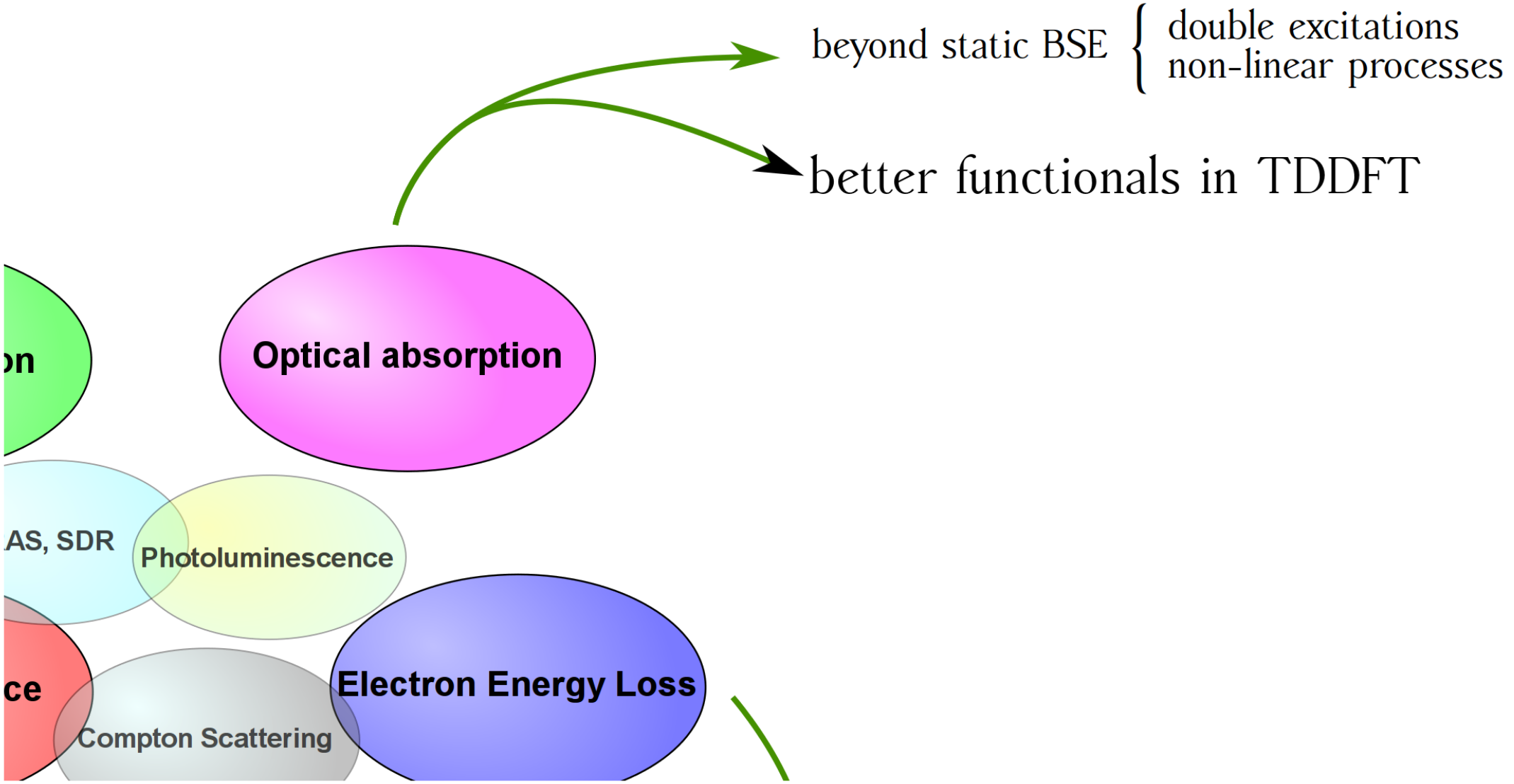
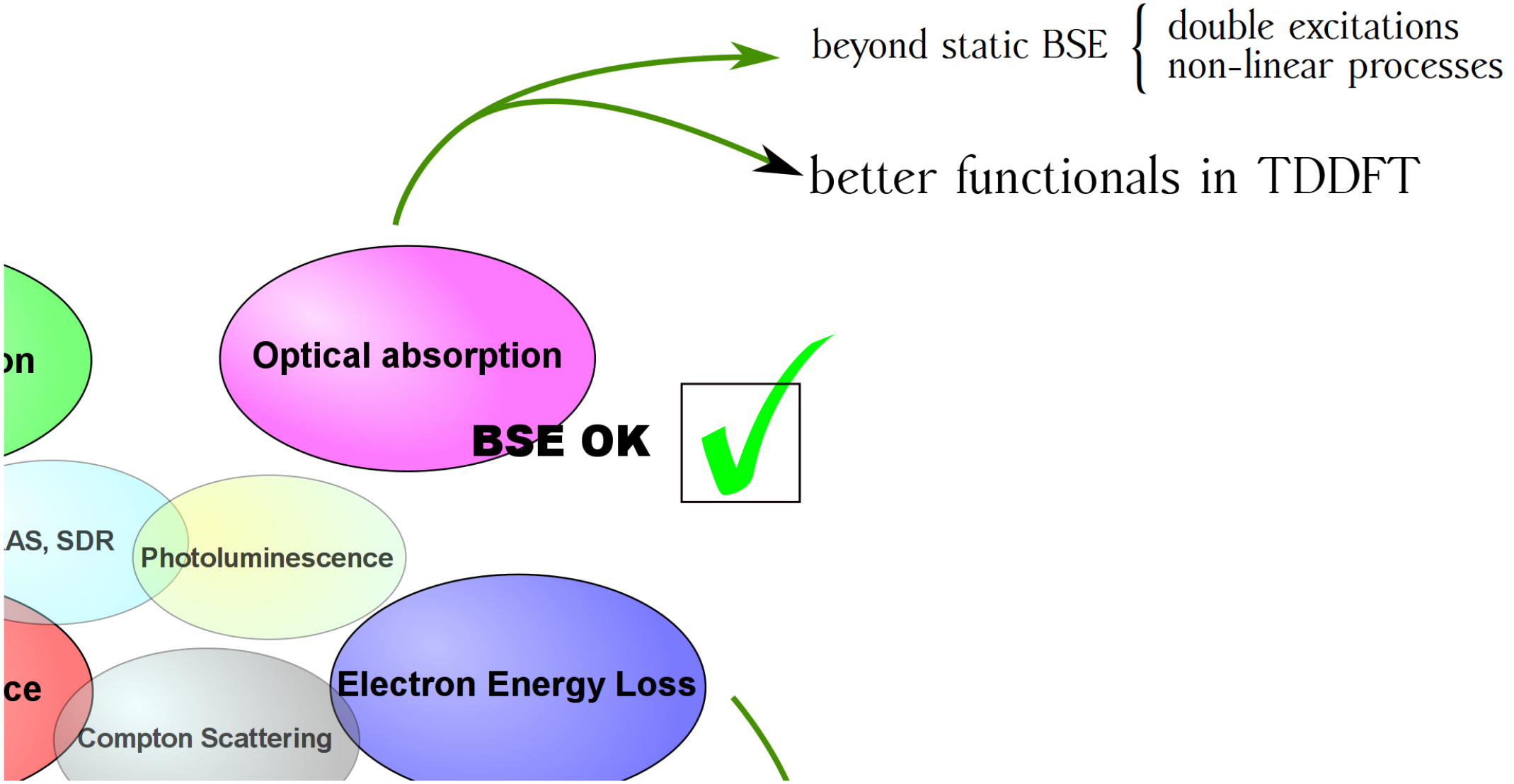
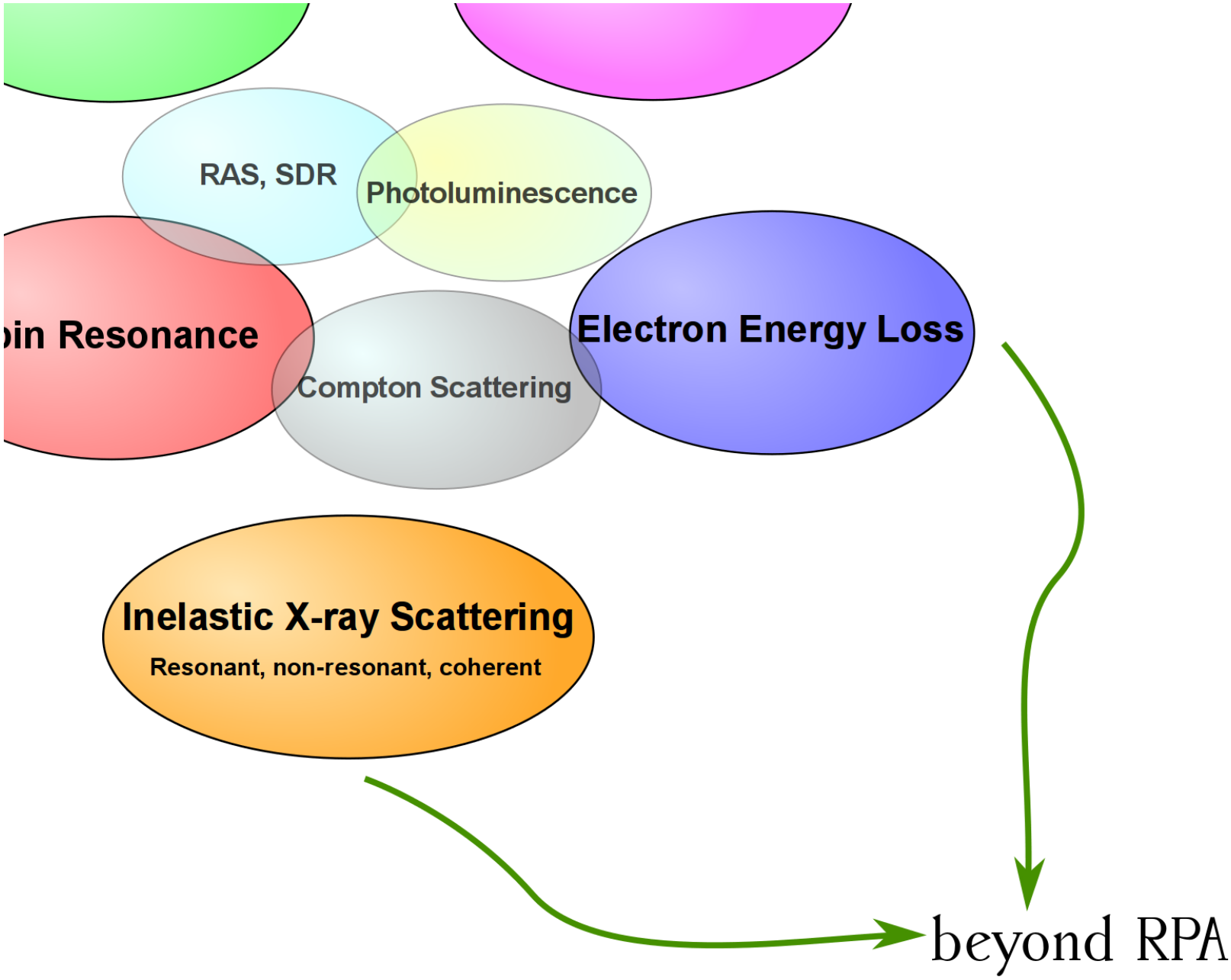


Photo-emission
Optical absorption
RAS, SDR
Photoluminescence
Spin Resonance
Compton Scattering
Electron Energy Loss
Inelastic X-ray Scattering
Resonant, non-resonant, coherent


beyond static BSE
double excitations
non-linear processes
better functionals in TDDFT
Photo-emission
Optical absorption
local
beyond
DMFT
beyond GW
RAS, SDR
Photoluminescence
Spin Resonance
Compton Scattering
Electron Energy Loss
Inelastic X-ray Scattering
Resonant, non-resonant, coherent
beyond RPA


beyond static BSE
double excitations
non-linear processes
better functionals in TDDFT
Optical absorption
AS, SDR
Photoluminescence
Electron Energy Loss
Compton Scattering


beyond static BSE
double excitations
non-linear processes
better functionals in TDDFT
Optical absorption
BSE OK
AS, SDR
Photoluminescence
Electron Energy Loss
Compton Scattering


RAS, SDR
Photoluminescence
in Resonance
Compton Scattering
Electron Energy Loss
Inelastic X-ray Scattering
Resonant, non-resonant, coherent
beyond RPA

Outline

- IXS, EELS beyond RPA
  - excitonic effects in IXS,EELS
  - exciton dispersion
  - visualisation tools
  - Coherent Inelastic X-ray Scattering
- Photo-emission beyond GW

ETSF
European Theoretical Spectroscopy Facility

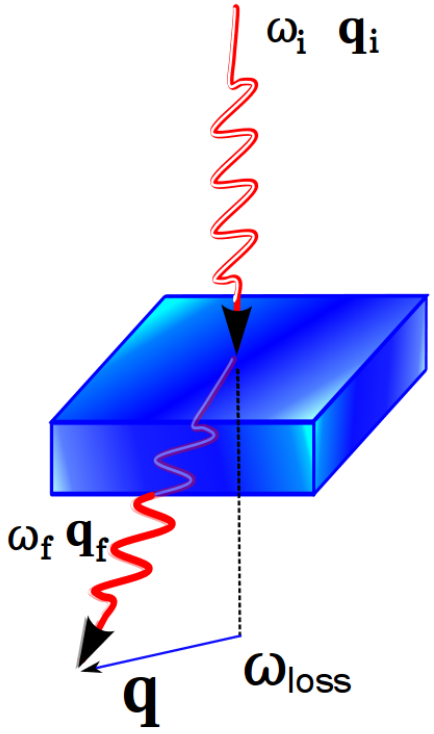
Theoretical Chemistry for Extended Systems: systematically improvable electronic structure methods
Toulouse - 23 May 2017

ÉCOLE POLYTECHNIQUE
UNIVERSITÉ PARIS-SACLAY

Inelastic X-ray Scattering

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

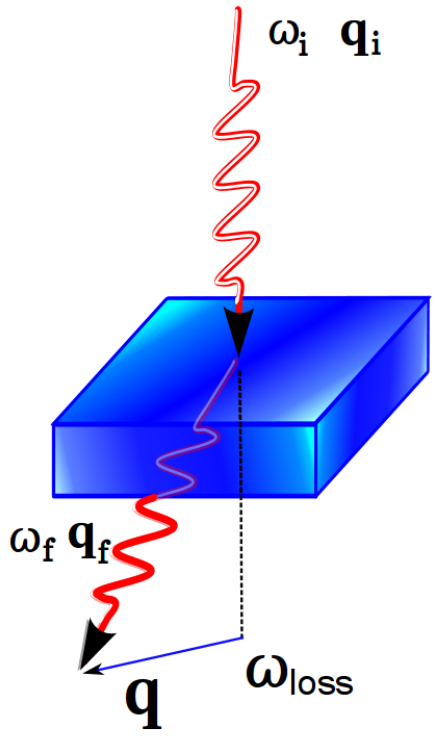
$$\varepsilon^{-1}(\mathbf{q},\omega) = 1 + v\chi$$



Inelastic X-ray Scattering

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

$$\varepsilon^{-1}(\mathbf{q},\omega) = 1 + v\chi$$



$$W = \varepsilon^{-1} v$$

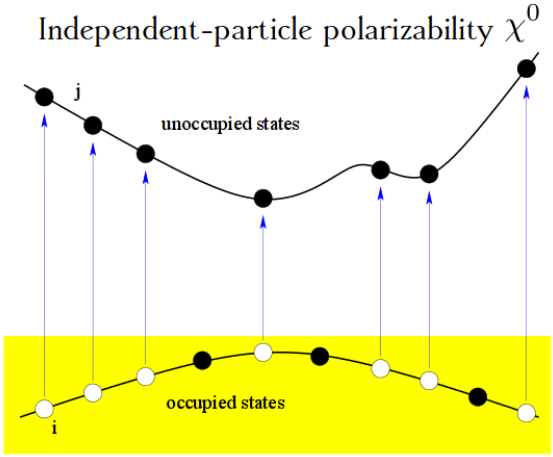
screening

$$\delta n = \chi V_{\mathrm{ext}}$$

density-density response function

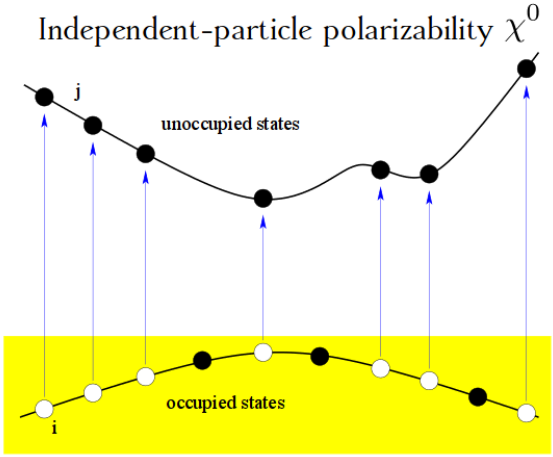
Polarizability

$$\chi = \chi^0 + \chi^0 \left(v + f_{xc}^{e-h} \right) \chi$$



Polarizability

$$\chi = \chi^0 + \chi^0 \left(v + f_{xc}^{e-h} \right) \chi$$



$$\chi^{\mathrm{RPA}} = \chi^0 + \chi^0 \left(v + \cancel{f_{xc}} \right) \chi^{\mathrm{RPA}}$$

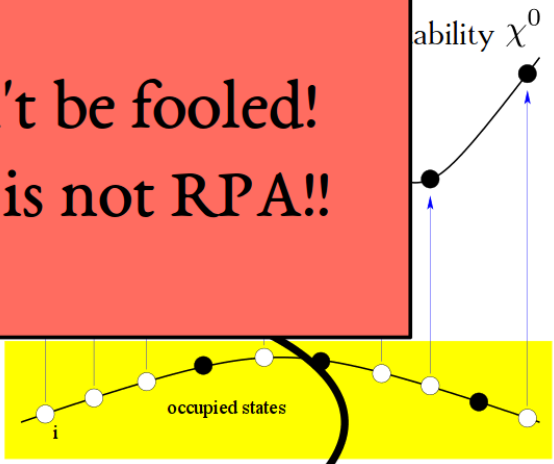
$$\chi^{\mathrm{ALDA}} = \chi^0 + \chi^0 \left(v + f_{xc}^{\mathrm{ALDA}} \right) \chi^{\mathrm{ALDA}}$$

$$\chi^{\mathrm{BSE}} = \chi^0_{\mathrm{GW}} + \chi^0_{\mathrm{GW}} \left(v - W \right) \chi^{\mathrm{BSE}}$$

Polarizability

$$\chi = \chi^0 + \chi^0 \left(v + f_{xc}^{e-h} \right)$$

Don't be fooled!
This is not RPA!!

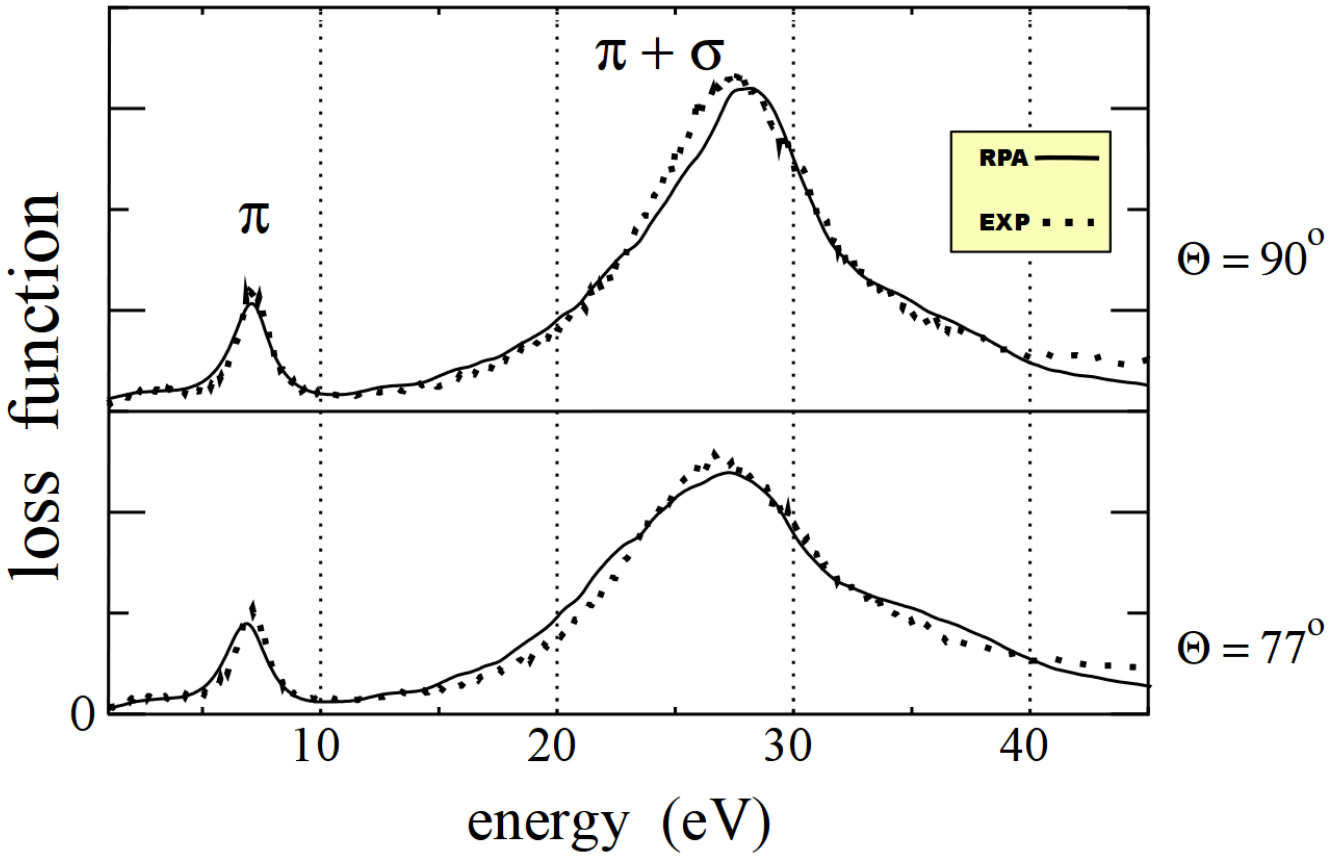


$$\chi^{\mathrm{RPA}} = \chi^0 + \chi^0 \left(v + \cancel{f_{xc}} \right) \chi^{\mathrm{RPA}}$$

$$\chi^{\mathrm{ALDA}} = \chi^0 + \chi^0 \left(v + f_{xc}^{\mathrm{ALDA}} \right) \chi^{\mathrm{ALDA}}$$

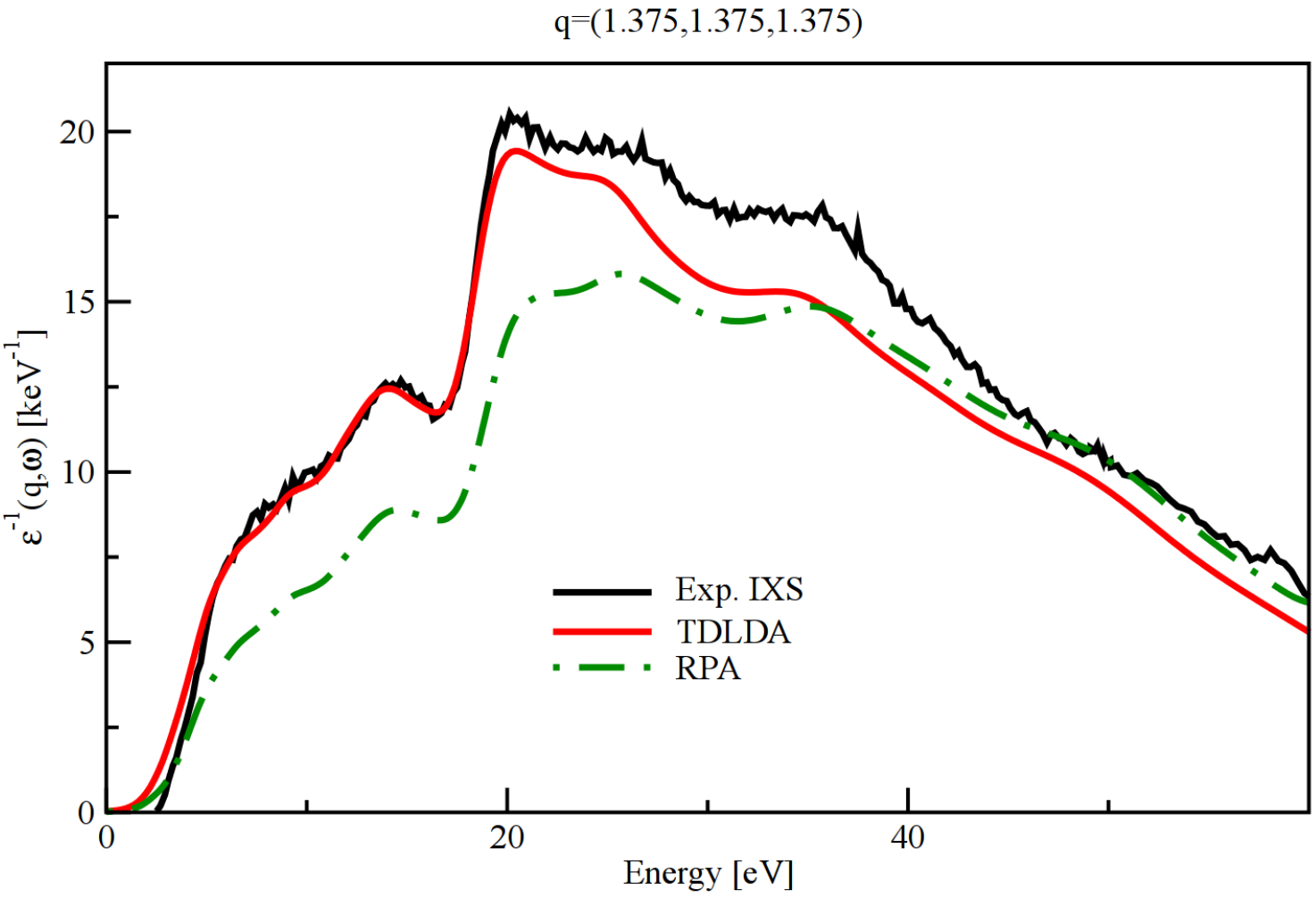
$$\chi^{\mathrm{BSE}} = \chi^0_{\mathrm{GW}} + \chi^0_{\mathrm{GW}} \left(v - W \right) \chi^{\mathrm{BSE}}$$

EELS of Graphite



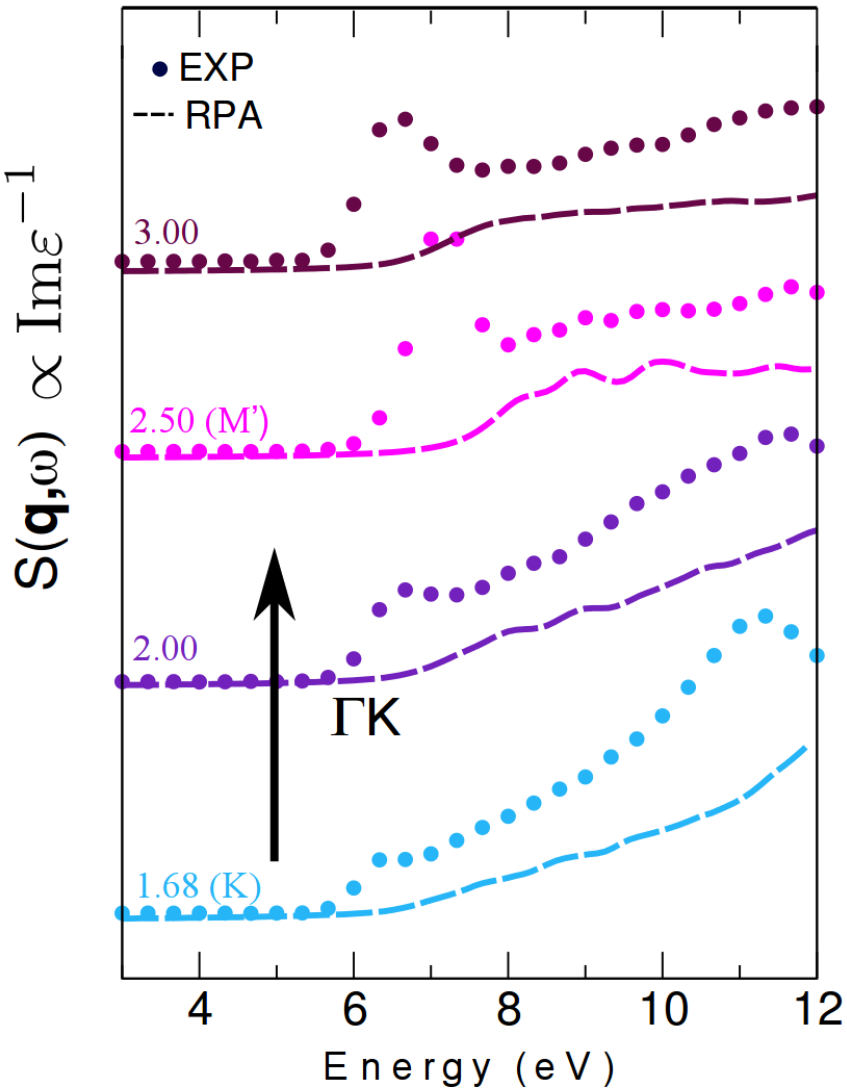
Marinopoulos *et al.* Phys. Rev. Lett. **89**, 076402 (2002)

IXS of Silicon



Weissker *et al.* Phys. Rev. Lett. **97,** 237602 (2006)

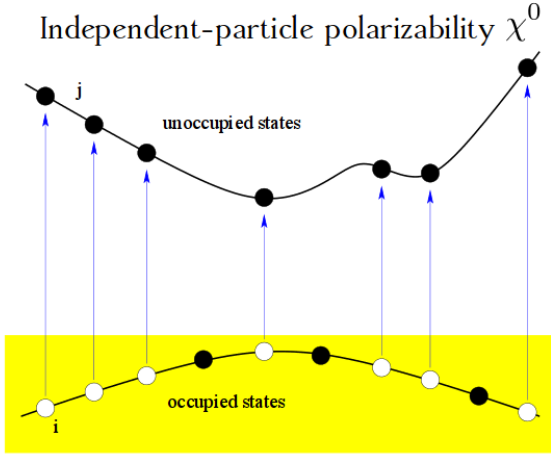
IXS of hBN



Galambosi *et al.* Phys. Rev. B **83**, 081413(R) (2011)

Polarizability

$$\chi = \chi^0 + \chi^0 \left(v + f_{xc}^{e-h} \right) \chi$$



$$\chi^{\mathrm{RPA}} = \chi^0 + \chi^0 \left(v + \cancel{f_{xc}} \right) \chi^{\mathrm{RPA}}$$

$$\chi^{\mathrm{ALDA}} = \chi^0 + \chi^0 \left(v + f_{xc}^{\mathrm{ALDA}} \right) \chi^{\mathrm{ALDA}}$$

$$\chi^{\mathrm{BSE}} = \chi^0_{\mathrm{GW}} + \chi^0_{\mathrm{GW}} \left(v - W \right) \chi^{\mathrm{BSE}}$$

$$\chi^{\mathrm{RPA}} = \chi^0 + \chi^0 \left(v + \cancel{f_{xc}}\right) \chi^{\mathrm{RP}}$$

$$\chi^{\mathrm{ALDA}} = \chi^0 + \chi^0 \left(v + f_{xc}^{\mathrm{ALDA}}\right) \chi$$

$$\chi^{\mathrm{BSE}} = \chi^0_{\mathrm{GW}} + \chi^0_{\mathrm{GW}} \left(v - W\right) \chi^{\mathrm{BSE}}$$

How do we describe excitons ?

$$\chi^0 = \sum_{vc} \frac{| < c|\mathbf{d}|v > |^2}{\omega - (\epsilon_c - \epsilon_v) + i\eta}$$

sum over independent transitions

no exciton by definition

independent-particle polarizability

How do we describe excitons ?

$$\chi^0 = \sum_{vc} \frac{| < c|\mathbf{d}|v > |^2}{\omega - (\epsilon_c - \epsilon_v) + i\eta}$$

sum over independent transitions

no exciton by definition

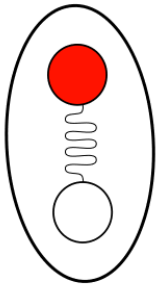
independent-particle polarizability

$$\chi = \sum_{\lambda} \frac{\left| \sum_{vc} A^{vc}_{\lambda} < c|\mathbf{d}|v > \right|^2}{\omega - E_{\lambda} + i\eta}$$

mixing of transitions

contains crystal local fields

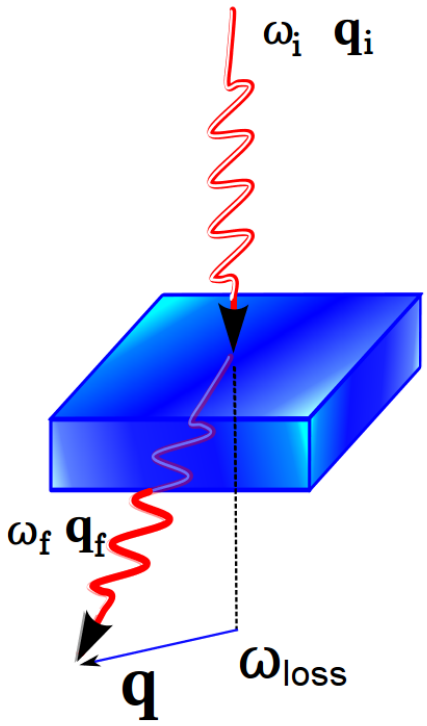
and excitonic effects



Bethe-Salpeter equation

well established, state-of-the-art theory for optical properties

IXS



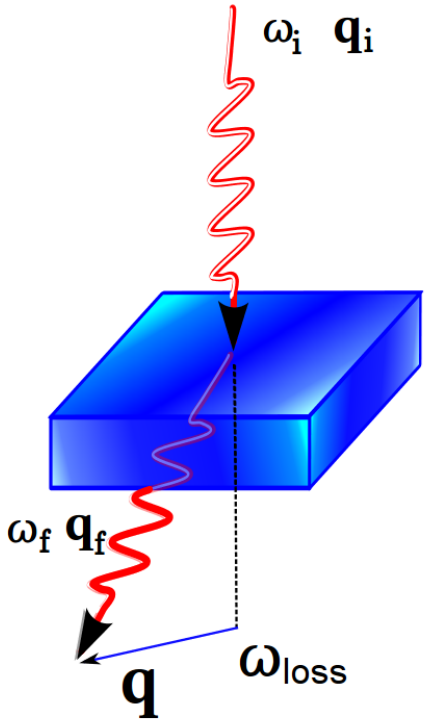
Exciton Dispersion

IXS

extension of the BSE to $\mathbf{q} \neq 0$

$$\chi = \sum_{\lambda} \frac{\left| \sum_{vc} A_{\lambda}^{vc} < c|\mathbf{d}|v > \right|^2}{\omega - E_{\lambda} + i\eta}$$

$$\chi(\mathbf{q},\omega) = \sum_{\lambda} \frac{\left| \sum_{vc} A_{\lambda}^{vc}(\mathbf{q}) < c|e^{i\mathbf{q}\cdot\mathbf{r}}|v > \right|^2}{\omega - E_{\lambda}(\mathbf{q}) + i\eta}$$



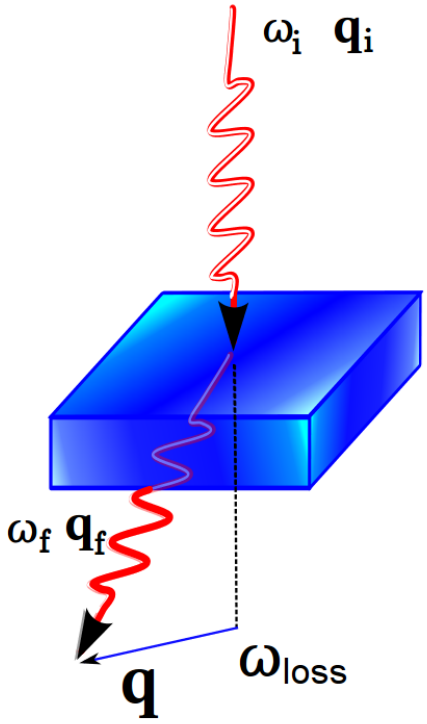
Exciton Dispersion

IXS

extension of the BSE to $\mathbf{q} \neq 0$

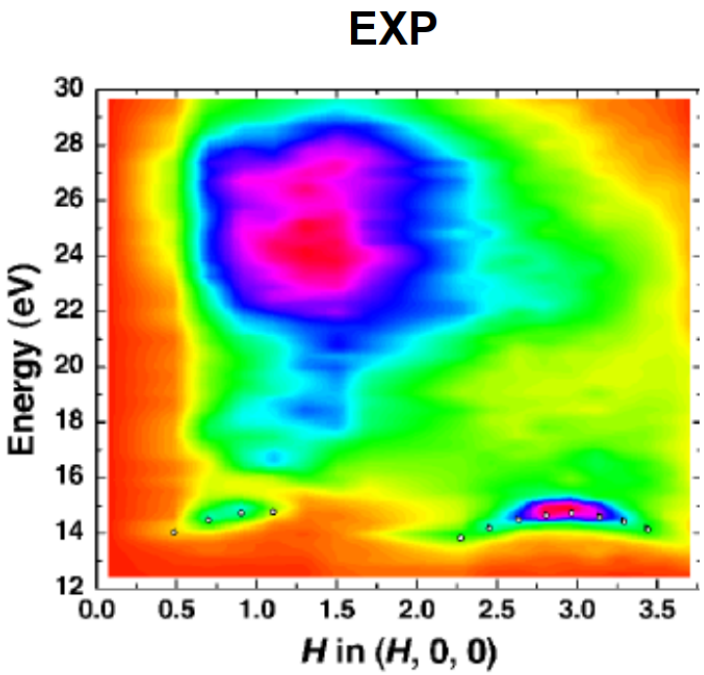
$$\chi = \sum_{\lambda} \frac{\left| \sum_{vc} A_{\lambda}^{vc} < c|\mathbf{d}|v > \right|^2}{\omega - E_{\lambda} + i\eta}$$

$$\chi(\mathbf{q},\omega) = \sum_{\lambda} \frac{\left| \sum_{vc} A_{\lambda}^{vc}(\mathbf{q}) < c|e^{i\mathbf{q}\cdot\mathbf{r}}|v > \right|^2}{\omega - E_{\lambda}(\mathbf{q}) + i\eta}$$

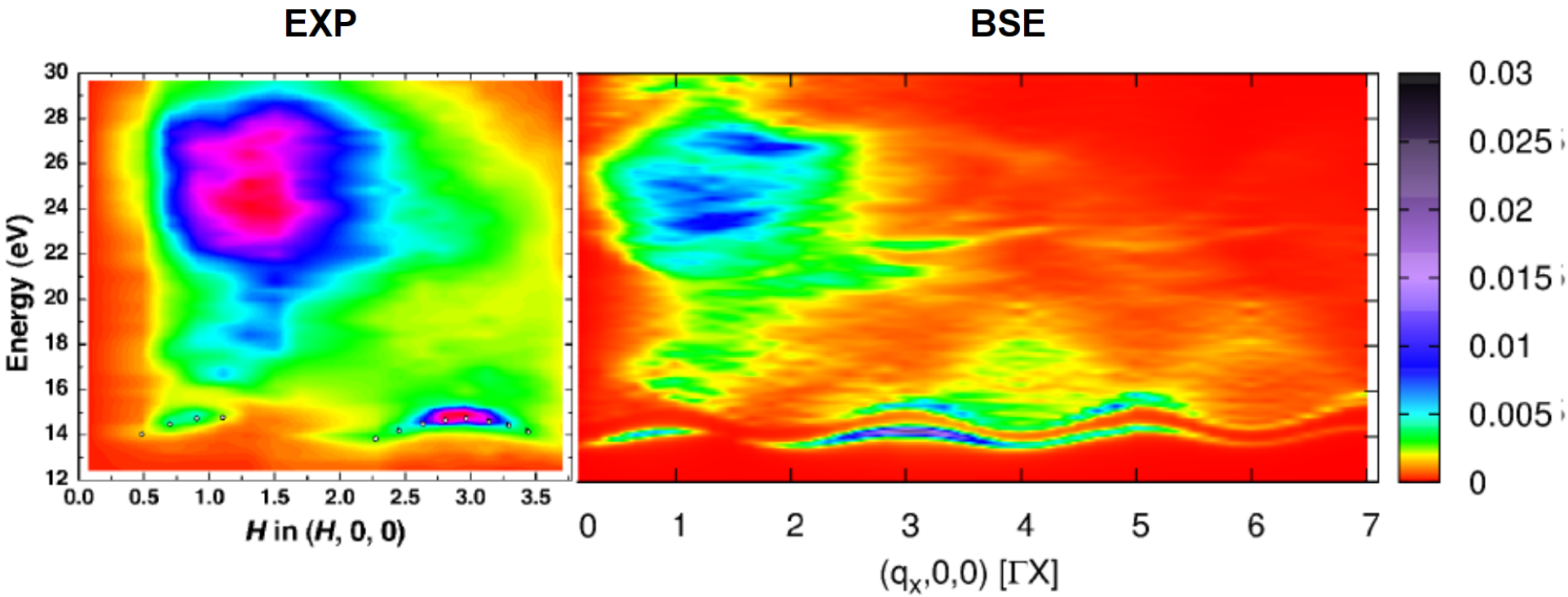


M. Gatti and F. Sottile PRB **88**, 85425 (2013)

The EXC code


EXP
Energy (eV)
30
28
26
24
22
20
18
16
14
12
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
H in (H, 0, 0)

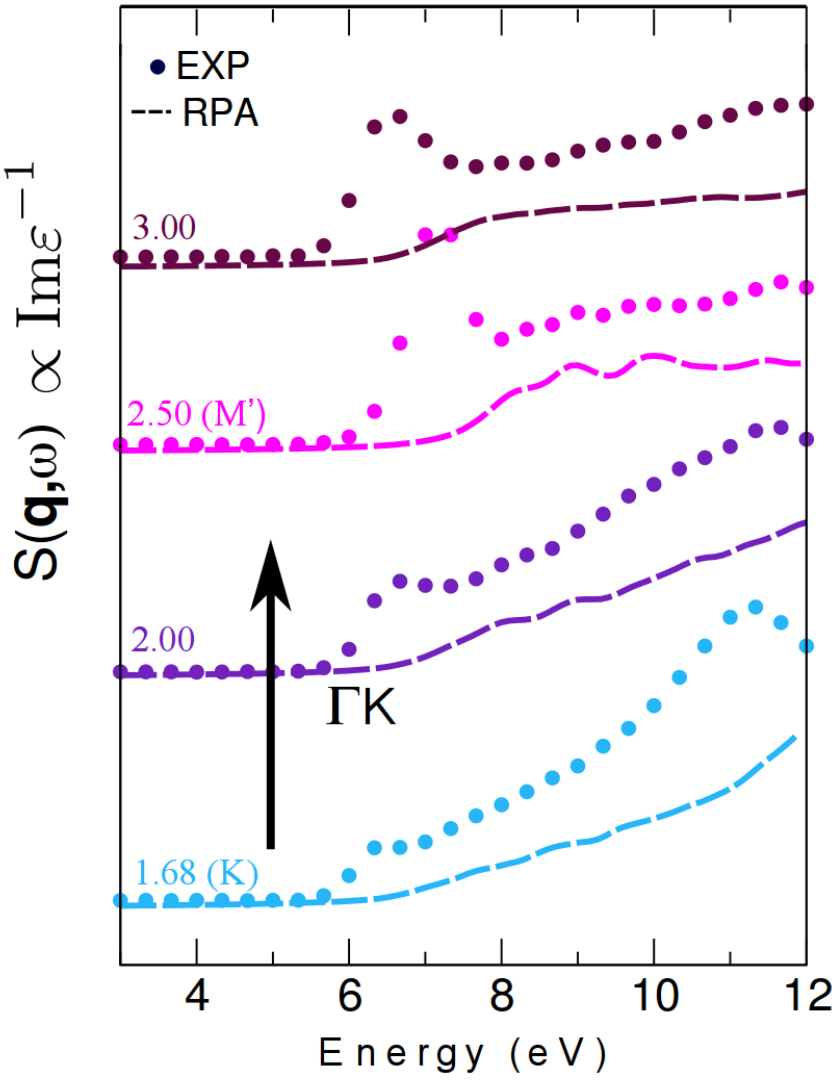
Dynamical Structure factor of LiF



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

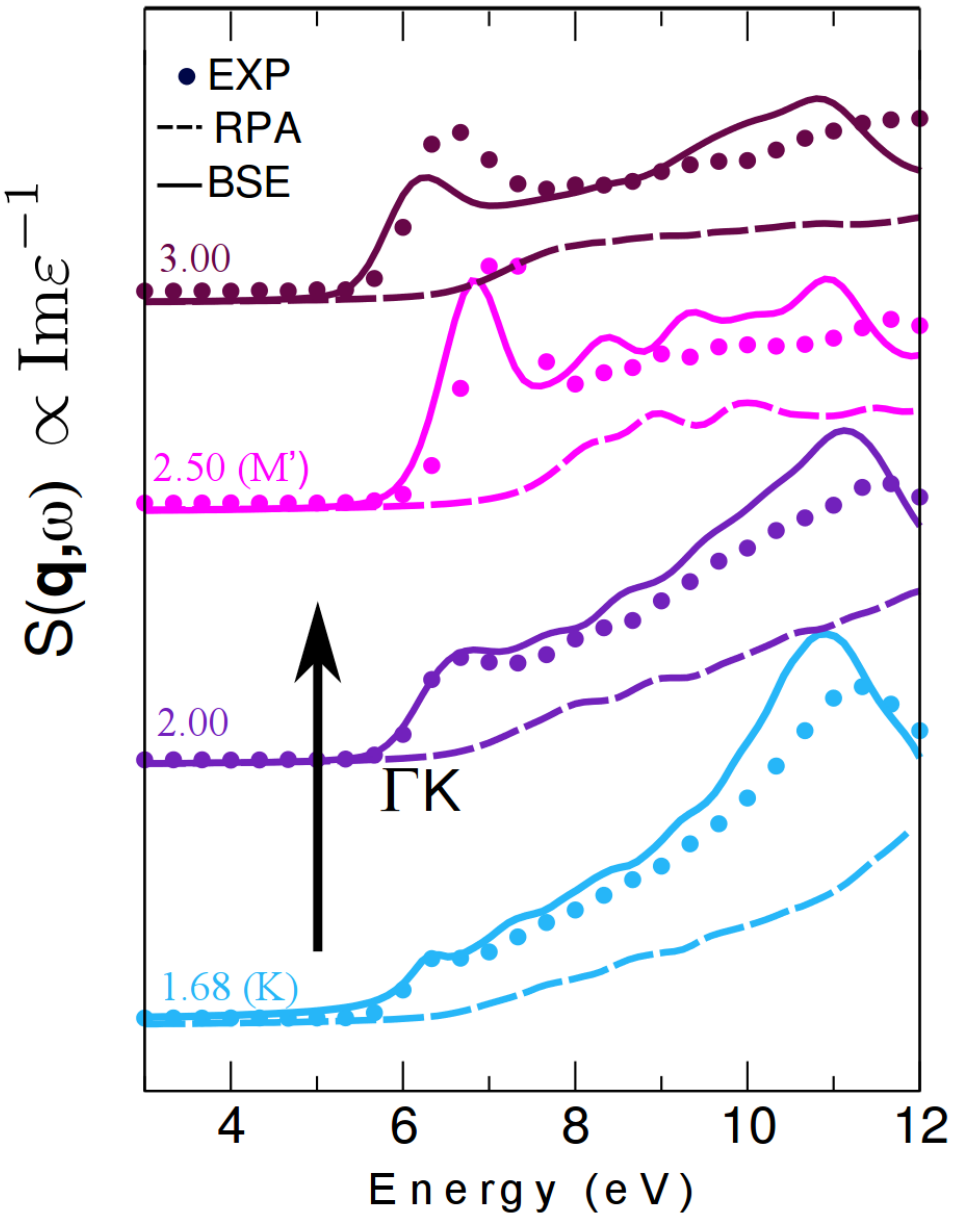
M. Gatti and F. Sottile PRB **88**, 85425 (2013)

IXS of hBN



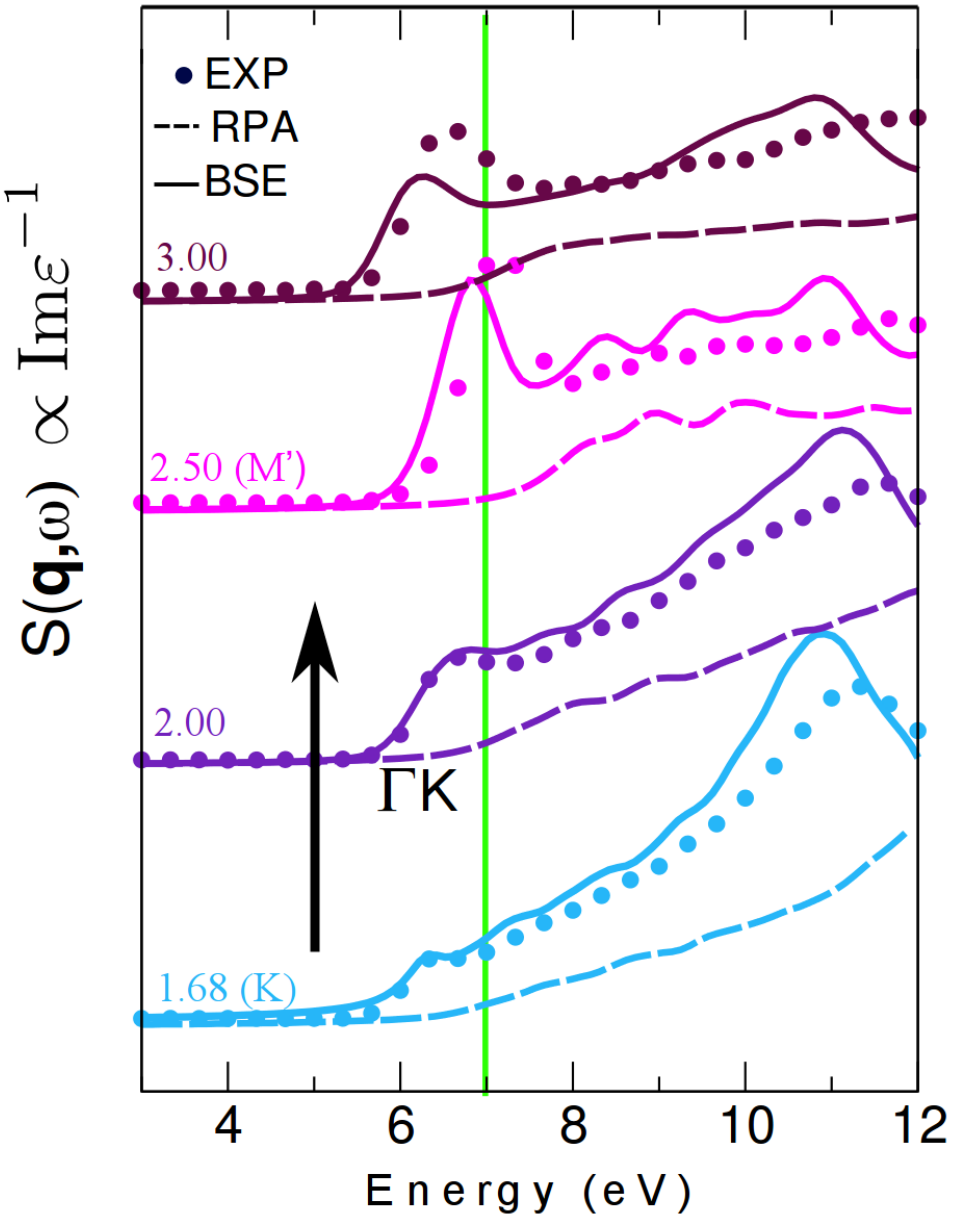
Galambosi *et al.* Phys. Rev. B **83**, 081413(R) (2011)

IXS of hBN



Fugallo *et al.* Phys. Rev. B **92**, 165122 (2015)

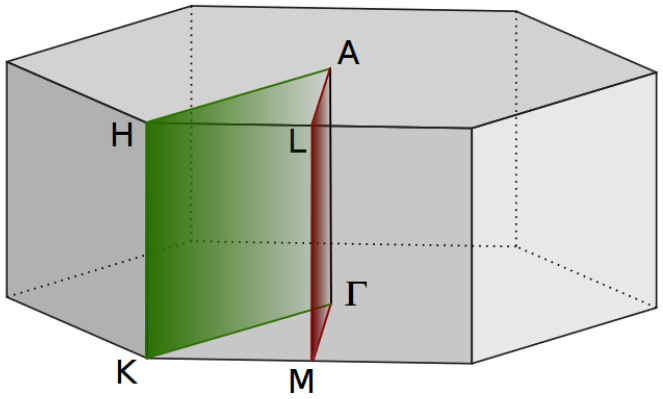
IXS of hBN

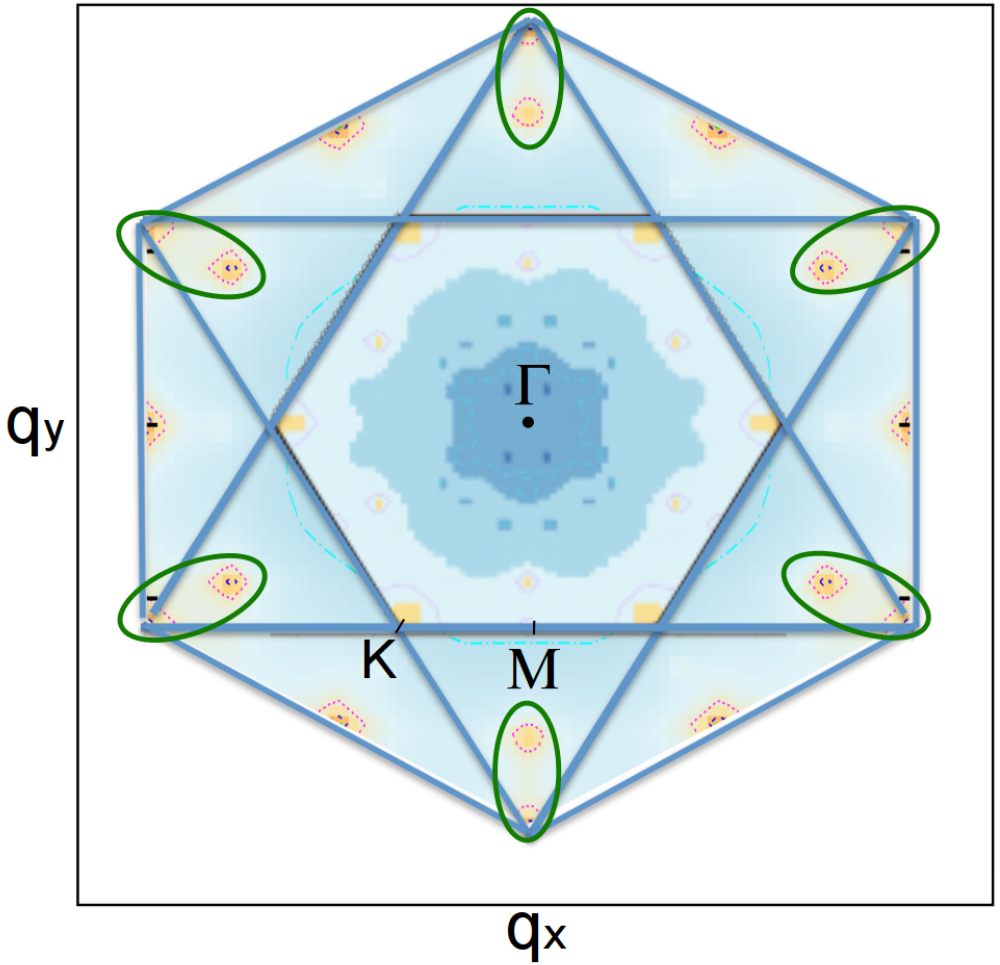


Fugallo *et al.* Phys. Rev. B **92**, 165122 (2015)

hexagonal Boron Nitride

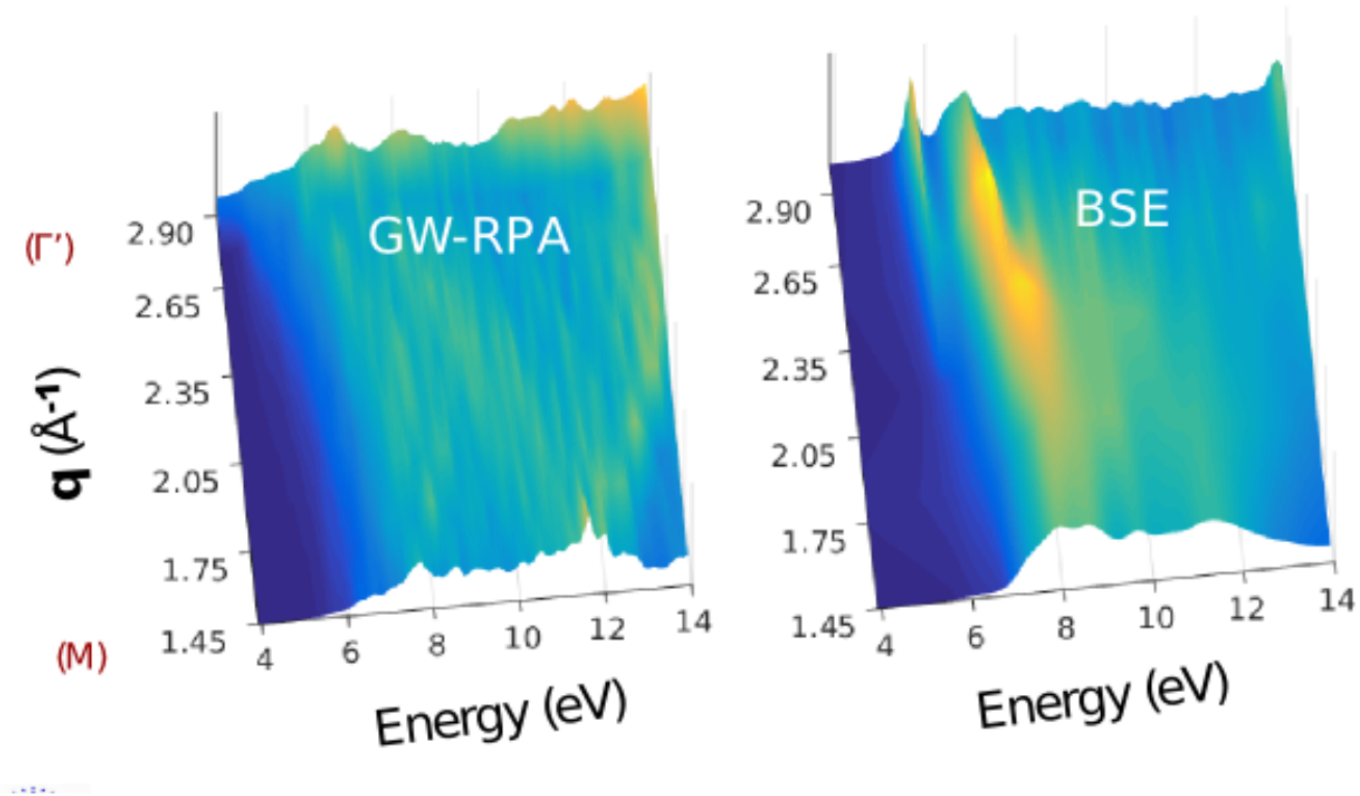
$$S(q, \omega = 7eV)$$





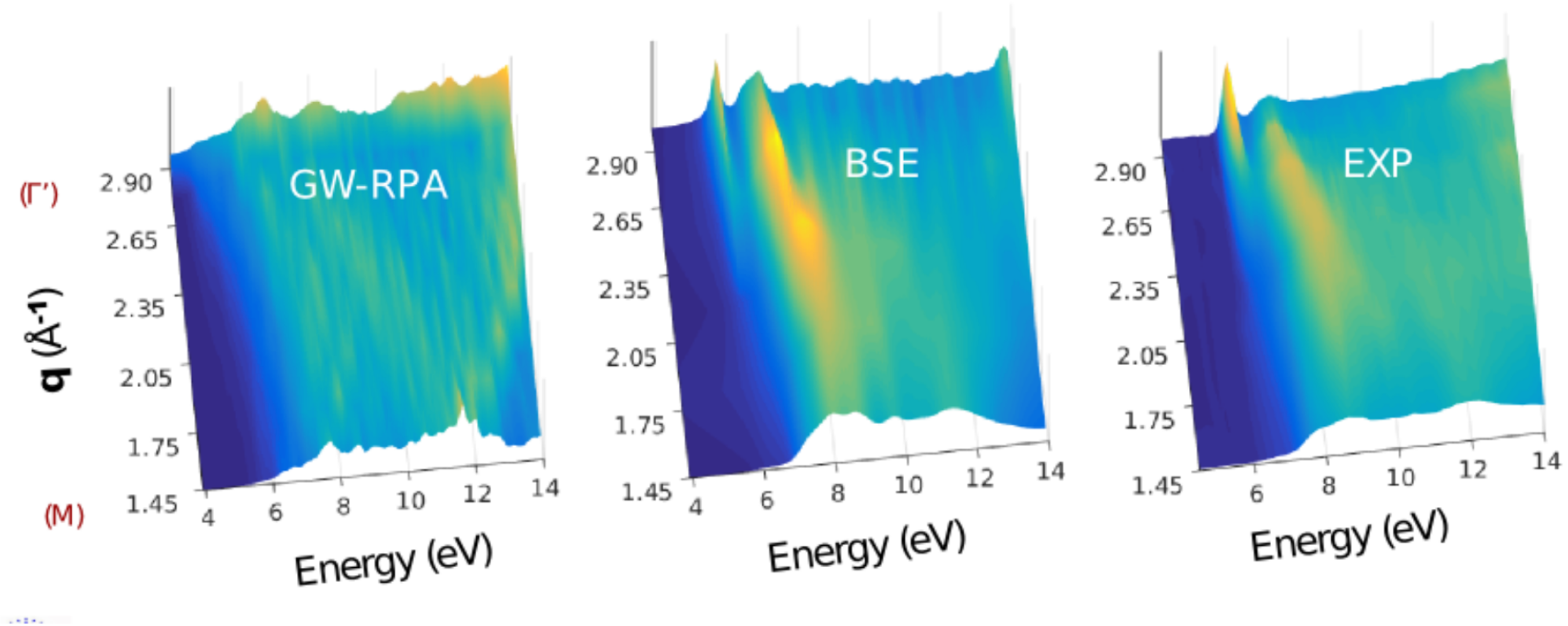
G. Fugallo *et al.* PRB **92**, 165122 (2015)

Exciton dispersion of h BN



G. Fugallo et al. Phys. Rev. B **92**, 165122 (2015)

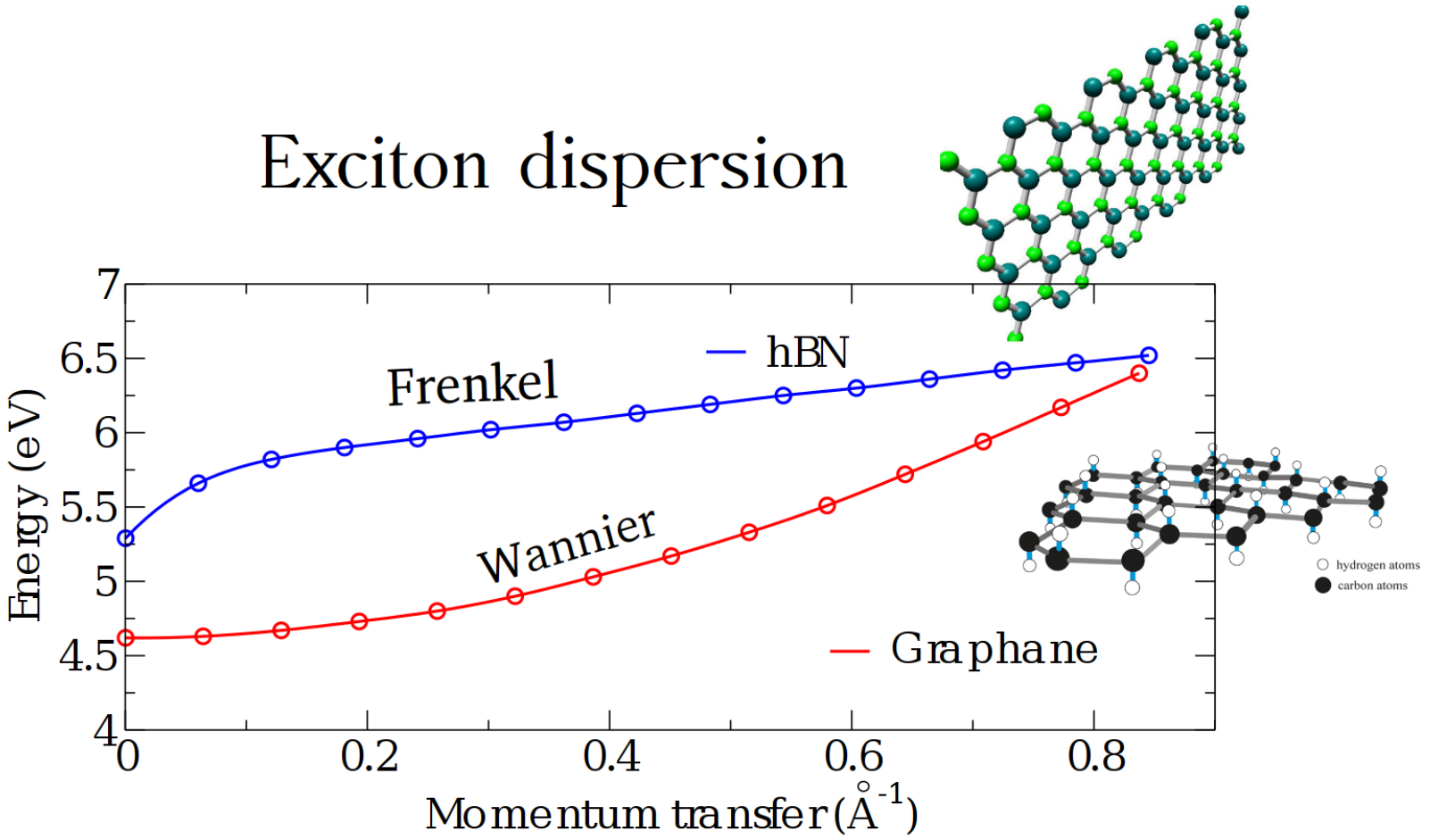
Exciton dispersion of h BN



ESRF ID20 beamline 5/2015

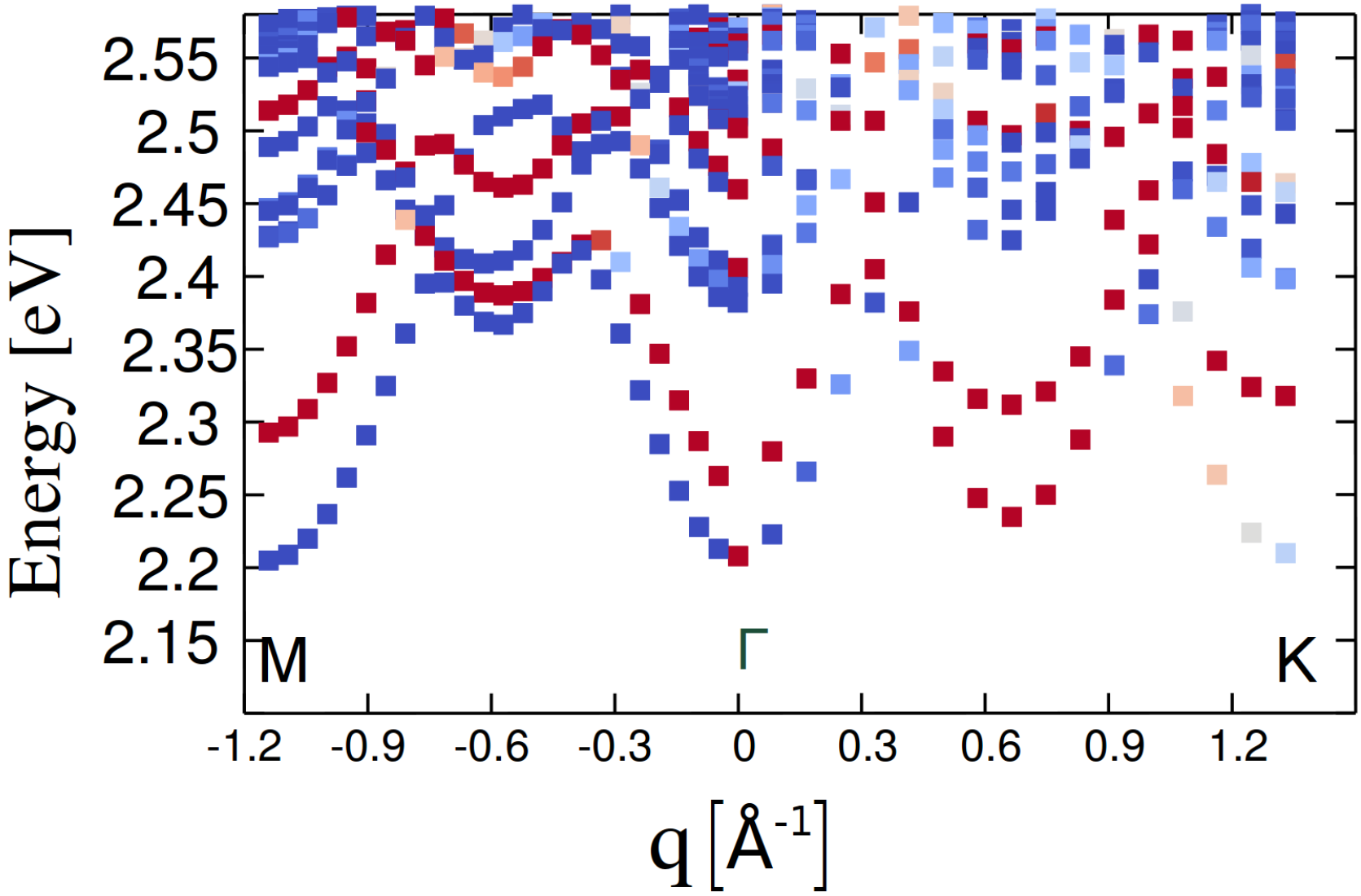
G. Fugallo et al. Phys. Rev. B **92**, 165122 (2015)

Theoretical predictions of 2D exciton dispersion



P. Cudazzo *et al.* PRL **116**, 066803 (2016)

Excitonic Band-structure of MoS_2 monolayer



Exciton Dispersion

$$\chi(\mathbf{q},\omega) = \sum_{\lambda} \frac{\left| \sum_{vc} A_{\lambda}^{vc}(\mathbf{q}) < c|e^{i\mathbf{q}\cdot\mathbf{r}}|v > \right|^2}{\omega - E_{\lambda}(\mathbf{q}) + i\eta}$$

Scattering experiments described and carefully analyzed

Dispersion predicted for 2D systems

Exciton Dispersion

$$\chi(\mathbf{q},\omega) = \sum_{\lambda} \frac{\left| \sum_{vc} A_{\lambda}^{vc}(\mathbf{q}) < c|e^{i\mathbf{q}\cdot\mathbf{r}}|v > \right|^2}{\omega - E_{\lambda}(\mathbf{q}) + i\eta}$$

Scattering experiments described and carefully analyzed

Dispersion predicted for 2D systems

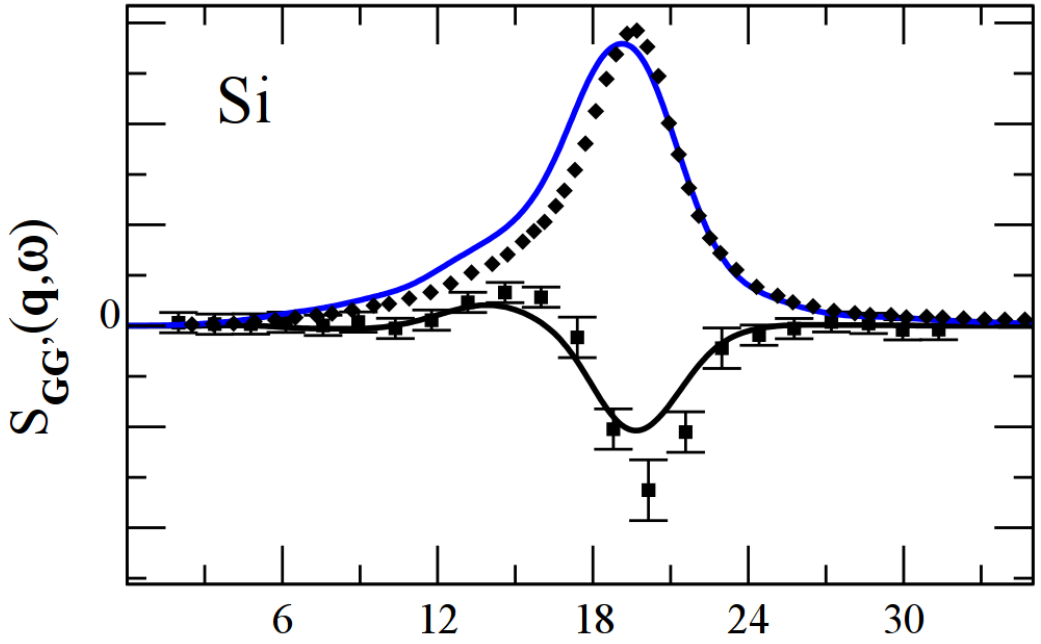
Opened a way of new series of tools and spectroscopies

Opened a way of new series of tools and spectroscopies

$$\chi(\mathbf{q},\omega) \Rightarrow \chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$$

non-diagonal response

q = (-1/2,-1/2,-1/2)
G = (1,1,1)
G' = (0,0,0)



Coherent Inelastic X-ray Scattering

- H.-C. Weissker PRL 2010
- W. Schulke and A. Kaprolat PRL 1991
- I. Reshetnyak PhD Thesis 2015

Opened a way of new series of tools and spectroscopies

$$\delta n(\mathbf{r},\omega) = \int d\mathbf{r}' \chi(\mathbf{r},\mathbf{r}',\omega)\delta V_{\mathrm{ext}}(\mathbf{r}',\omega)$$

Opened a way of new series of tools and spectroscopies

$$\delta n(\mathbf{r},t) = \int d\omega \sum_{\mathbf{q},\mathbf{G},\mathbf{G}'} \chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) V_{ext}(\mathbf{q}+\mathbf{G}',\omega) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} e^{-i\omega t}$$

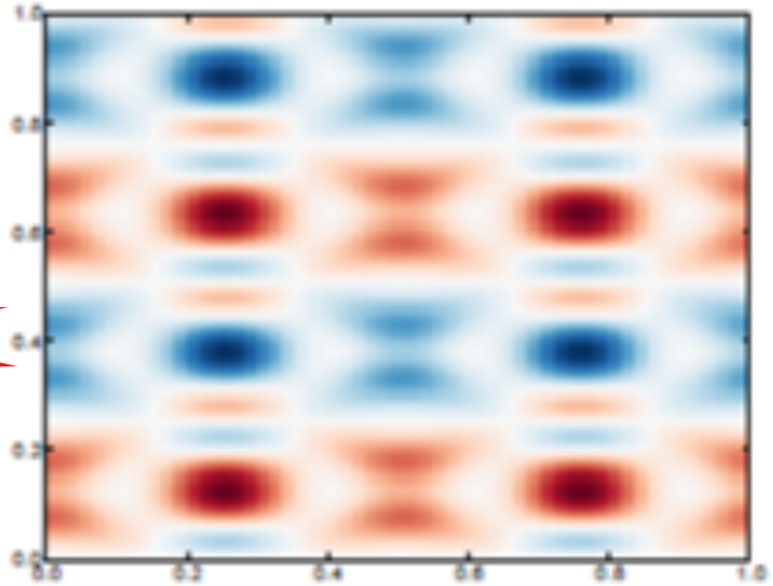
Opened a way of new series of tools and spectroscopies

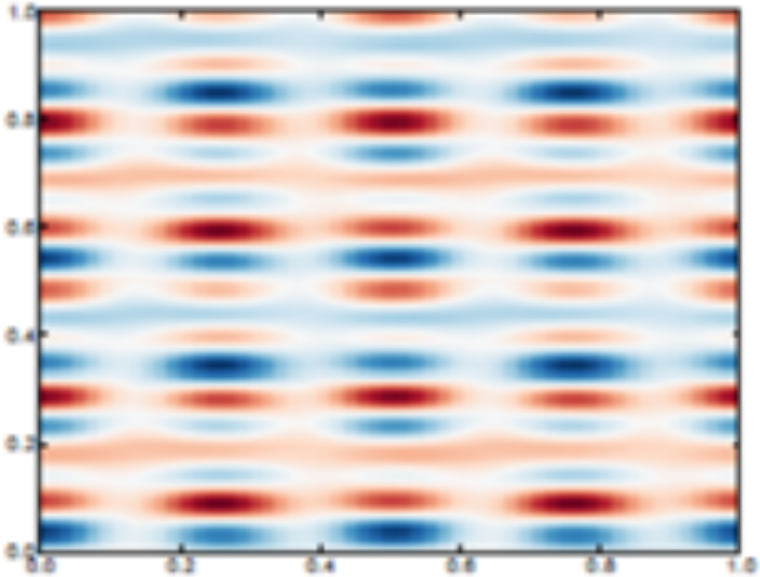
visualization of induced charge (LiF)

$$\delta n(\mathbf{r},t) = \int d\omega \sum_{\mathbf{q},\mathbf{G},\mathbf{G}'} \chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) V_{ext}(\mathbf{q}+\mathbf{G}',\omega) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}} e^{-i\omega t}$$

RPA

~~**exciton**~~





BSE

exciton

R. Hambach PhD Thesis 2010

I. Reshetnyak PhD Thesis 2015

Outline

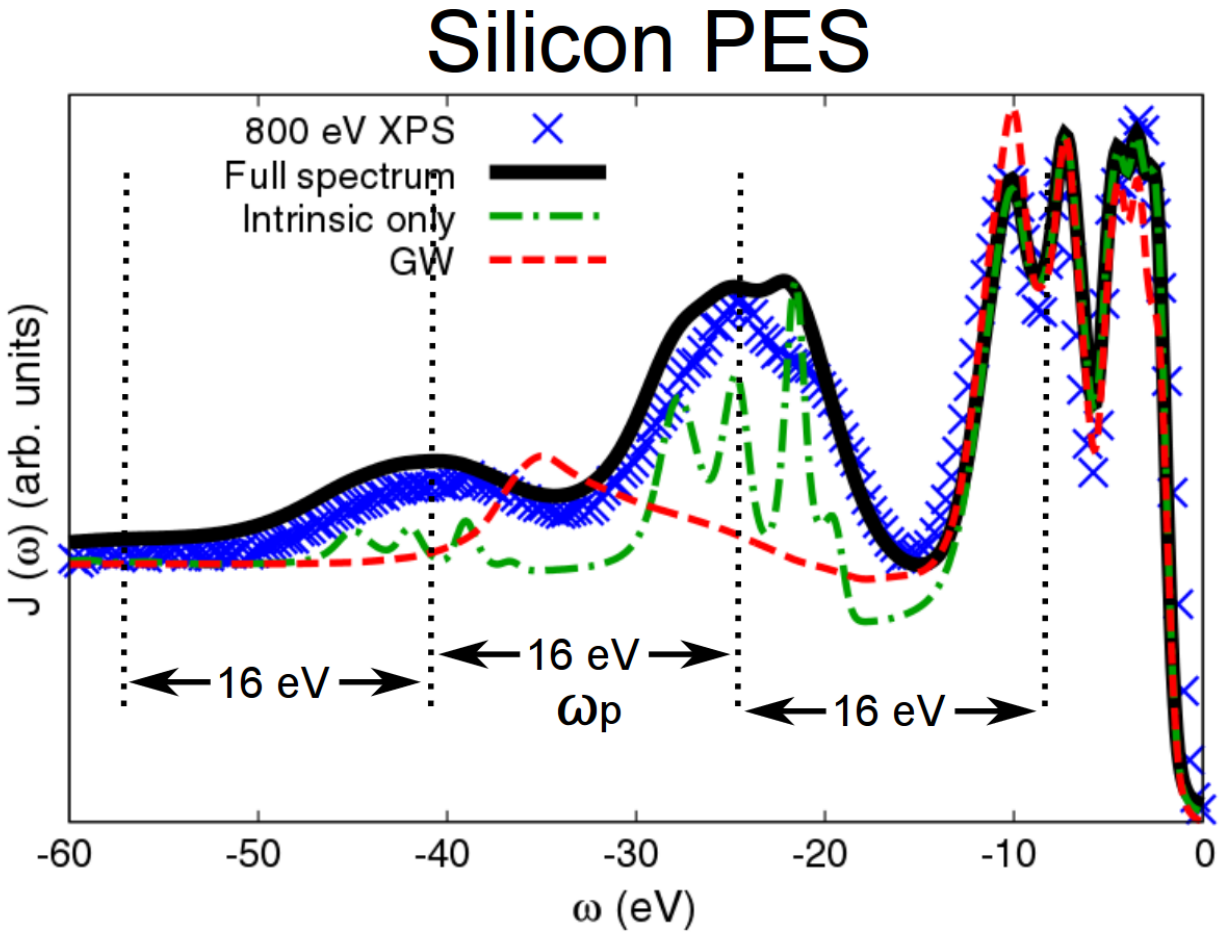
- IXS, EELS beyond RPA
  - excitonic effects in IXS,EELS
  - exciton dispersion
  - visualisation tools
  - Coherent Inelastic X-ray Scattering
- Photo-emission beyond GW

Satellites in Photoemission

Plasmon Satellites

Cumulant expansion
(well beyond GW)

Main ingredient ::
Loss function

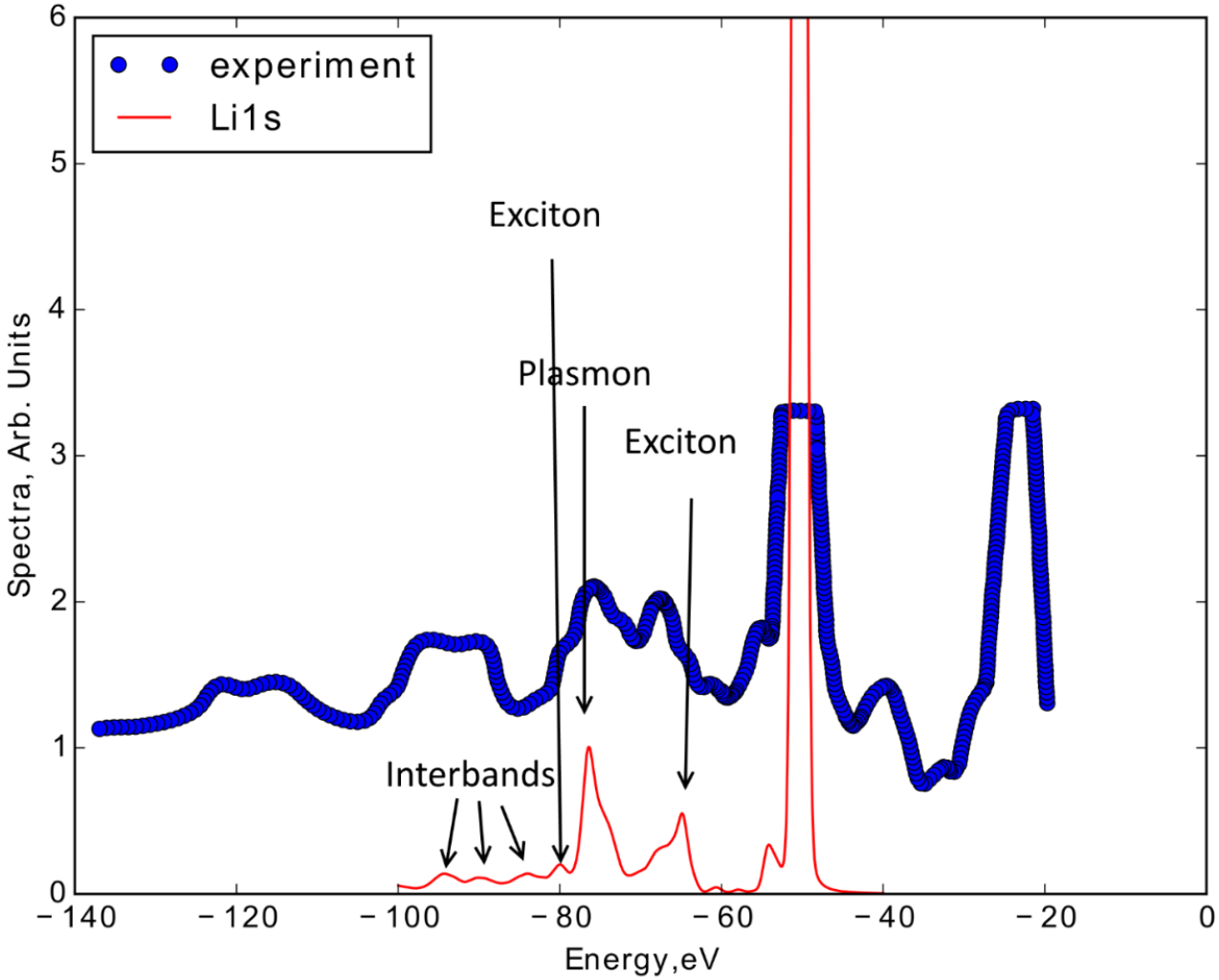


M. Guzzo et al. PRL **107**, 166401 (2011).

Satellites in Photoemission

What about exciton satellites ?

Photo-emission spectra of LiF



M. Scrocco PRB **32**, 1306 (1985)

I. Reshetnyak PhD Thesis 2015

Conclusions

added new dimensions (q,G,G') to the problem

- ✓ exciton dispersion (bulk, layered, 2D systems)
- ✓ excitonic band structure
- ✓ new spectroscopies (Coherent Inelastic X-ray Scattering)
- ✓ visualization tools
- ✓ tackle new challenges in theory (exciton satellites)

- new spectroscopies (Resonant Inelastic X-ray Scattering)
- ...influence of excitonic W (GW, DMFT, condensation,etc.)

Acknowledgments

- **Matteo Gatti** extension of the BSE to $\mathbf{q} \neq 0$
- **Pierluigi Cudazzo, Giorgia Fugallo**
  exciton dispersion of layered and 2D systems
- **Lucia Reining, Matteo Guzzo, Igor Reshetnyak**
  non-diagonal response, exciton satellites
- **Fausto Sirotti (SOLEIL), Simo Huotari (ESRF)**
  our friends from the dark side (experimentalists)
- **Theoretical Spectroscopy Group in Palaiseau**

Thank you