Theoretical Spectroscopy
new frontiers for photoemission and inelastic X-ray scattering

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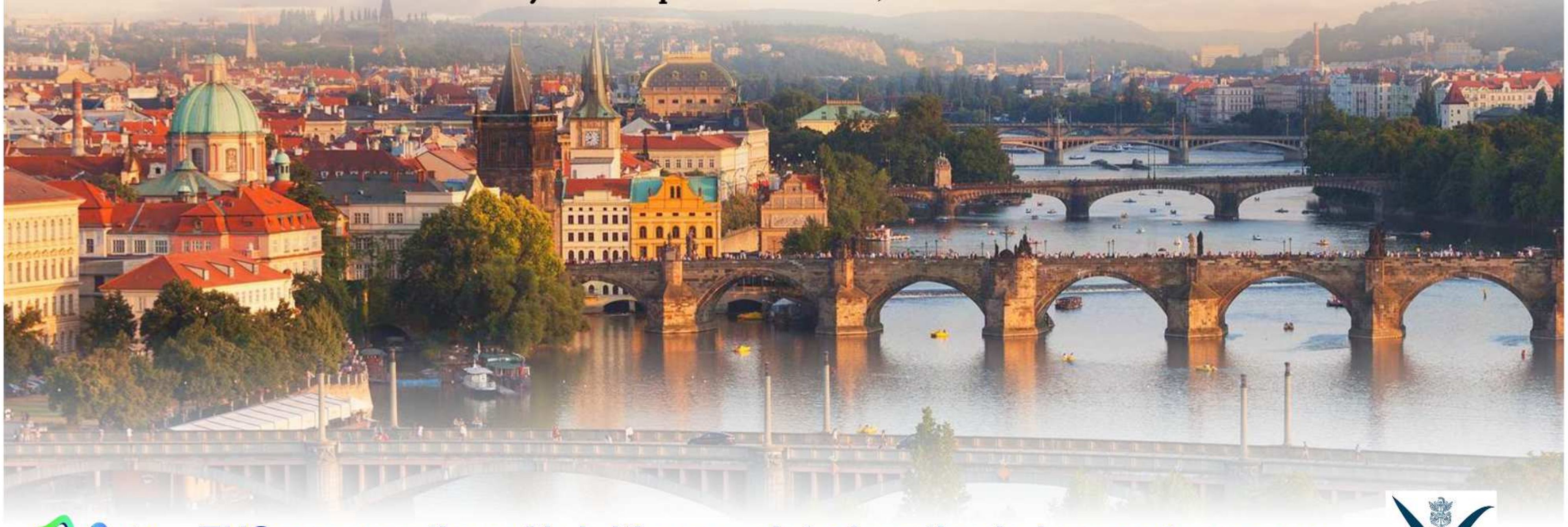


EUSpec meeting: Ab-initio correlated methods in spectroscopy
Prague - 8 February 2017

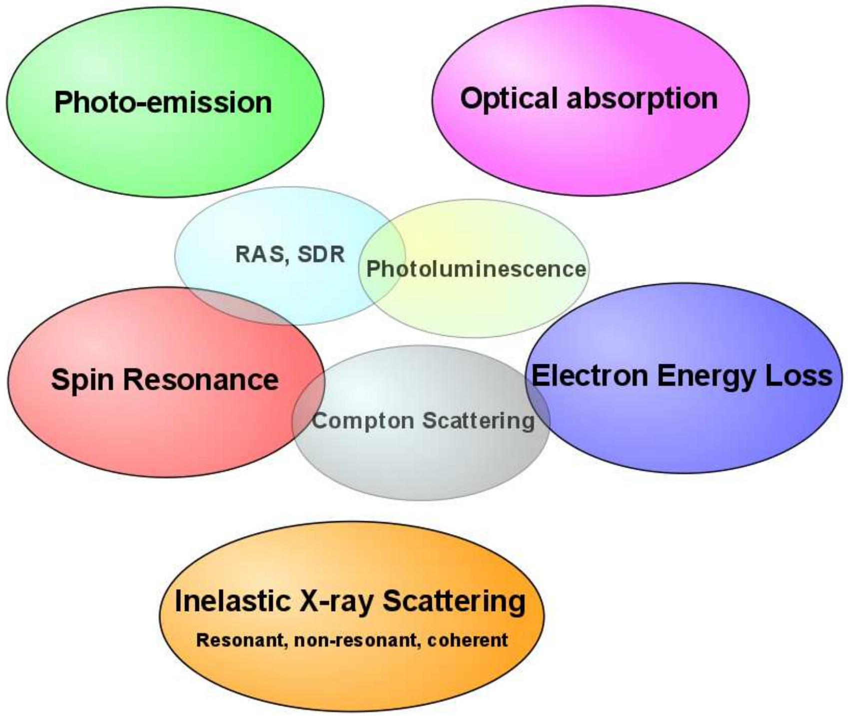
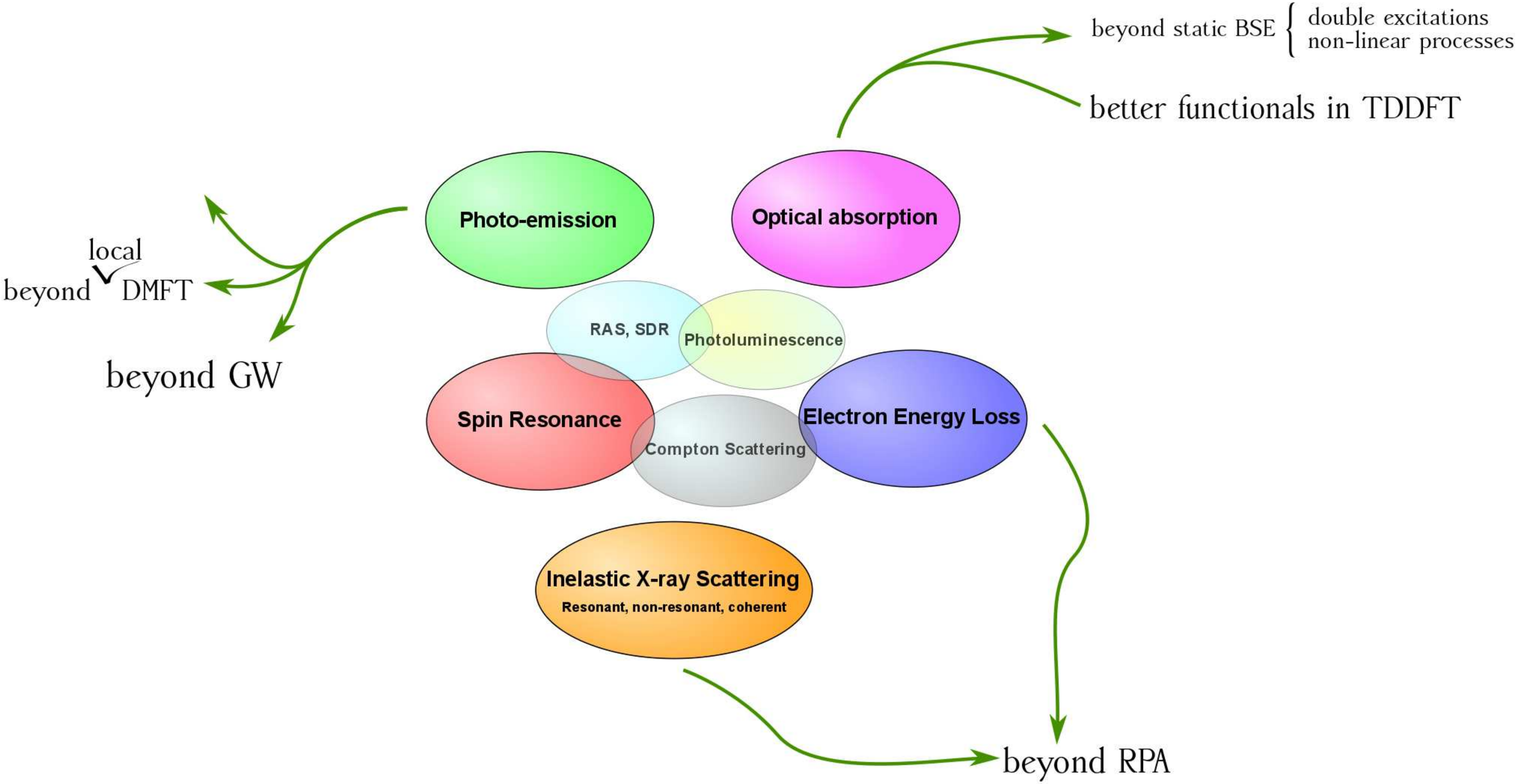


Photo-emission
Optical absorption
RAS, SDR
Photoluminescence
Spin Resonance
Compton Scattering
Electron Energy Loss
Inelastic X-ray Scattering
Resonant, non-resonant, coherent

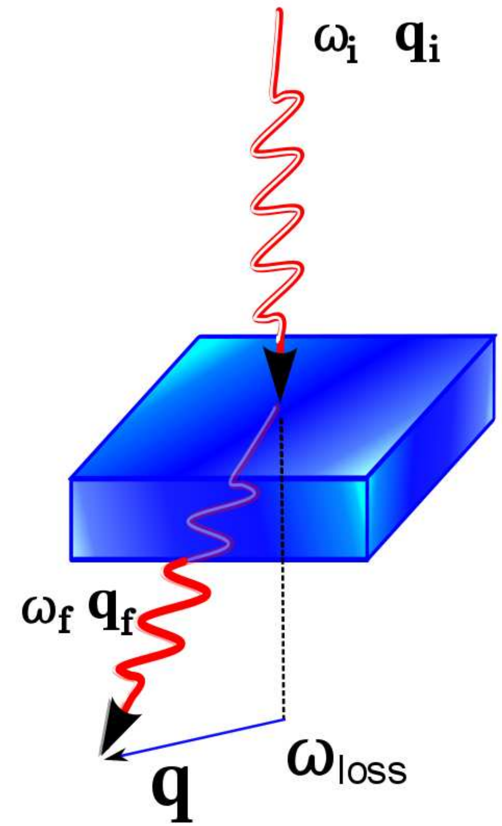

beyond static BSE
double excitations
non-linear processes
better functionals in TDDFT
Photo-emission
Optical absorption
local
beyond DMFT
RAS, SDR
Photoluminescence
beyond GW
Spin Resonance
Electron Energy Loss
Compton Scattering
Inelastic X-ray Scattering
Resonant, non-resonant, coherent
beyond RPA

Outline

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

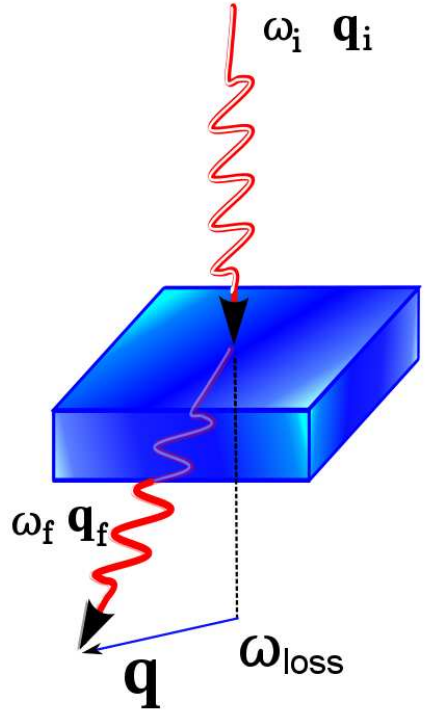
Inelastic X-ray Scattering

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



Inelastic X-ray Scattering

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



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

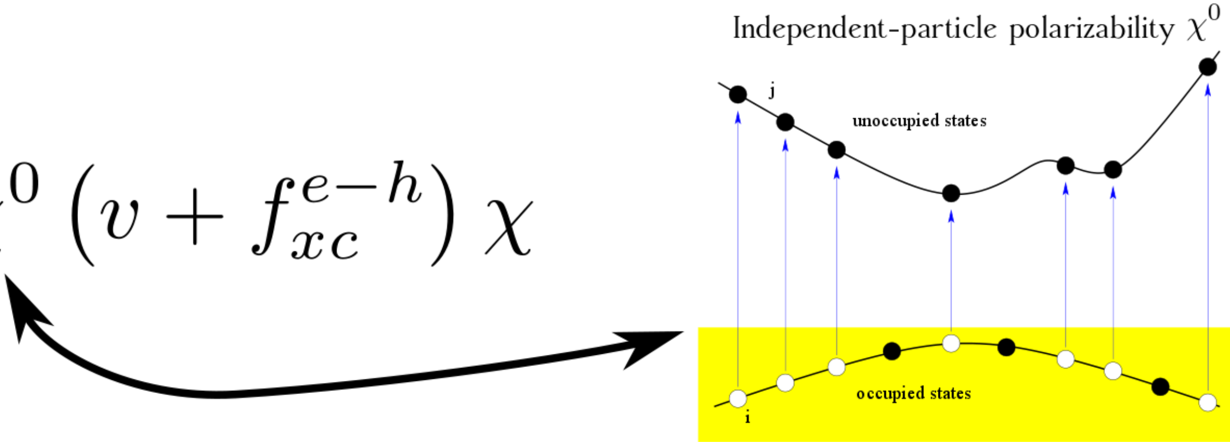
screening

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

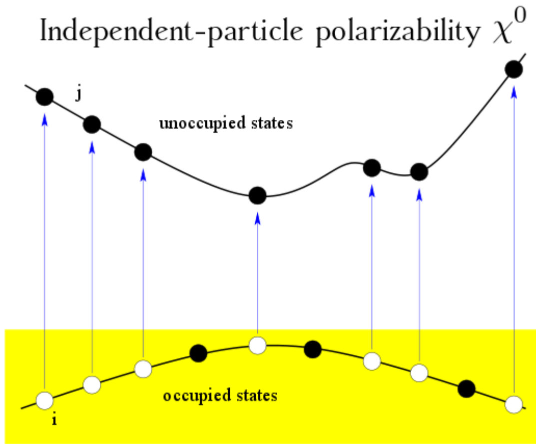
density-density response function

Polarizability

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



Polarizability



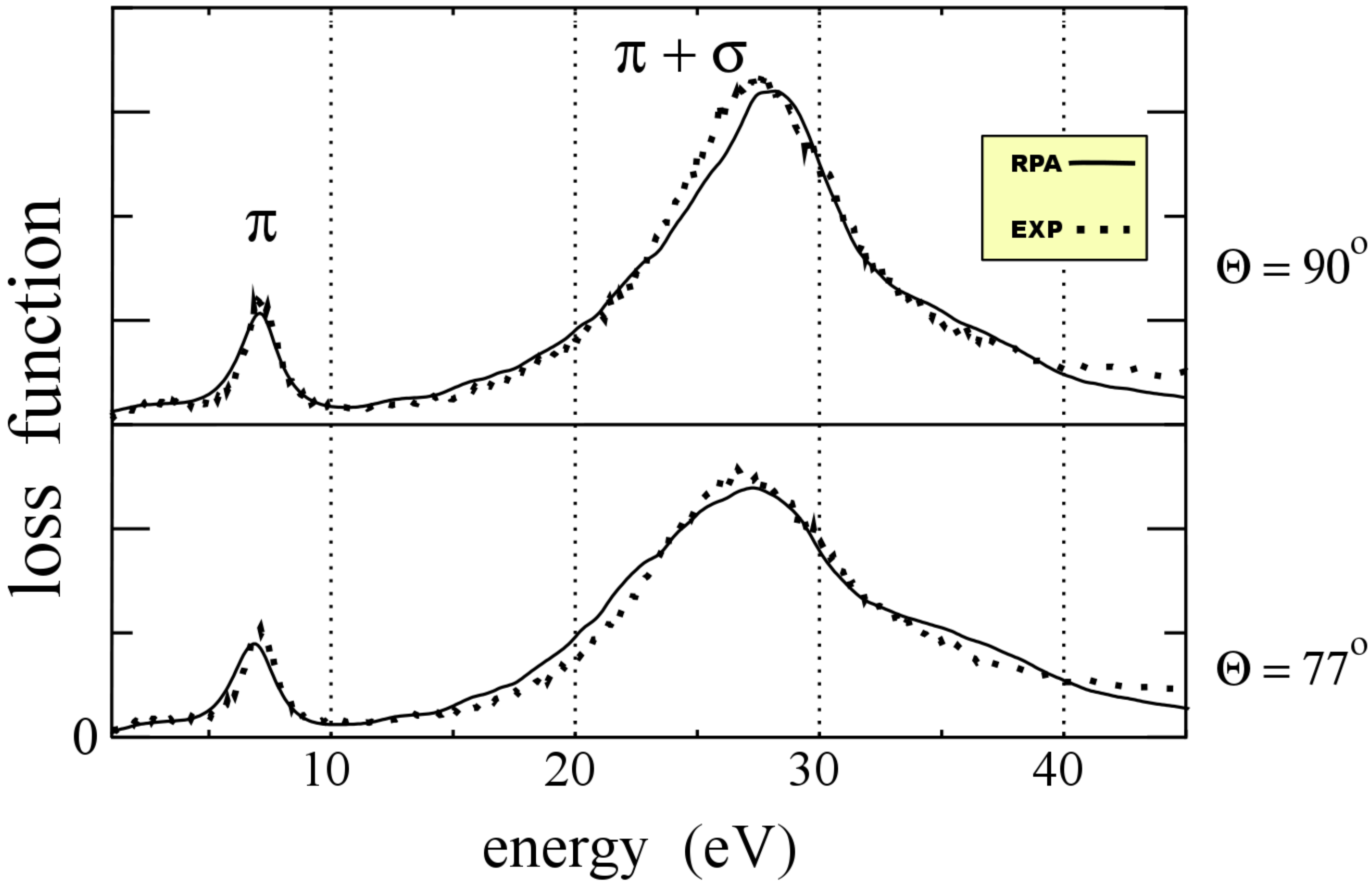
$$\chi = \chi^0 + \chi^0 \left(v + f_{xc}^{e-h}\right) \chi$$

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

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

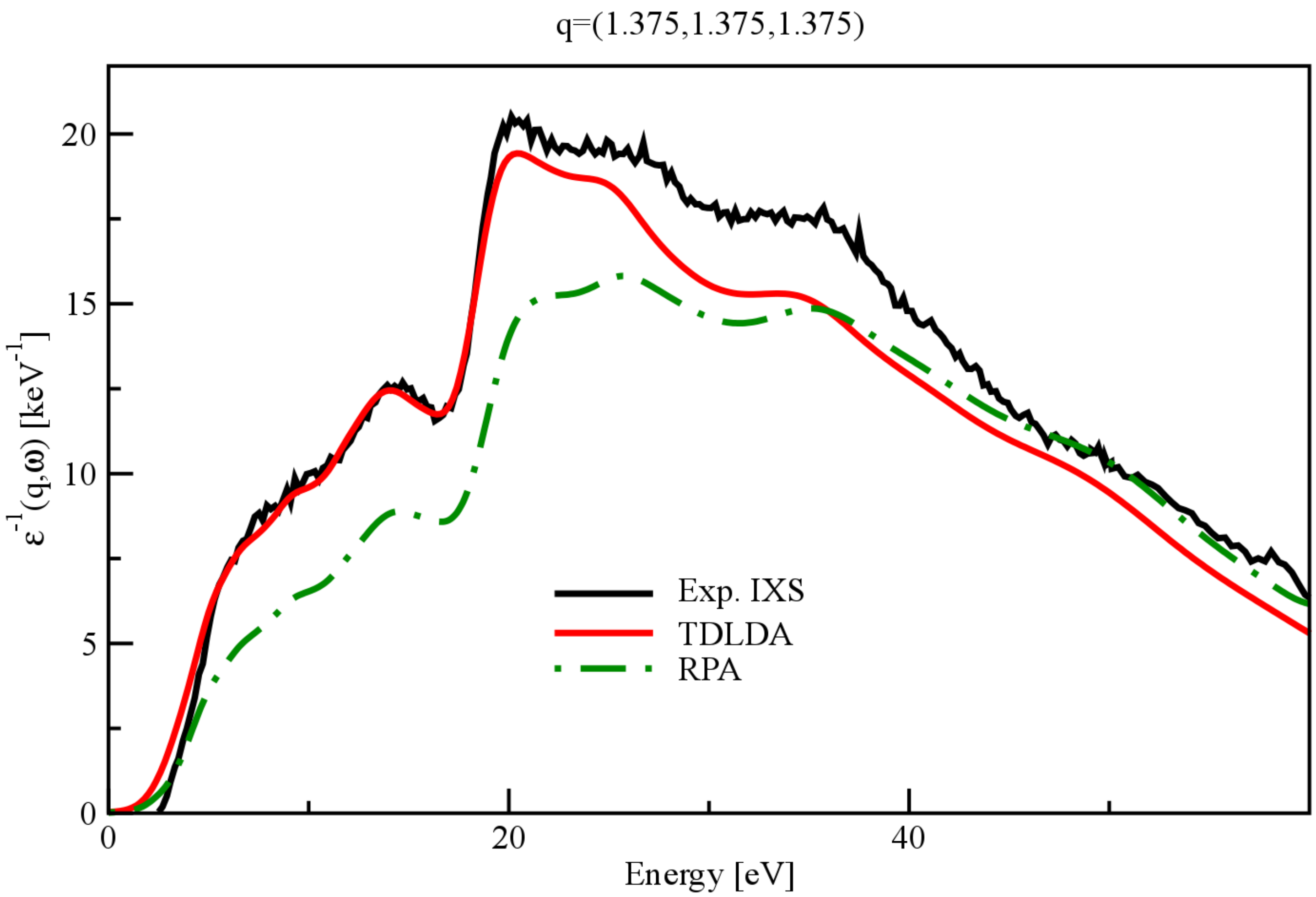
$$\chi^{\mathrm{BSE}} = \chi^0_{\mathrm{GW}} + \chi^0_{\mathrm{GW}} \left(v - W\right) \chi^{\mathrm{BSE}}$$

EELS of Graphite



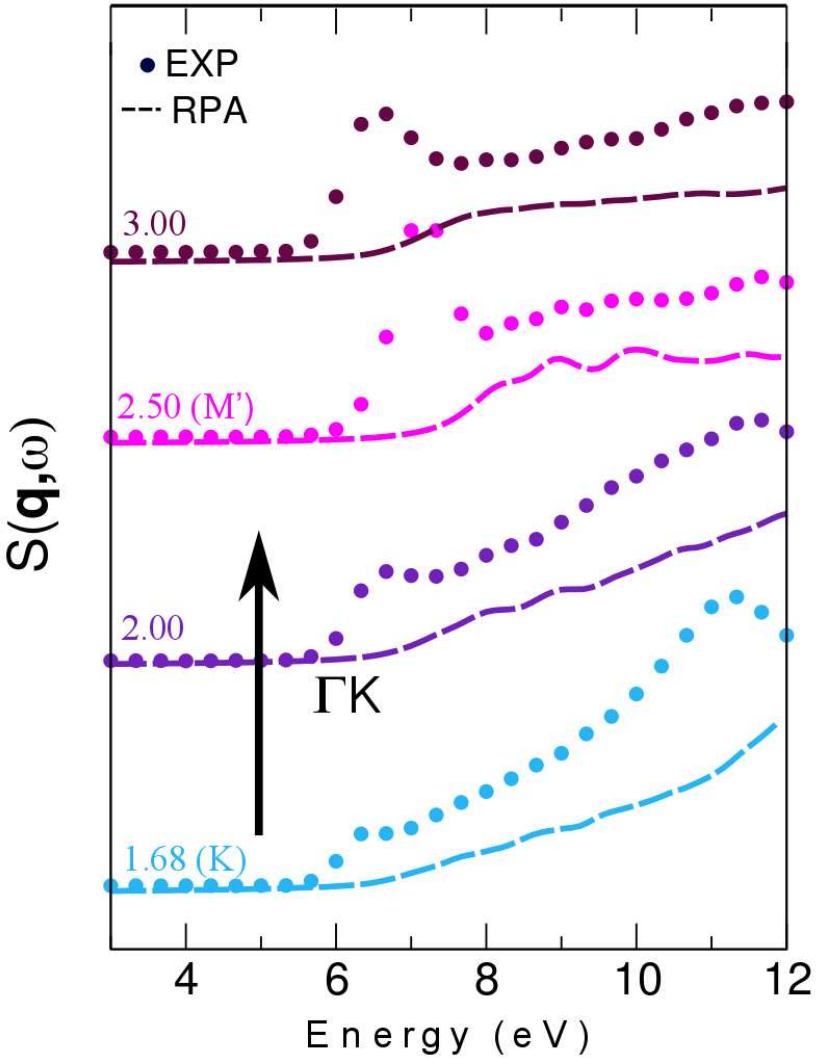
Marinopoulos *et al.* Phys. Rev. Lett. **89**, 076402 (2002)

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)

Ab initio description of 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

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

mixing of transitions
contains crystal local fields
and excitonic effects

Bethe-Salpeter equation

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

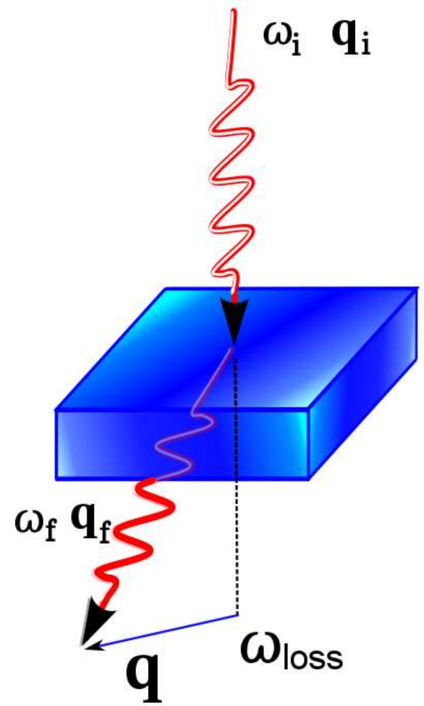
Exciton Dispersion

IXS

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

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

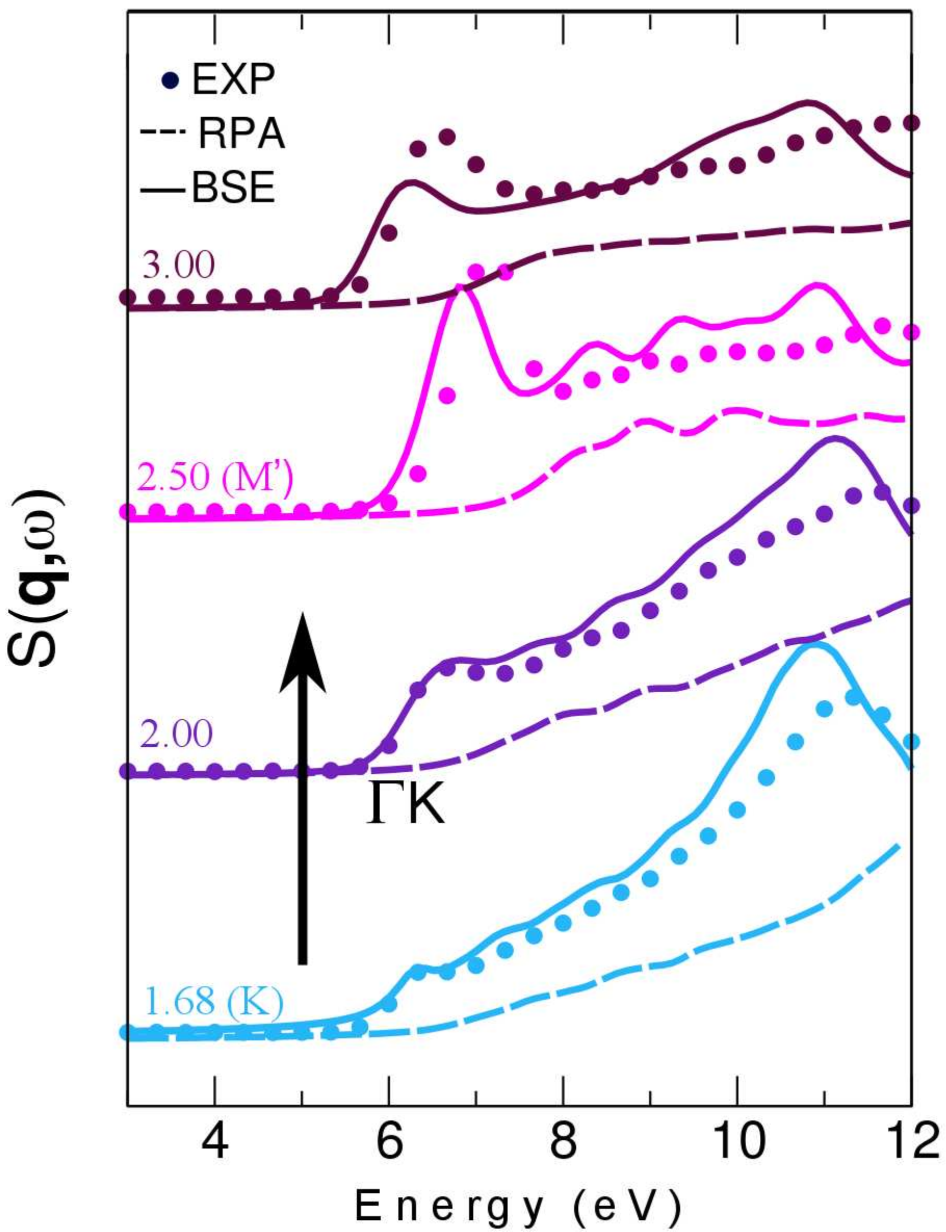
$$\chi(\mathbf{q}, \omega) = \sum_\lambda \frac{\left| \sum_{vc} A_\lambda^{vc}(\mathbf{q}) < c|e^{i\mathbf{q}\cdot\mathbf{r}}|v > \right|^2}{\omega - E_\lambda(\mathbf{q}) + i\eta}$$



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

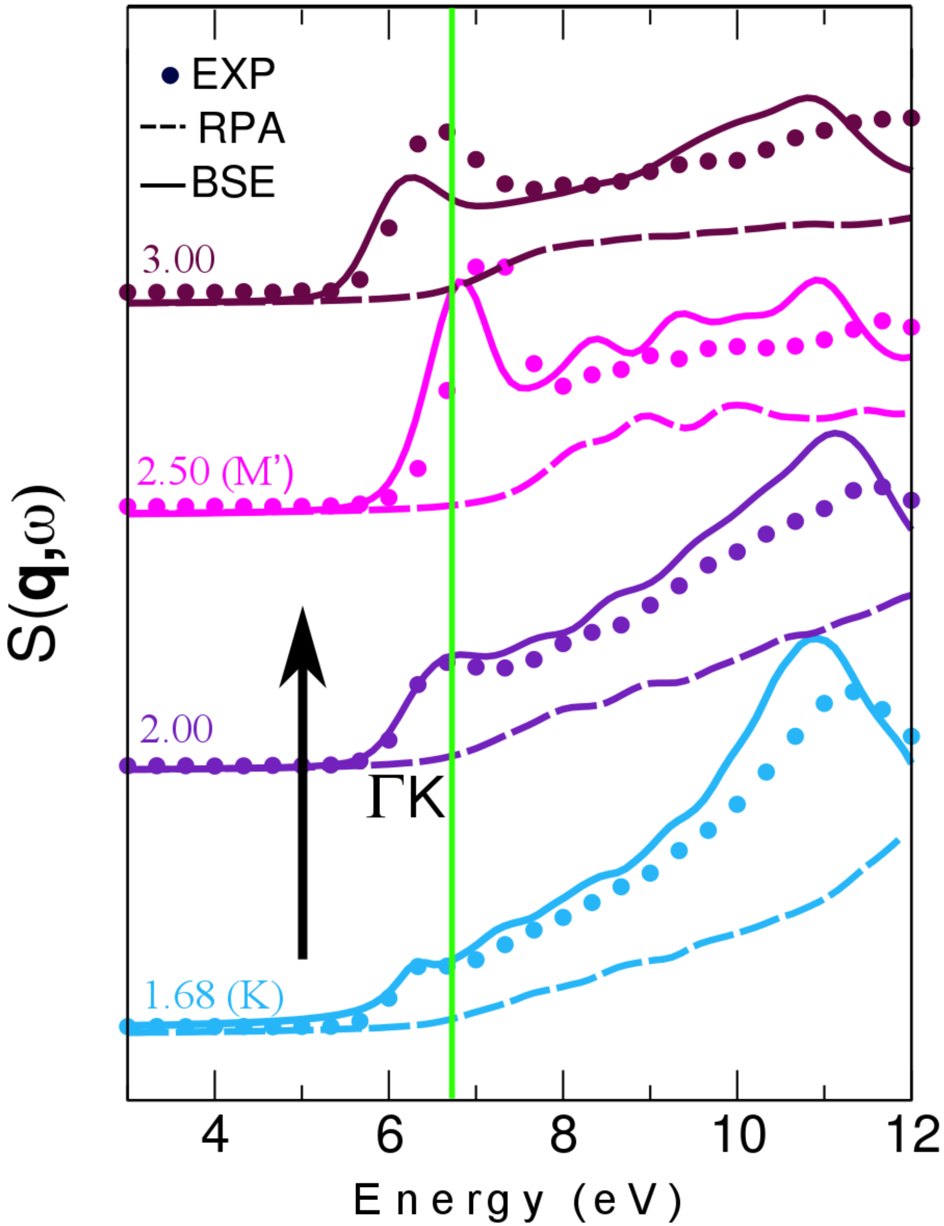
The EXC code

IXS of hBN



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

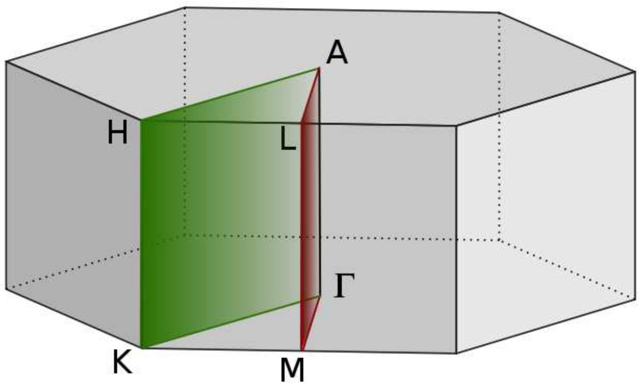
IXS of hBN

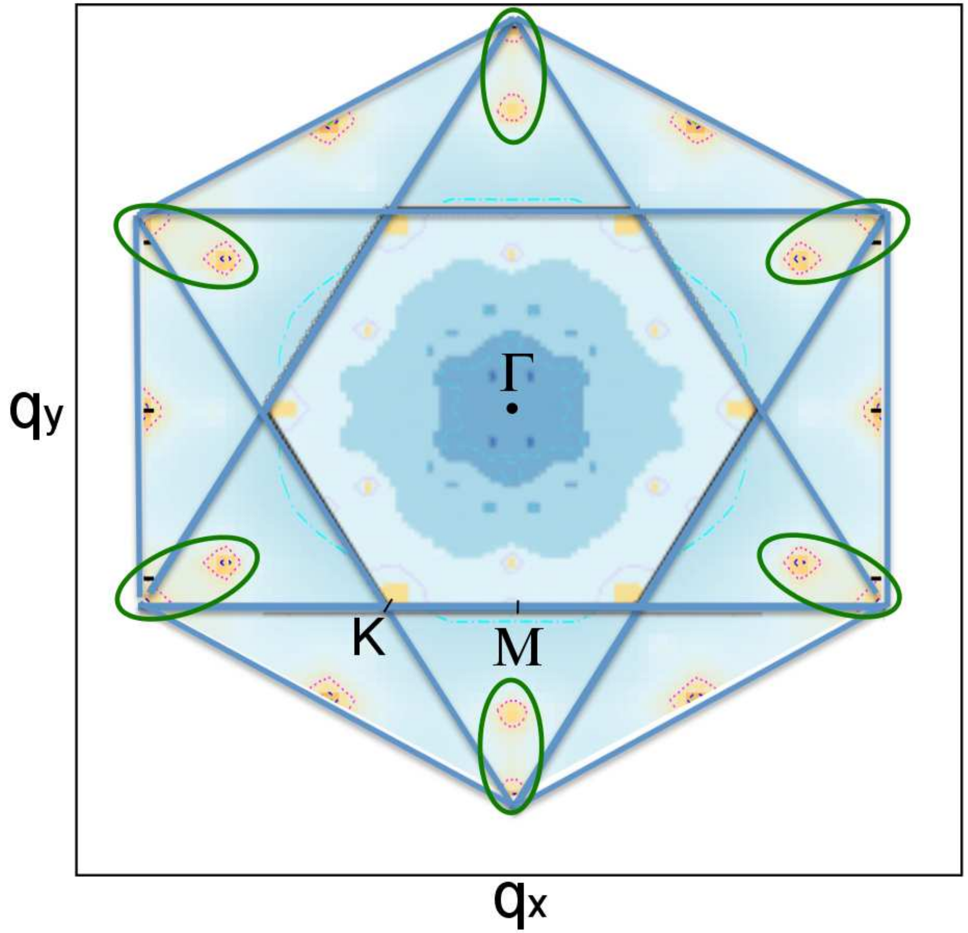


Fugallo *et al.* Phys. Rev. B **92**, 165122 (2015)

hexagonal Boron Nitride

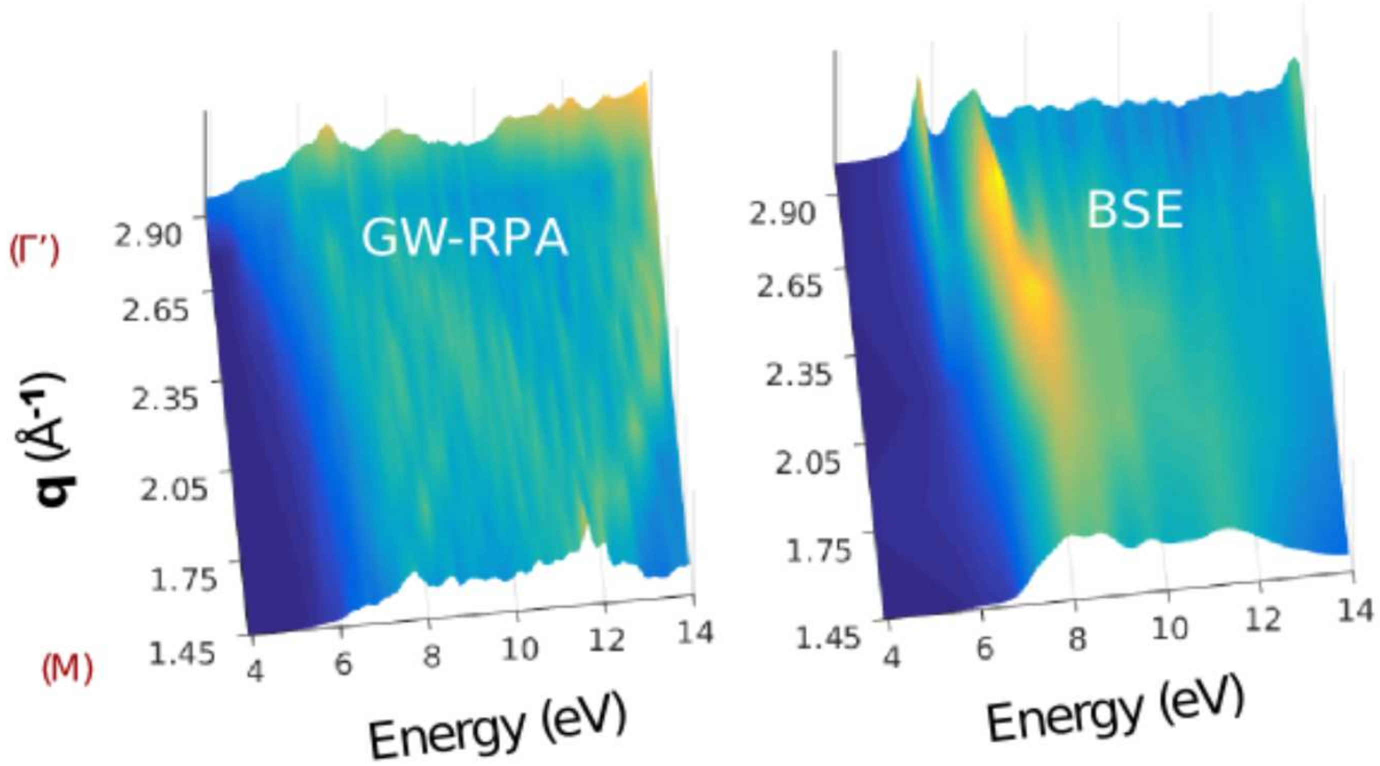
$$S(q, \omega = 7eV)$$





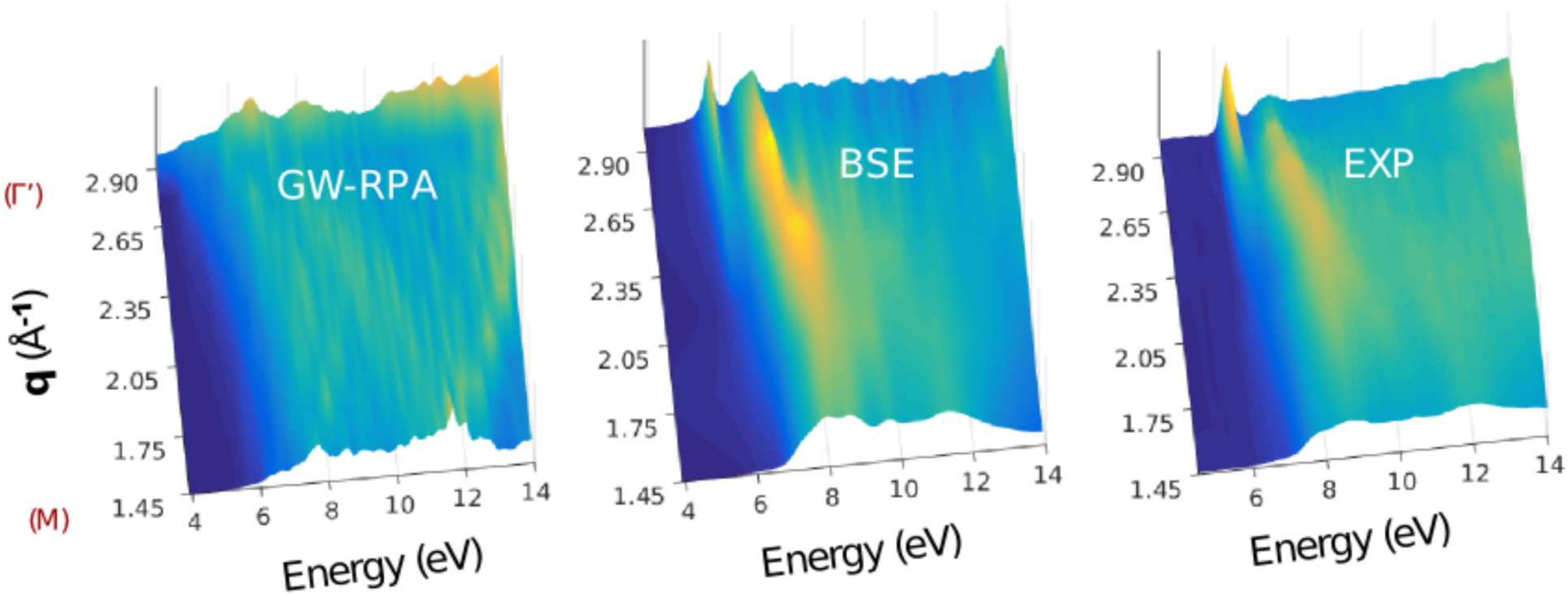
G. Fugallo *et al.* PRB **92**, 165122 (2015)

Exciton dispersion of h BN



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

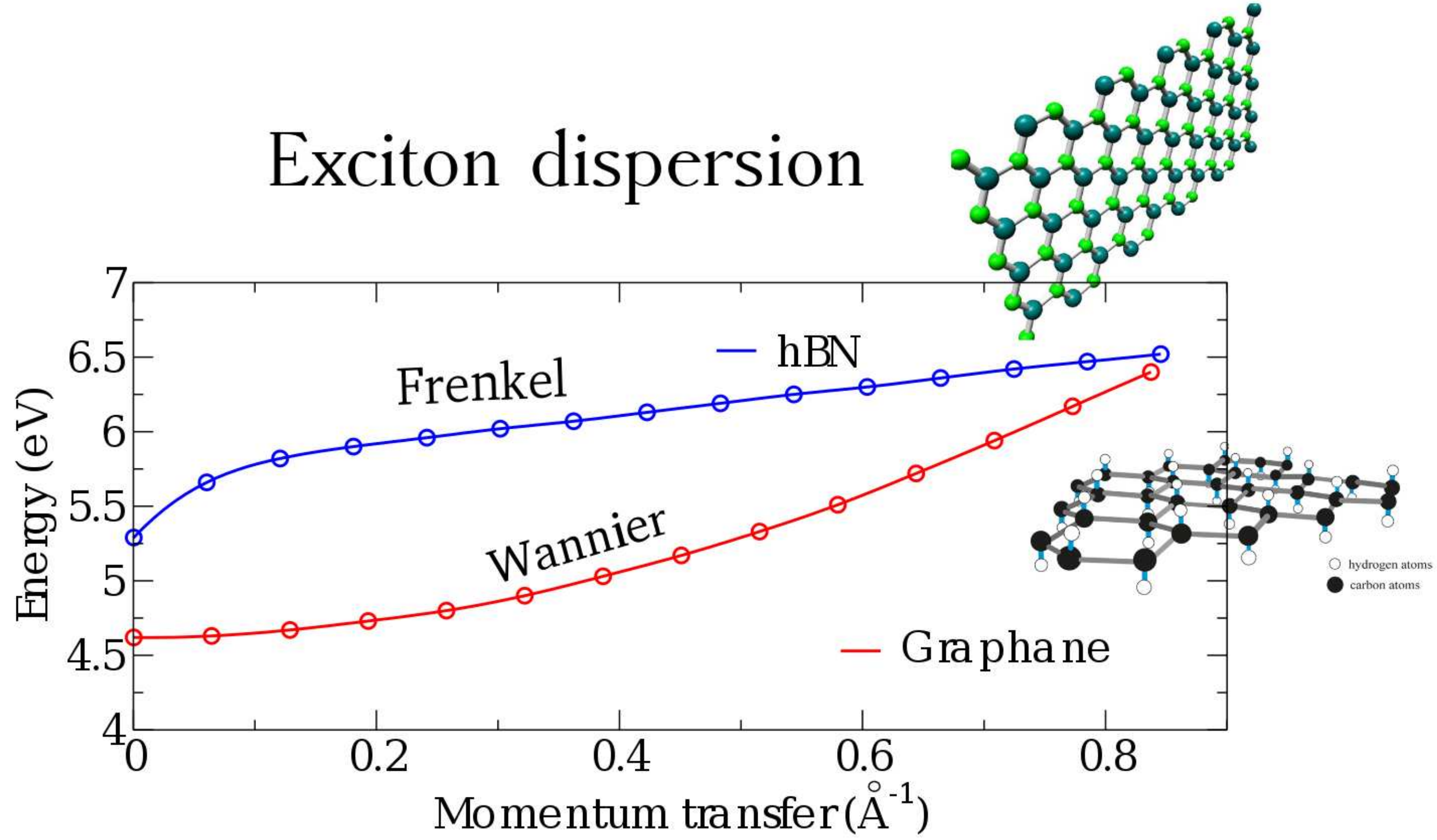
Exciton dispersion of h BN



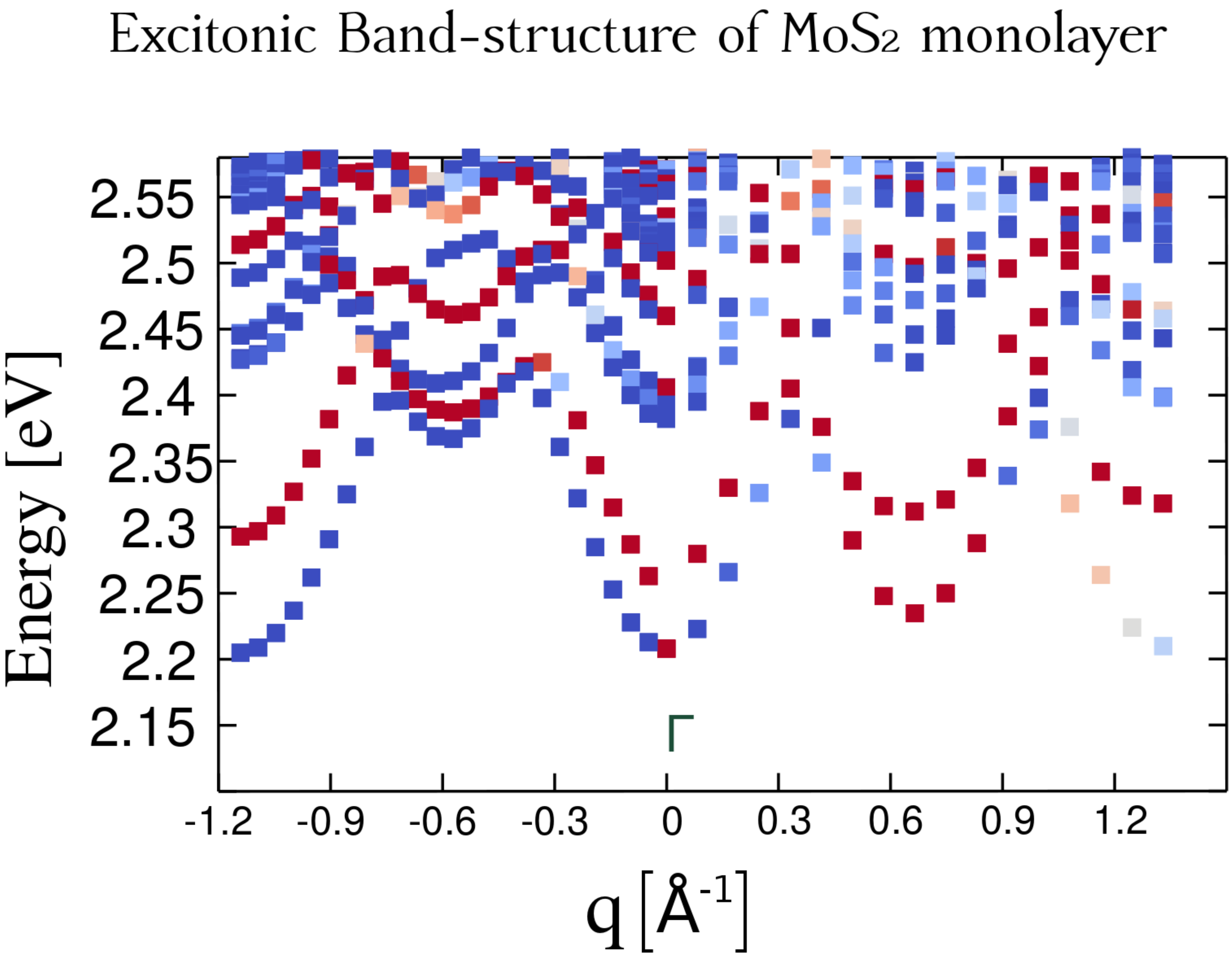
ID20 beamline 5/2015

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 MoS2 monolayer
Energy [eV]
2.55
2.5
2.45
2.4
2.35
2.3
2.25
2.2
2.15
Γ
-1.2
-0.9
-0.6
-0.3
0
0.3
0.6
0.9
1.2
q [Å-1]

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

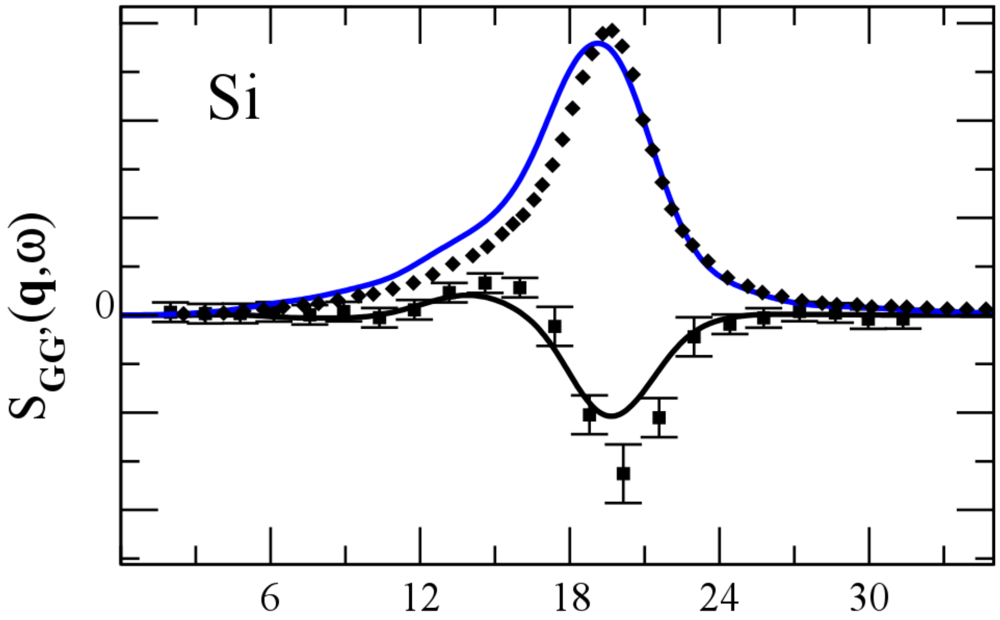
$$\chi(\mathbf{q},\omega) \Rightarrow \chi_{\mathbf{GG'}}(\mathbf{q},\omega)$$

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

visualization of induced charge (LiF)

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

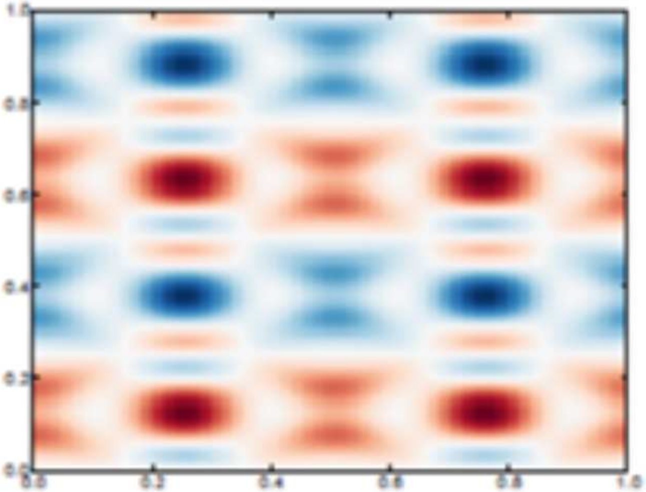
Opened a way of new series of tools and spectroscopies

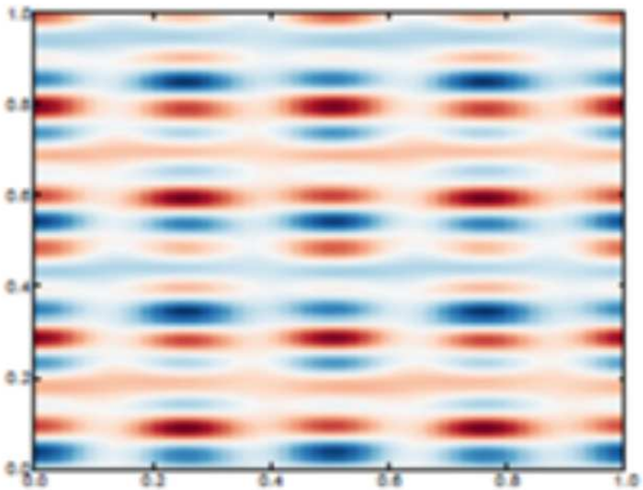
visualization of induced charge (LiF)

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

RPA

~~exciton~~





BSE

exciton

R. Hambach PhD Thesis 2010

I. Reshetnyak PhD Thesis 2015

Outline

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

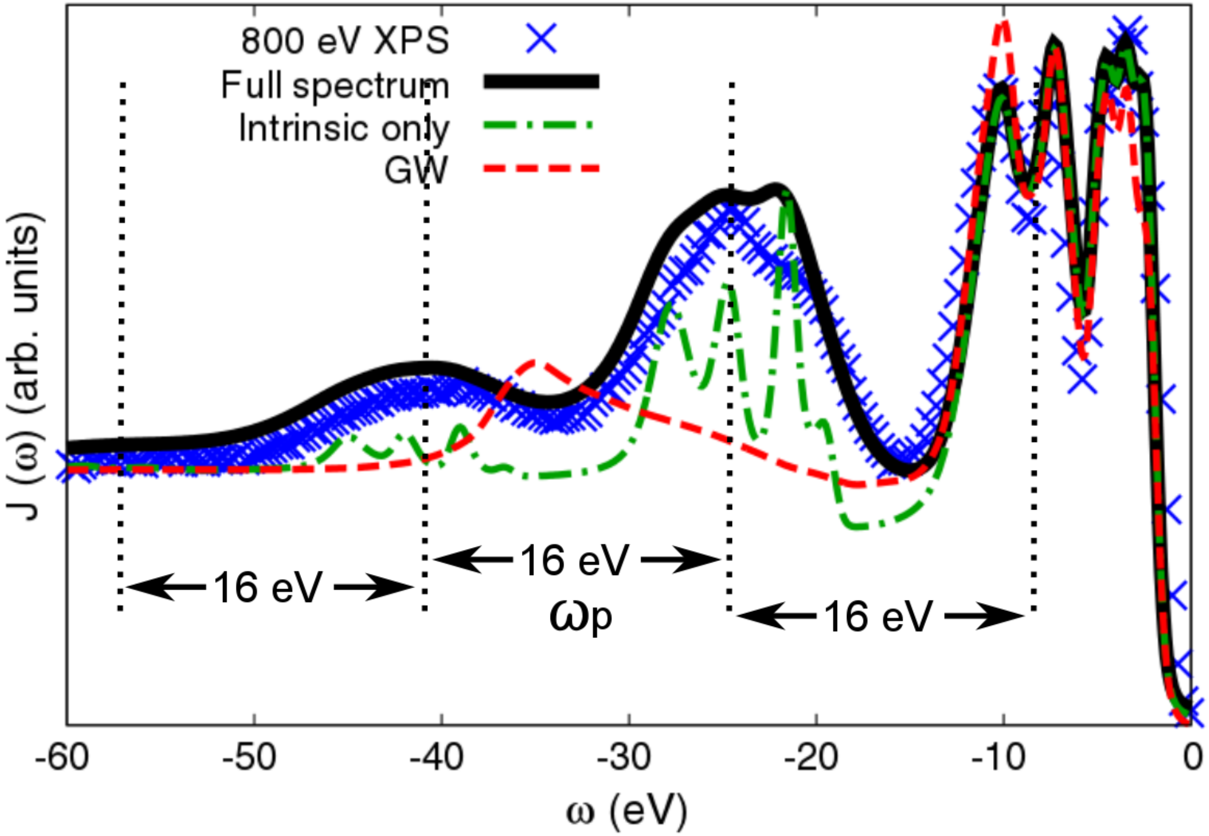
Satellites in Photoemission

Plasmon Satellites

Cumulant expansion
(well beyond GW)

Main ingredient ::
Loss function

Silicon PES

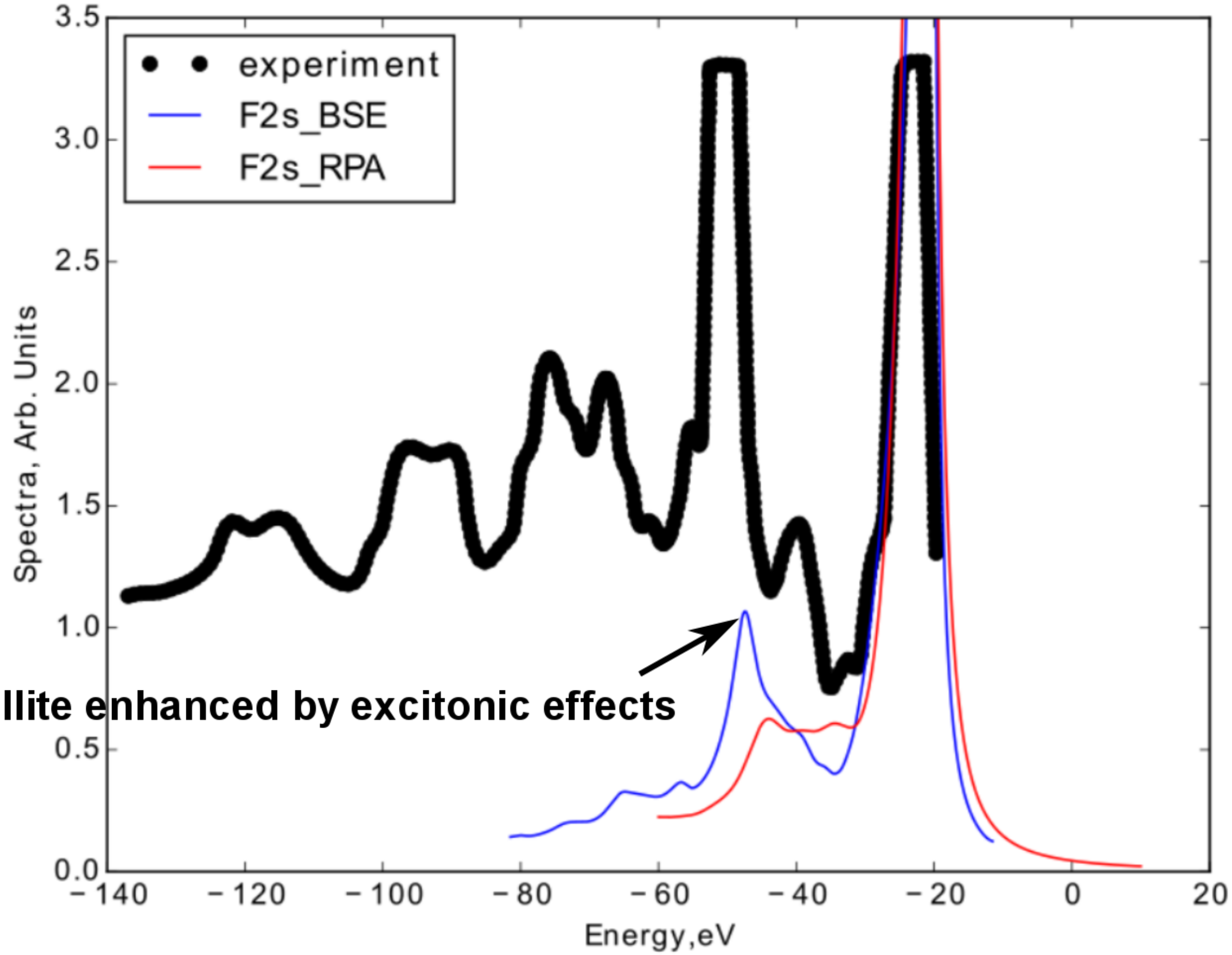


M. Guzzo et al. PRL **107**, 166401 (2011).

Satellites in Photoemission

What about exciton satellites ?

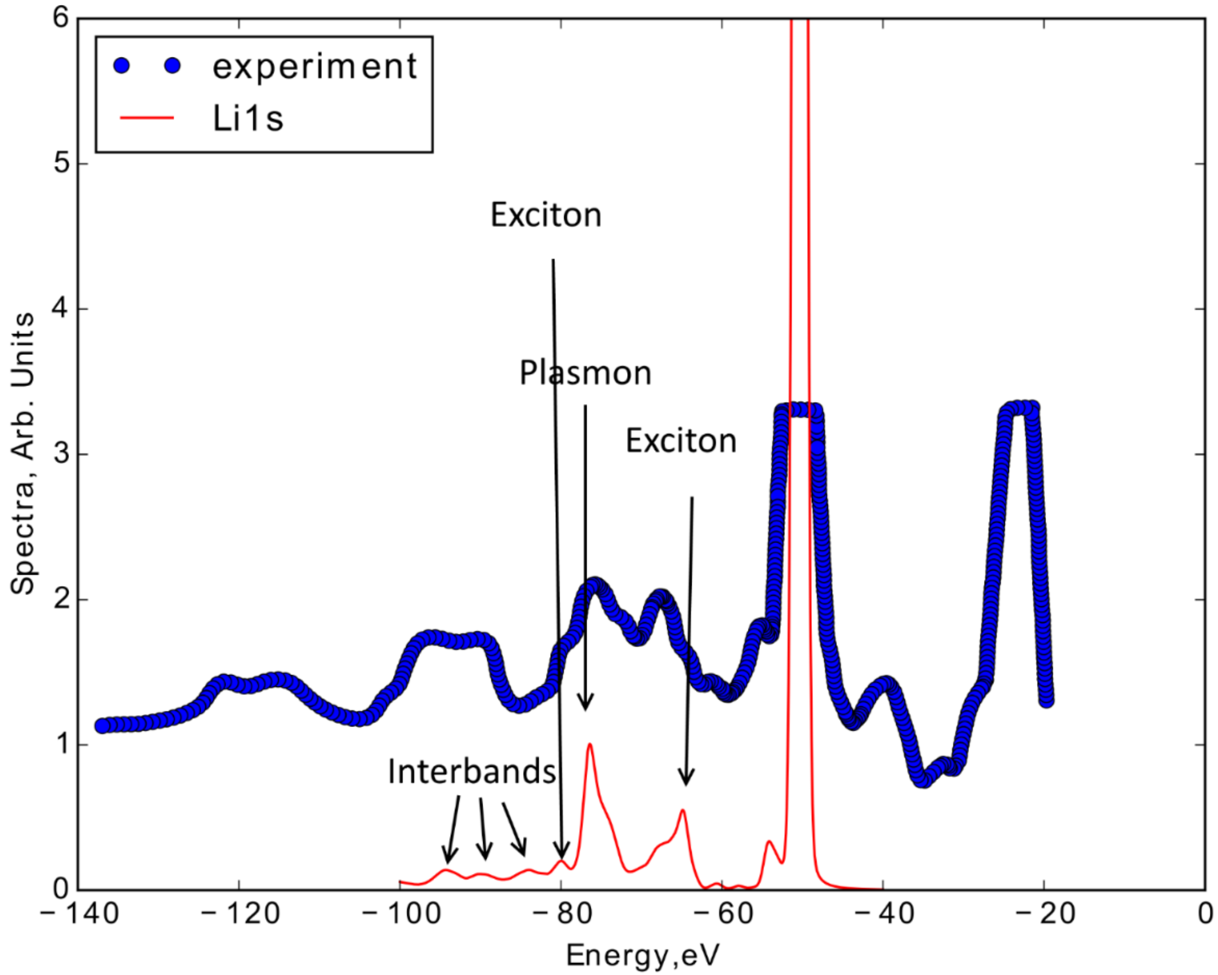
Photo-emission spectra of LiF



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

I. Reshetnyak PhD Thesis 2015

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