X-ray spectroscopies via Green's functions Theory

the importance of excitonic (many-body) signatures

Francesco Sottile

LSI, Ecole Polytechnique, Palaiseau and ETSF - France

19th November 2024, Campus Luminy, Marseille

Theory around XFELs

ÉCOLE POLYTECHNIQUE

IP PARIS

ETSF

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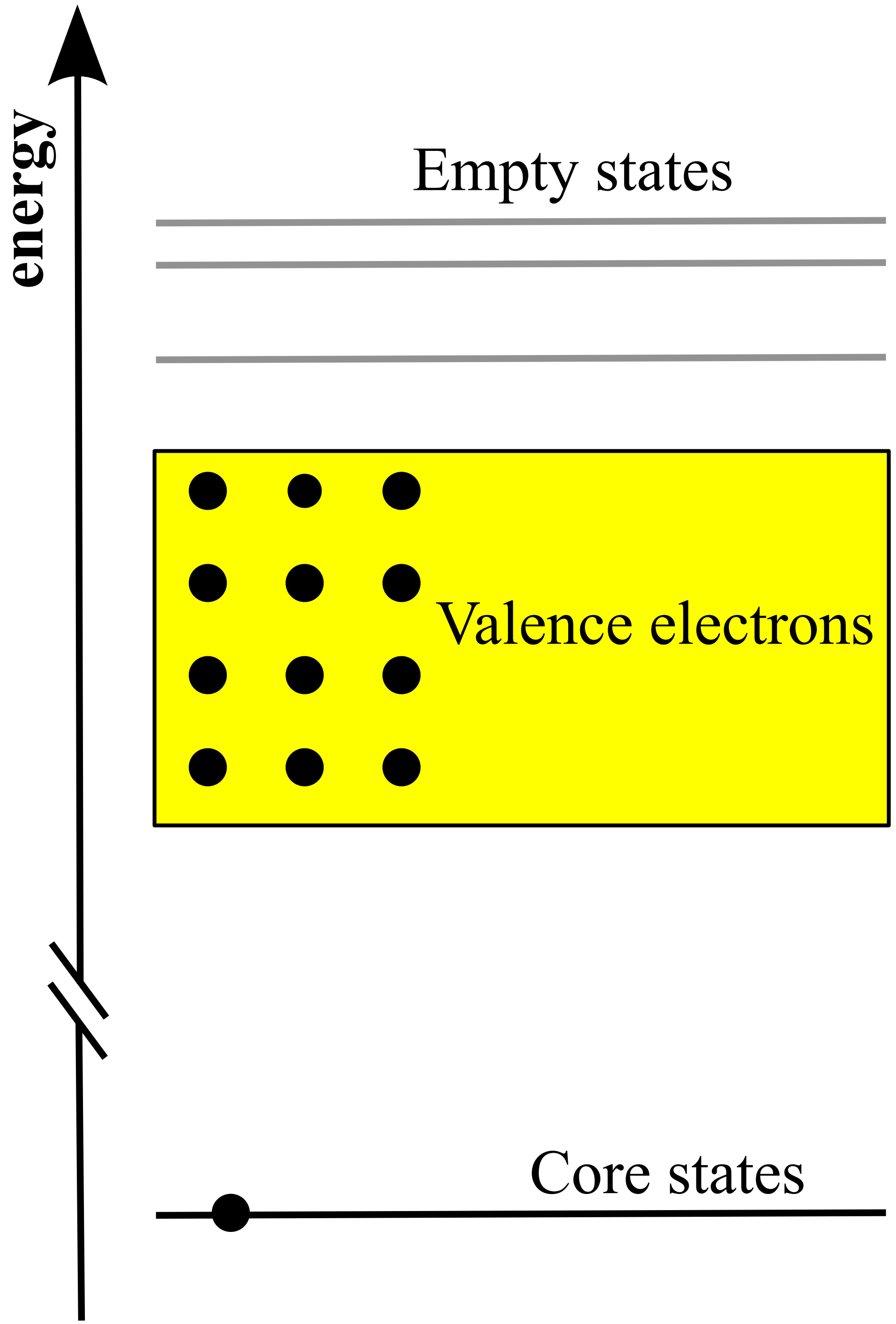
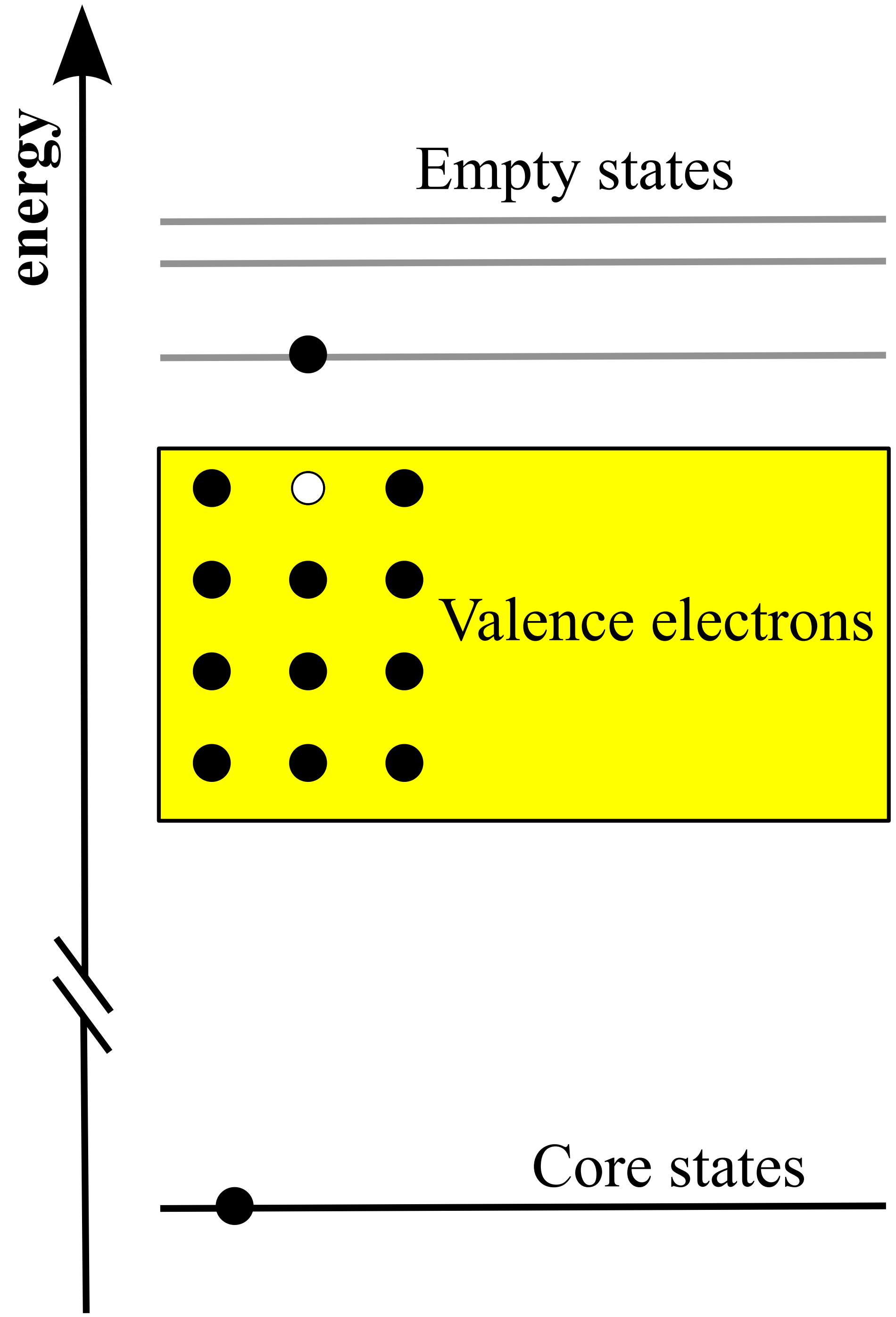

energy
Empty states
Valence electrons
Core states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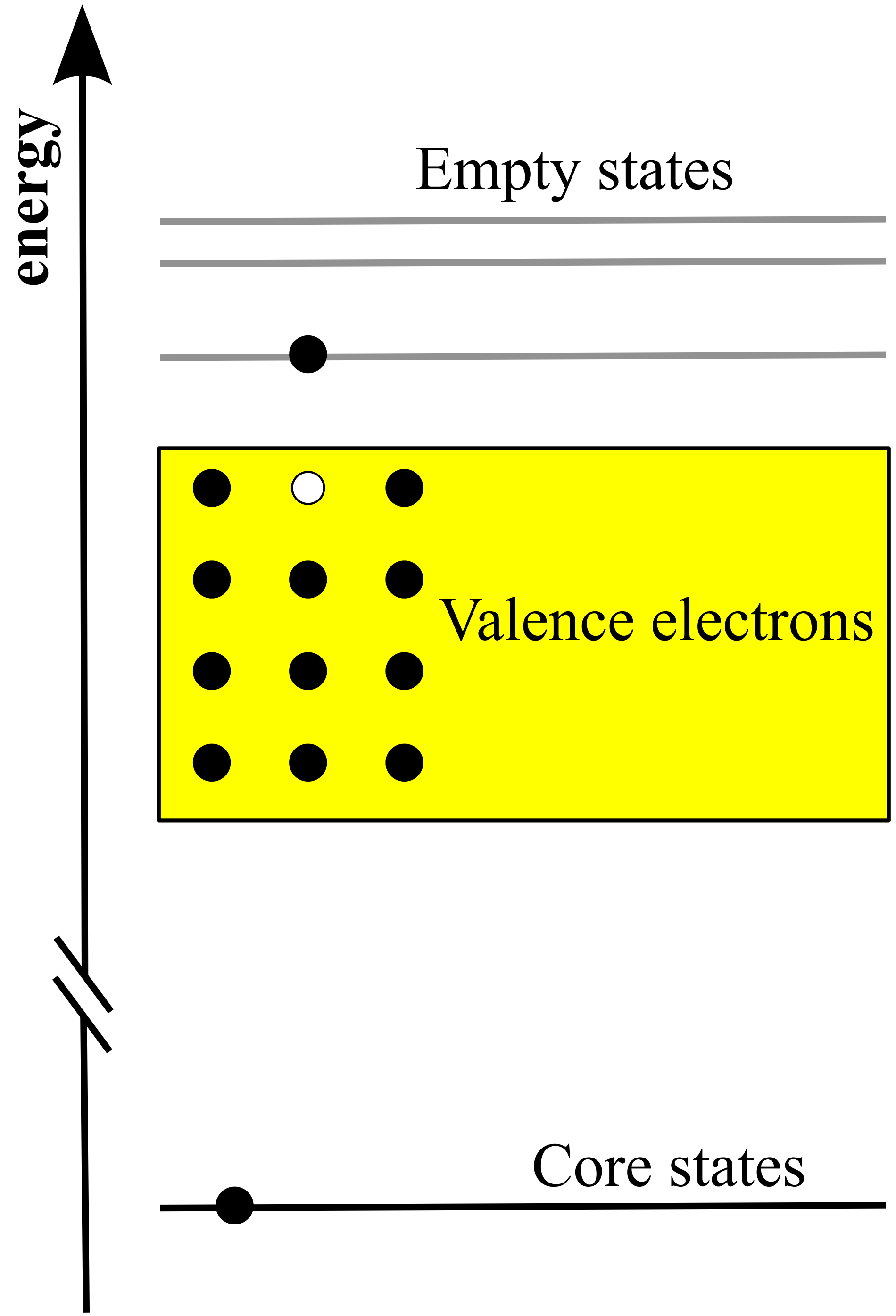
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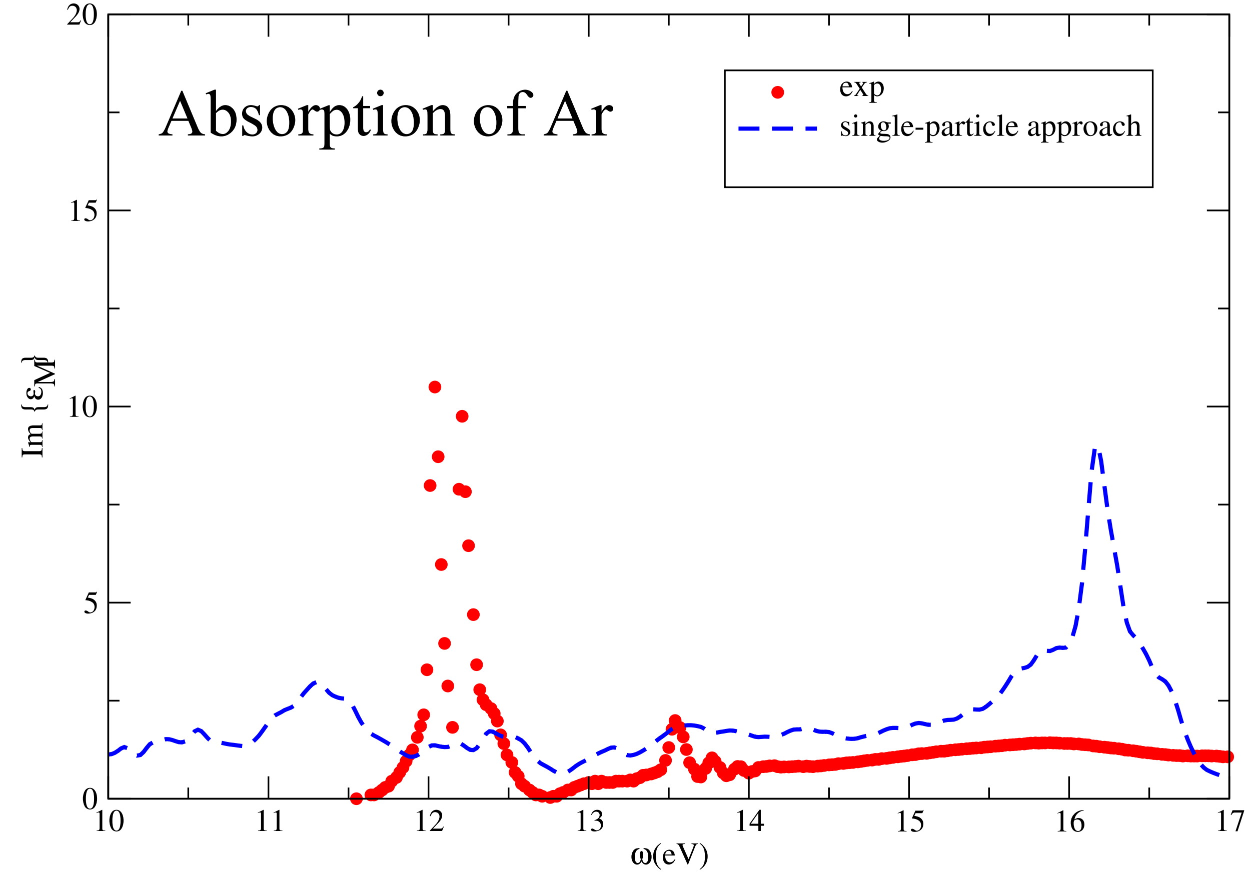
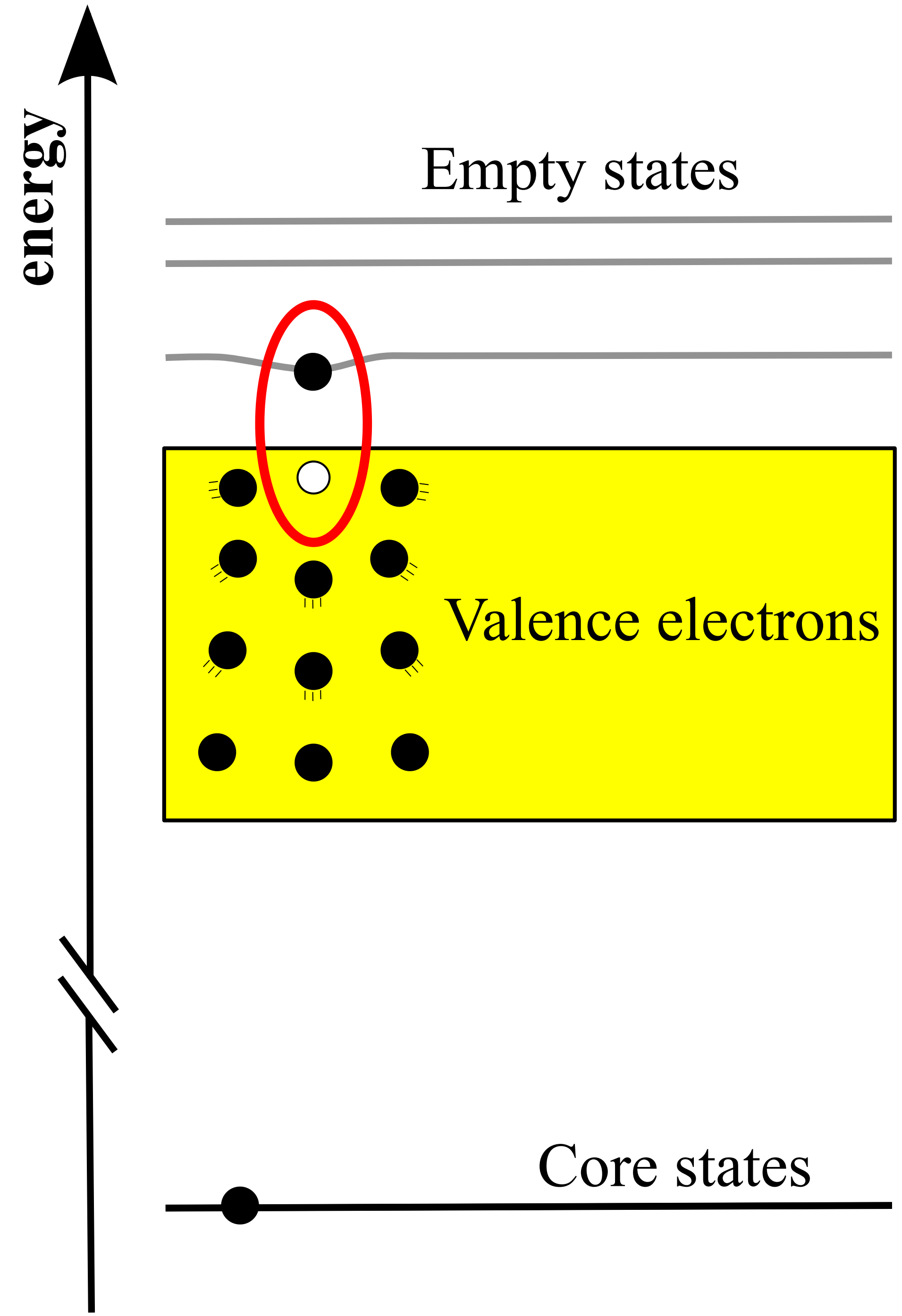
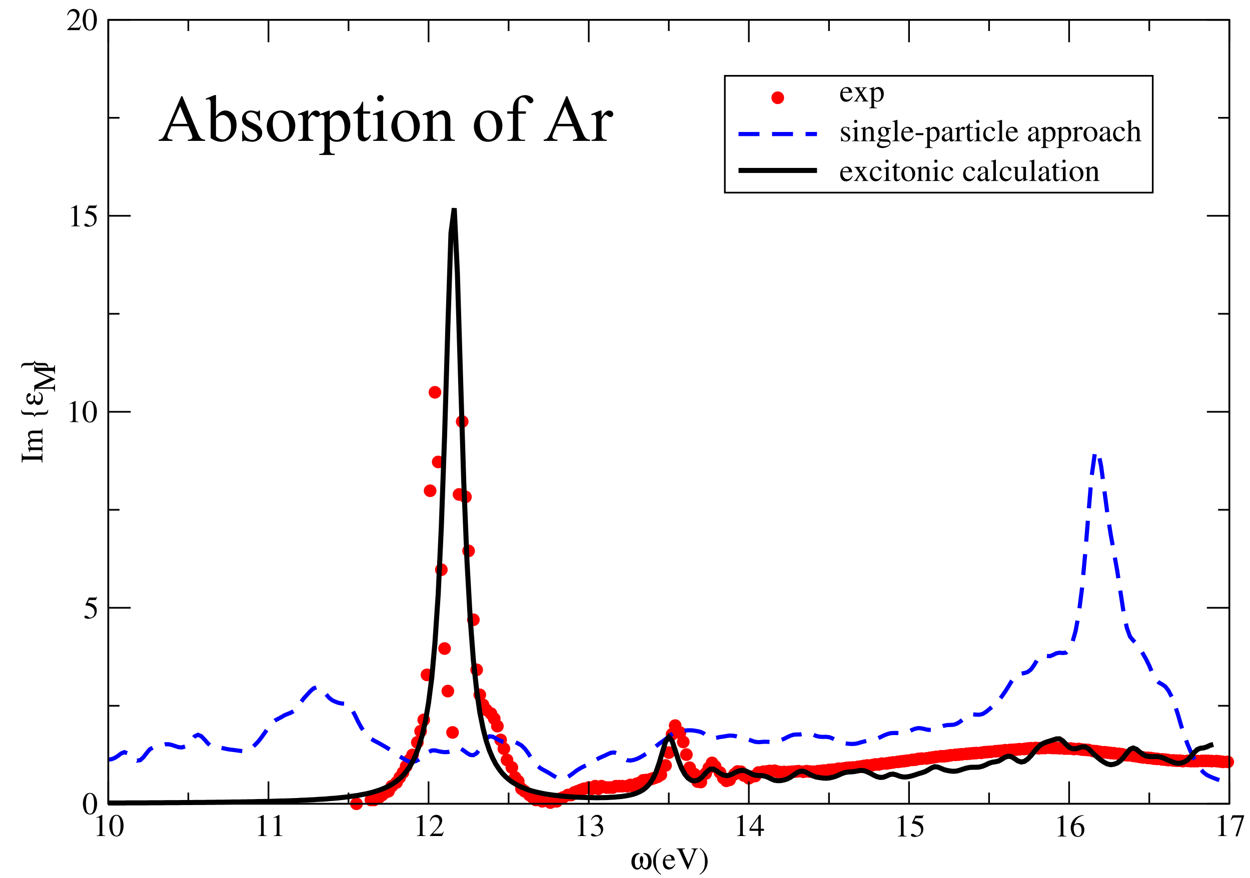

Absorption of Ar
exp
single-particle approach
Im {ε_M}
ω(eV)
0
5
10
15
20
10
11
12
13
14
15
16
17



energy
Empty states
Valence electrons
Core states



Absorption of Ar
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excitonic calculation
Im {ε_M}
ω(eV)
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- Excitons via Green's functions many-body theory

  Signatures in absorption

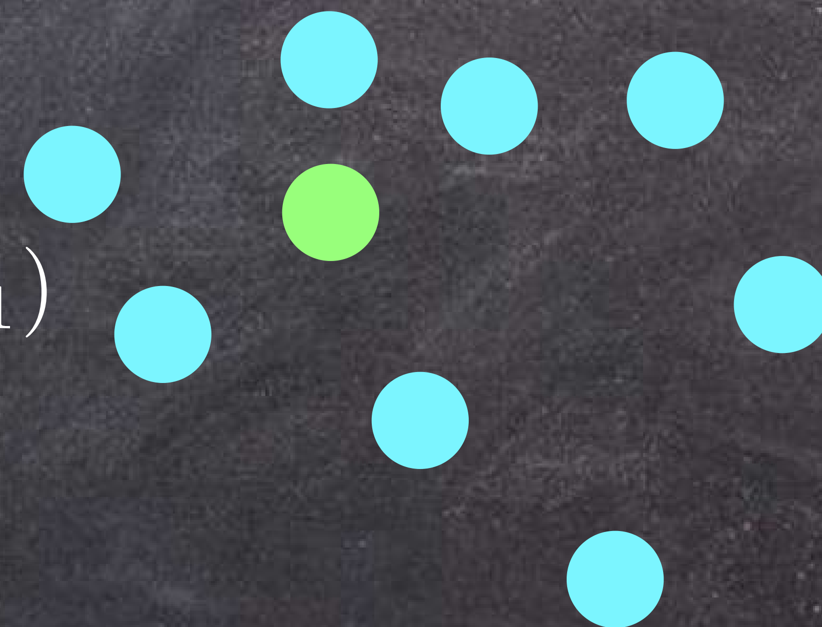
- (N,C,R) Inelastic X-ray scattering within GFs

- What about XFELs ?

The Green's functions mb formalism

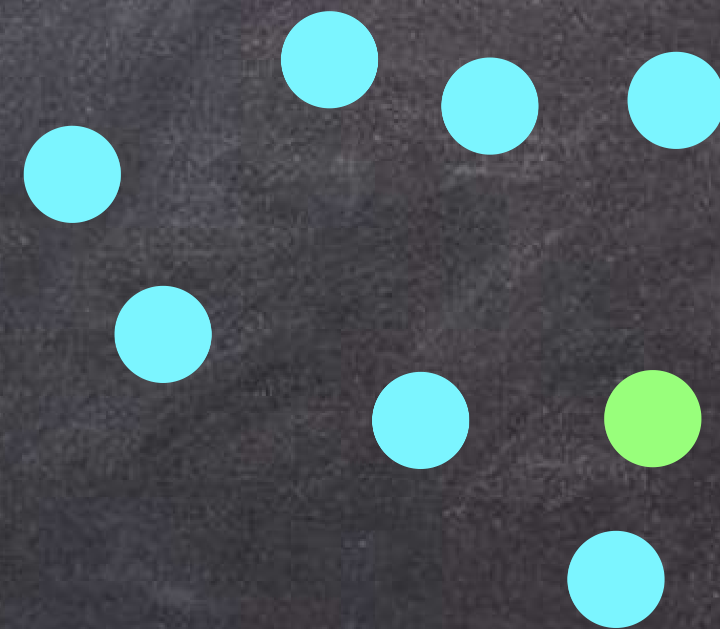
$$G(1,2)$$

$$1 = (\mathbf{r}_1, t_1, \sigma_1)$$



The Green's functions mb formalism

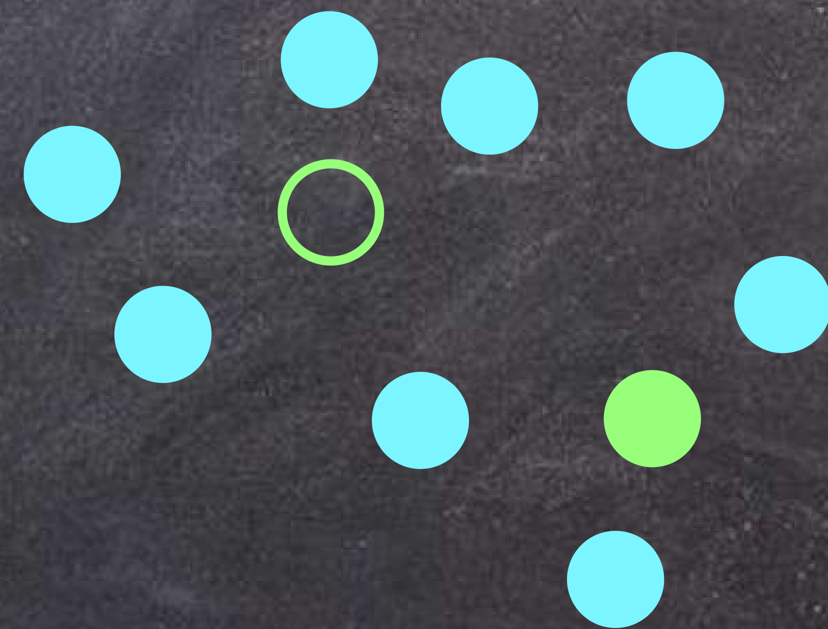
$$G(1,2)$$



$$2 = (\mathbf{r}_2, t_2, \sigma_2)$$

The Green's functions mb formalism

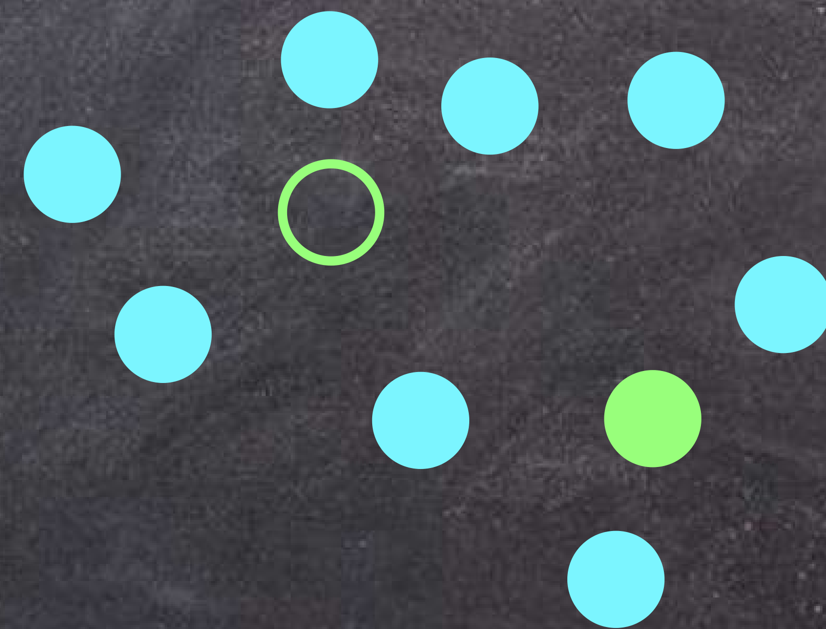
$$G(1,2)$$



$$G^{(2)}(1,2,3,4)$$

The Green's functions mb formalism

$$G(1,2)$$



$$G^{(2)}(1,2,3,4) - G(1,2)G(3,4) = -iL(1,2,3,4) = \frac{\delta G(1,3)}{\delta V_{ext}(2,4)}$$

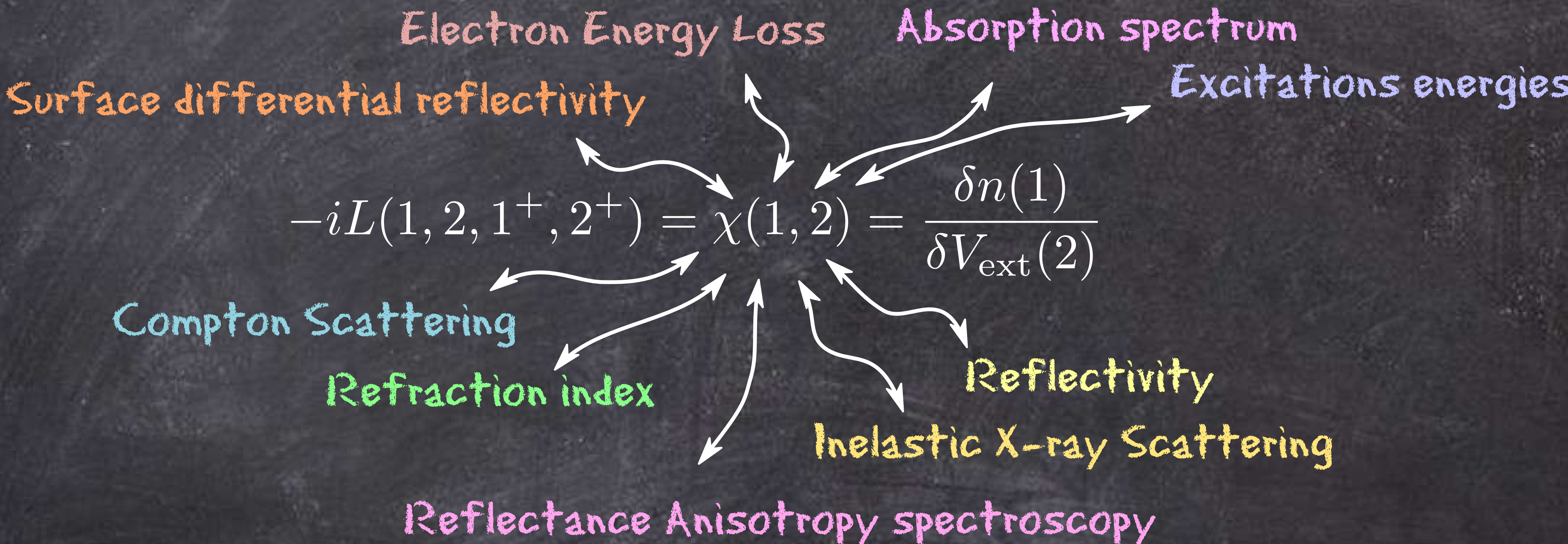
$$-iL(1,2,1^+,2^+) = \chi(1,2) = \frac{\delta n(1)}{\delta V_{\text{ext}}(2)}$$

Electron Energy Loss

Excitations energies

$$-iL(1,2,1^+,2^+) = \chi(1,2) = \frac{\delta n(1)}{\delta V_{\text{ext}}(2)}$$

Inelastic X-ray Scattering

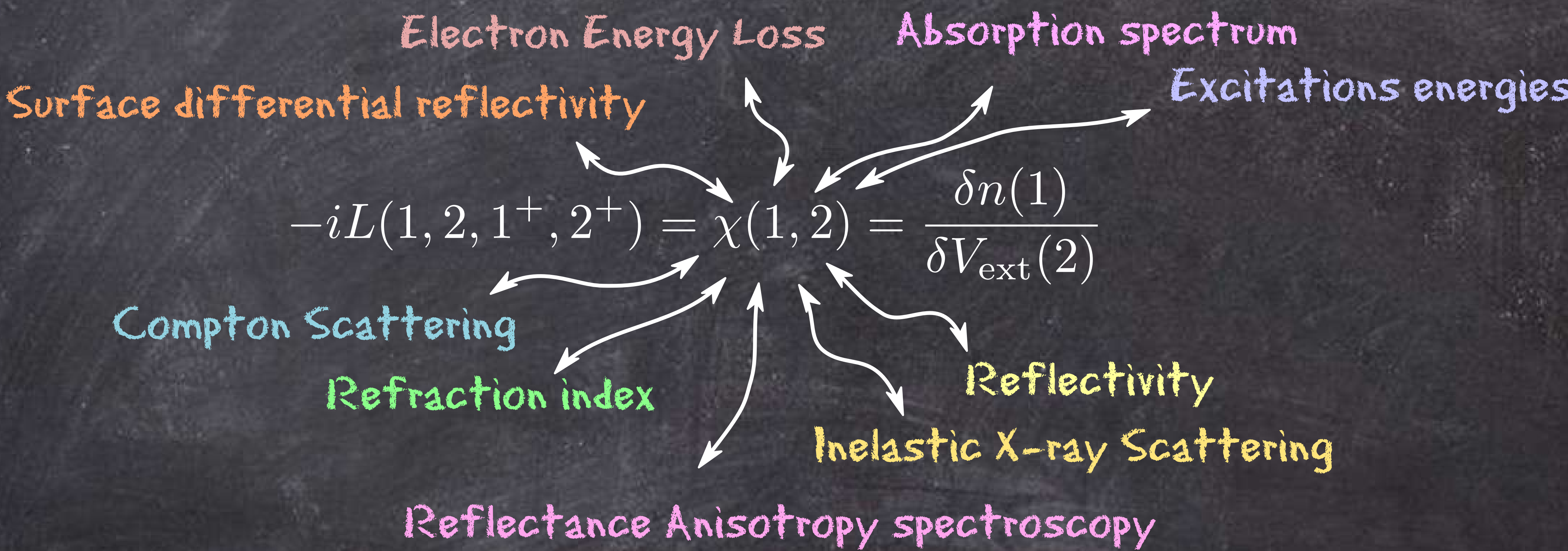

Electron Energy Loss
Absorption spectrum
Excitations energies
Surface differential reflectivity
$-iL(1,2,1^+,2^+) = \chi(1,2) = \frac{\delta n(1)}{\delta V_{\text{ext}}(2)}$
Compton Scattering
Refraction index
Reflectivity
Inelastic X-ray Scattering
Reflectance Anisotropy spectroscopy

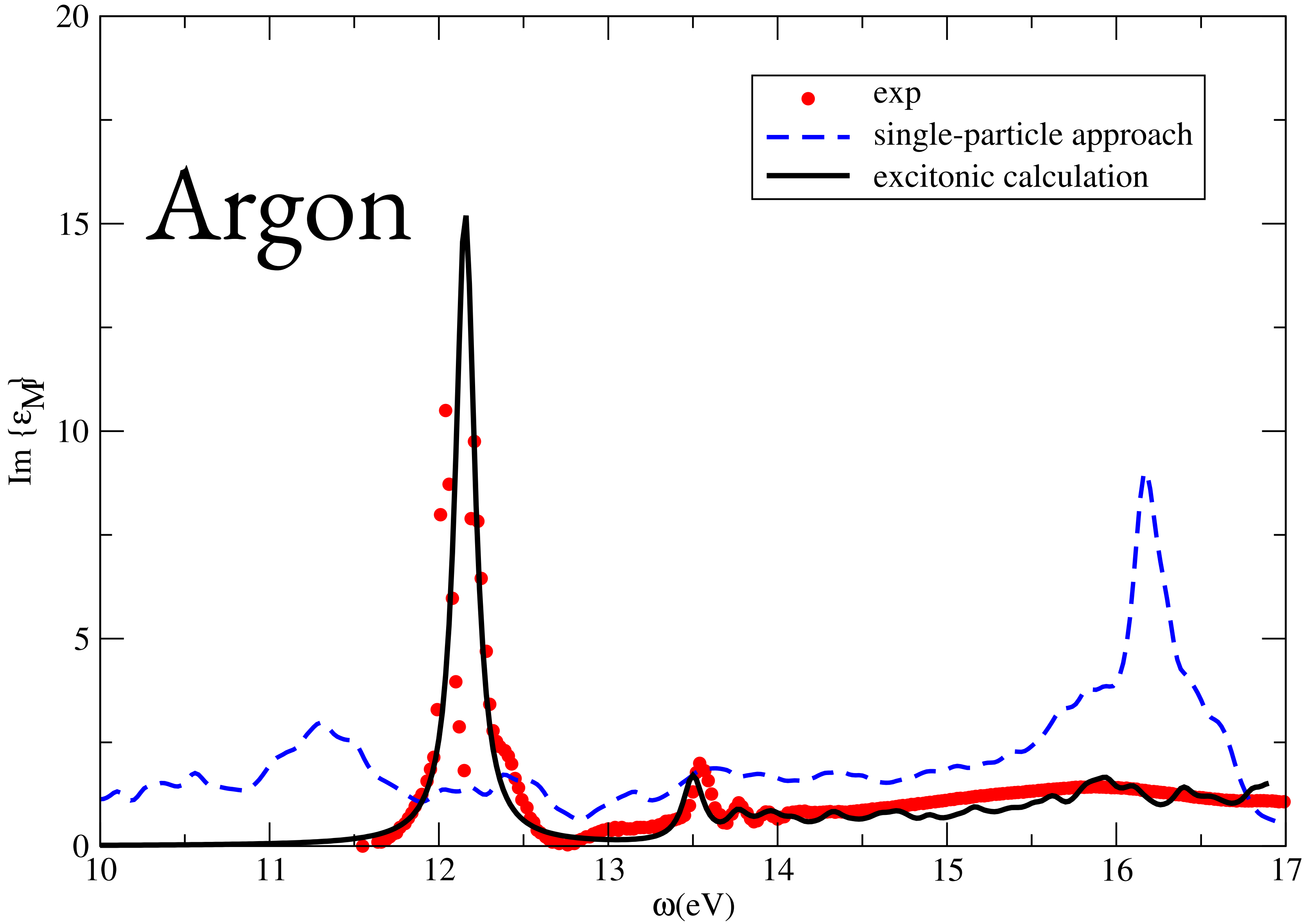
The Bethe-Salpeter Equation

$$L(1,2,3,4) = L^0(1,2,3,4) + L^0(1,2,5,6)\left[v(5,7)\delta(5,6)\delta(7,8) + i\frac{\delta\Sigma(5,6)}{\delta G(7,8)}\right]L(7,8,3,4)$$

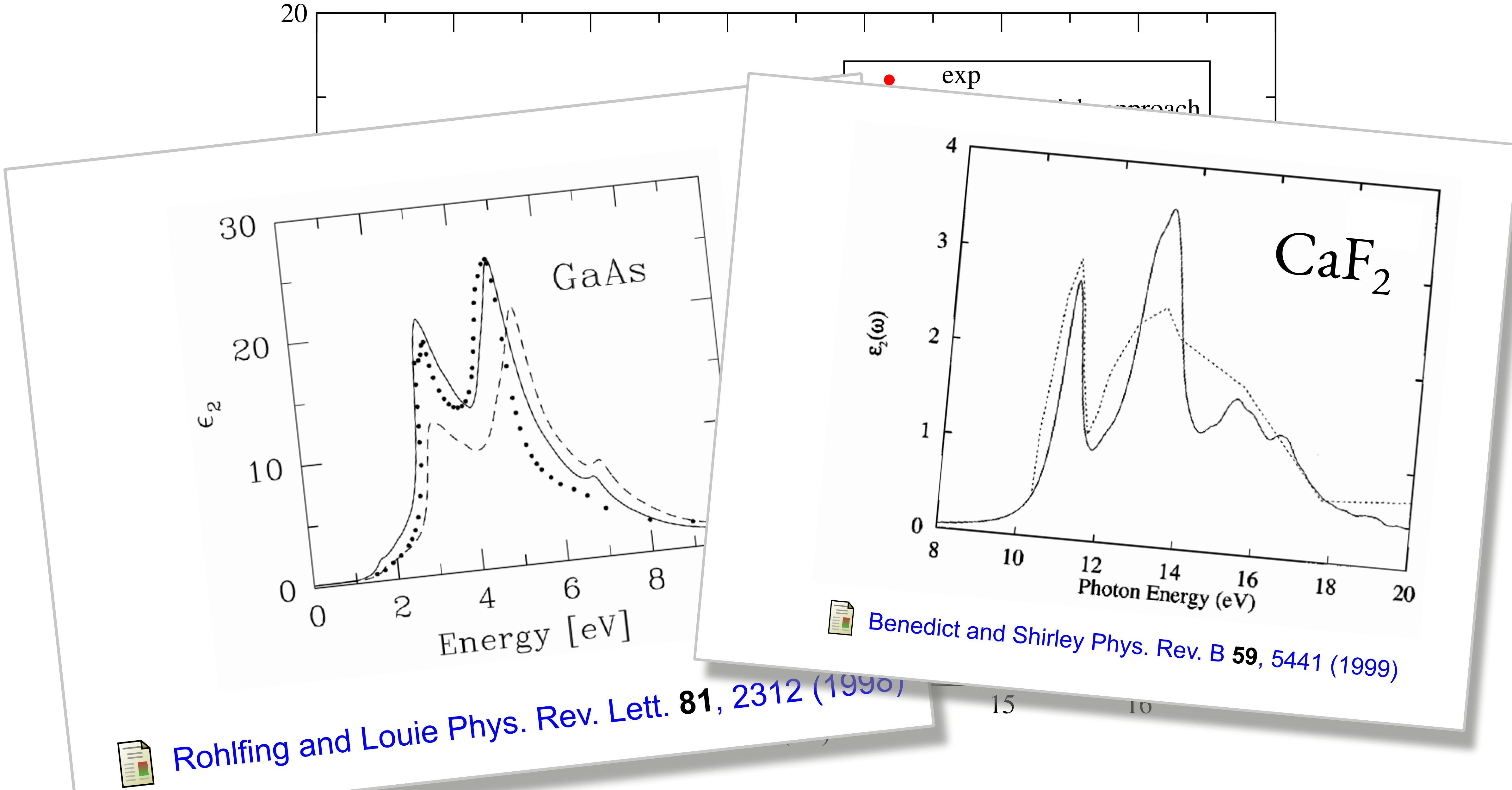
$$L^0(1,2,3,4) = G(1,2)G(3,4)$$

$$-iL(1,2,1^+,2^+) = \chi(1,2) = \frac{\delta n(1)}{\delta V_{\text{ext}}(2)}$$





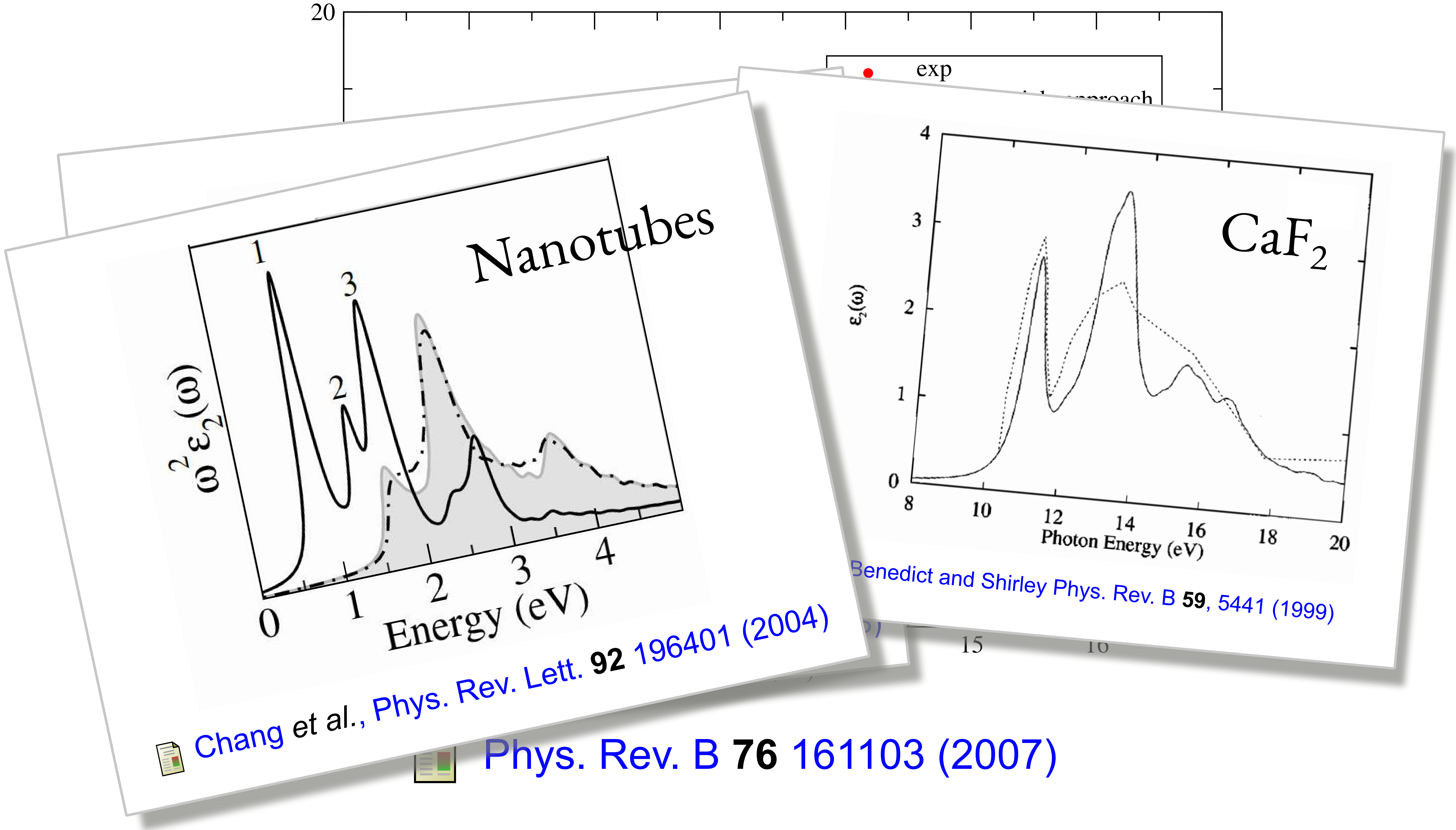
Phys. Rev. B **76** 161103 (2007)



Rohlfing and Louie Phys. Rev. Lett. **81**, 2312 (1998)

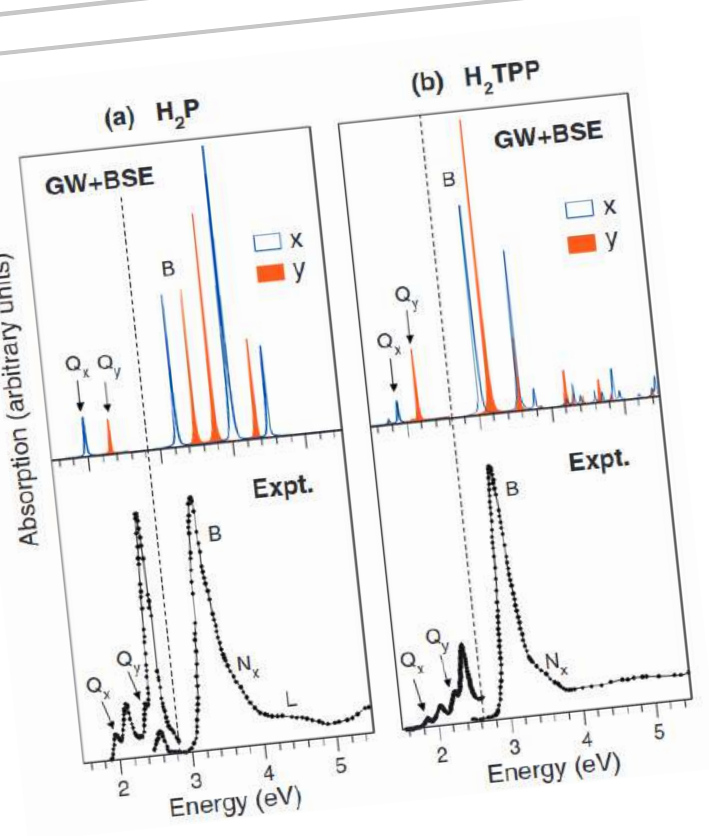
Benedict and Shirley Phys. Rev. B **59**, 5441 (1999)

Phys. Rev. B **76** 161103 (2007)



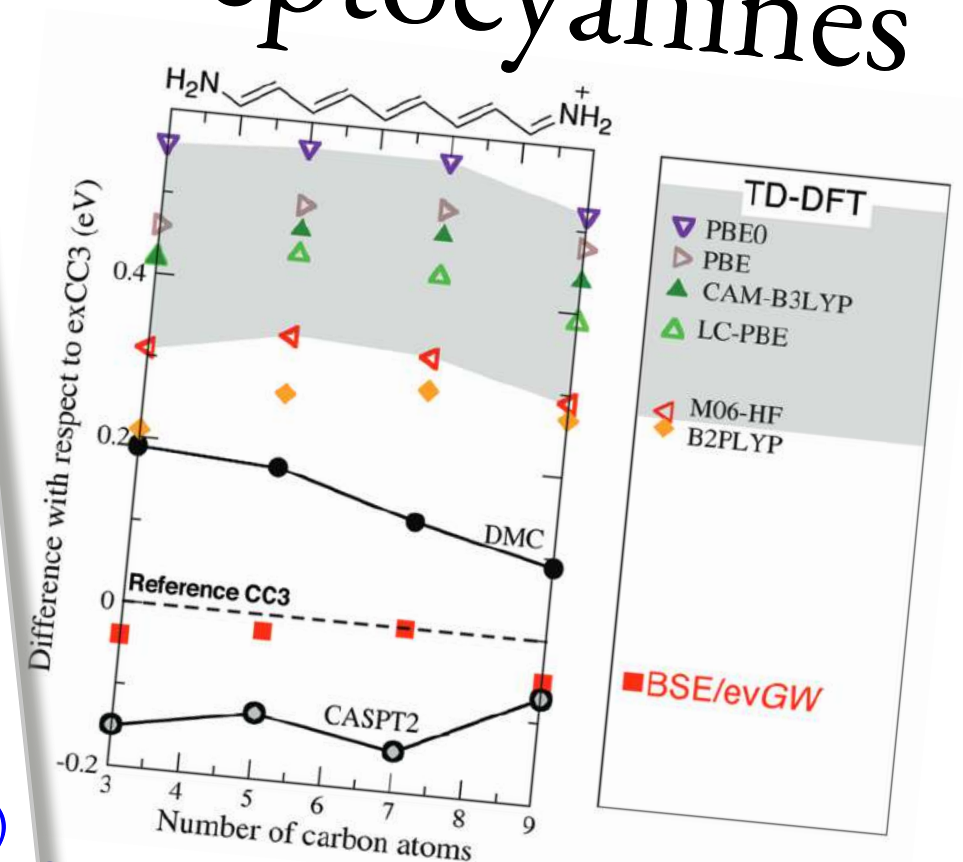
20
exp
Nanotubes
$\omega^2\varepsilon_2(\omega)$
1
2
3
0
1
2
3
4
Energy (eV)
Chang et al., Phys. Rev. Lett. **92** 196401 (2004)
CaF$_2$
$\varepsilon_2(\omega)$
0
1
2
3
4
8
10
12
14
16
18
20
Photon Energy (eV)
Benedict and Shirley Phys. Rev. B **59**, 5441 (1999)
15
16
Phys. Rev. B **76** 161103 (2007)

Porphyrins



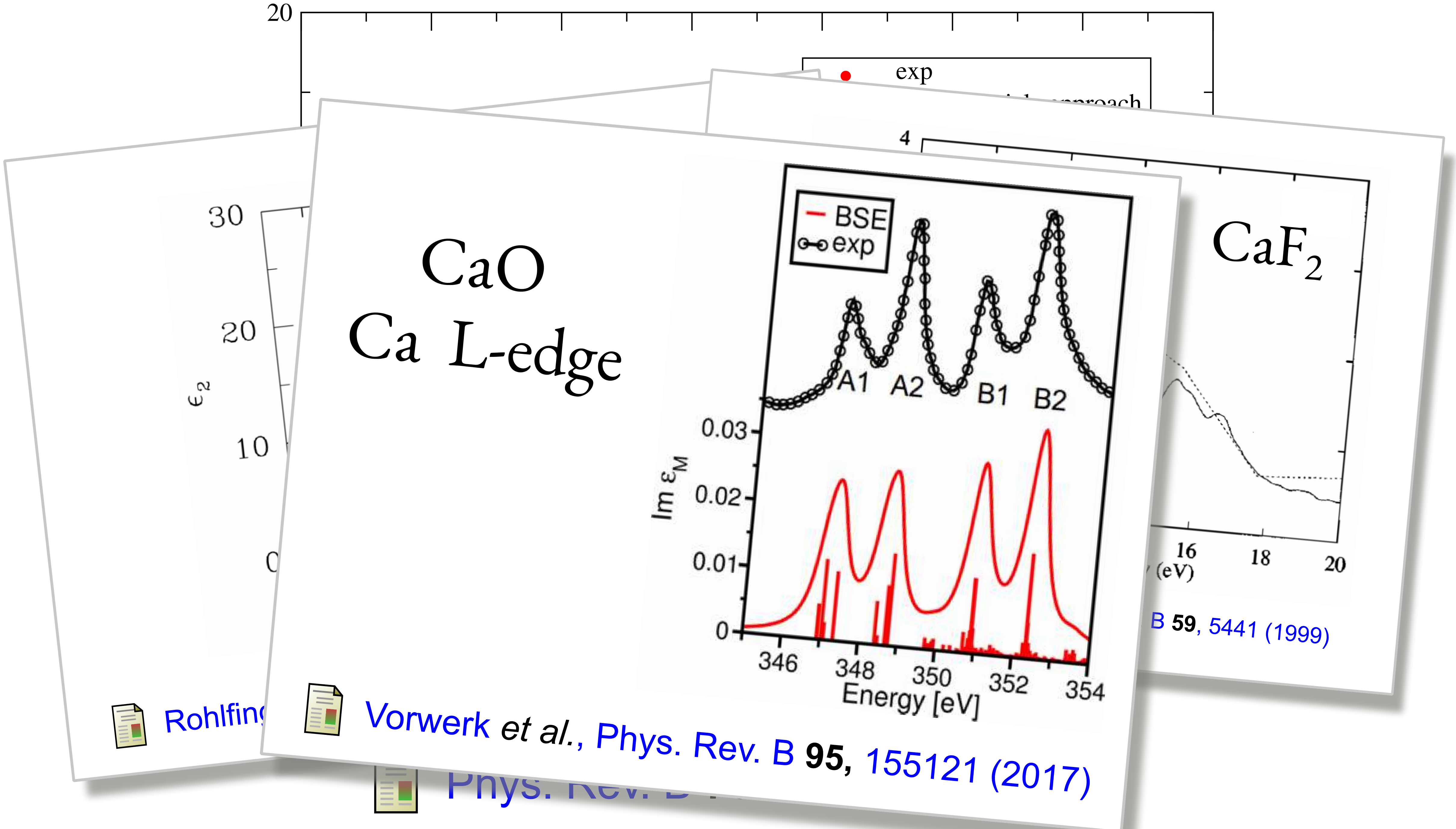
Palummo *et al.*, J. Chem. Phys. **131** 084102 (2009)

streptocyanines



ase *et al.* Chem. Soc. Rev. **47**, 1022 (2018)

Phys. Rev. B **76** 161103 (2007)


CaO
Ca L-edge
BSE
exp
A1
A2
B1
B2
Im ε_M
0.03
0.02
0.01
0
346
348
350
352
354
Energy [eV]
Vorwerk *et al.*, Phys. Rev. B **95**, 155121 (2017)
CaF$_2$
B **59**, 5441 (1999)
Rohlfing
ϵ_2
30
20
10
exp

Green's function approach has been (is) successful

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- it captures the physics of the electron-hole interaction

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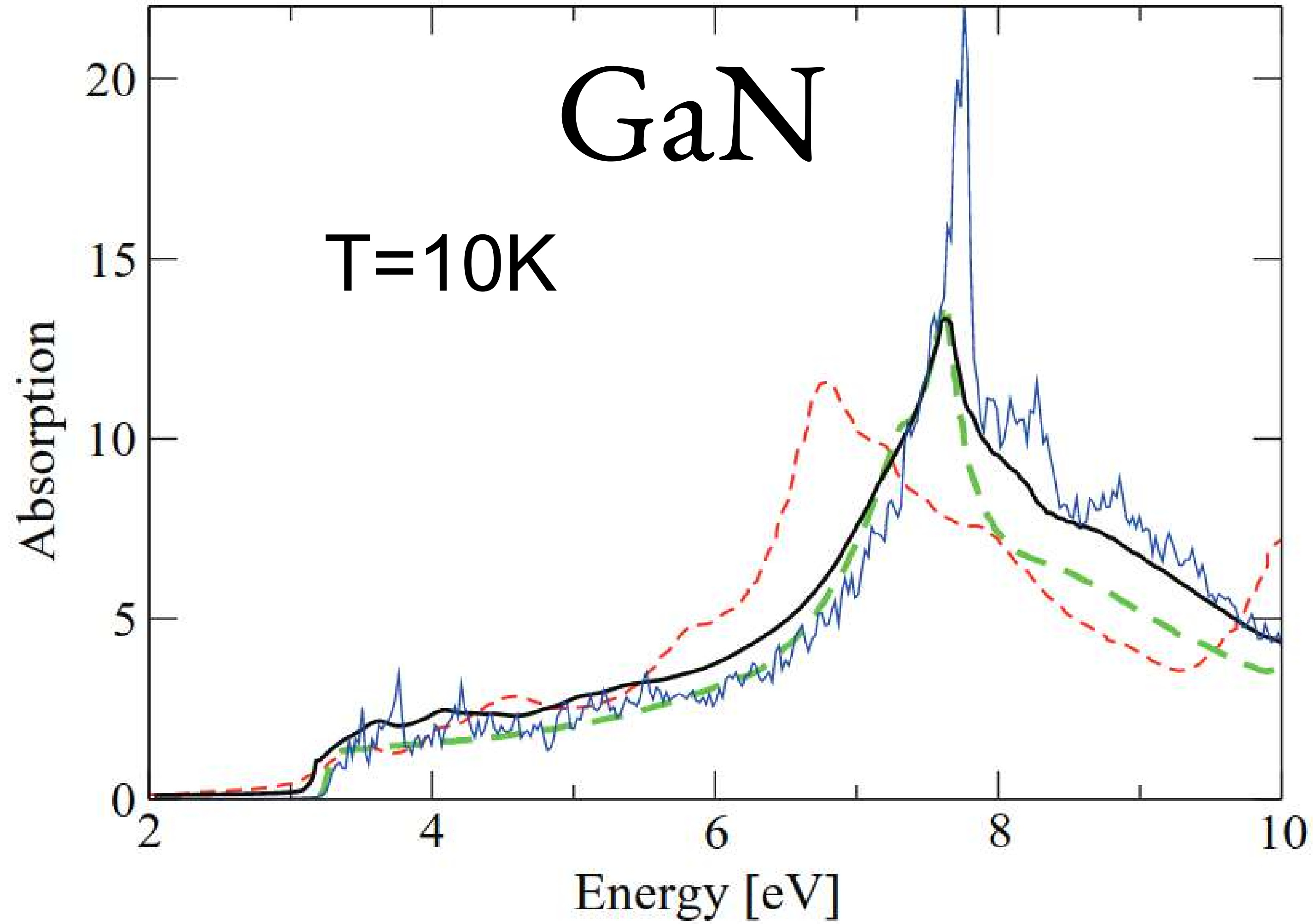
- it can (automatically) profit from extensions

Temperature
electron-phonon



Kawai *et al.* Phys. Rev. B **89**, 085202 (2014)

Evidence of ideal excitonic insulator in bulk MoS_2 under pressure

S. Samaneh Ataei[a,1], Daniele Varsano[a,1], Elisa Molinari[a,b], and Massimo Rontani[a,2]

PNAS 2021 Vol. 118 No. 13 e2010110118 https://doi.org/10.1073/pnas.2010110118

PHYSICAL REVIEW B, VOLUME 65, 155332

Bethe-Salpeter equation for magnetoexcitons in quantum wells

Z. G. Koinov*
Department of Physics & Astronomy, University of Texas at San Antonio, San Antonio, Texas 78249

(Received 10 December 2001; published 11 April 2002)

PRL **116,** 196804 (2016) PHYSICAL REVIEW LETTERS week ending 13 MAY 2016

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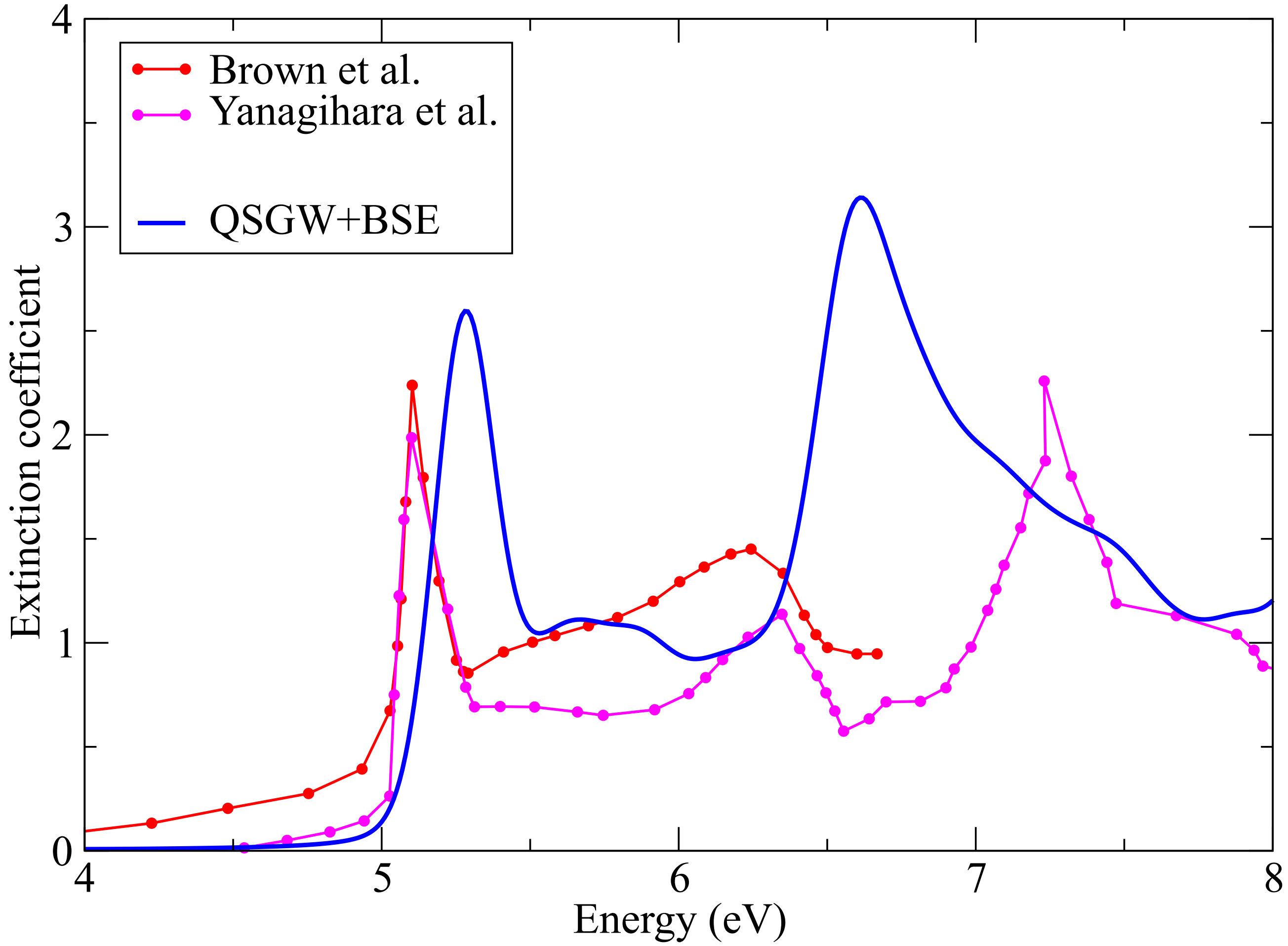
- it captures the physics of the electron-hole interaction
- it can (automatically) profit from extensions
- *ab initio* → predictions
- analysis tools (why? how? who is responsable?)

AgCl extinction coefficient



Lorin *et al.* Phys. Rev. B **104**, 235149 (2021)

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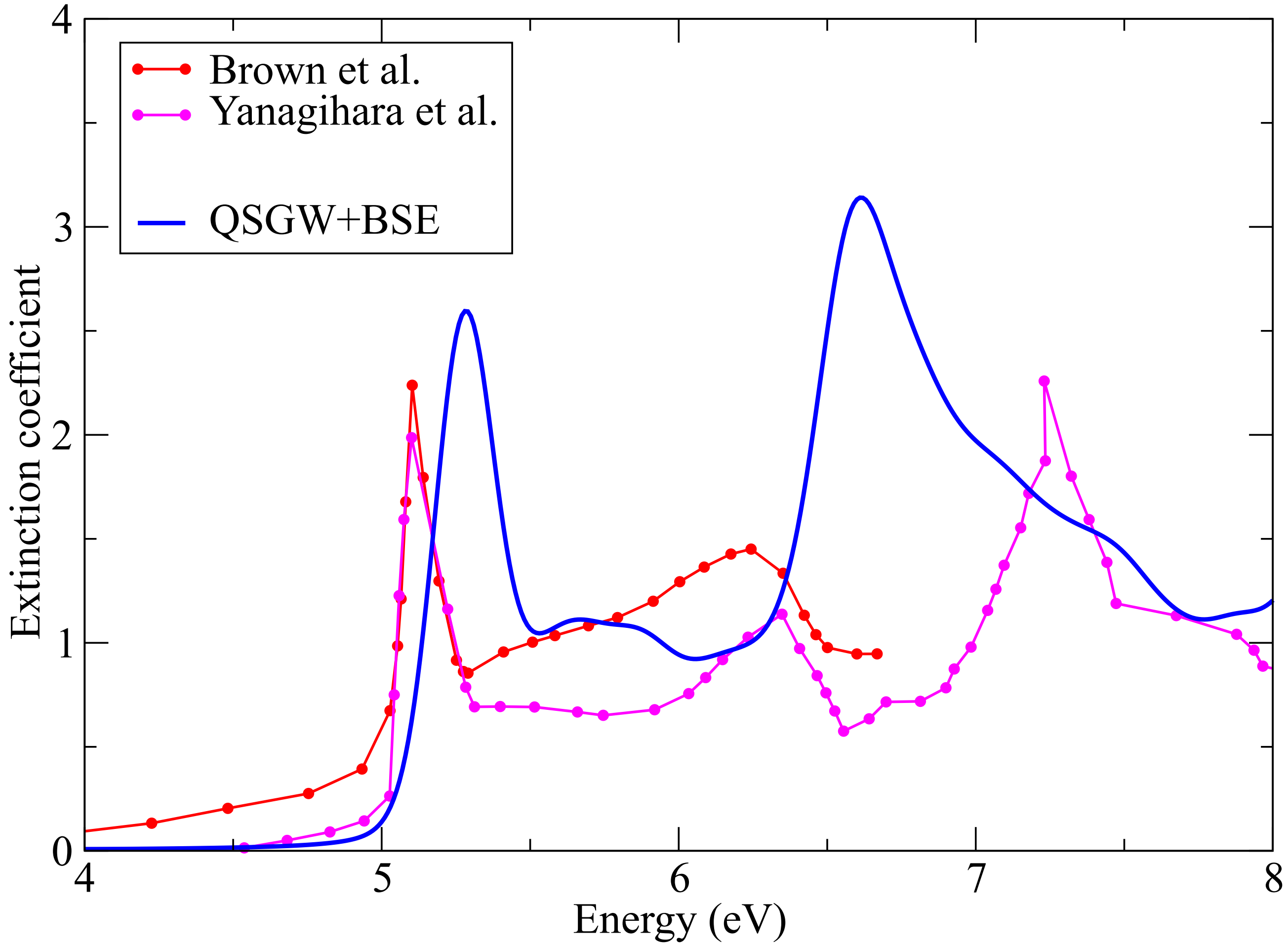

$$\chi_M = \sum_\lambda \frac{\left|\sum_{vc\mathbf{k}} A_\lambda^{vc\mathbf{k}} \langle c\mathbf{k}|\hat{\mathbf{d}}|v\mathbf{k}\rangle\right|^2}{\omega - E_\lambda + i\eta}$$

$$\kappa = \mathrm{Im}\sqrt{\frac{1}{1+v_0\chi_M}}$$

Lorin *et al.* Phys. Rev. B **104**, 235149 (2021)

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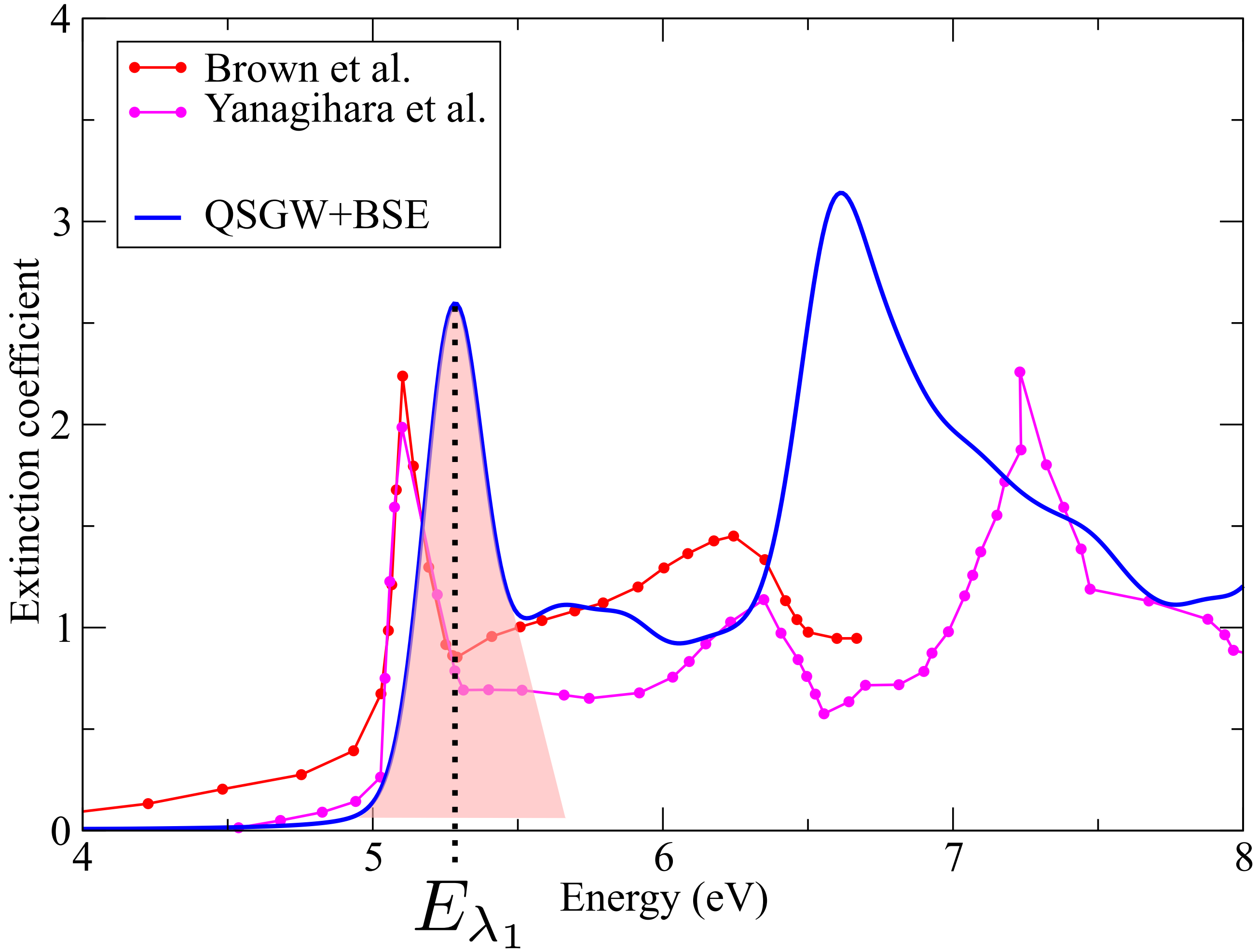

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AgCl extinction coefficient

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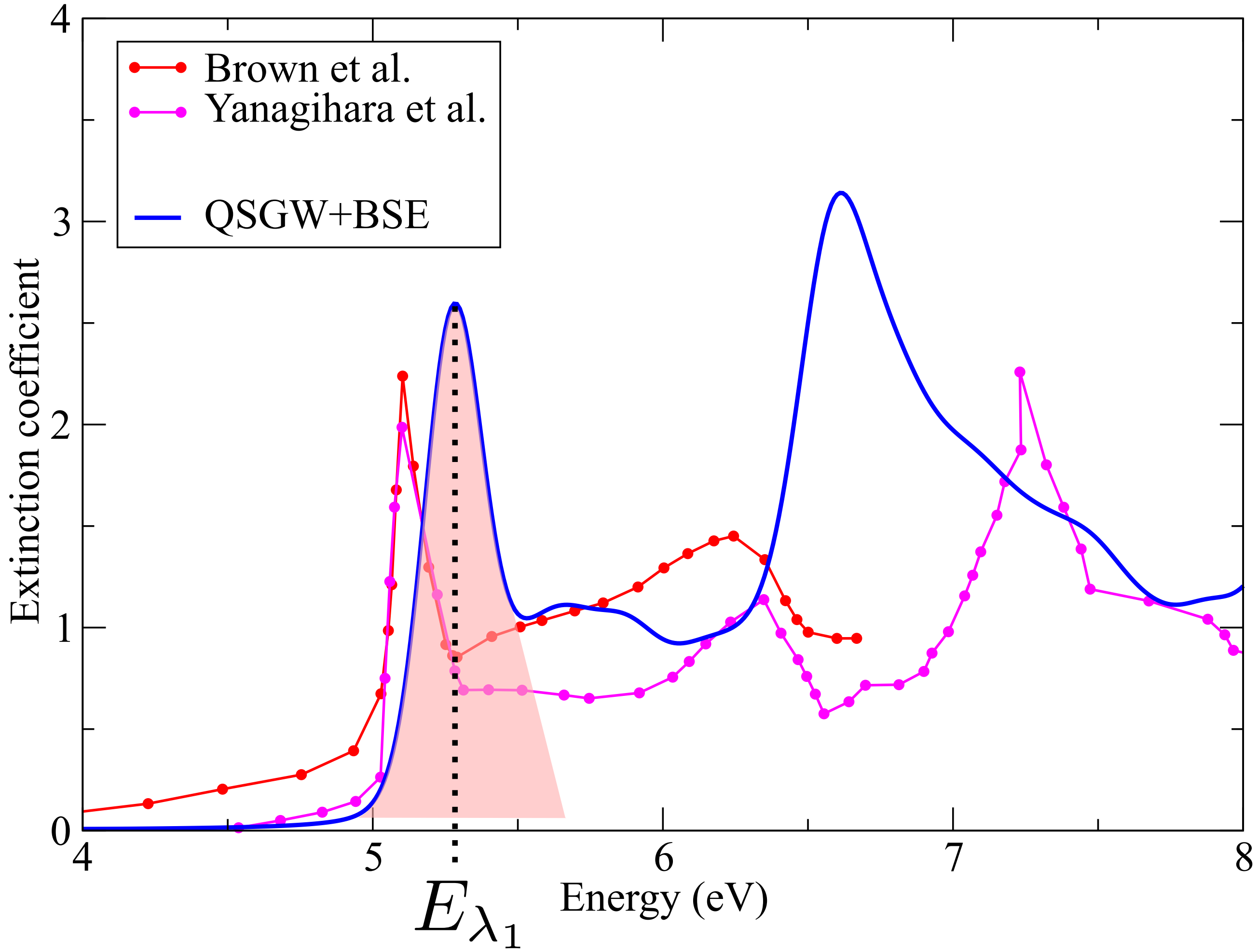
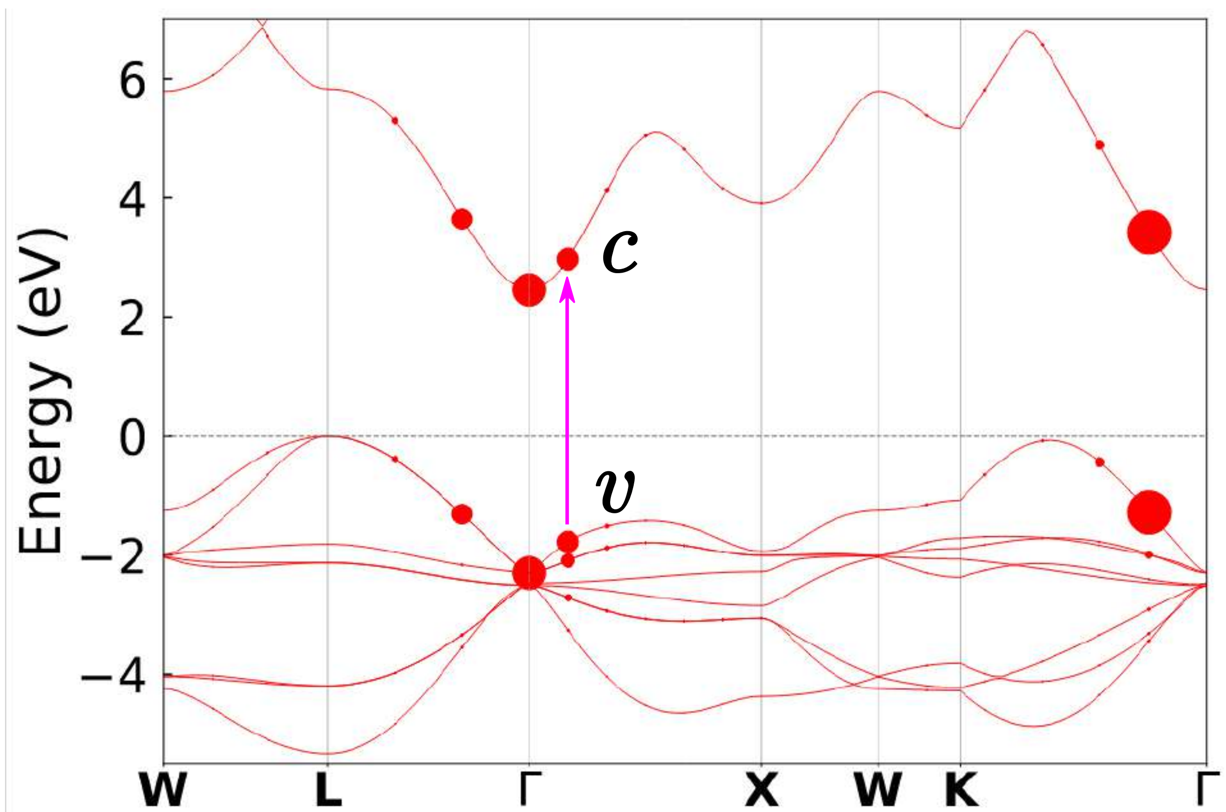




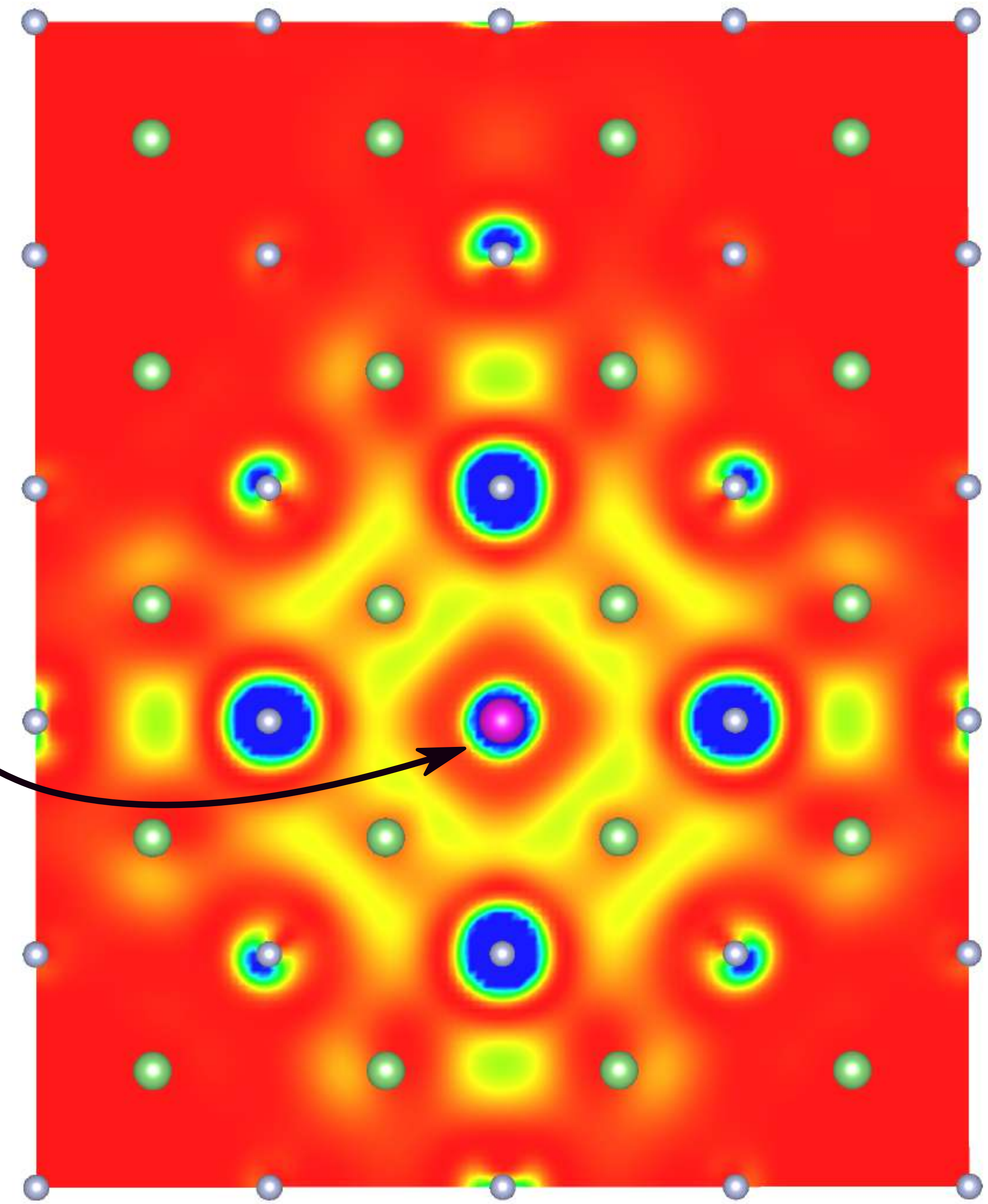
Lorin *et al.* Phys. Rev. B **104**, 235149 (2021)

Excitonic wavefunction of LiF

$$\Psi_\lambda(\mathbf{r}_e, \mathbf{r}_h) \;=\; \sum_{vc\mathbf{k}} A_\lambda^{vc\mathbf{k}} \psi_{c\mathbf{k}}^*(\mathbf{r}_e)\psi_{v\mathbf{k}}(\mathbf{r}_h)$$

Excitonic wavefunction of LiF

$$|\Psi_\lambda(\mathbf{r}_e,\mathbf{r}_h)|^2 = \left|\sum_{vc\mathbf{k}} A_\lambda^{vc\mathbf{k}} \psi^*_{c\mathbf{k}}(\mathbf{r}_e)\psi_{v\mathbf{k}}(\mathbf{r}_h)\right|^2$$



- where is the exciton localised ?
- how much ?

Gatti and Sottile, Phys. Rev. B **98**, 155113 (2013)

- Excitons via Green's functions many-body theory
  - Signatures in absorption
- (N,C,R) Inelastic X-ray scattering within GFs
- What about XFELs ?

Christian Vorwerk (thesis with C. Draxl)

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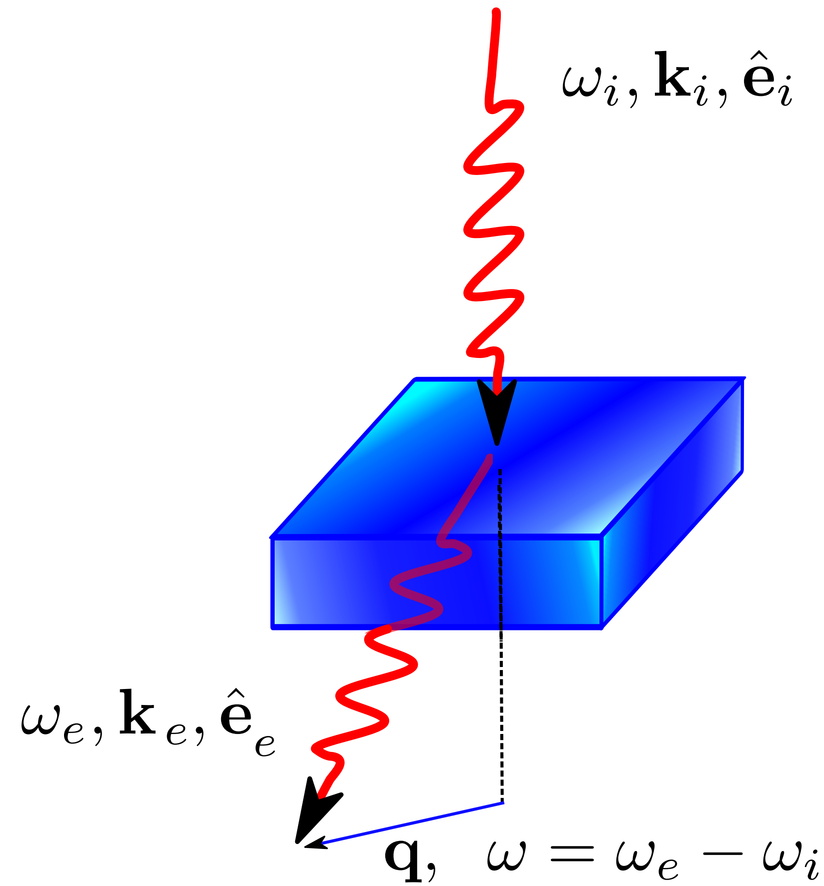
Matteo Gatti

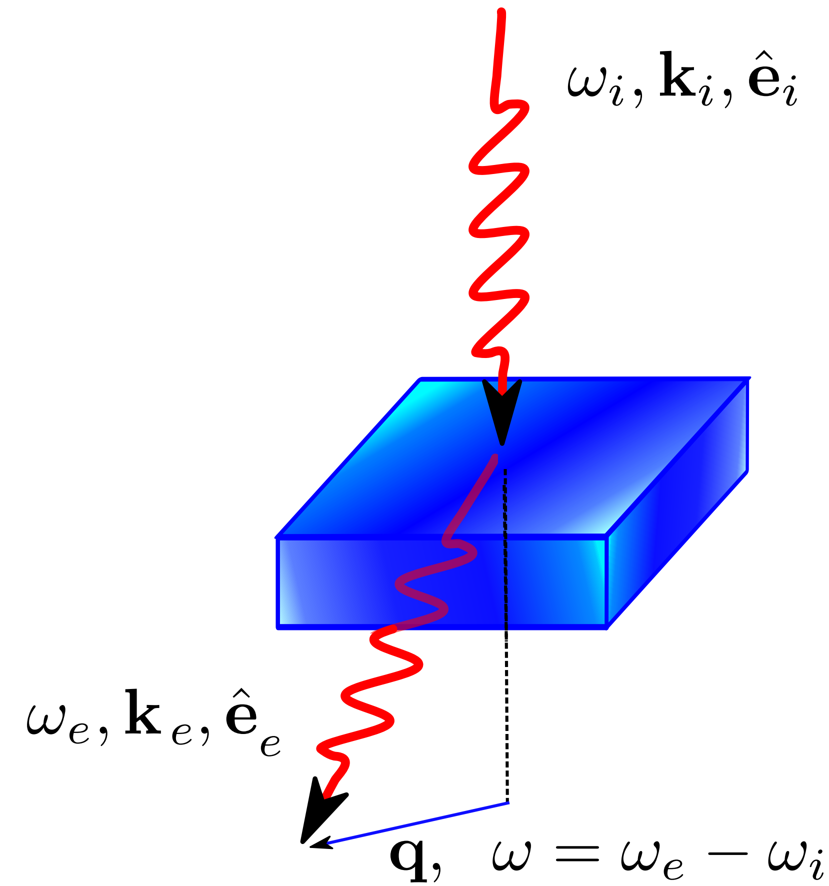
Laura Urquiza

X-ray scattering



$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \langle f | e^{i\mathbf{q}\cdot\mathbf{r}} | 0 \rangle - \frac{i\omega_{i/e}}{2mc^2} \sum_n \frac{\langle f | e^{-i\mathbf{k}_f\cdot\mathbf{r}} \nabla | n \rangle \; \langle n | e^{i\mathbf{k}_i\cdot\mathbf{r}} \nabla | 0 \rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

X-ray scattering



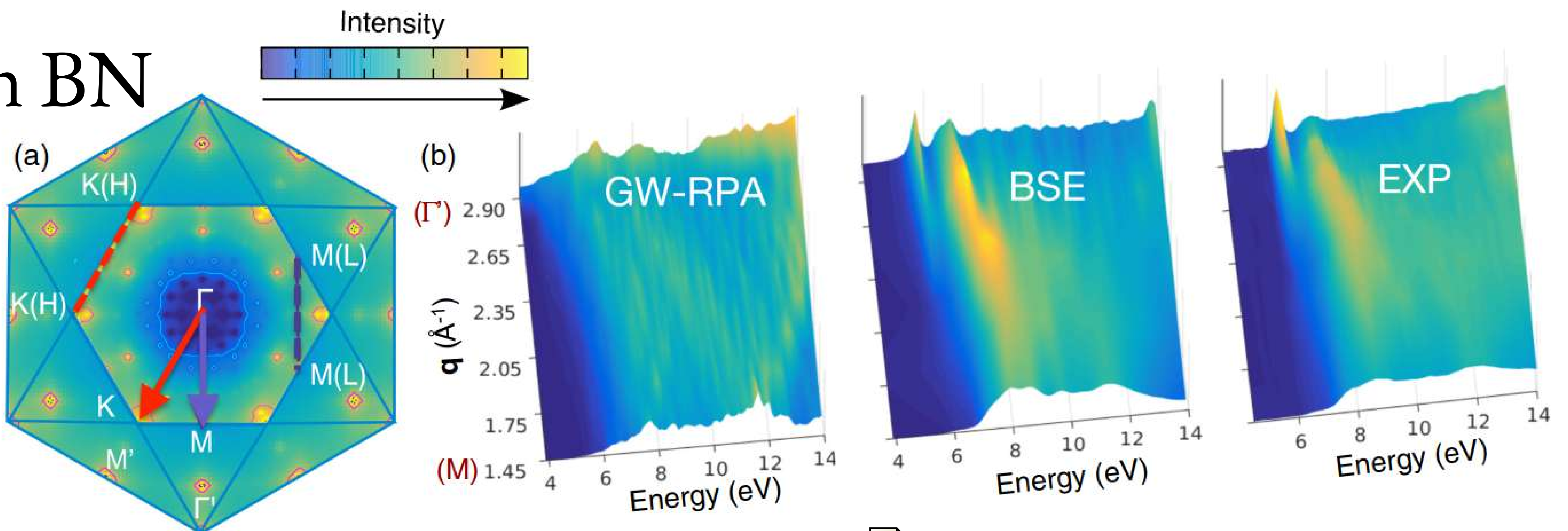
non-Resonant IXS

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \langle f | e^{i\mathbf{q}\cdot\mathbf{r}} | 0 \rangle - \frac{i\omega_{i/e}}{2mc^2} \sum_n \frac{\langle f | e^{-i\mathbf{k}_f\cdot\mathbf{r}} \nabla | n \rangle \ \langle n | e^{i\mathbf{k}_i\cdot\mathbf{r}} \nabla | 0 \rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

Bethe-Salpeter Equation - finite momentum transfer

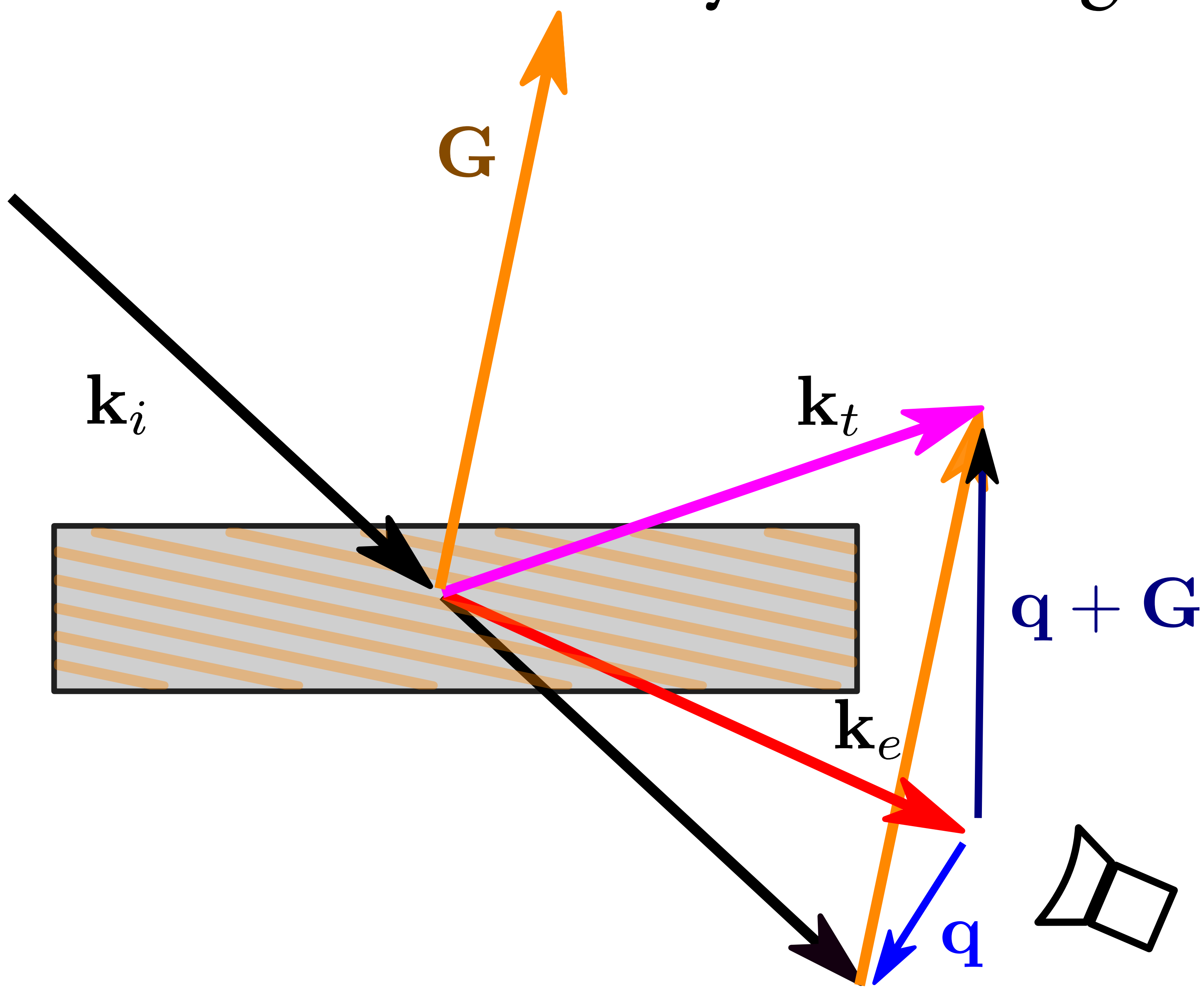
$$S(\mathbf{q},\omega) \propto \chi_M(\mathbf{q},\omega) = \sum_\lambda \frac{\left|\sum_{vc} A_\lambda^{vc,\mathbf{q}} \langle c|e^{i\mathbf{q}\cdot\mathbf{r}}|v\rangle\right|^2}{\omega - E_\lambda(\mathbf{q}) + i\eta}$$

h BN



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

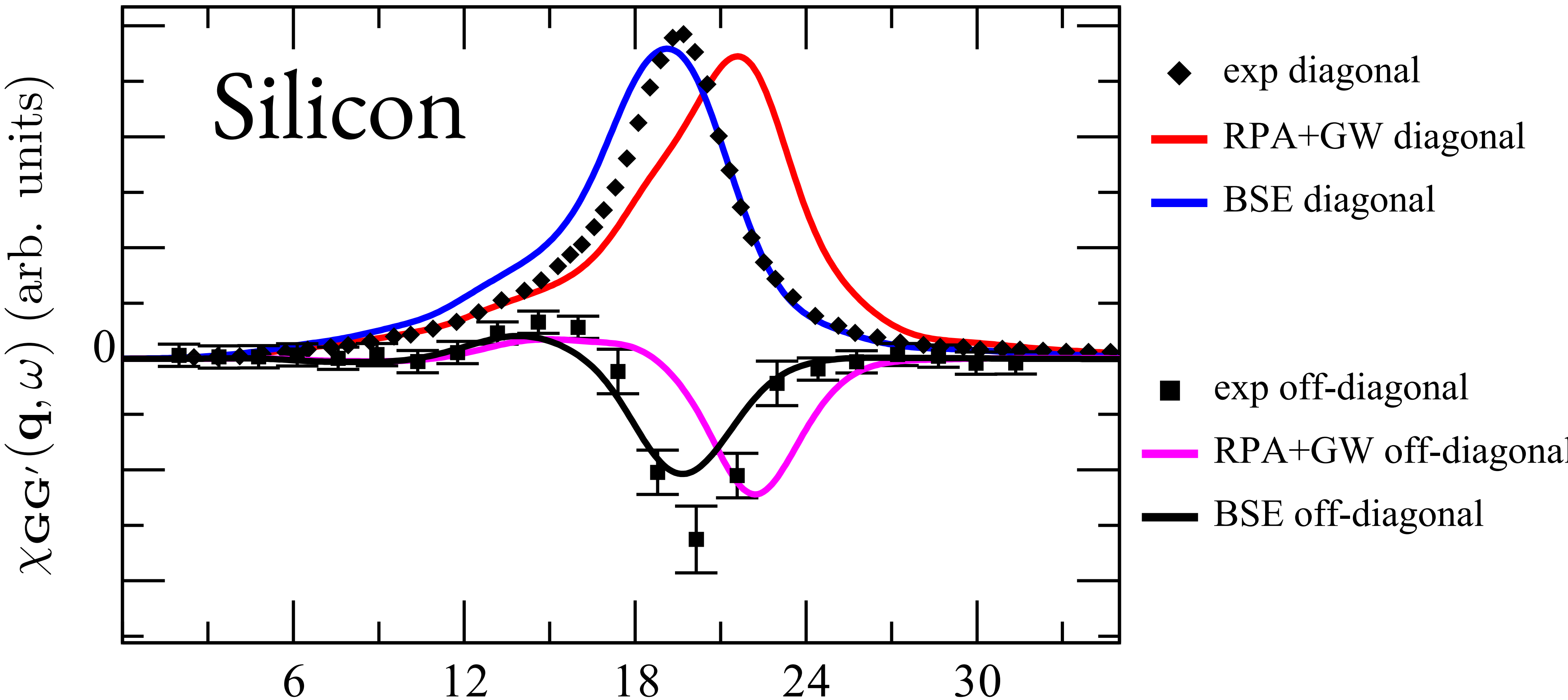
Coherent Inelastic X-ray scattering



Coherent Inelastic X-ray scattering

$$\chi(\mathbf{q},\mathbf{q}+\mathbf{G},\omega)=\sum_{\lambda\lambda'}\frac{\sum_{vc}A_\lambda^{vc,\mathbf{q}}\langle c|e^{-i\mathbf{q}\cdot\mathbf{r}}|v\rangle\,S^{-1}_{\lambda\lambda'}\sum_{v'c'}A_\lambda^{*,v'c',\mathbf{q}}\langle v'|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c'\rangle}{\omega-E_\lambda(\mathbf{q})+i\eta}$$

Igor Reshetnyak *et al.* Phys. Rev. Research **1**, 032010(R) (2019)



Schülke and Kaprolat, Phys. Rev. Lett. **67**, 879 (1991).

Weissker *et al.* Phys. Rev. B **81**, 085104 (2010).

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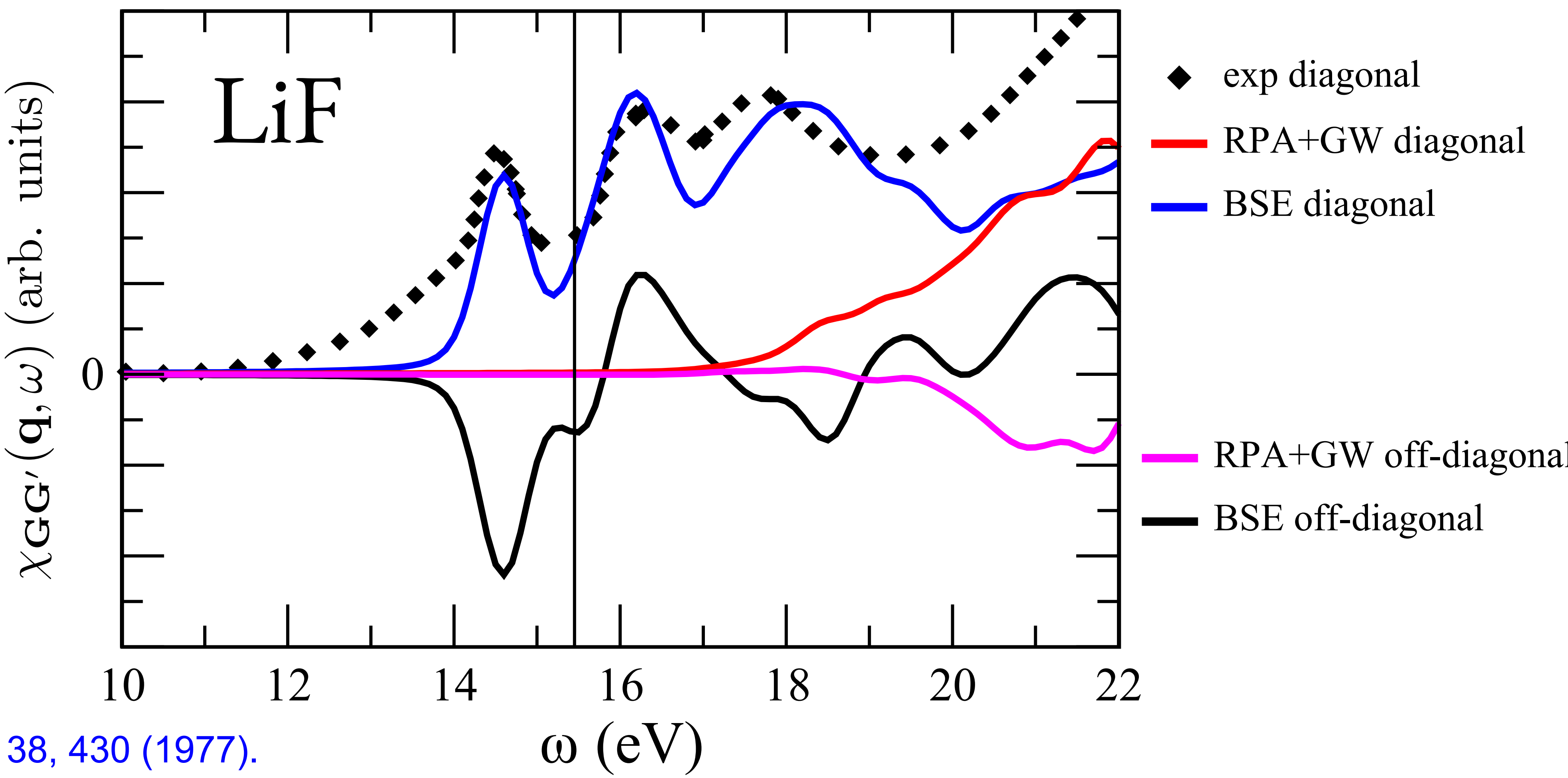

Fields *et al.* Phys. Rev. Lett. 38, 430 (1977).

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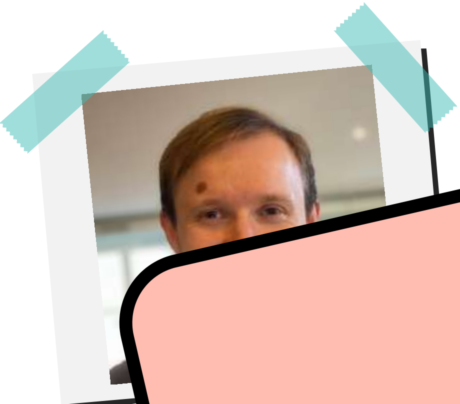

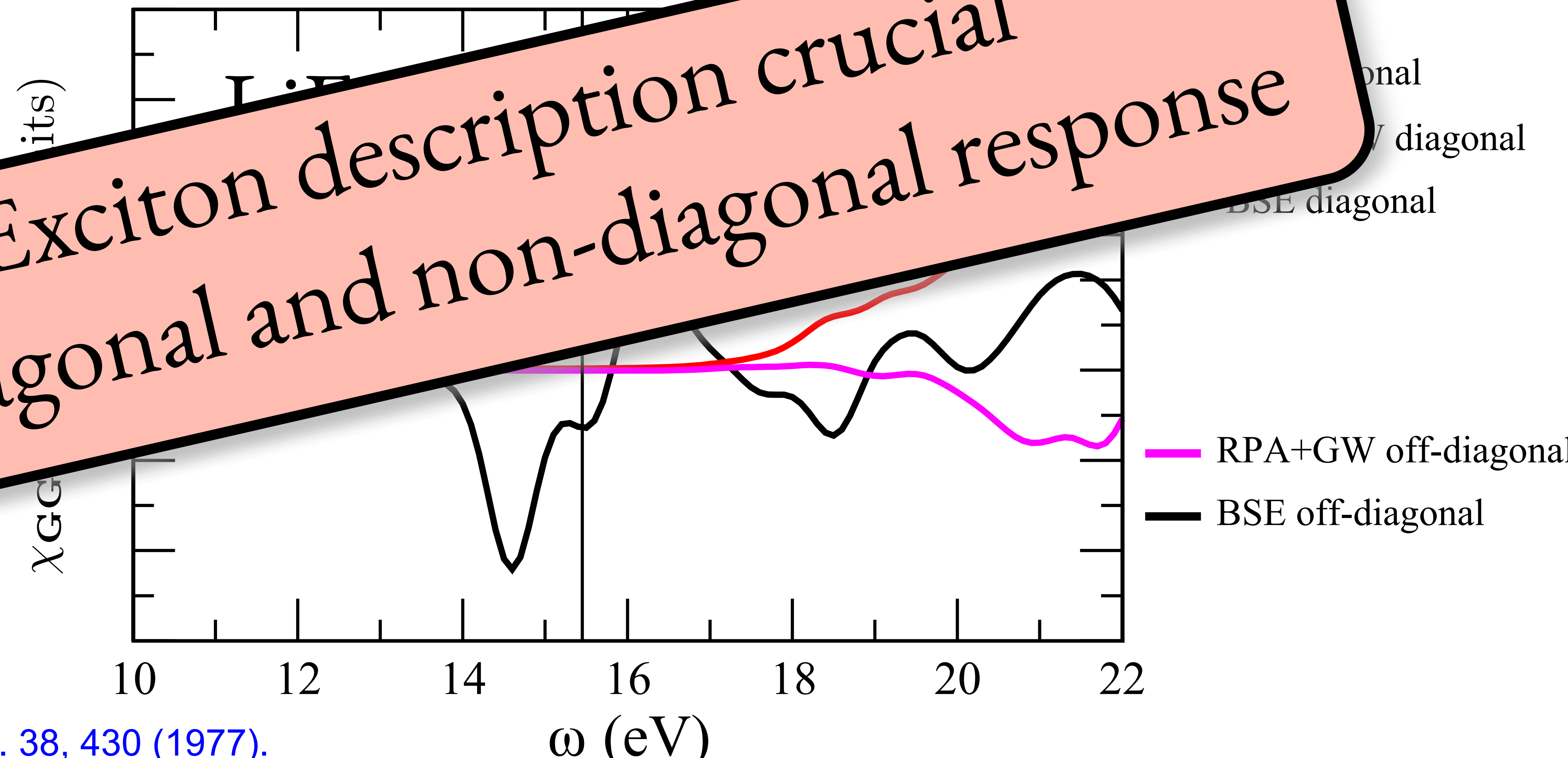

Exciton description crucial for diagonal and non-diagonal response

Igor Re
Phys. R
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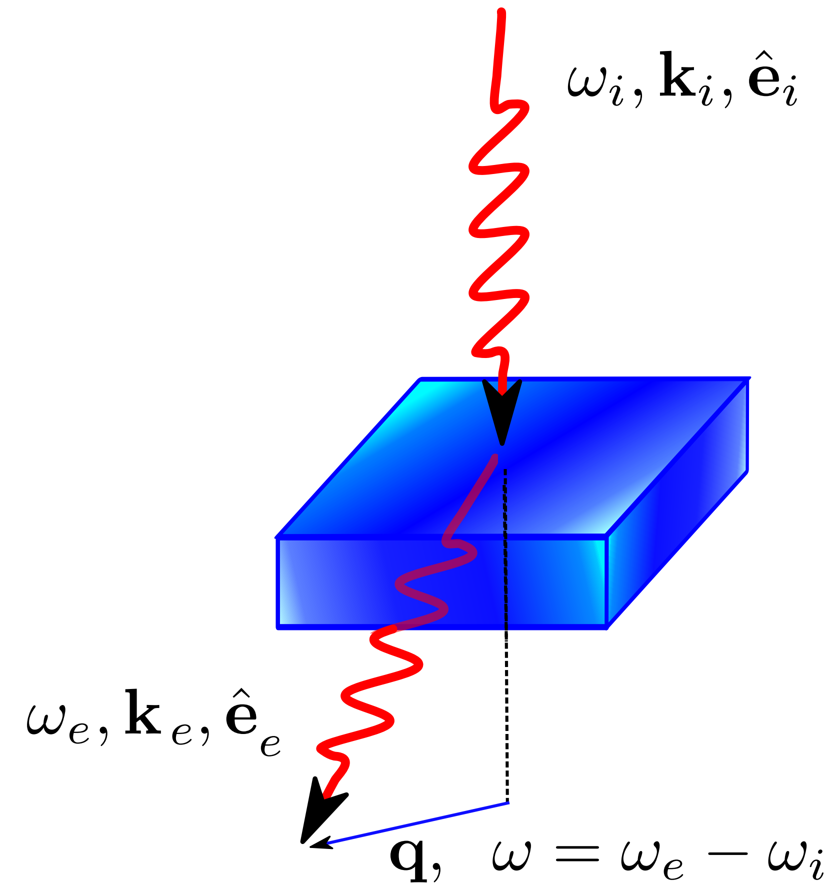
Fields *et al.* Phys. Rev. Lett. 38, 430 (1977).

X-ray scattering



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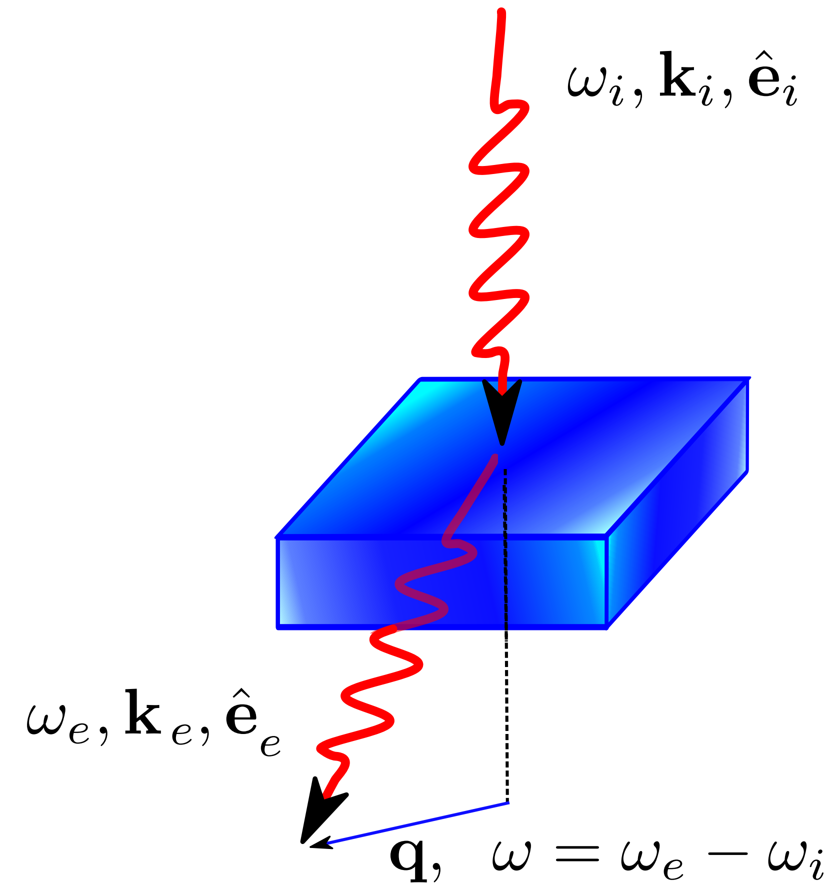
X-ray scattering



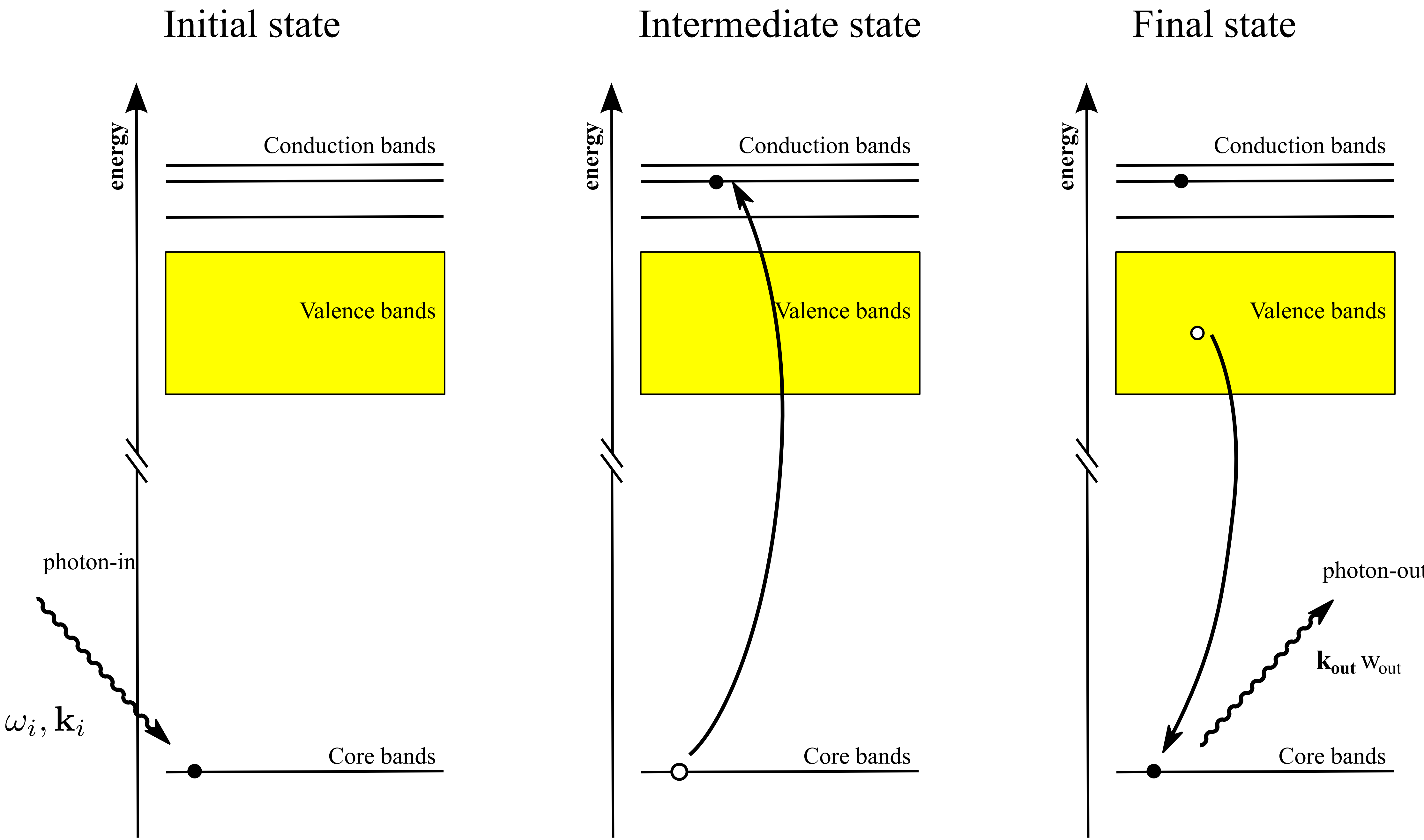
non-Resonant IXS

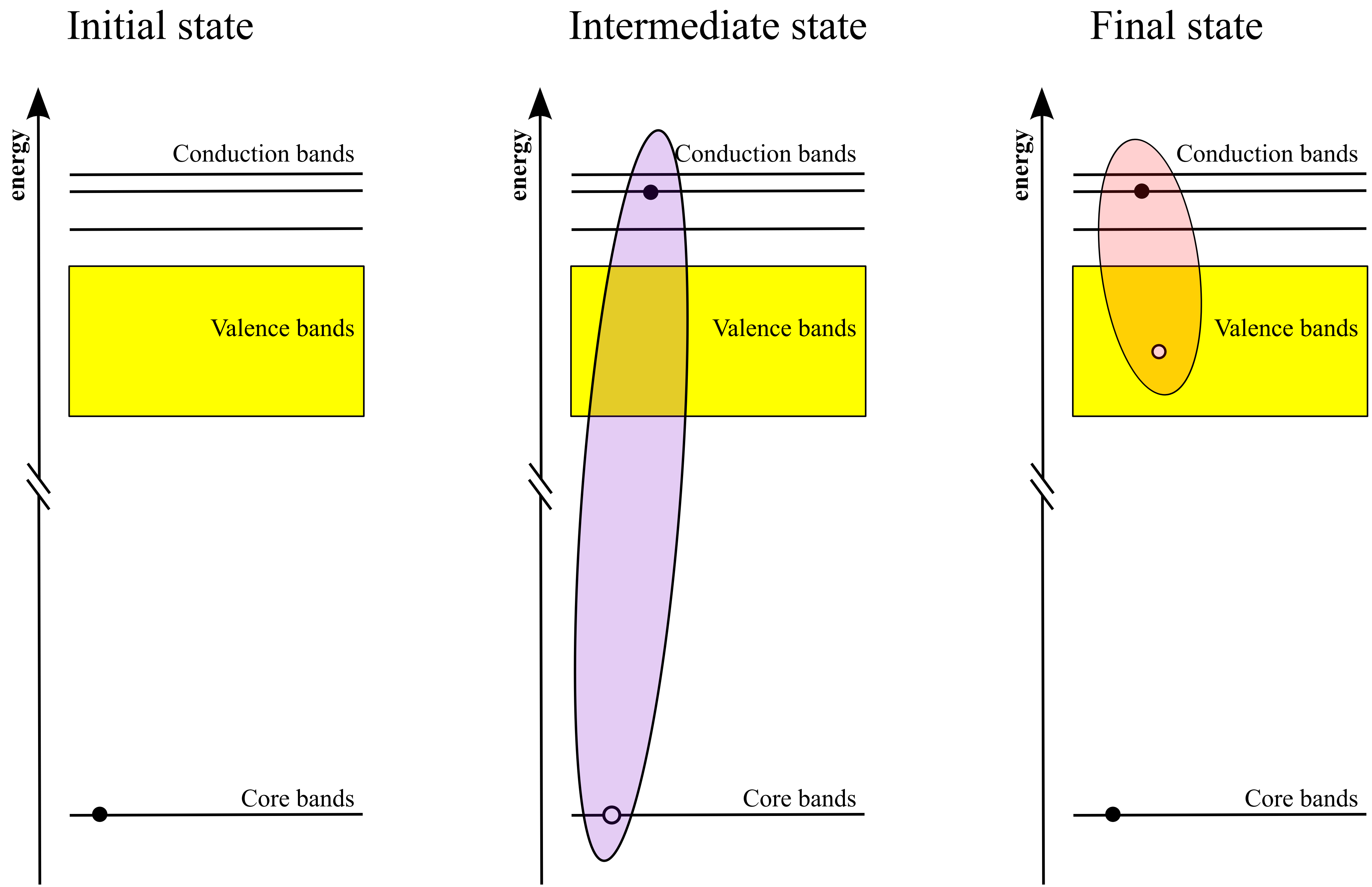
Resonant IXS

$$\frac{d^2\sigma}{d\Omega_2 d\omega_e} \propto \sum_f \left| \langle f | e^{i\mathbf{q}\cdot\mathbf{r}} | 0 \rangle - \frac{i\omega_{i/e}}{2mc^2} \sum_n \frac{\langle f | e^{-i\mathbf{k}_f\cdot\mathbf{r}} \nabla | n \rangle \ \langle n | e^{i\mathbf{k}_i\cdot\mathbf{r}} \nabla | 0 \rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

Resonant IXS

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2\mathrm{d}\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f|e^{-i\mathbf{k}_f\cdot\mathbf{r}}\nabla|n\rangle\ \langle n|e^{i\mathbf{k}_i\cdot\mathbf{r}}\nabla|0\rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$


Initial state
Intermediate state
Final state
energy
energy
energy
Conduction bands
Conduction bands
Conduction bands
Valence bands
Valence bands
Valence bands
photon-in
$\omega_i, \mathbf{k}_i$
Core bands
Core bands
Core bands
photon-out
$\mathbf{k}_{out}$ w_{out}



Initial state
Intermediate state
Final state
energy
Conduction bands
Valence bands
Core bands
energy
Conduction bands
Valence bands
Core bands
energy
Conduction bands
Valence bands
Core bands

Resonant Inelastic X-ray scattering

via excitonic pathways in BSE

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f | e^{-i\mathbf{k}_f \cdot \mathbf{r}} \nabla | n \rangle \, \langle n | e^{i\mathbf{k}_i \cdot \mathbf{r}} \nabla | 0 \rangle}{\omega_i - (E_n - E_0)} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

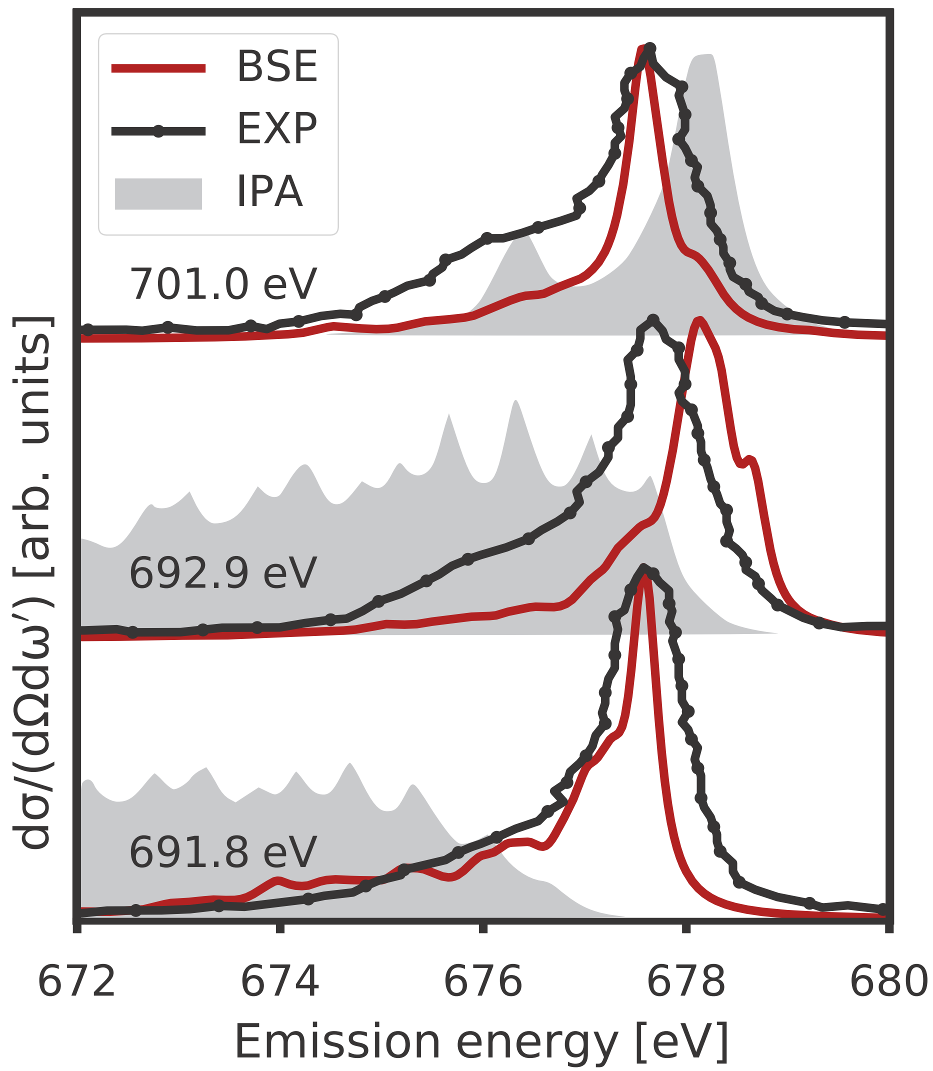
↓

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \quad \mathrm{Im} \sum_{\substack{\mu\mu'' \\ \lambda'_c \lambda_c \lambda}} \sum_{\substack{vv' \\ cc''}} \left[\frac{t^{(1)}_{\lambda'_c} \, A^{\mu c}_{\lambda'_c} \, \tilde{\rho}_{\mu v}}{\omega_i - E_{\lambda'_c} + i\eta} \right]^* \frac{A^{vc}_{\lambda} A^{*v'c''}_{\lambda}}{\omega - E_{\lambda} + i\eta} \left[\frac{\tilde{\rho}^*_{\mu'' v'} \, A^{\mu'' c''}_{\lambda_c} \, t^{(1)}_{\lambda_c}}{\omega_i - E_{\lambda_c} + i\eta} \right]$$

Vorwerk, Sottile, Draxl, Phys. Rev. Research **2**, 042003(R) (2020)

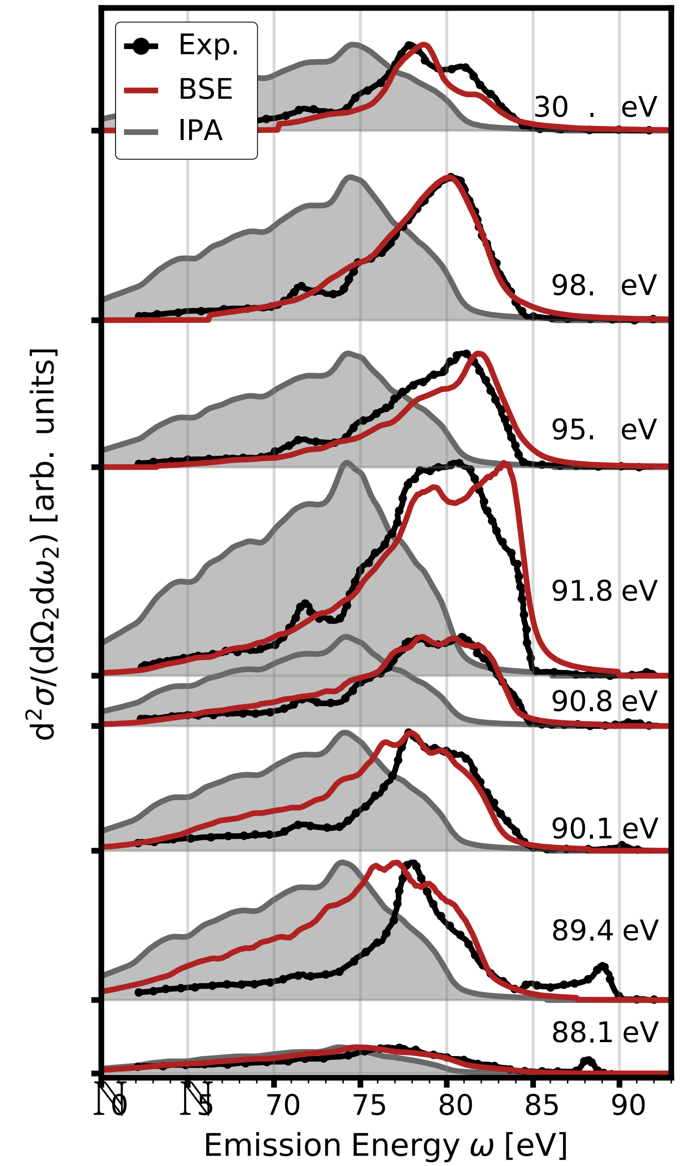
https://github.com/exciting/BRIXS

LiF



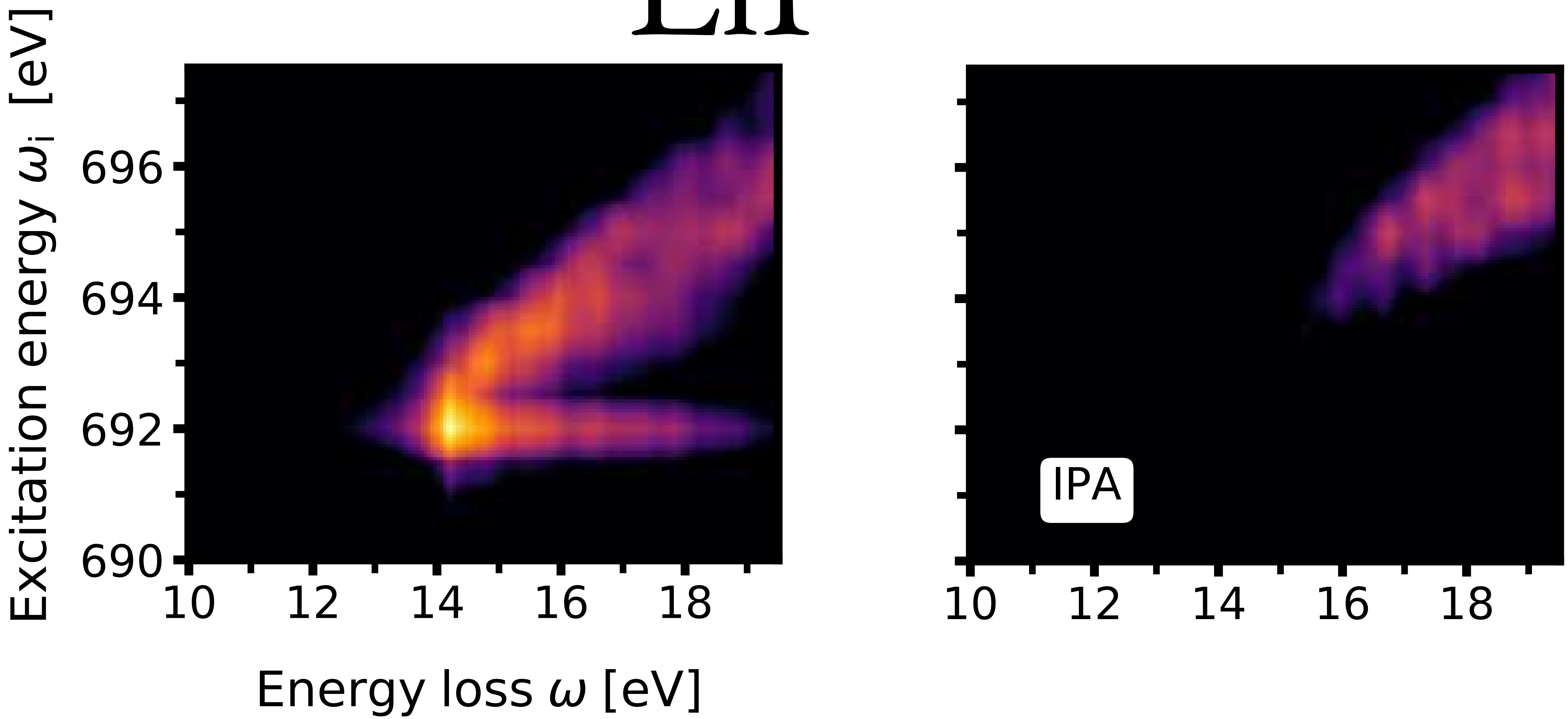
Vorwerk *et al.* Phys. Rev. Research **2**, 042003(R) (2020)

Diamond



Vorwerk *et al.* Phys. Chem. Chem. Phys. **24**, 17439 (2022).

LiF



Vorwerk *et al.* Phys. Rev. Research **2**, 042003(R) (2020)

Conclusions

- Absorption and RIXS accurate within BSE
- Ab initio and predictive, and permits analysis

Conclusions

- Absorption and RIXS accurate within BSE
- Ab initio and predictive, and permits analysis
- Rely on the description of the initial (ground) state
- Cumbersome calculations

Perspectives (with XFEL in mind)

- Tackle small (fragile) systems

  probe-before-damage

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Perspectives (with XFEL in mind)

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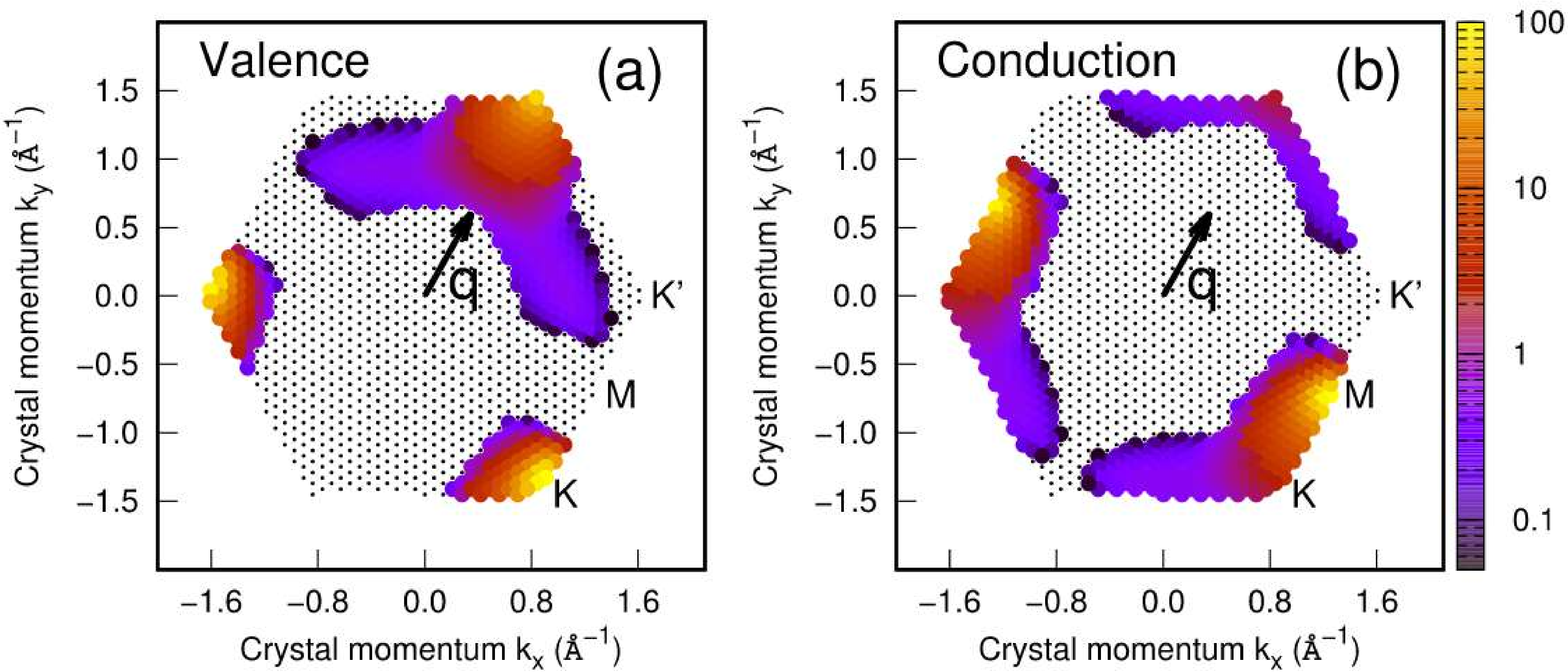
  - time-dependent RIXS (fs resolution)
  - stimulated RIXS (non-linear regime)

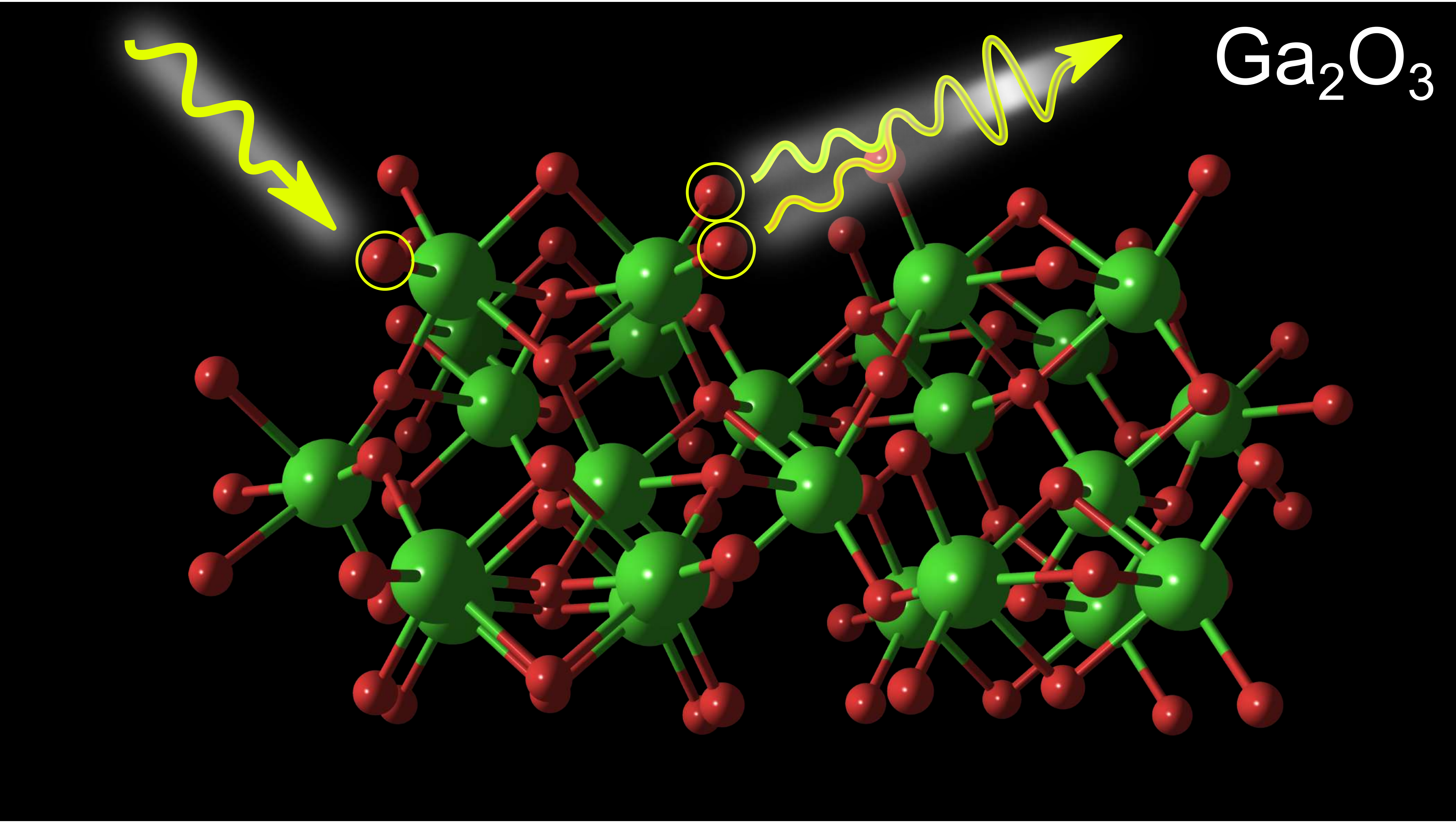
Thanks to the Theoretical Spectroscopy Group

and to You

Excitons in hexagonal BN

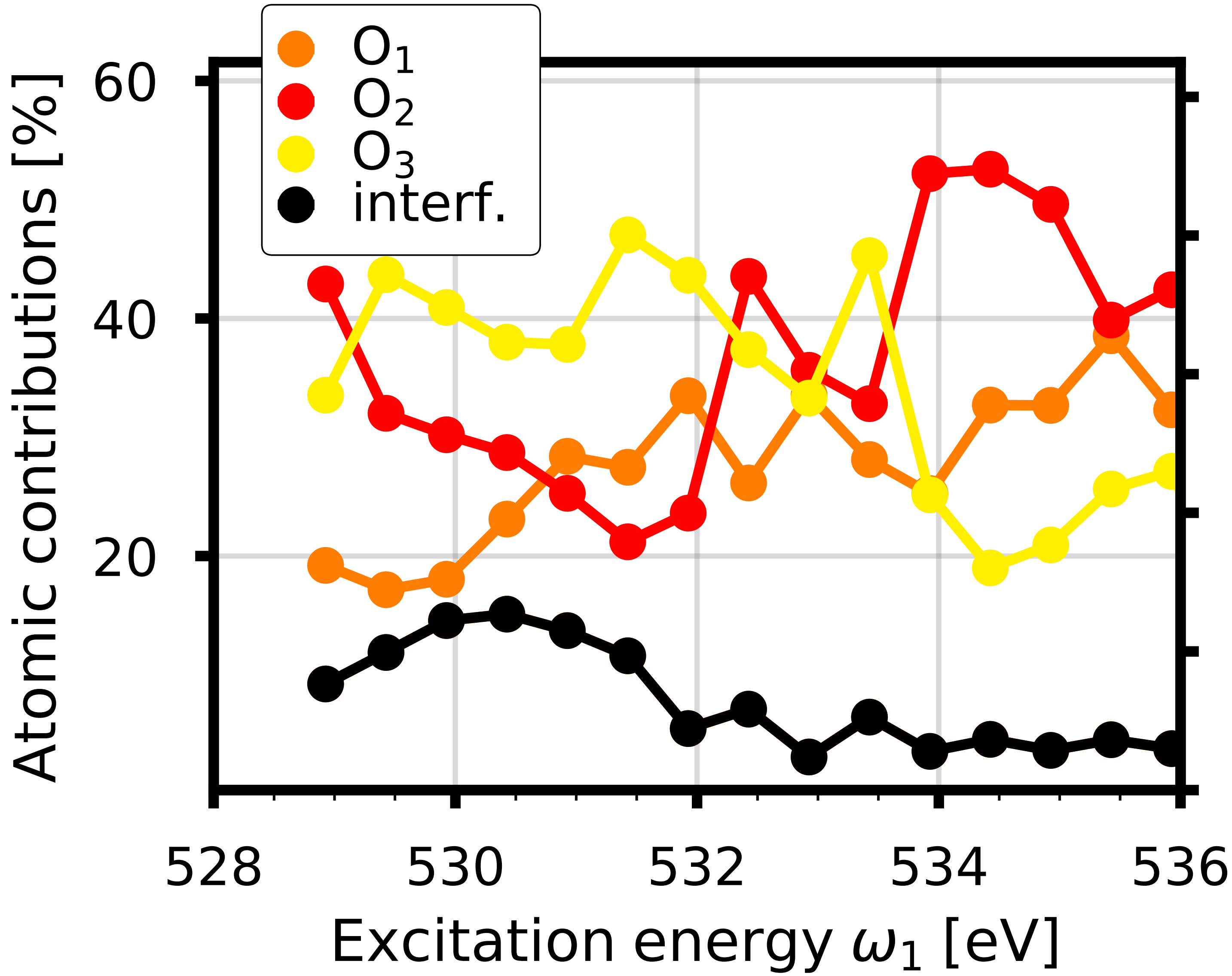


Sponza *et al.* Phys. Rev. B **97**, 075121 (2018)


Ga_2O_3

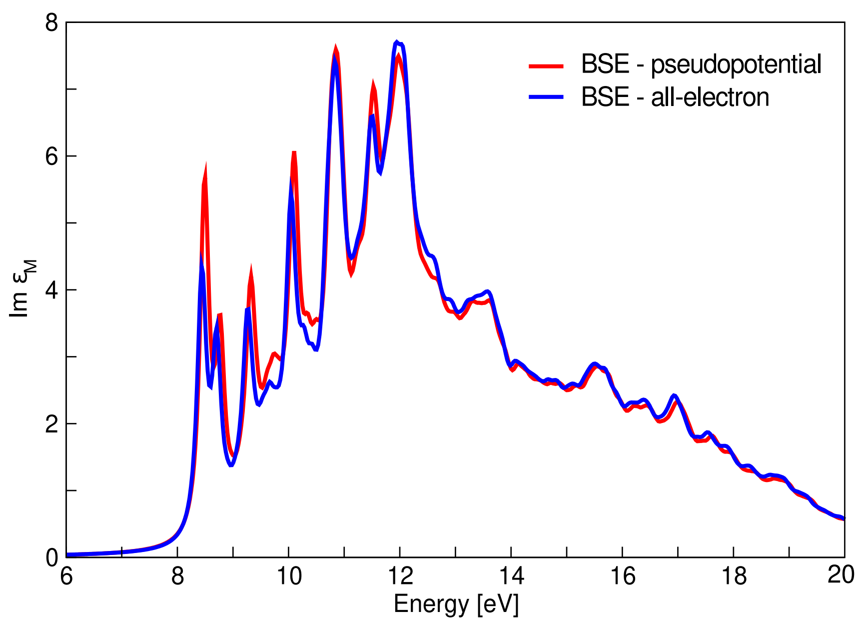
O-K Ga_2O_3

3 inequivalent oxigens

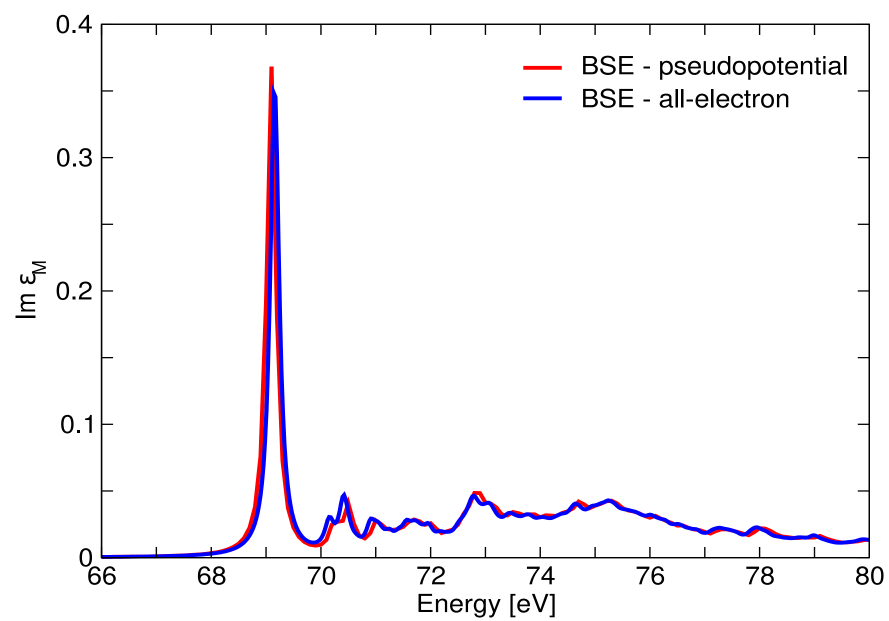


Vorwerk *et al.* Phys. Chem. Chem. Phys. **24**, 17439 (2022).

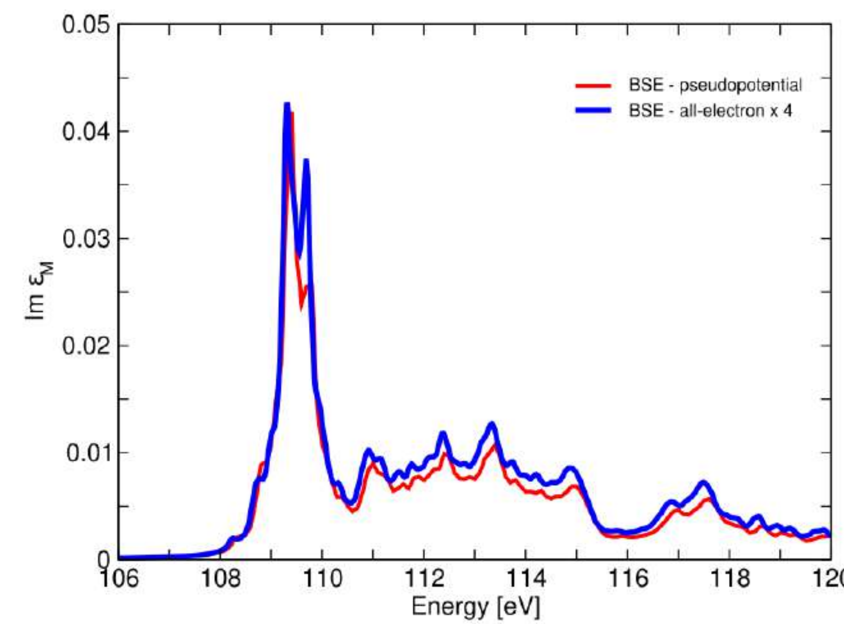
Optical and X-ray absorption of Al_2O_3
All-electron vs pseudo-potential



optical



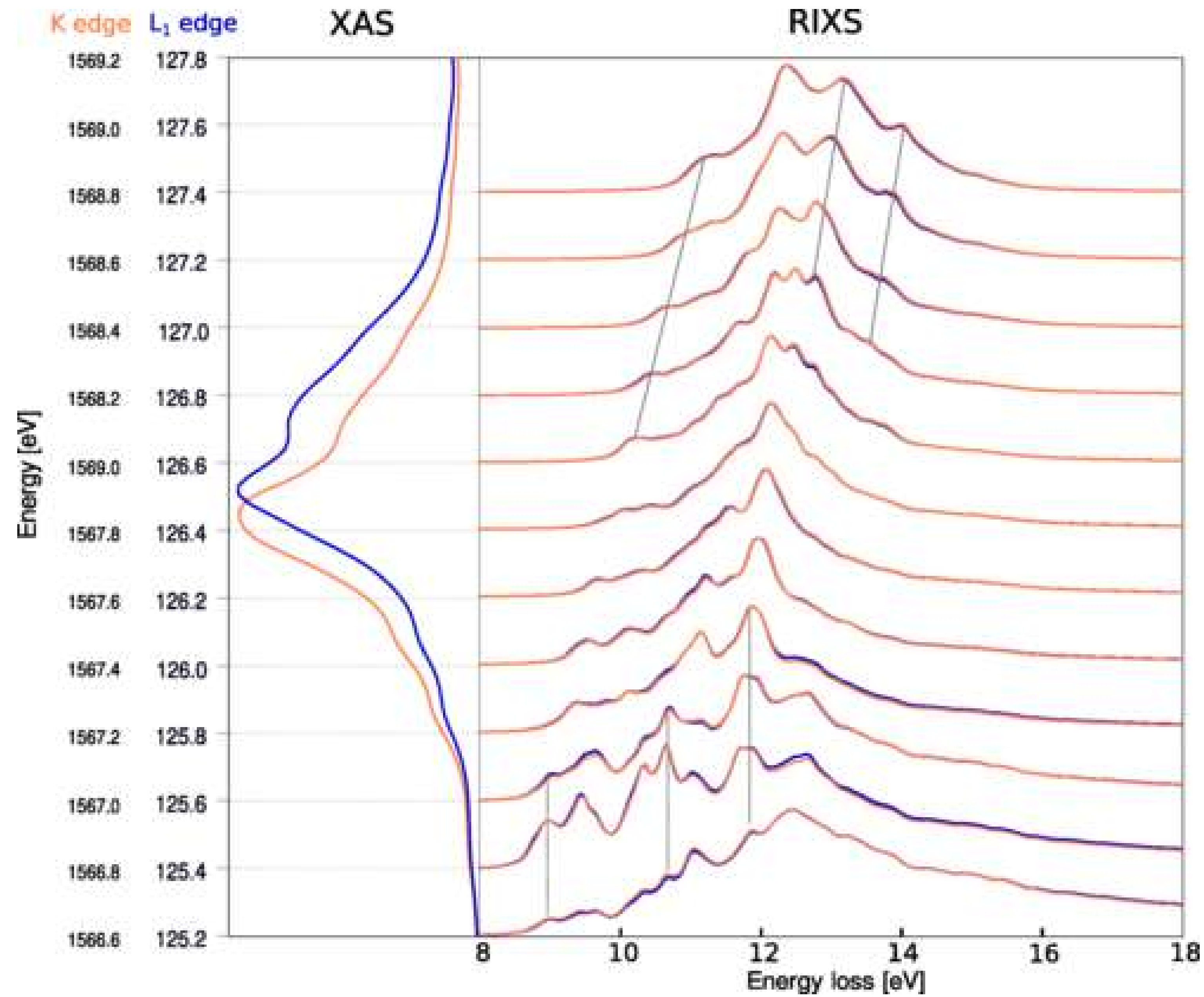
$L_{2,3}$



L_1

M.L. Urquiza, M. Gatti, F. Sottile, Phys. Rev. B **107**, 205148 (2023)

Al_2O_3



Urquiza *et al.*, Phys. Rev. B **109**, 115157 (2024)

Urquiza *et al.*, Phys. Rev. B **107**, 205148 (2023)