Signatures of correlation

from excitons to satellites

Workshop on Next Generation Quantum Materials
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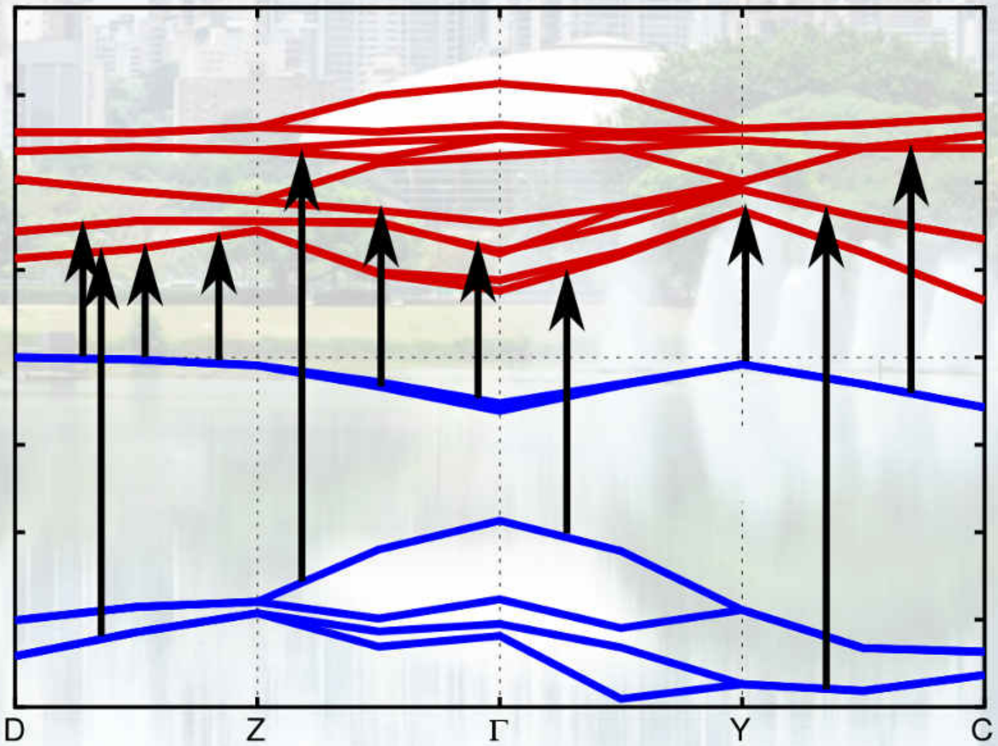
Exciton as signature of correlation

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

sum over independent transitions

no exciton by definition

independent-particle polarizability



Exciton as signature of correlation

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

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

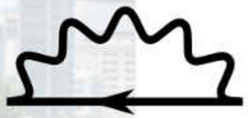
$$= G^e G^h \Gamma = \chi^0 + \chi^0 (v - W)\chi$$

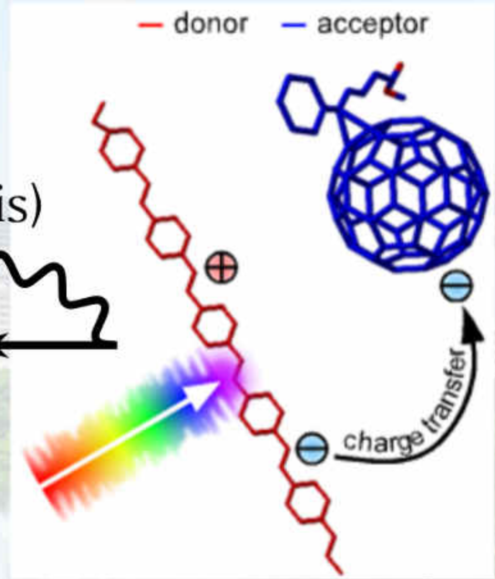
$$\varepsilon^{-1} = 1 + v\chi$$

Why Excitons ....

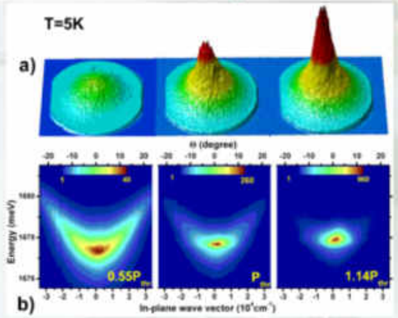
- properties of matter { optical spectroscopy / inelastic X-ray scattering / electron energy loss spectroscopy

- tunability of optical gap (opto-electronics, photo-voltaics/catalysis)

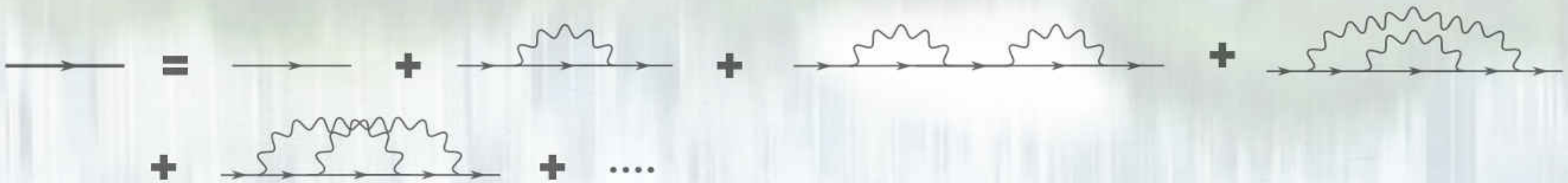




- e-h screening crucial ingredient in theory (GW, DMFT)
  and spectroscopies (PES, RIXS)



- Challenges of theory
  (electron-exciton satellites, cumulant, BEC of excitons)

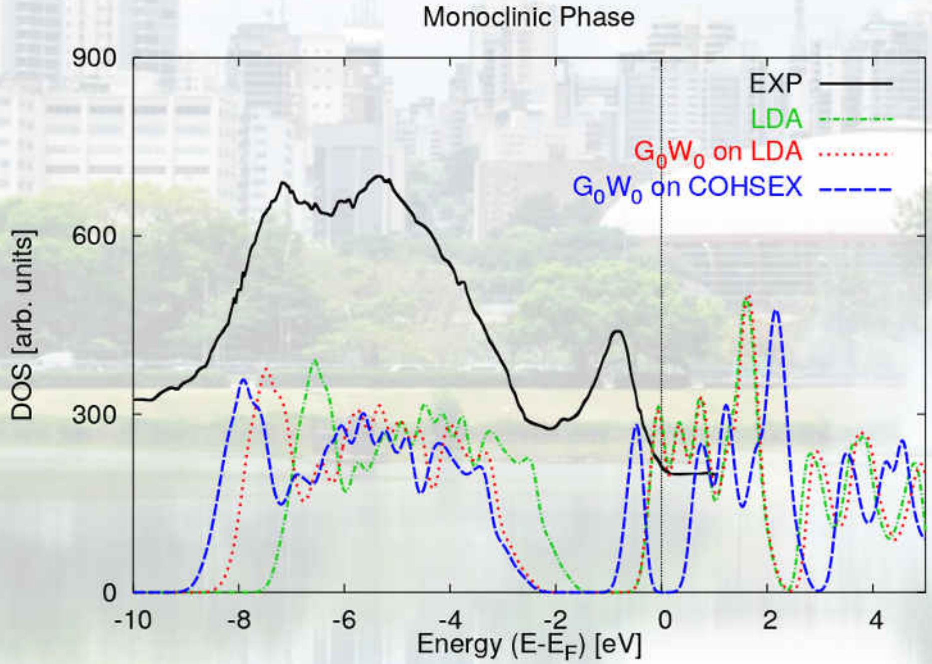


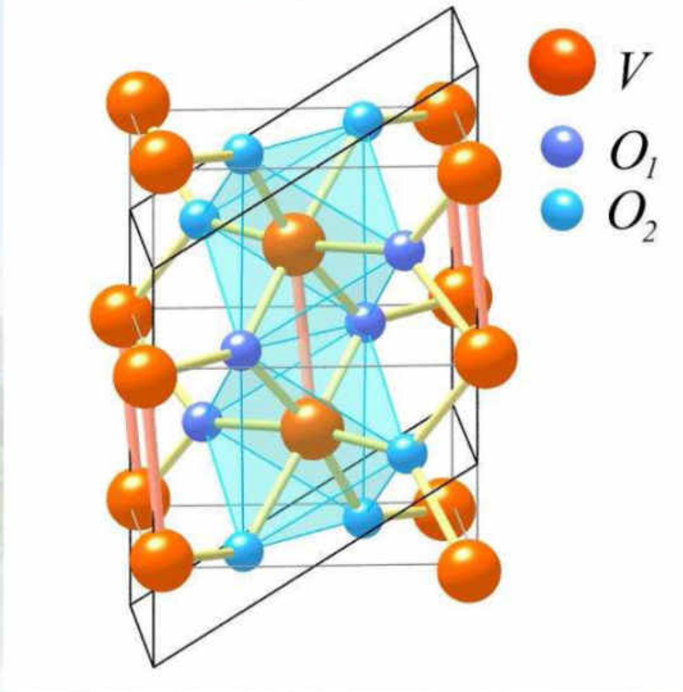
Outline

- Optical properties of VO_2
- Exciton dispersion
- Excitonic effects in PES satellites

Monoclinic (insulating) VO_2

LDA gives metallic phase





scCOHSEX+GW

M. Gatti *et al.* PRL **99**, 266402 (2007)

Monoclinic (insulating) VO_2

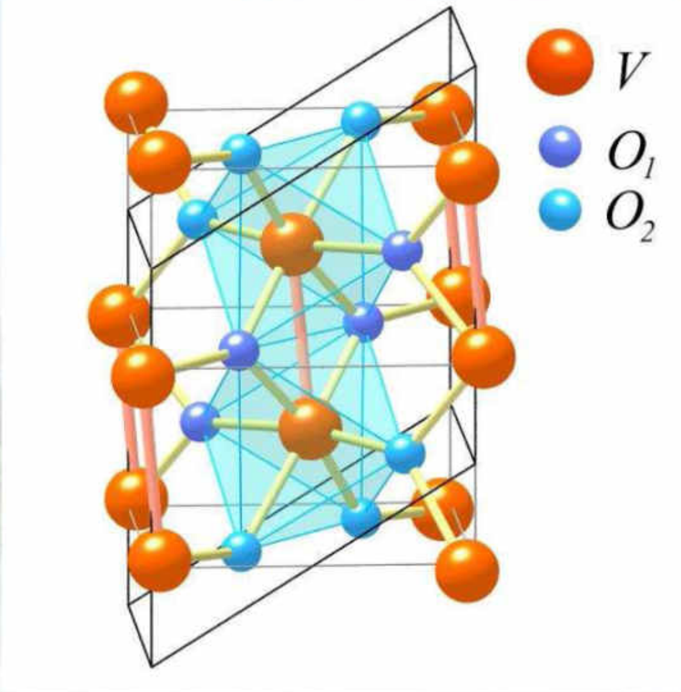
Bethe-Salpeter equation

$$^4\chi = \chi^0_{GW} + \chi^0_{GW}(v - W)\chi$$

$$^4\chi = GG + GG\,(v - W)\chi$$

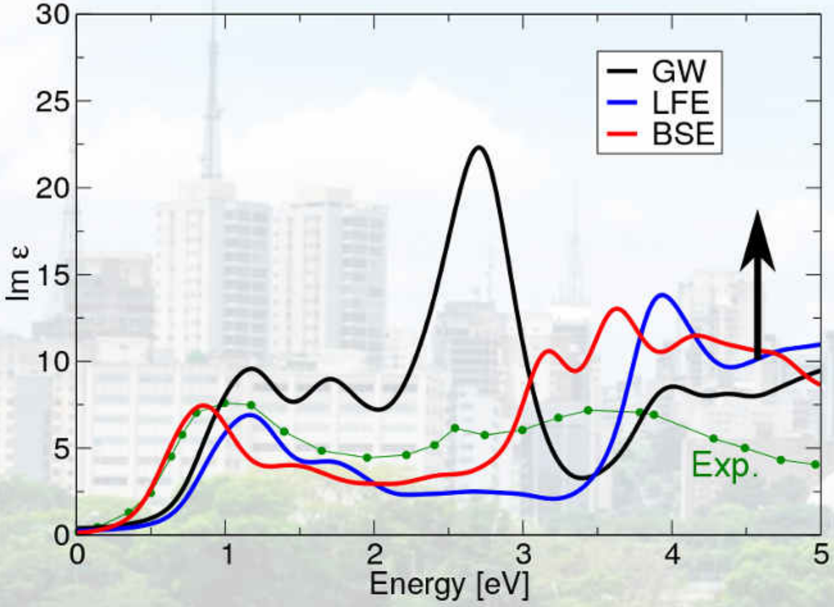
local fields

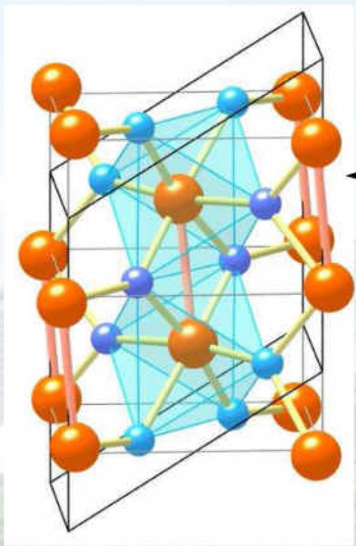
e-h interaction

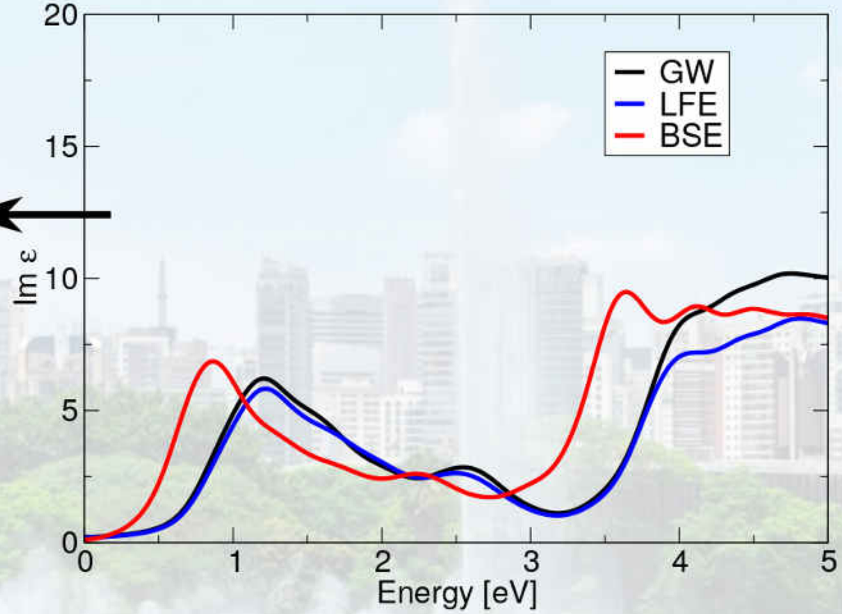


F. Sottile *et al.* The EXC code , Ab initio solution of the Bethe-Salpeter equation

Monoclinic (insulating) VO_2







- ✓ strong anisotropy (one dimensionality)
- ✓ strong local fields
- ✓ strong exciton (binding energy 0.3 eV)

M. Gatti *et al.* PRB **91**, 195137 (2015)

H.W. Verleur *et al.* PR **172**, 788 (1968)

Outline

- Optical properties of VO_2
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Exciton Dispersion

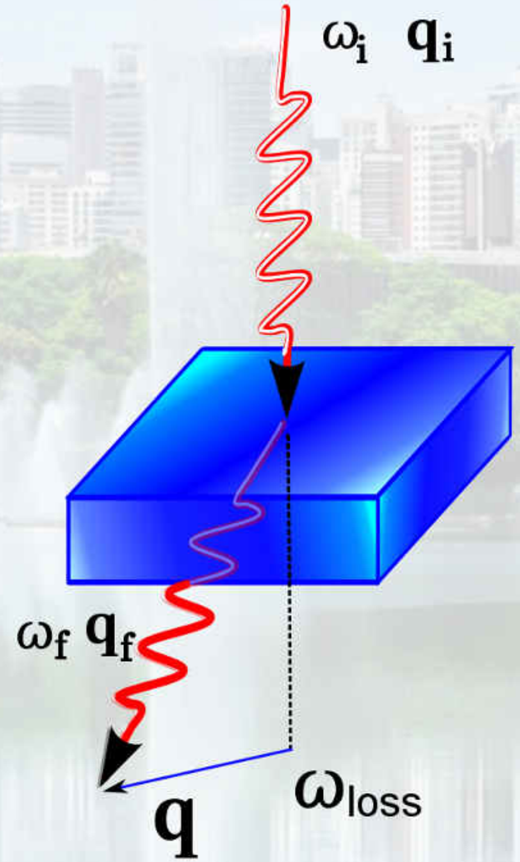
- First step towards exciton dynamics
- Analysis of different (scattering) spectroscopies

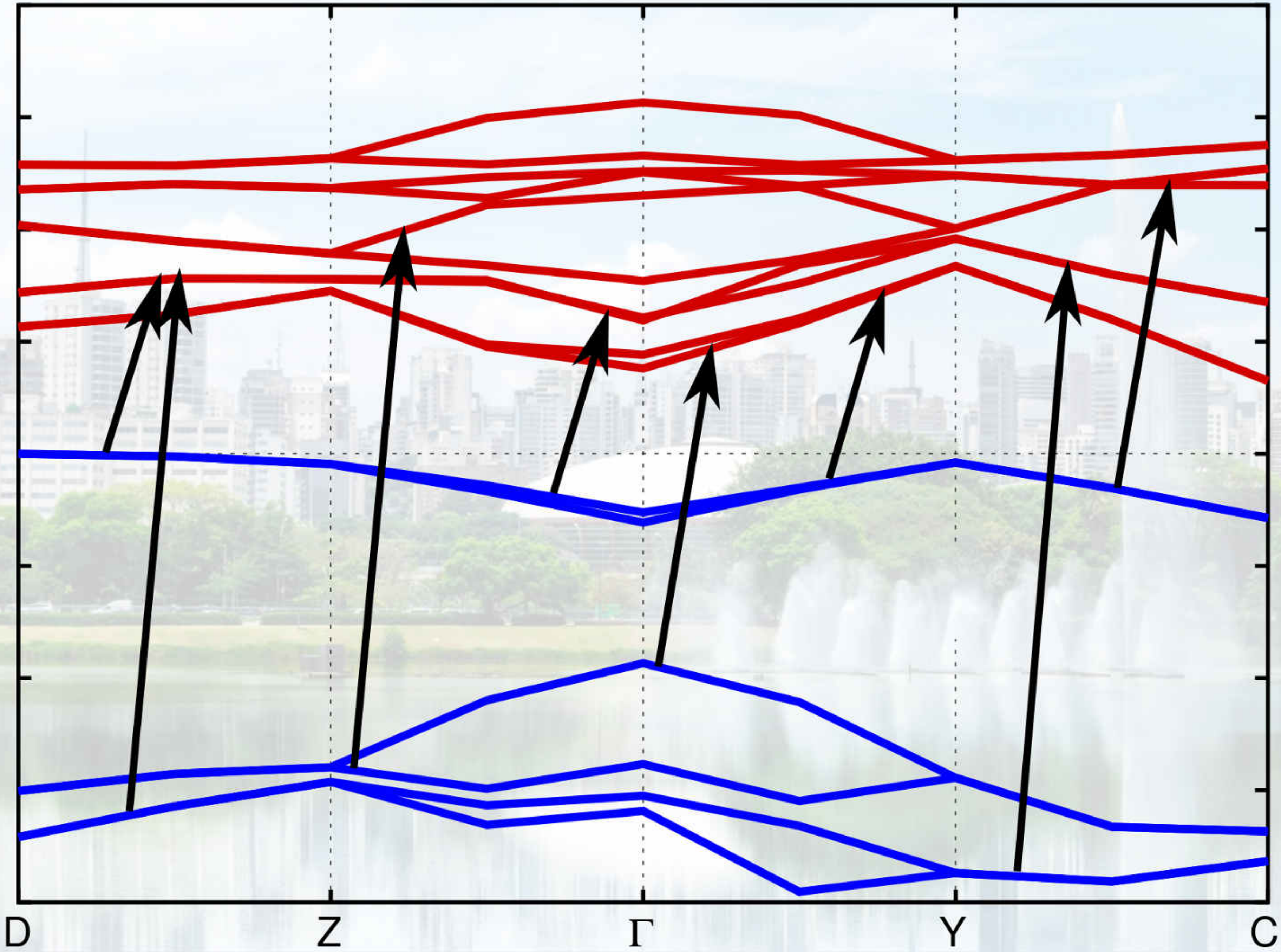
$$\chi = \sum_\lambda \frac{\left| \sum_{vc} A_\lambda^{vc} < c|\mathbf{d}|v > \right|^2}{\omega - E_\lambda + i\eta}$$

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

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

IXS

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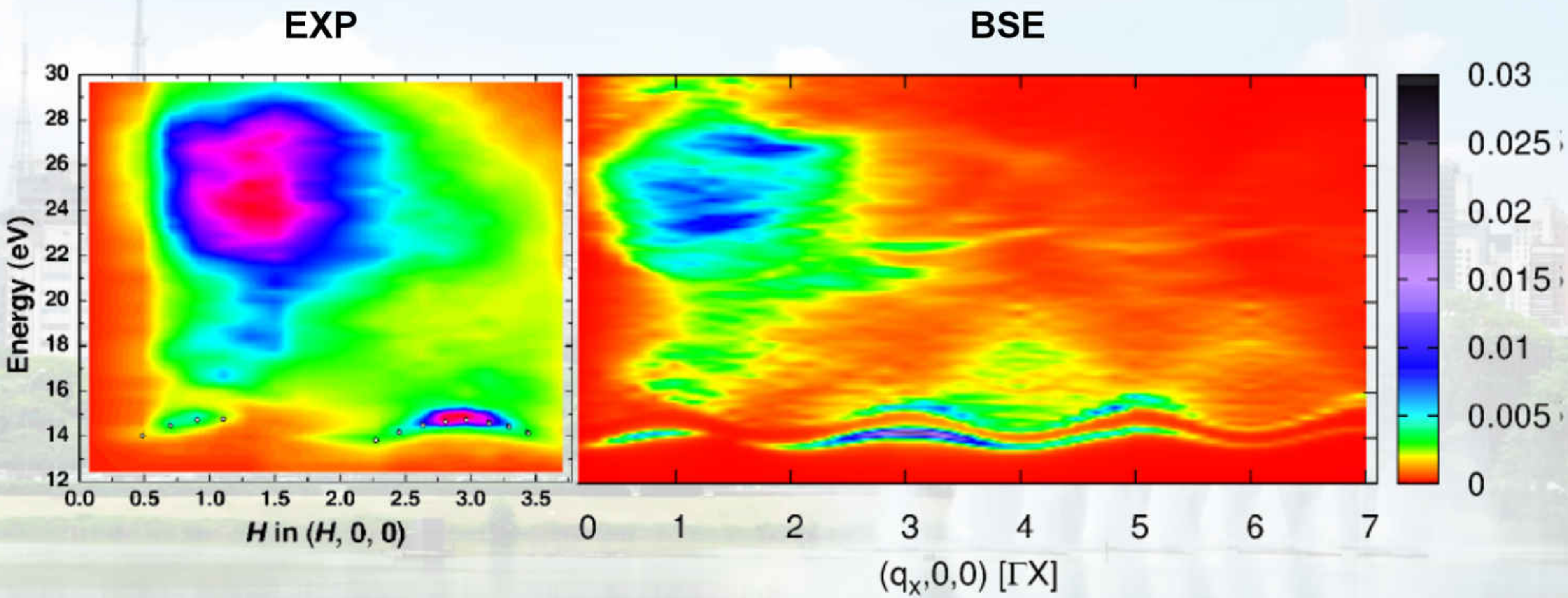
PRL **111,** 157401 (2013) PHYSICAL REVIEW LETTERS week ending 11 OCTOBER 2013

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.

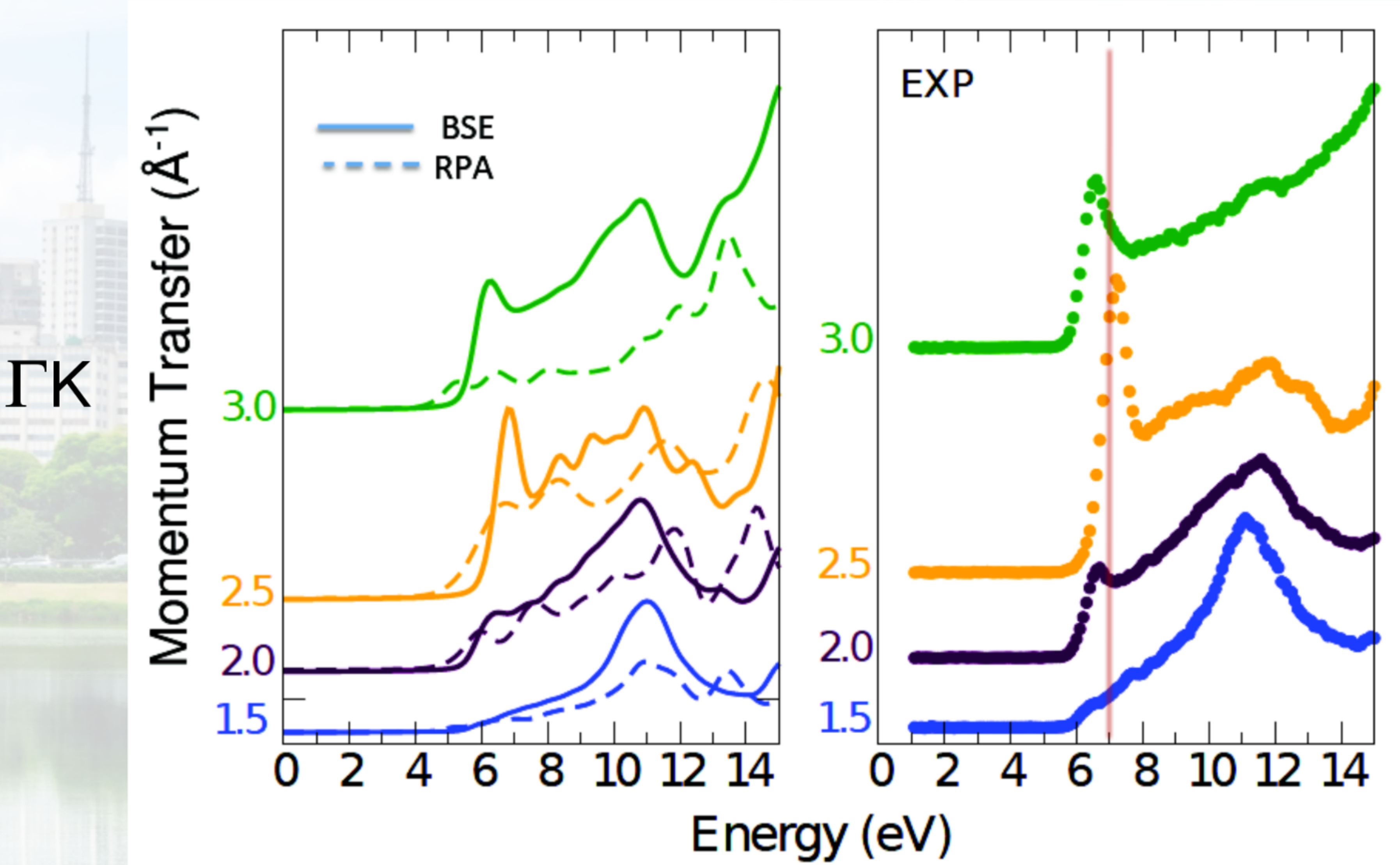
Dynamical Structure factor of LiF



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

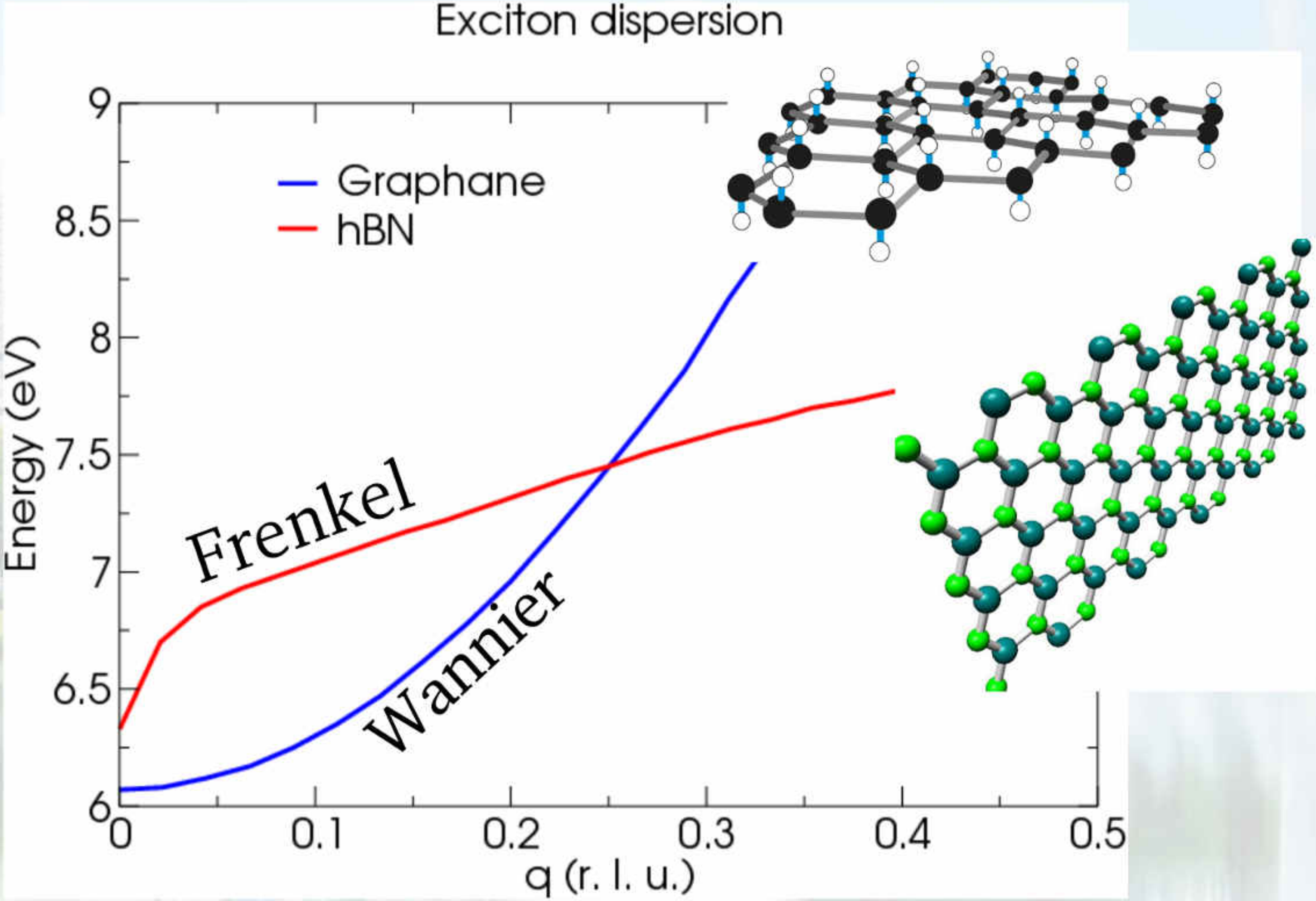
M. Gatti and F. Sottile PRB **88**, 85425 (2013)

hexagonal Boron Nitride



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

Theoretical predictions of 2D exciton dispersion



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

Exciton Dispersion

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

New experiments described and carefully analyzed

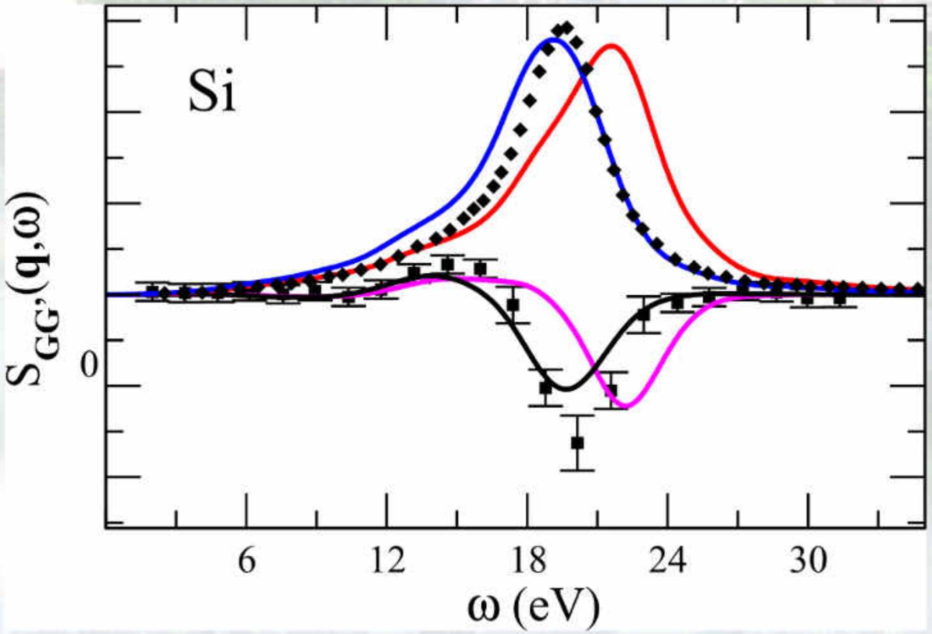
Opened a way of new series of tools and spectroscopies

Opened a way of new series of tools and spectroscopies

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

non-diagonal response

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



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

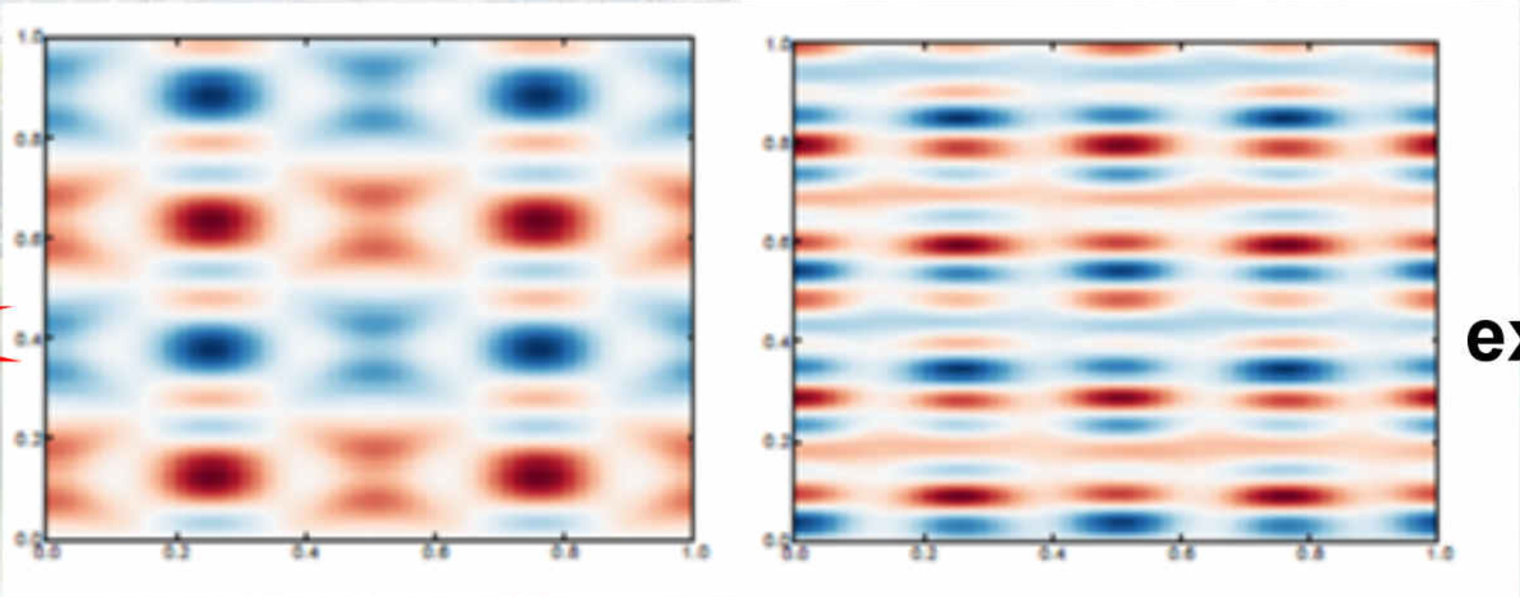
Opened a way of new series of tools and spectroscopies

visualization of induced charge (LiF)

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

RPA

~~**exciton**~~



BSE

exciton

I. Reshetnyak PhD Thesis 2015

Outline

- Optical properties of VO_2
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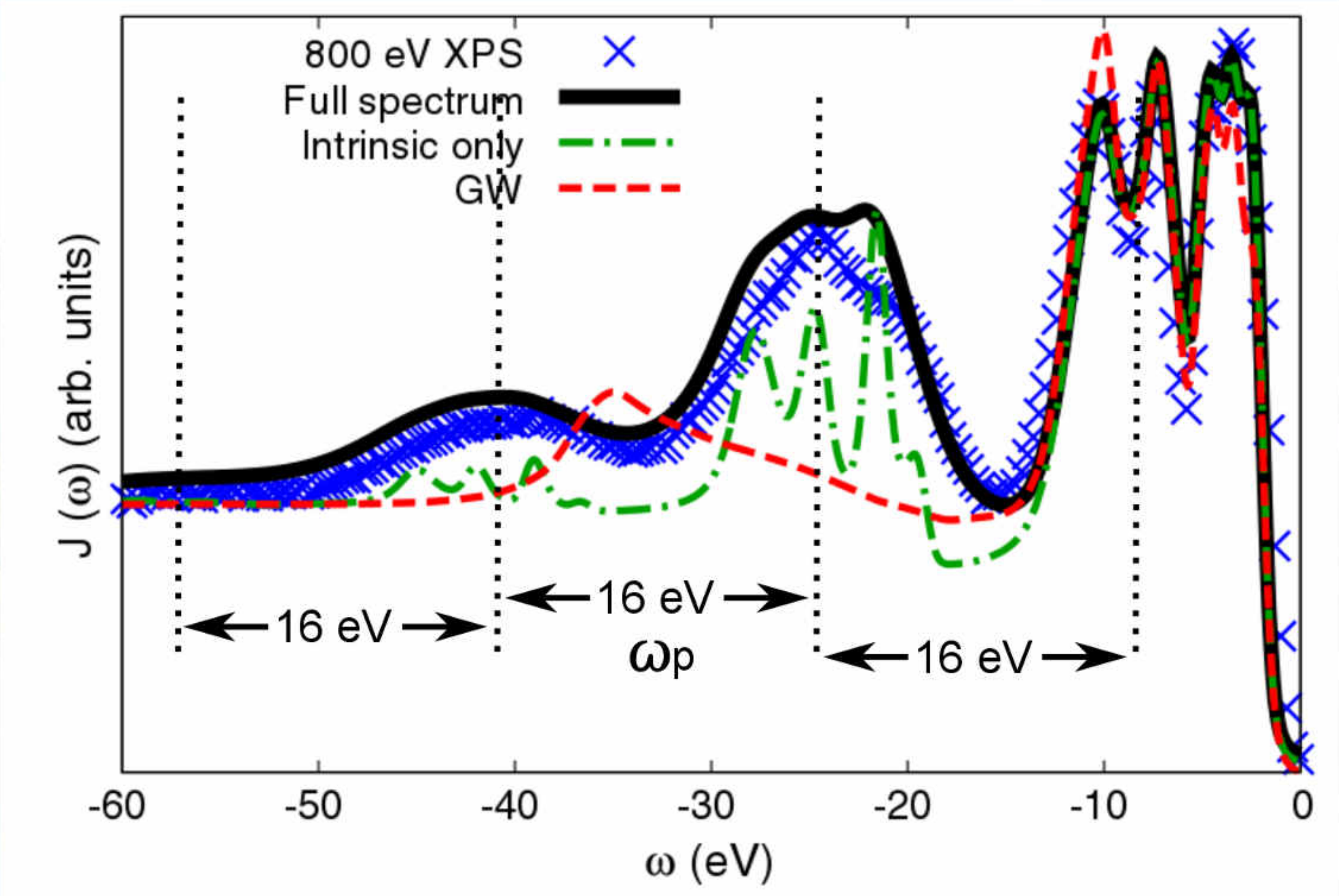
- Excitonic effects in PES satellites

Satellites in Photoemission

Silicon PES

Plasmon Satellites

Main ingredient ::
Loss function

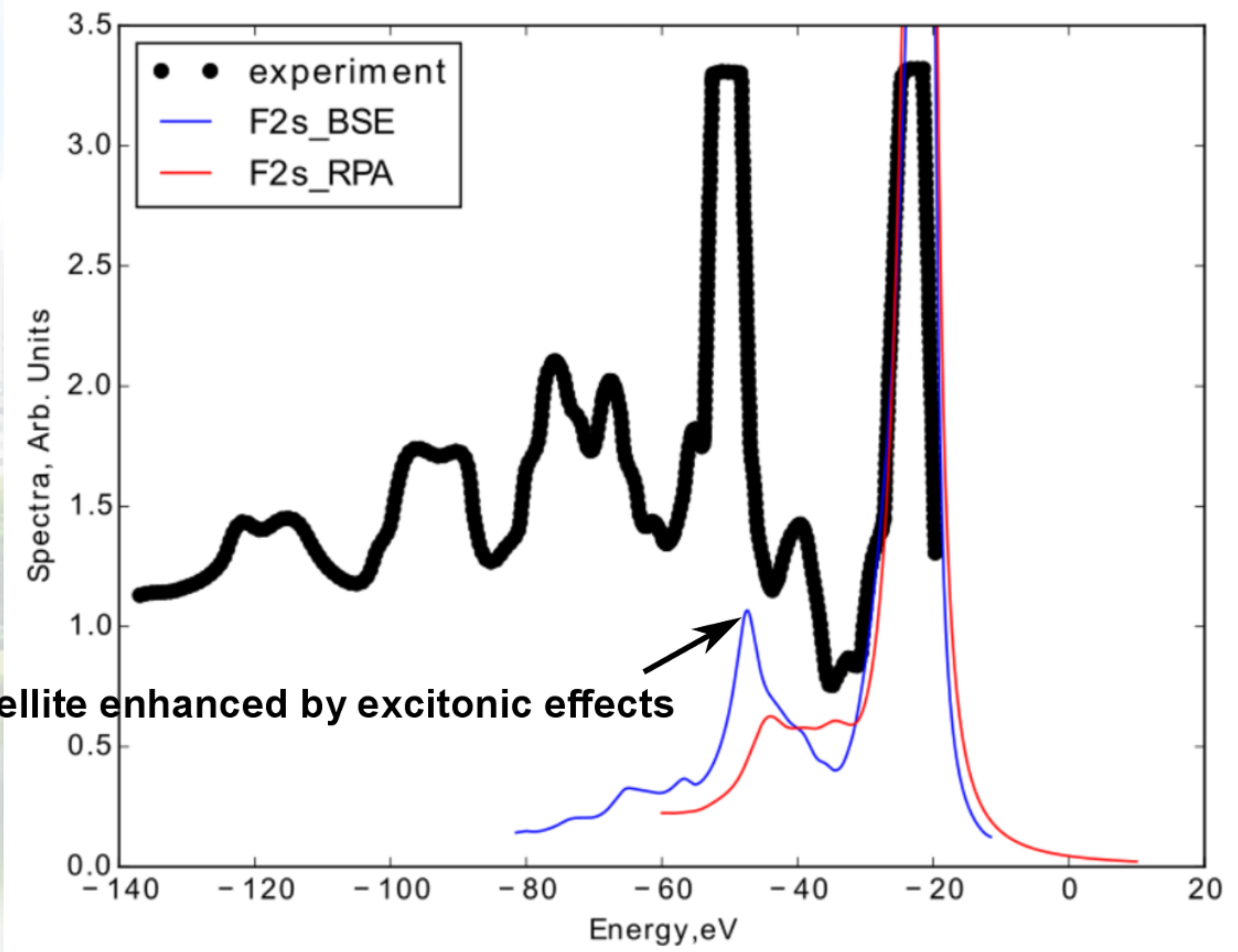


M. Guzzo et al. PRL **107**, 166401 (2011).

Satellites in Photoemission

What about exciton satellites ?

Photo-emission spectra of LiF

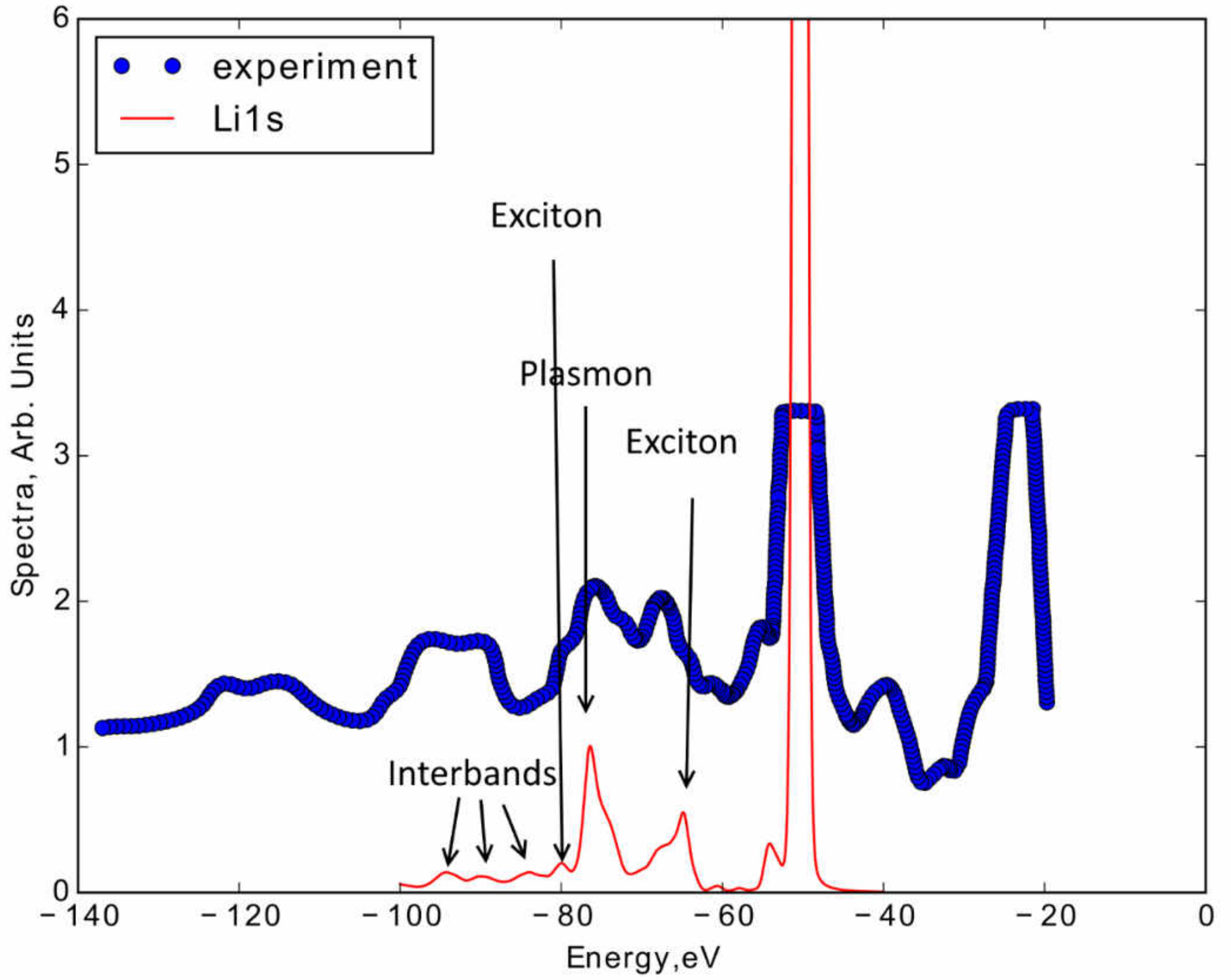


plasmon satellite enhanced by excitonic effects

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

I. Reshetnyak PhD Thesis 2015

Photo-emission spectra of LiF



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

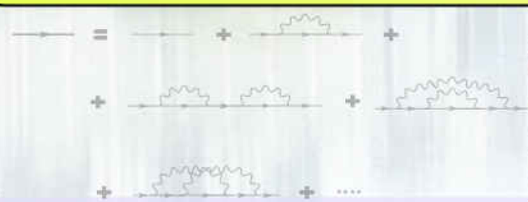
I. Reshetnyak PhD Thesis 2015

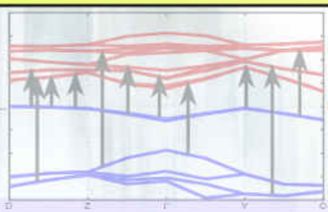
Conclusions

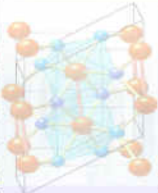
✓ established the importance of excitonic effects (VO_2,etc)

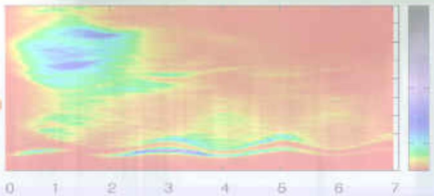
added new dimensions (q,G,G') to the problem

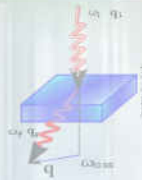
- ✓ exciton dispersion (bulk, layered, 2D systems)
- ✓ excitonic band structure
- ✓ new spectroscopies (Coherent Inelastic X-ray Scattering)
- ✓ visualization tools
- ✓ tackle new challenges in theory (exciton satellites)

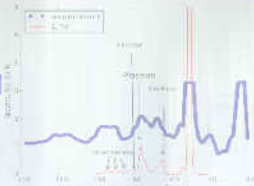












Acknowledgments

- **Matteo Gatti** extension of the BSE to $\mathbf{q} \neq 0$
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  exciton dispersion of layered and 2D systems
- **Lucia Reining, Matteo Guzzo, Igor Reshetnyak**
  non-diagonal response, exciton satellites
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Thank you