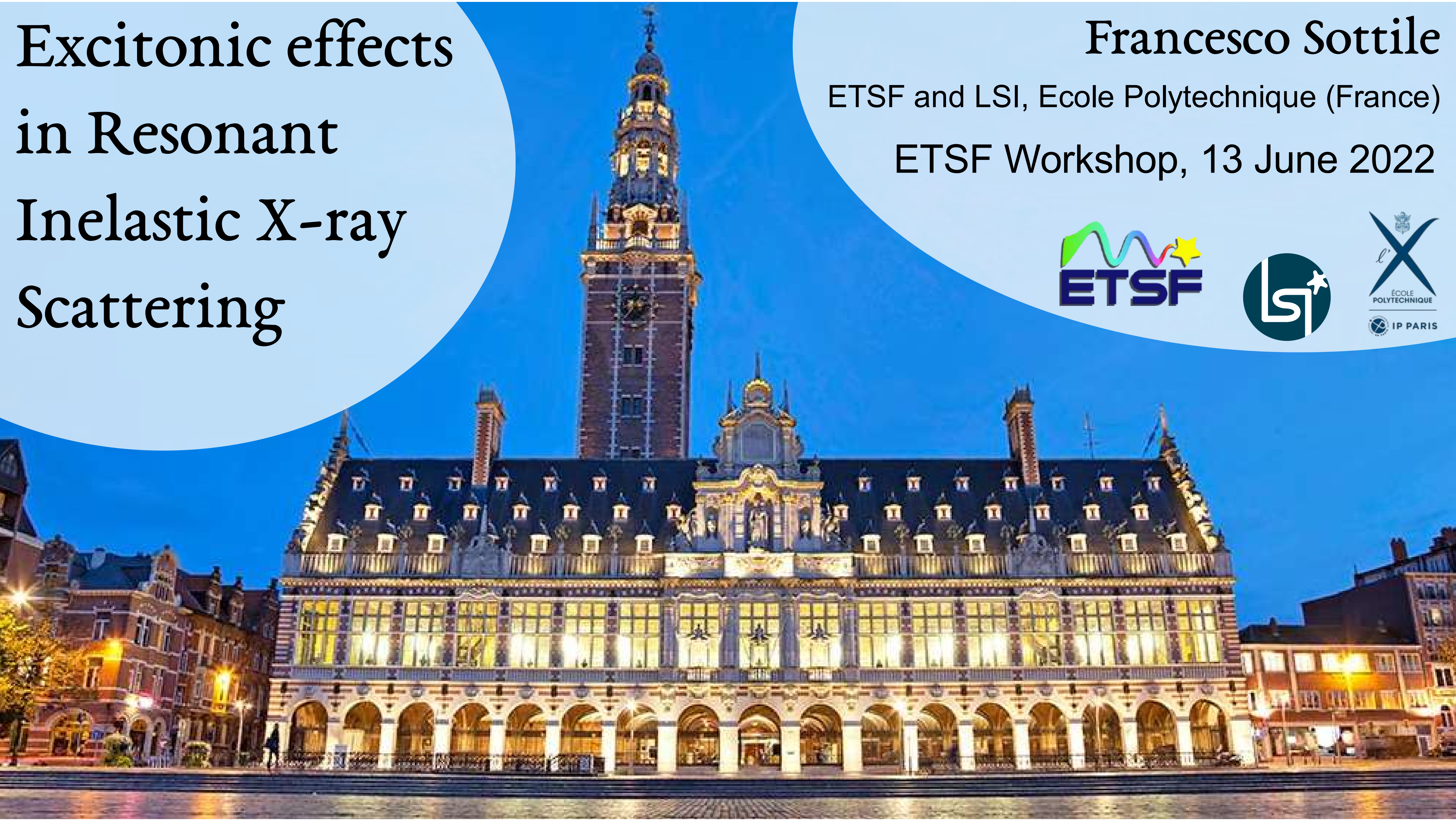
Excitonic effects in Resonant Inelastic X-ray Scattering

Francesco Sottile

ETSF and LSI, Ecole Polytechnique (France)

ETSF Workshop, 13 June 2022



Excitonic effects
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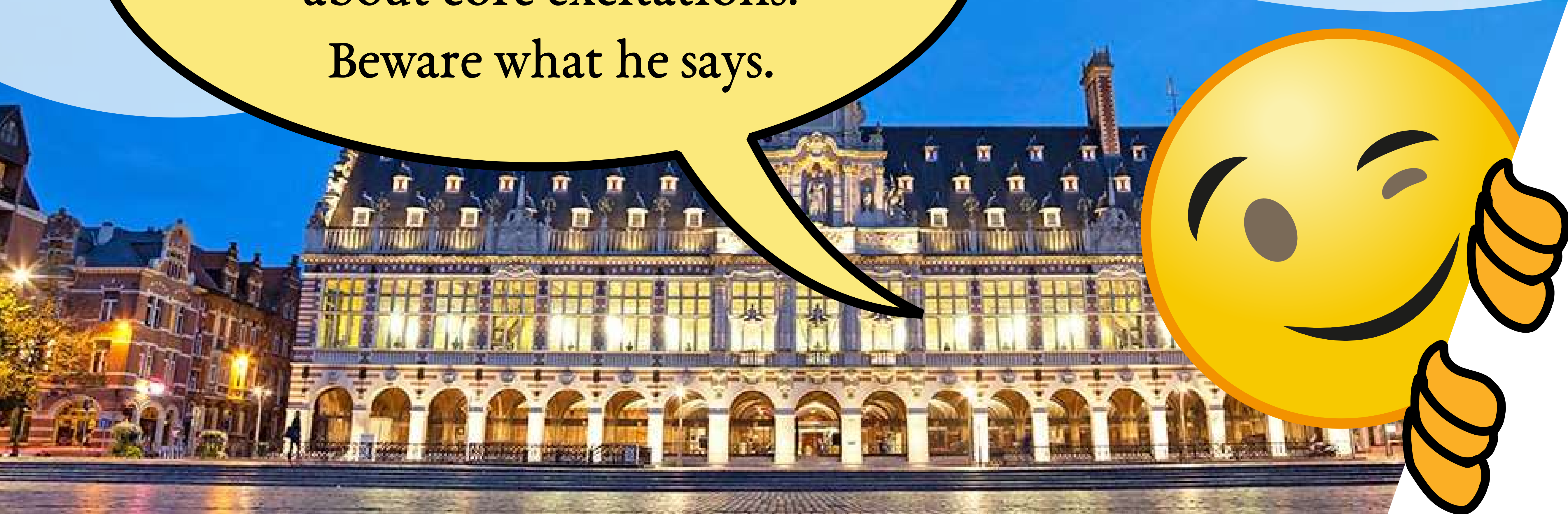


Christian Vorwerk's

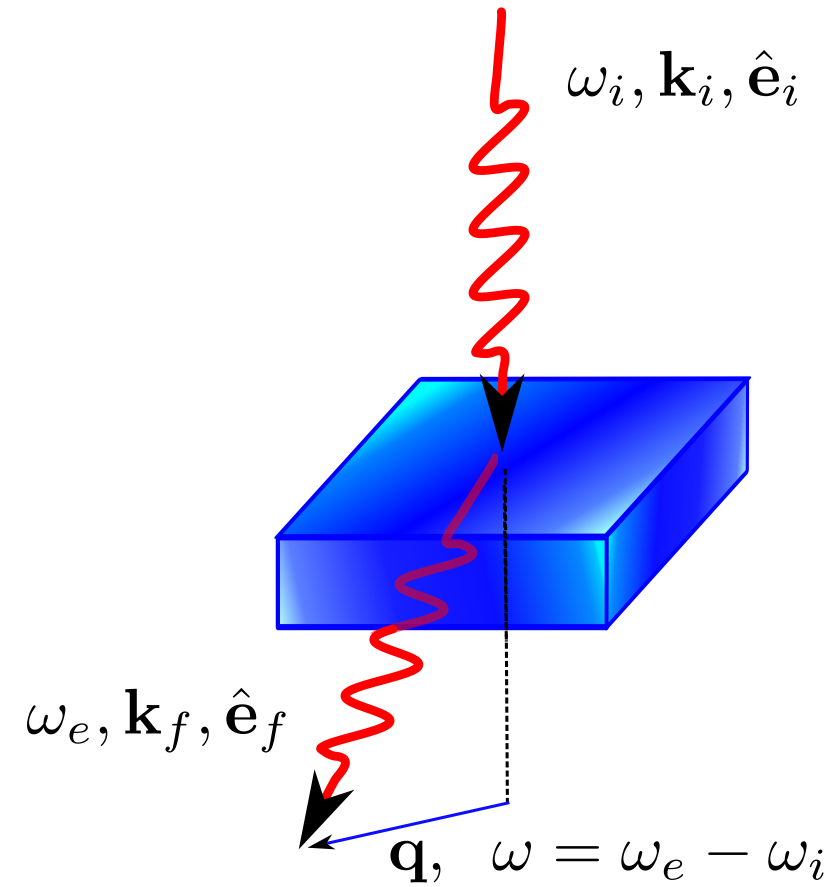
PhD Thesis (2020)

Laura Urquiza's Postdoc

Poster on Al_2O_3

- RIXS scheme
- Derivation in terms of excitation pathways
- Example :: LiF
- Atomic Coherence in RIXS

X-ray scattering

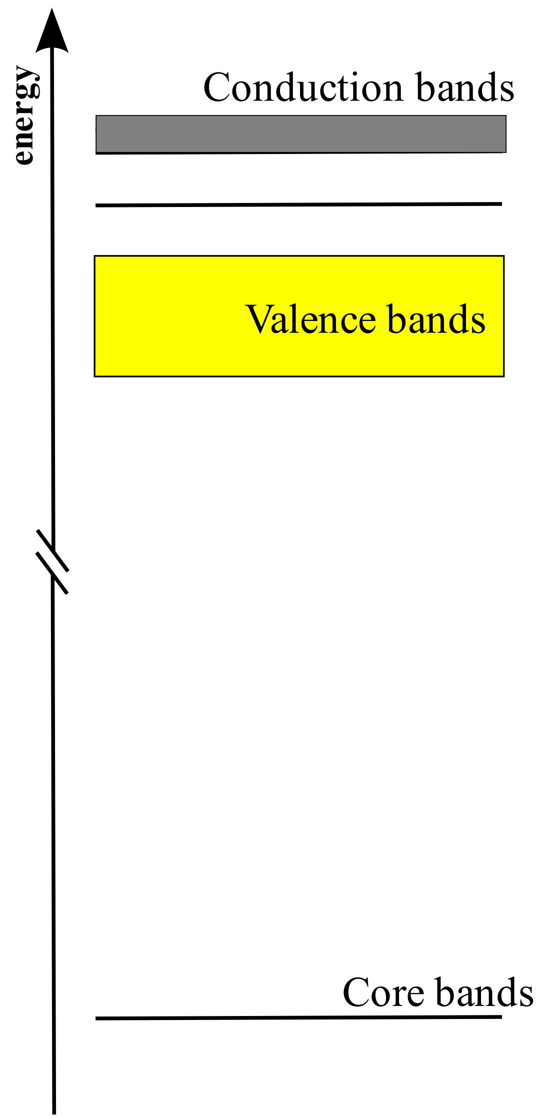


non-Resonant IXS

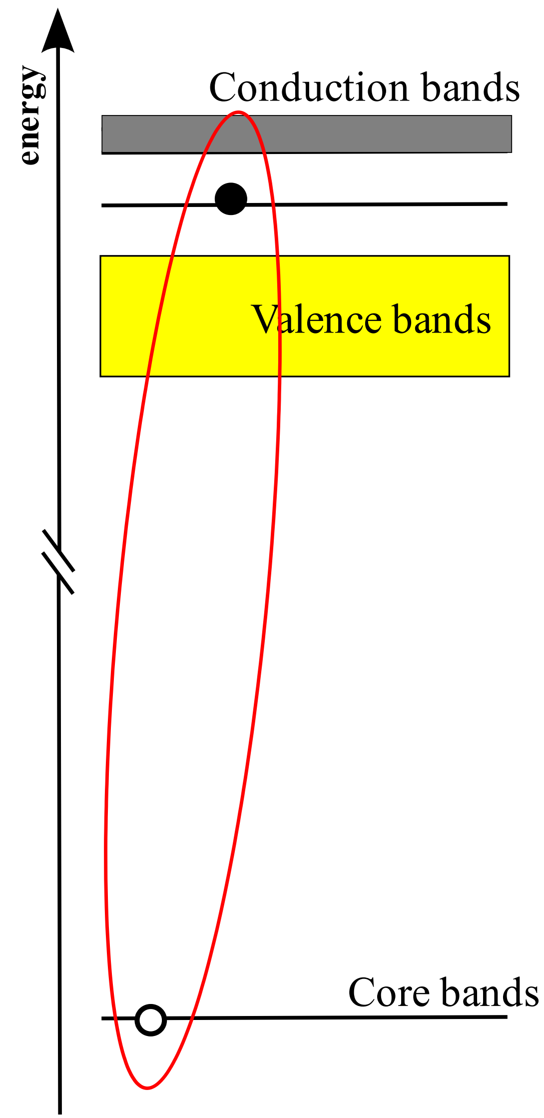
Resonant IXS

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

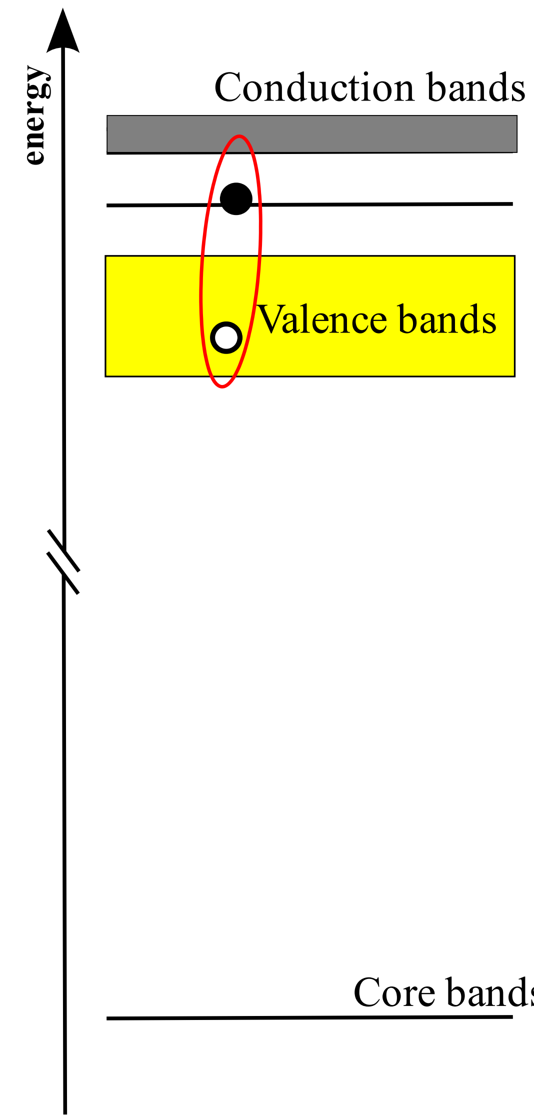
Ground state

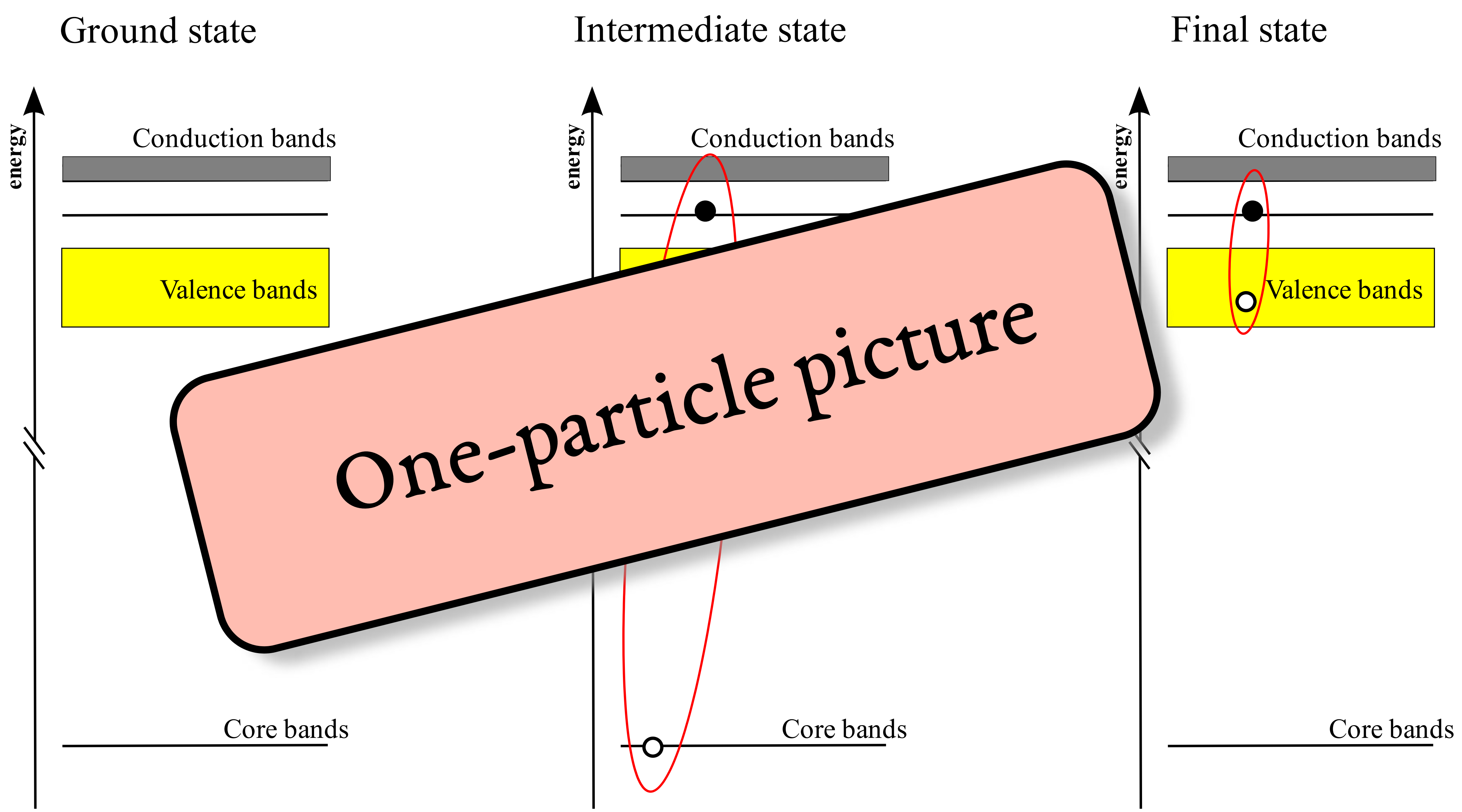


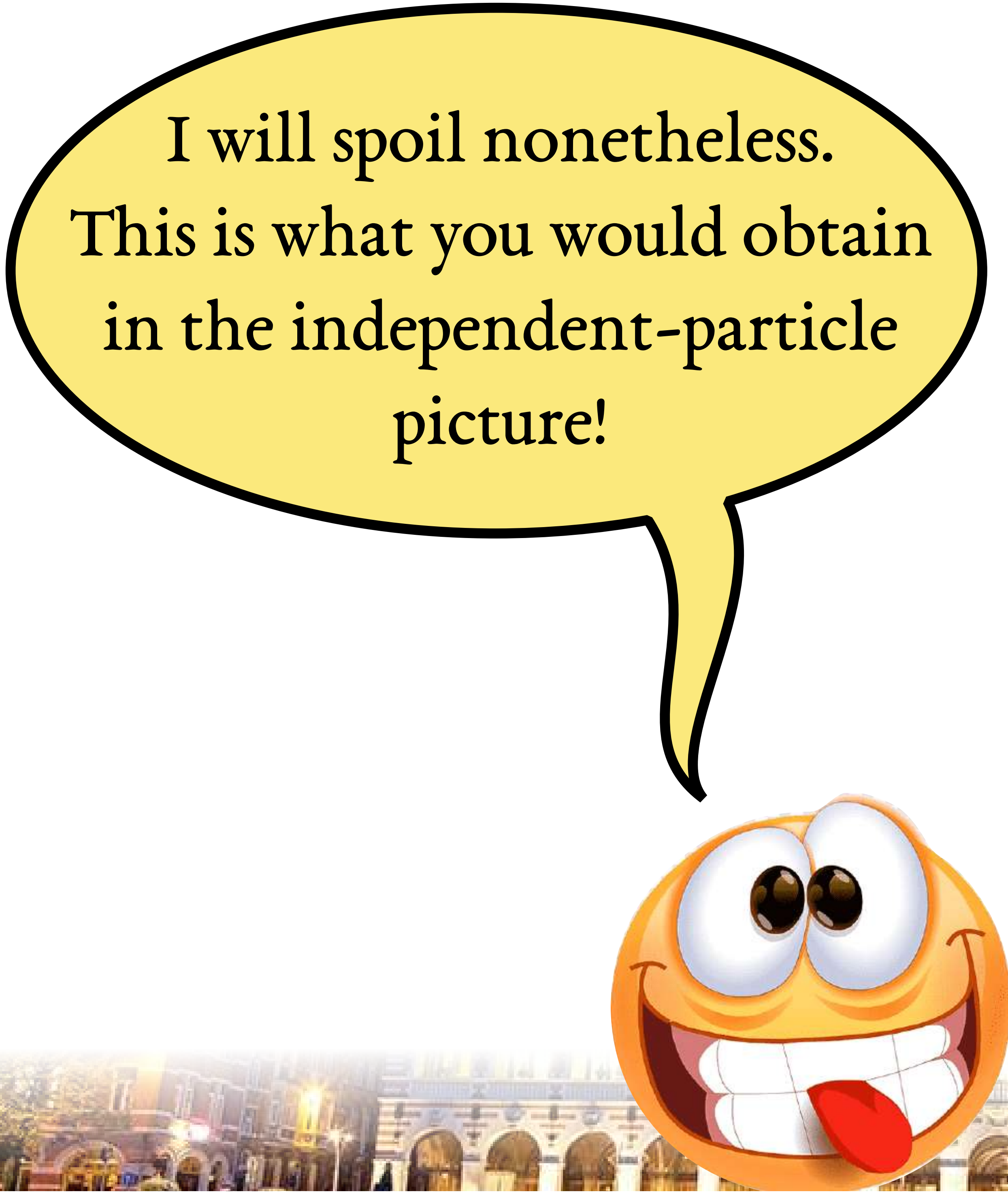
Intermediate state

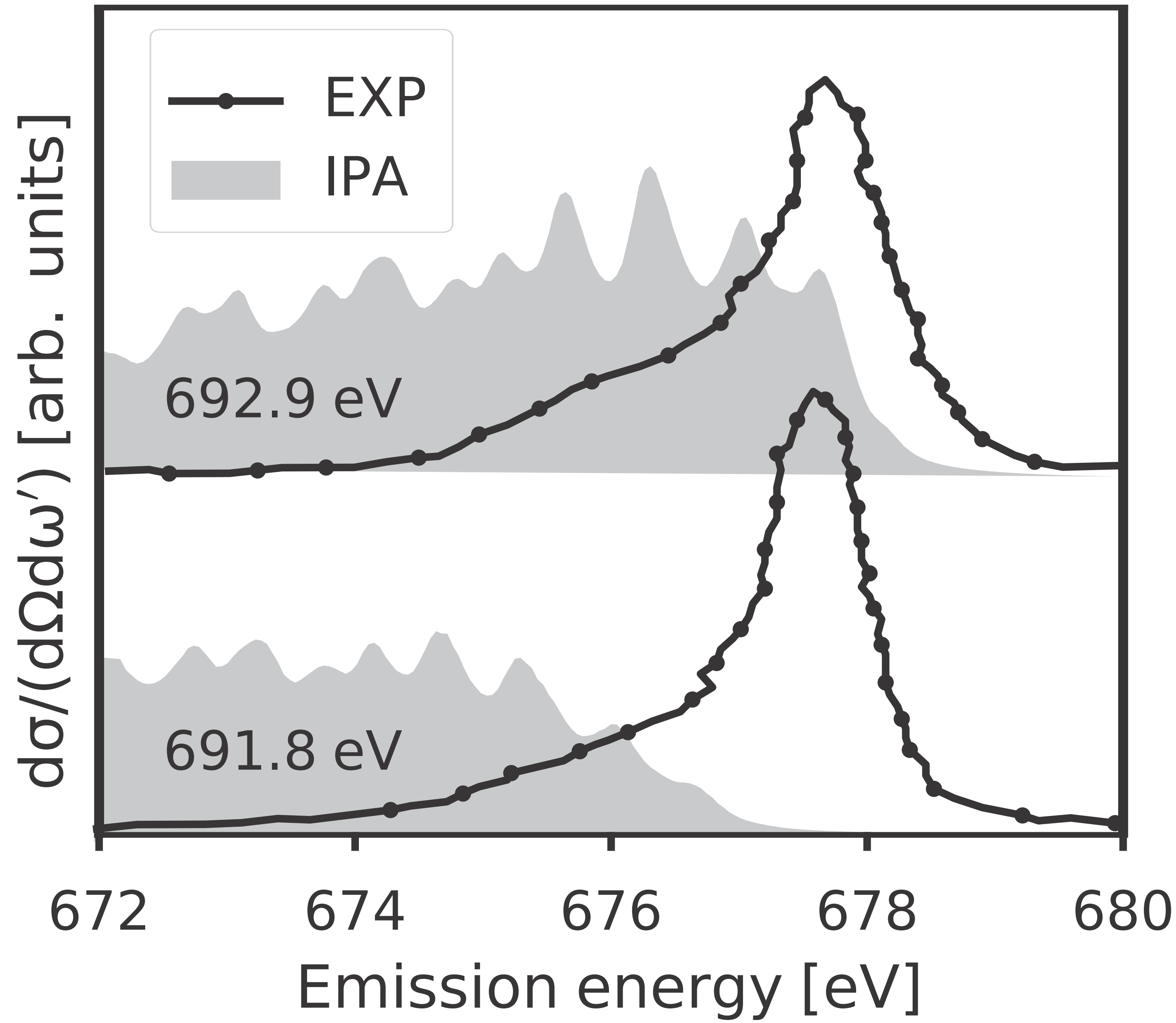


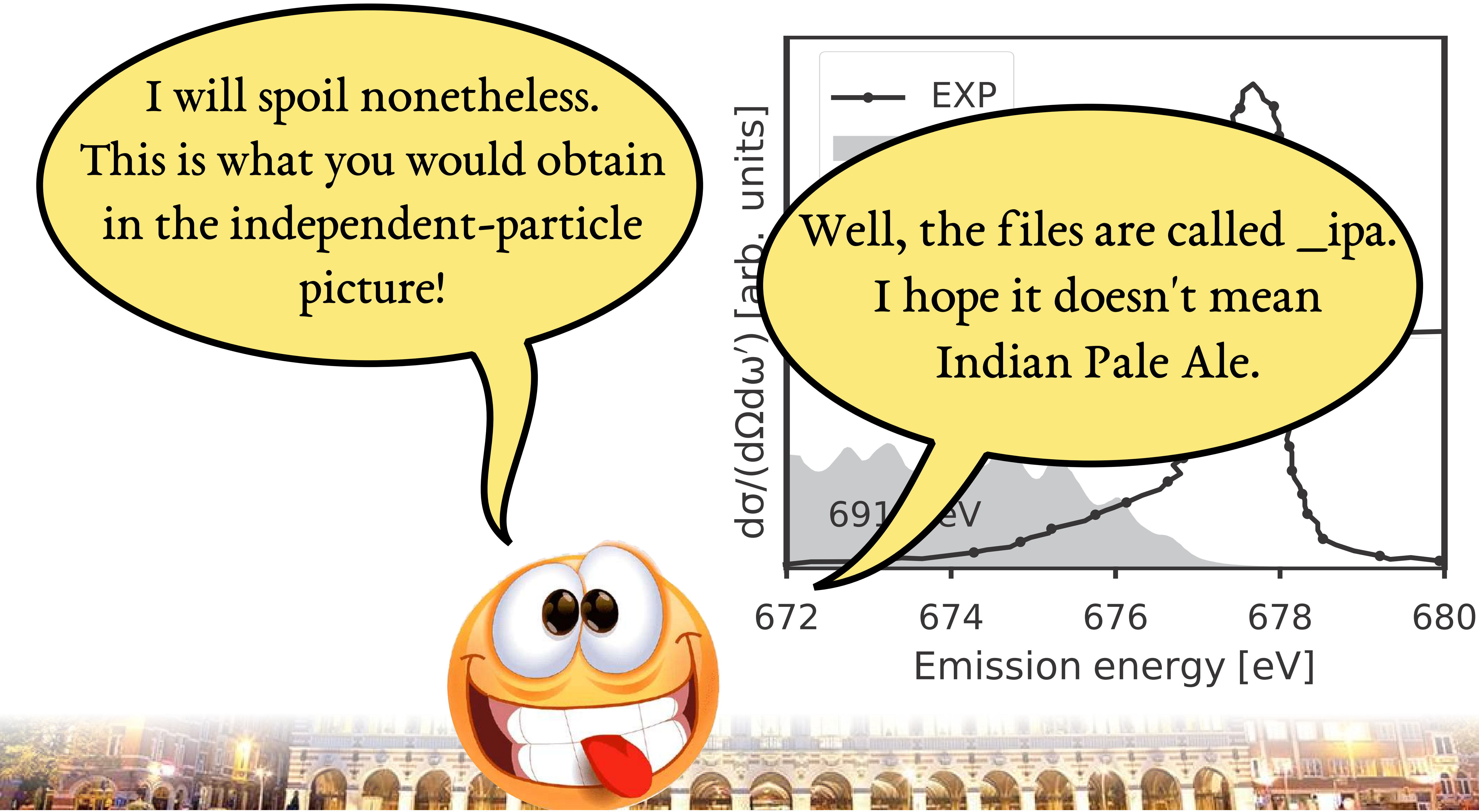
Final state

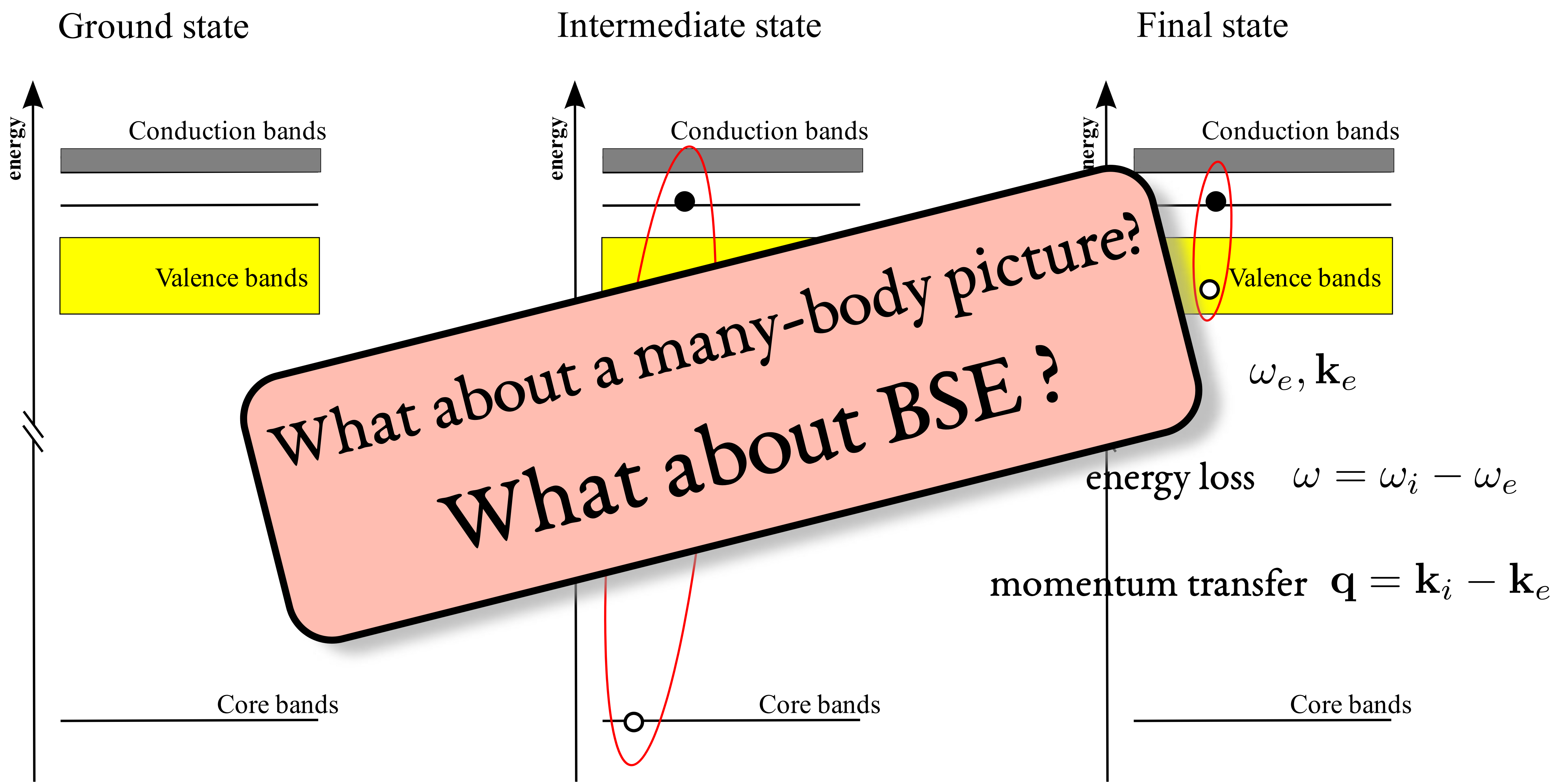



Ground state
Intermediate state
Final state
energy
Conduction bands
Valence bands
Core bands
One-particle picture


I will spoil nonetheless.
This is what you would obtain
in the independent-particle
picture!


EXP
IPA
692.9 eV
691.8 eV
dσ/(dΩdω′) [arb. units]
672
674
676
678
680
Emission energy [eV]


I will spoil nonetheless. This is what you would obtain in the independent-particle picture!
Well, the files are called _ipa. I hope it doesn't mean Indian Pale Ale.
EXP
dσ/(dΩdω') [arb. units]
672
674
676
678
680
Emission energy [eV]



What about a many-body picture?

What about BSE ?

energy loss $\omega = \omega_i - \omega_e$

momentum transfer $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_e$

Resonant IXS via BSE ?

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2\mathrm{d}\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f|\hat{\mathbf{d}}|n\rangle \; \langle n|\hat{\mathbf{d}}|0\rangle}{\omega_i - (E_n - E_0) + i\eta} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

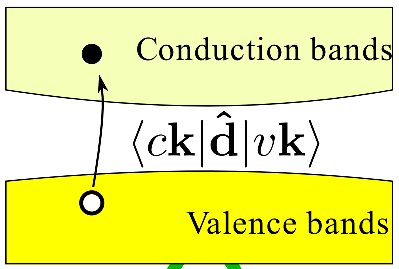
- Shirley, Phys. Rev. Lett. **80**, 794 (1998)
- Vinson *et al.*, Phys. Rev. B **94**, 035163 (2016)
- Geondzhian and Gilmore, Phys. Rev. B **98**, 214305 (2018)

Resonant IXS via BSE ?

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f|\hat{\mathbf{d}}|n\rangle \; \langle n|\hat{\mathbf{d}}|0\rangle}{\omega_i - (E_n - E_0) + i\eta} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

Absorption
$\longrightarrow$
via BSE

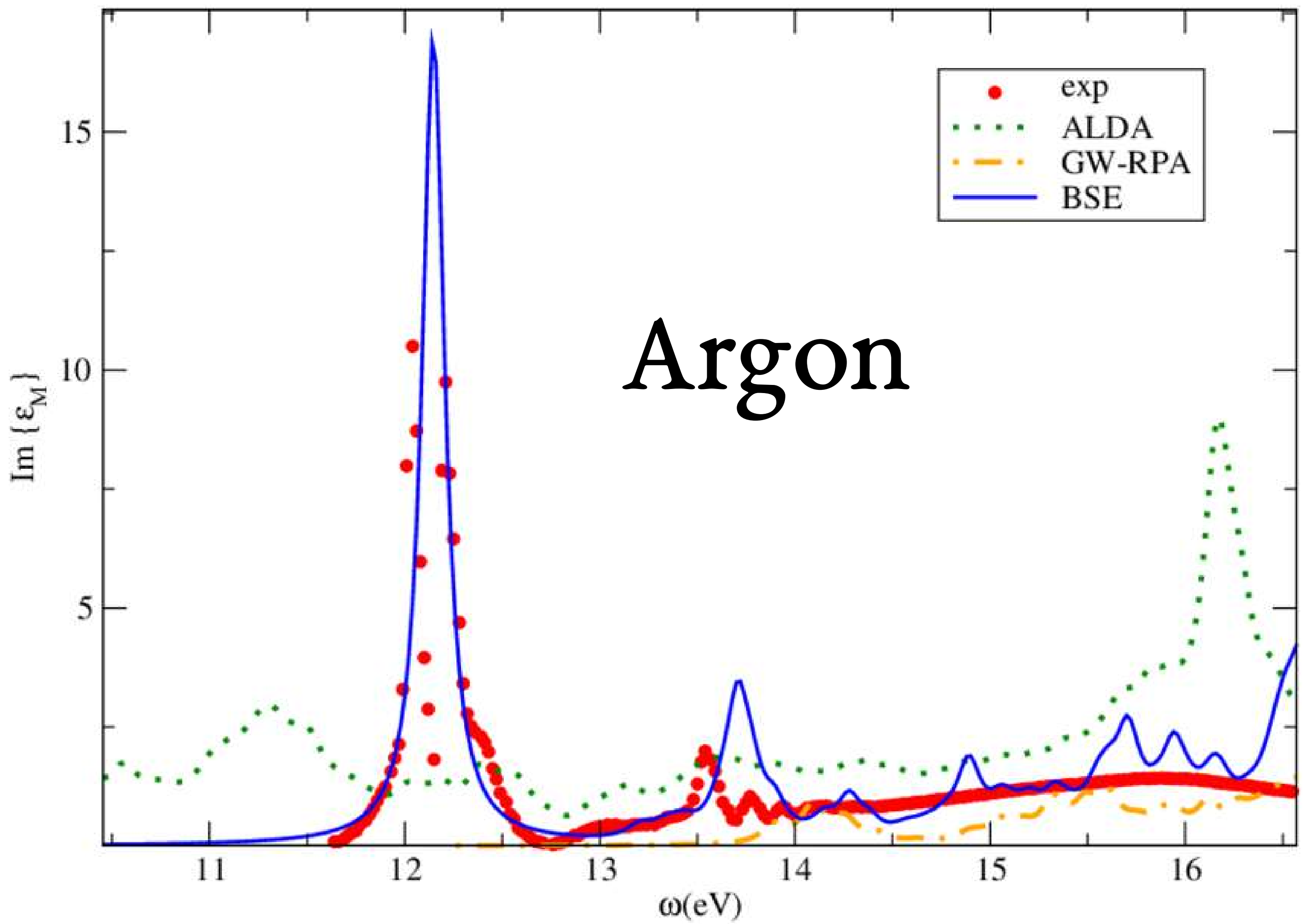
$$\mathrm{Abs}(\omega) \propto \sum_f \frac{\left|\langle f|\hat{\mathbf{d}}|0\rangle\right|^2}{\omega - (E_f - E_0) + i\eta} = \sum_\lambda \frac{\left|\sum_{vc\mathbf{k}} A_\lambda^{vc\mathbf{k}} \tilde{\rho}_{vc\mathbf{k}}\right|^2}{\omega - E_\lambda + i\eta}$$



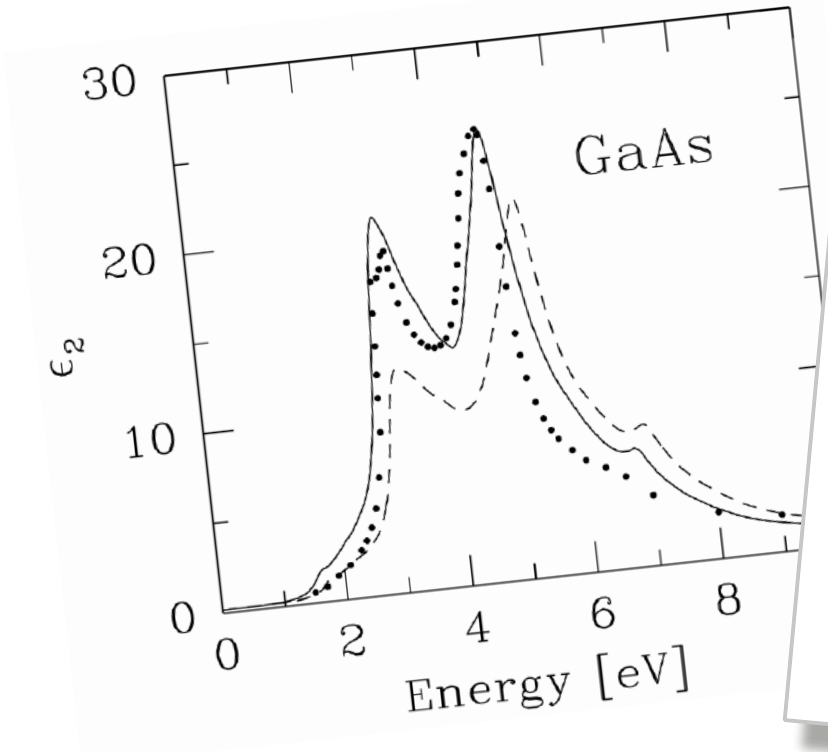
$$\sum_{\lambda} \frac{\left|\sum_{vc\mathbf{k}} A_{\lambda}^{vc\mathbf{k}} \tilde{\rho}_{vc\mathbf{k}}\right|^2}{\omega - E_{\lambda} + i\eta}$$

eigenvectors(values) of the exc Hamiltonian

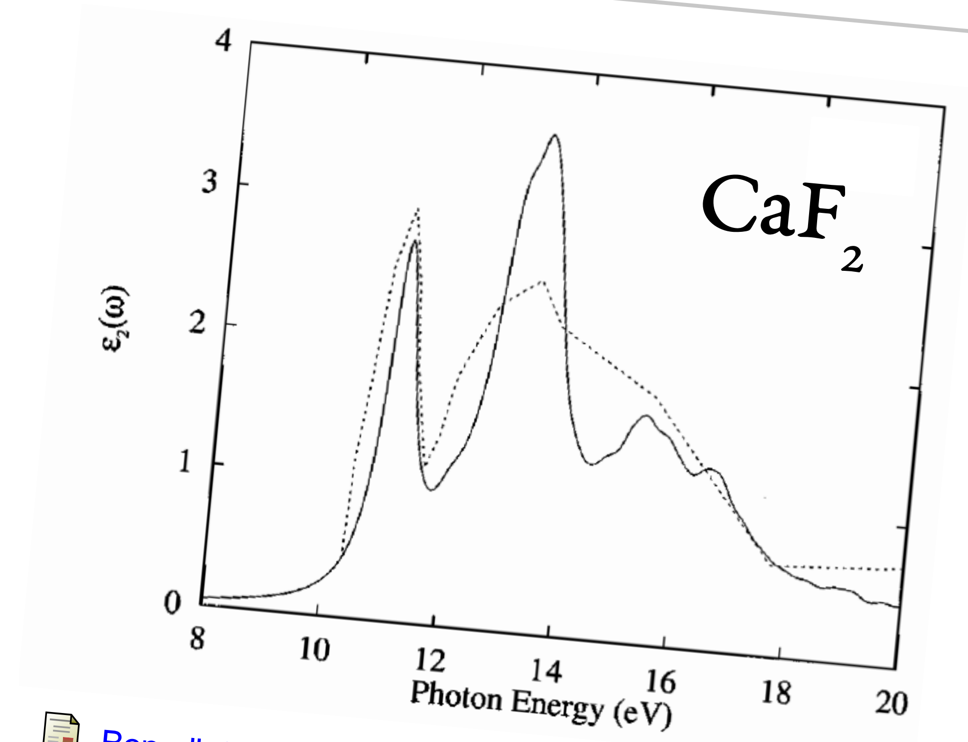
dipole matrix-elements
between one-particle states



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

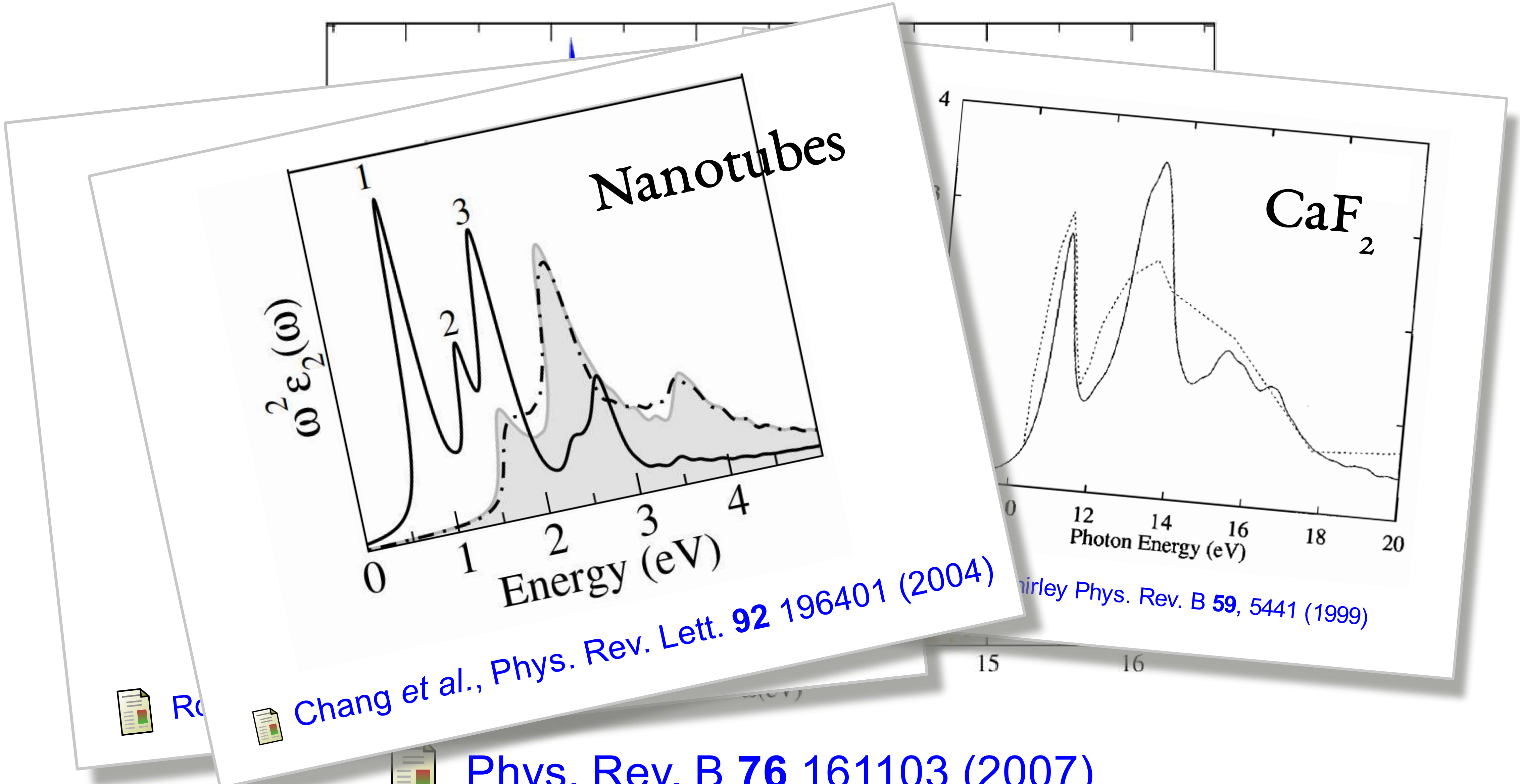


Rohlfing and Louie Phys. Rev. Lett. **81**, 2312 (1998)

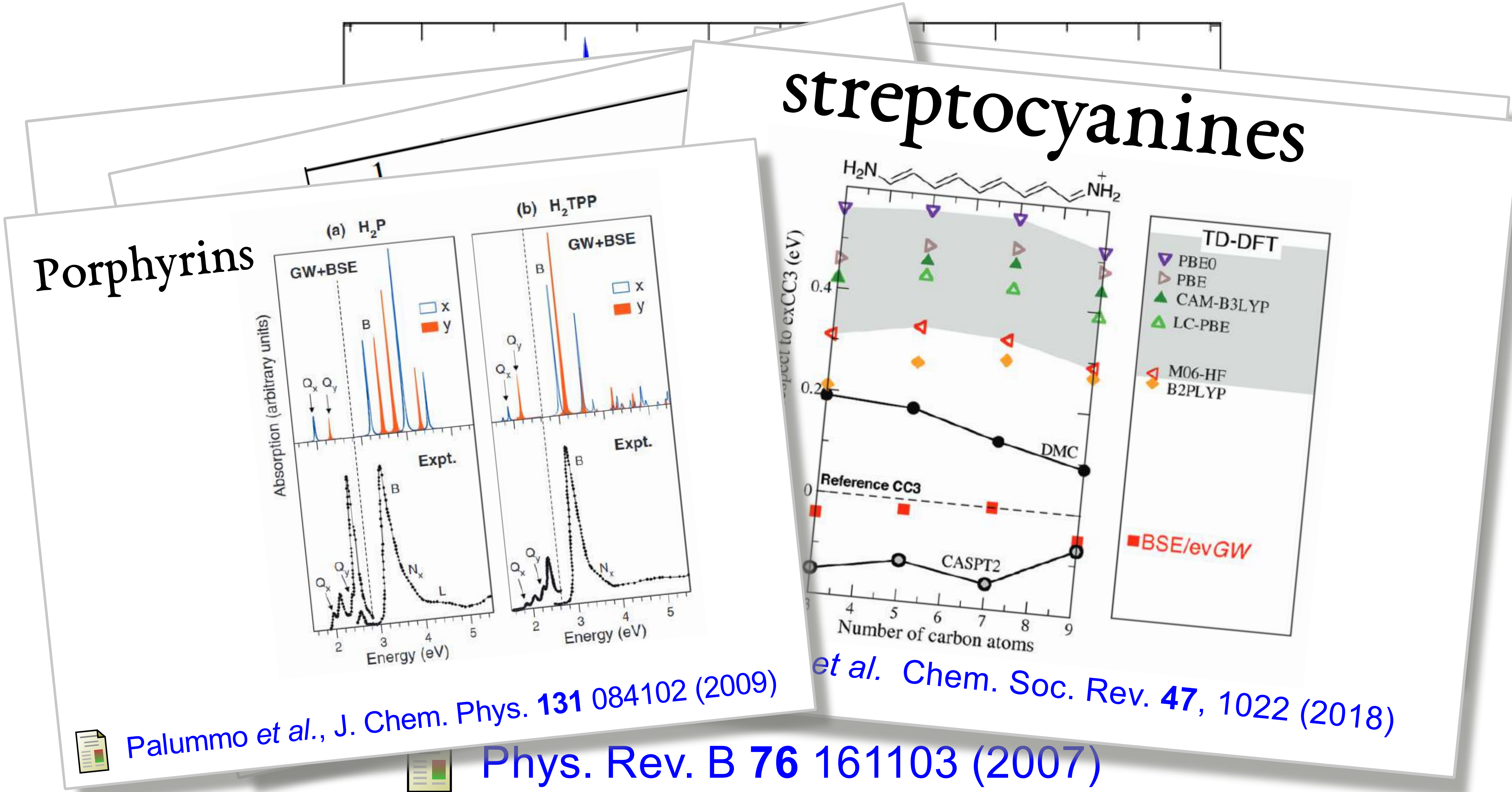


Benedict and Shirley Phys. Rev. B **59**, 5441 (1999)

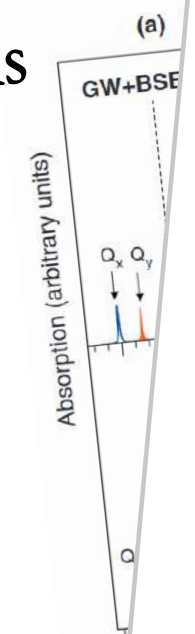
Phys. Rev. B **76** 161103 (2007)



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

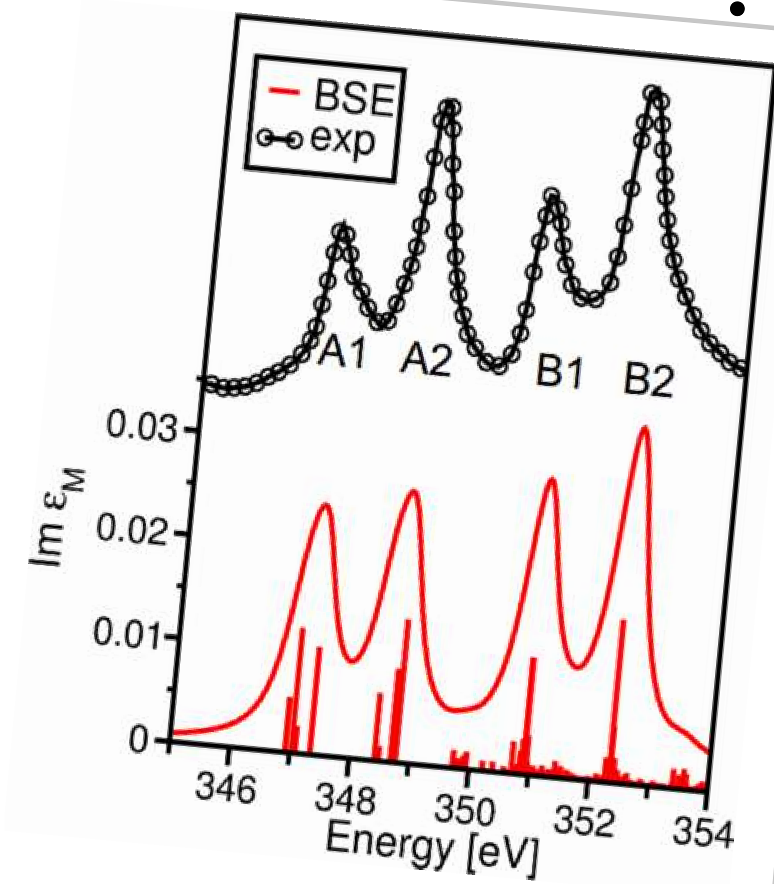

Porphyrins
(a) H2P
(b) H2TPP
GW+BSE
Expt.
Absorption (arbitrary units)
Energy (eV)
Palummo et al., J. Chem. Phys. 131 084102 (2009)
streptocyanines
TD-DFT
PBE0
PBE
CAM-B3LYP
LC-PBE
M06-HF
B2PLYP
DMC
Reference CC3
CASPT2
BSE/evGW
Number of carbon atoms
et al. Chem. Soc. Rev. 47, 1022 (2018)
Phys. Rev. B 76 161103 (2007)

Porphyrins



Palummo *et al.*, J. Chem...

CaO
Ca L-edge

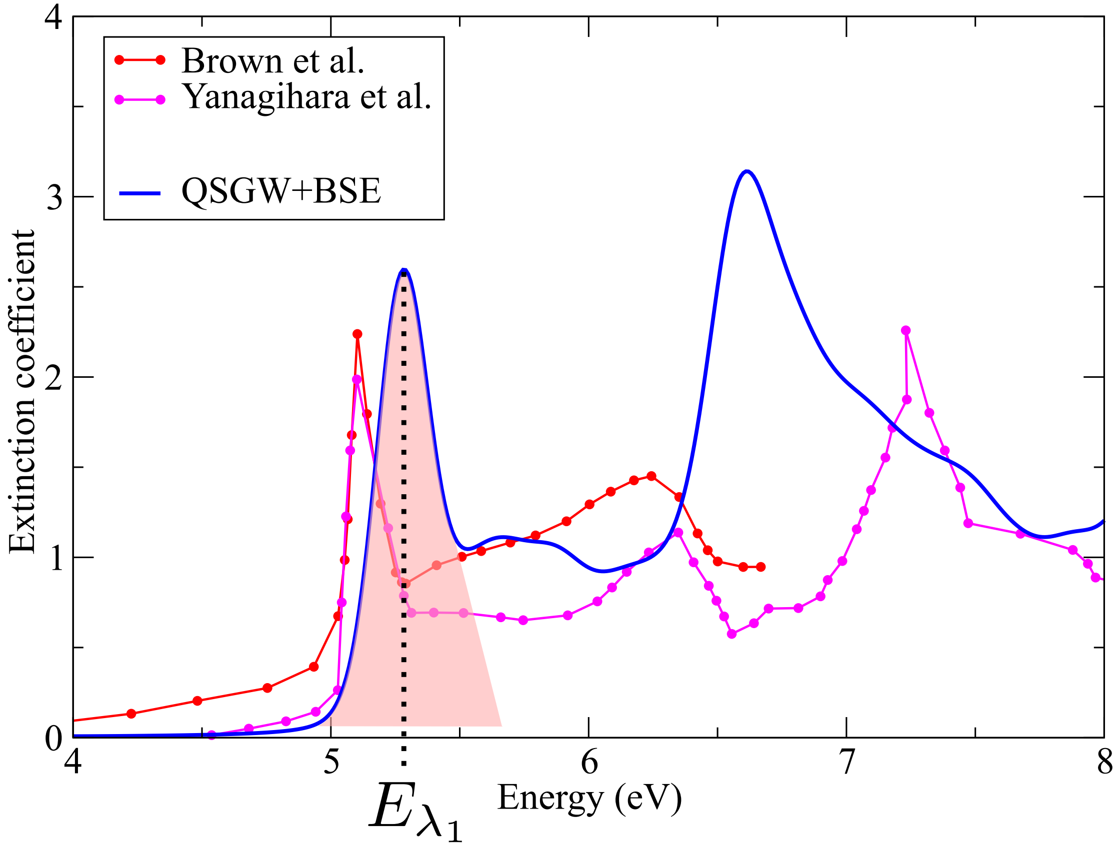


Vorwerk *et al.*, Phys. Rev. B **95**, 155121 (2017)

...1022 (2018)

Phys. Rev. B **76** 161103 (200...)

AgCl absorption

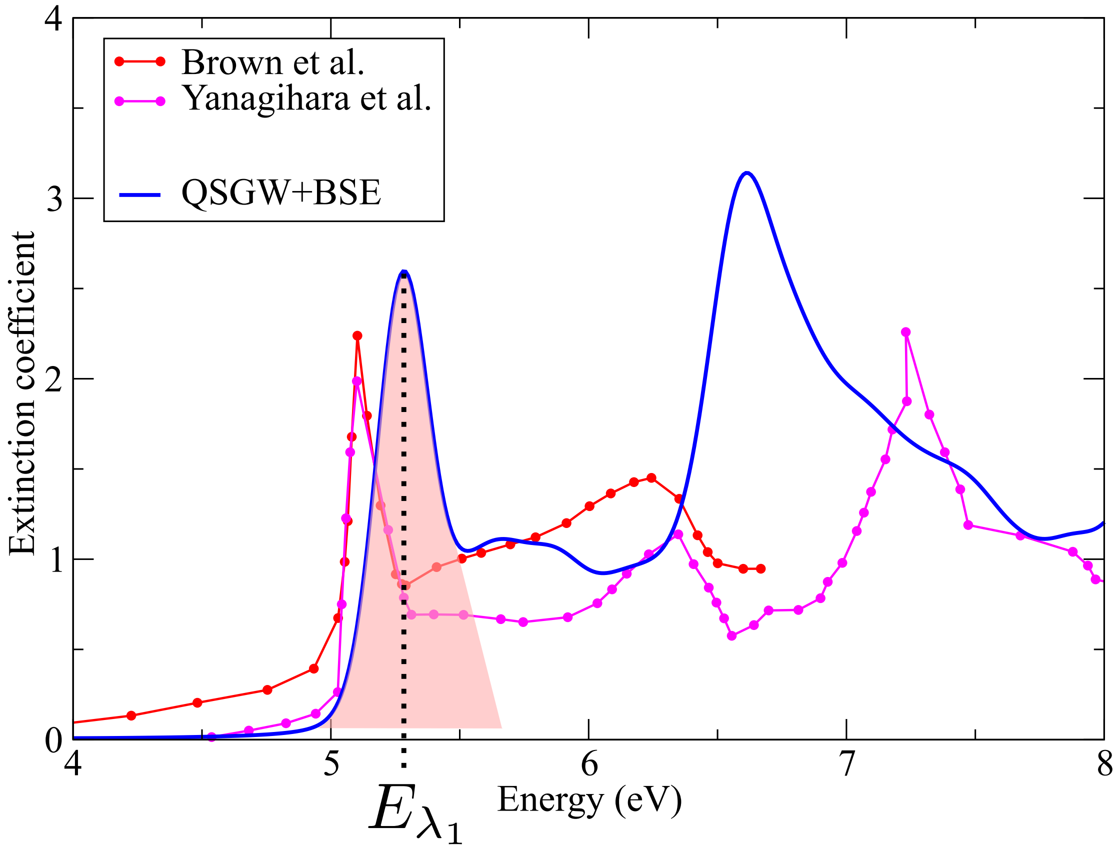


$$\chi_M = \sum_\lambda \frac{\left|\sum_{vc\mathbf{k}} A_\lambda^{vc\mathbf{k}} \langle c\mathbf{k}|\hat{\mathbf{d}}|v\mathbf{k}\rangle\right|^2}{\omega - E_\lambda + i\eta}$$

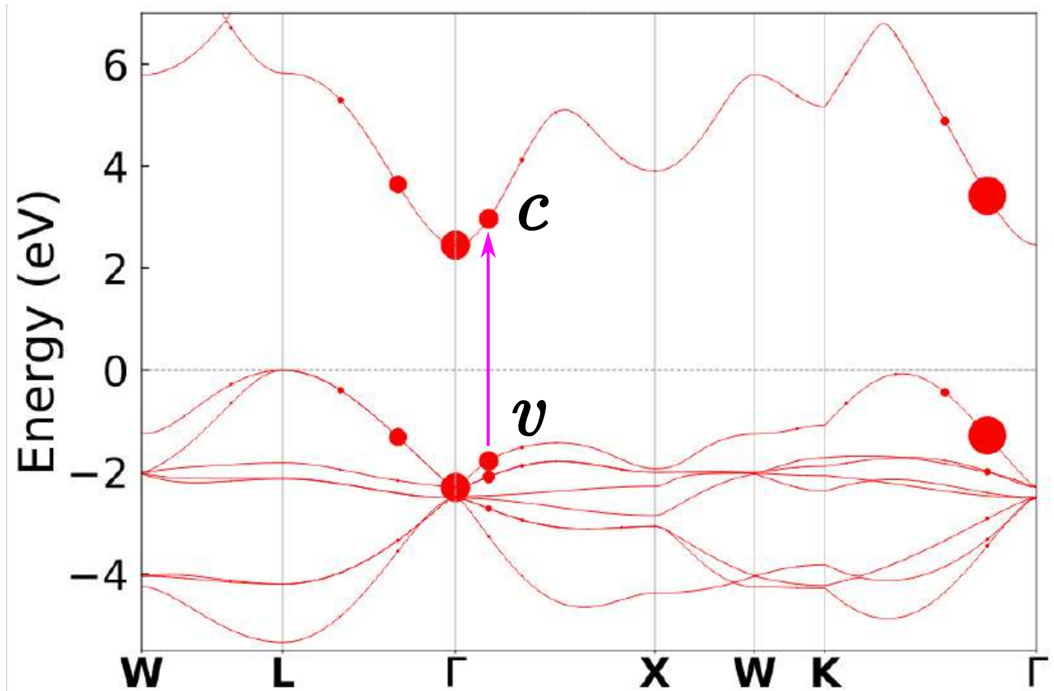
$$\kappa = \mathrm{Im}\sqrt{\frac{1}{1+v_0\chi_M}}$$

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

AgCl absorption



$$\chi_M = \sum_{\lambda} \frac{\left| \sum_{vc\mathbf{k}} A_{\lambda_1}^{vc\mathbf{k}} \langle c\mathbf{k} | \hat{\mathbf{d}} | v\mathbf{k} \rangle \right|^2}{\omega - E_\lambda + i\eta}$$



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

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f|\hat{\mathbf{d}}|n\rangle \ \langle n|\hat{\mathbf{d}}|0\rangle}{\omega_i - (E_n - E_0) + i\eta} \right|^{\mathbf{2}} \times \boldsymbol{\delta\left(\omega - (E_f - E_0)\right)}$$

$\mathbb{1}$ $\mathbb{1}$ $\mathbb{1}$ $\mathbb{1}$

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \mathrm{Im} \sum_f \sum_n \frac{\langle 0|\hat{\mathbf{d}}|n\rangle \ \langle 0|\hat{\mathbf{d}}|f\rangle}{\omega_i - (E_n - E_0) + i\eta} \sum_n \frac{\langle f|\hat{\mathbf{d}}|n\rangle \ \langle n|\hat{\mathbf{d}}|0\rangle}{\omega_i - (E_n - E_0) + i\eta} \times \frac{1}{\omega - (E_f - E_0) + i\eta}$$

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2\mathrm{d}\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f|\hat{\mathbf{d}}|n\rangle \ \langle n|\hat{\mathbf{d}}|0\rangle}{\omega_i - (E_n - E_0) + i\eta} \right|^2 \times \boldsymbol{\delta\left(\omega - (E_f - E_0)\right)}$$

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2\mathrm{d}\omega_e} \propto \ \mathrm{Im} \sum_{\substack{vv' \\ cc'c''c''' \\ \mu\mu'\mu''\mu'''}} \left[\tilde{\rho}^*_{\mu v} \cdot \chi^{c'\mu'}_{c\mu}(\omega_i) \cdot \tilde{\rho}_{c'\mu'}\right]^* \chi^{c''v'}_{cv}(\omega) \left[\tilde{\rho}^*_{\mu''v'} \cdot \chi^{c'''\mu'''}_{c''\mu''}(\omega_i) \cdot \tilde{\rho}_{c'''\mu'''}\right]$$

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \ \mathrm{Im} \sum_{\substack{vv' \\ cc'c''c''' \\ \mu\mu'\mu''\mu'''}} \left[\tilde{\rho}^*_{\mu v} \cdot \chi^{c'\mu'}_{c\mu}(\omega_i) \cdot \tilde{\rho}_{c'\mu'}\right]^* \chi^{c''v'}_{cv}(\omega) \left[\tilde{\rho}^*_{\mu''v'} \cdot \chi^{c'''\mu'''}_{c''\mu''}(\omega_i) \cdot \tilde{\rho}_{c'''\mu'''}\right]$$

$c \rightarrow$ conduction state

$v \rightarrow$ valence state

$\mu \rightarrow$ core state

$$\chi^{v'c'}_{vc}(\omega) = \int d\mathbf{r}d\mathbf{r}' \ \psi^*_c(\mathbf{r})\psi_v(\mathbf{r}) \ \chi(\mathbf{r}, \mathbf{r}', \omega) \ \psi^*_{v'}(\mathbf{r})\psi_{c'}(\mathbf{r})$$

$$= \sum_\lambda \frac{A^{vc}_\lambda A^{*v'c'}_\lambda}{\omega - E_\lambda + i\eta}$$

$$\tilde{\rho}_{vc} = \langle c|\hat{\mathbf{d}}|v\rangle = \int d\mathbf{r} \, \psi^*_c(\mathbf{r}) \, \hat{\mathbf{d}} \, \psi_v(\mathbf{r})$$

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2\mathrm{d}\omega_e} \propto \mathrm{Im} \sum_{\substack{vv'\\cc'c''c'''\\\mu\mu'\mu''\mu'''}} \left[\tilde{\rho}^*_{\mu v}\cdot\chi^{c'\mu'}_{c\mu}(\omega_i)\cdot\tilde{\rho}_{c'\mu'}\right]^*\chi^{c''v'}_{cv}(\omega)\left[\tilde{\rho}^*_{\mu''v'}\cdot\chi^{c'''\mu'''}_{c''\mu''}(\omega_i)\cdot\tilde{\rho}_{c'''\mu'''}\right]$$

- core-excitation polarizability (x-ray absorption) — **BSE calculation**
- valence-excitation polarizability (optical absorption) — **BSE calculation**
- core-valence matrix elements (new ingredients) — **simple calculation**

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2\mathrm{d}\omega_e} \propto \mathrm{Im} \sum_{\substack{vv' \\ cc'c''c''' \\ \mu\mu'\mu''\mu'''}} \left[\tilde{\rho}^*_{\mu v} \cdot \chi^{c'\mu'}_{c\mu}(\omega_i) \cdot \tilde{\rho}_{c'\mu'}\right]^* \chi^{c''v'}_{cv}(\omega) \left[\tilde{\rho}^*_{\mu''v'} \cdot \chi^{c'''\mu'''}_{c''\mu''}(\omega_i) \cdot \tilde{\rho}_{c'''\mu'''}\right]$$

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \ \mathrm{Im} \sum_{\substack{vv' \\ cc'c''c''' \\ \mu\mu'\mu''\mu'''}} \left[\tilde{\rho}^*_{\mu v} \cdot \chi^{c'\mu'}_{c\mu}(\omega_i) \cdot \tilde{\rho}_{c'\mu'}\right]^* \chi^{c''v'}_{cv}(\omega) \left[\tilde{\rho}^*_{\mu''v'} \cdot \chi^{c'''\mu'''}_{c''\mu''}(\omega_i) \cdot \tilde{\rho}_{c'''\mu'''}\right]$$

$$\sum_{c'''\mu''\mu'''} \left[\tilde{\rho}_{\mu''v'} \cdot \chi^{c'''\mu'''}_{c''\mu''}(\omega_i) \cdot \tilde{\rho}_{c'''\mu'''}\right] = \sum_{\boldsymbol{c'''}\mu''\boldsymbol{\mu'''}} \sum_{\lambda_c} \tilde{\rho}_{\mu''v'} \frac{A^{\mu''c''}_{\lambda_c} \boldsymbol{A^{*\mu'''c'''}_{\lambda_c}}}{\omega_i - E_{\lambda_c} + i\eta} \boldsymbol{\tilde{\rho}_{c'''\mu'''}}$$

$$= \sum_{\mu'',\lambda_c} \frac{A^{\mu''c''}_{\lambda_c} t^{(1)}_{\lambda_c}}{\omega_i - E_{\lambda_c} + i\eta}$$

$$t^{(1)}_{\lambda_c} = \sum_{c'''\mu'''} A^{*\mu'''c'''}_{\lambda_c} \tilde{\rho}_{c'''\mu'''}$$

oscillator strength of the excitation

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

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

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

$$t^{(2)}_{\lambda_c\lambda} = \sum_{vc\mu} A^{*\mu c}_{\lambda_c} \tilde{\rho}^*_{\mu v} A^{vc}_{\lambda}$$

excitation pathway

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2\mathrm{d}\omega_e} \propto \quad \mathrm{Im} \sum_{\lambda} \frac{\left| \sum_{\lambda_c} \frac{t^{(2)}_{\lambda_c\lambda} t^{(1)}_{\lambda_c}}{\omega_i - E_{\lambda_c} + i\eta} \right|^2}{\omega - E_\lambda + i\eta}$$

← **RIXS oscillator strength**

$$t^{(2)}_{\lambda_c\lambda} = \sum_{vc\mu} A^{*\mu c}_{\lambda_c}\, \tilde{\rho}^{*}_{\mu v}\, A^{vc}_{\lambda}$$

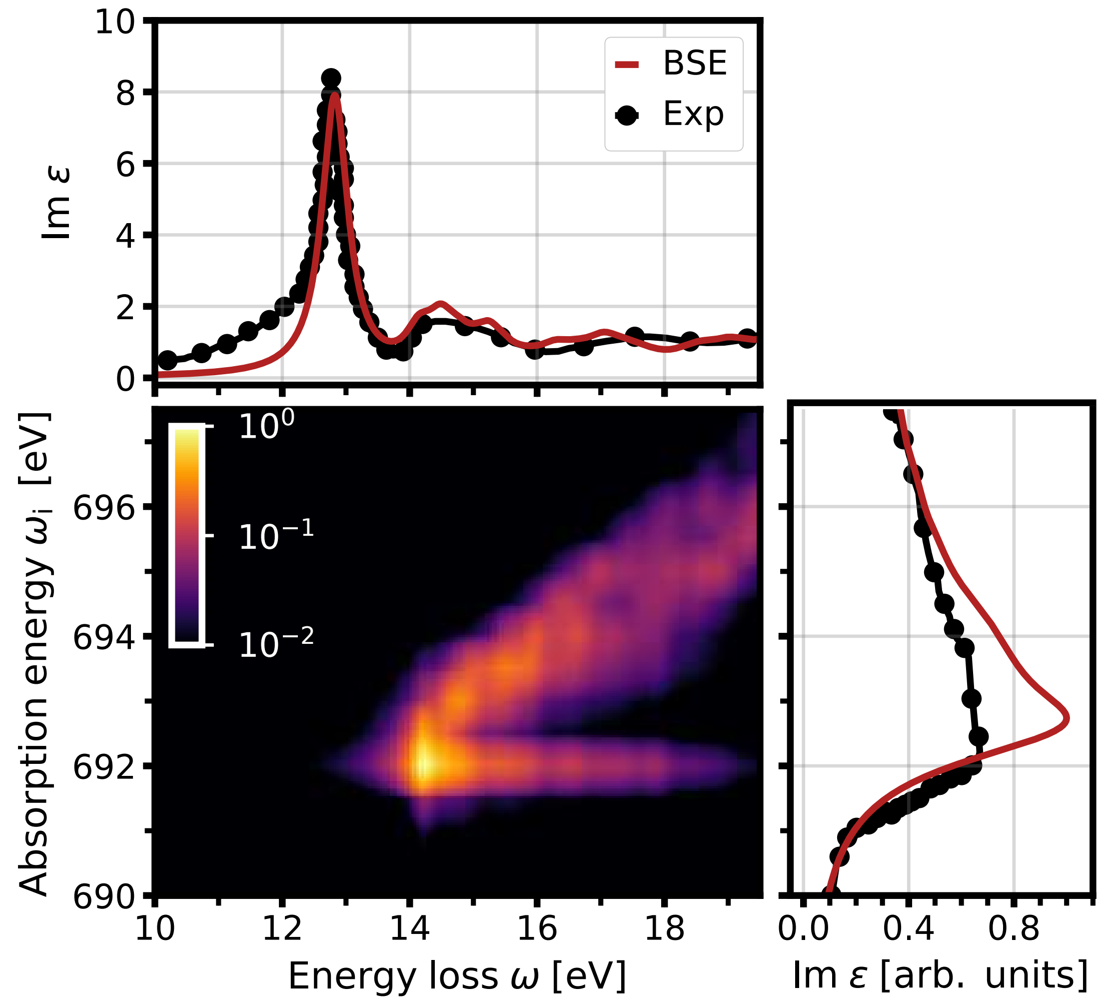
excitation pathway

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \quad \mathrm{Im} \sum_{\lambda} \frac{\left| \sum_{\lambda_c} \frac{t^{(2)}_{\lambda_c\lambda} t^{(1)}_{\lambda_c}}{\omega_i - E_{\lambda_c} + i\eta} \right|^2}{\omega - E_\lambda + i\eta}$$

RIXS oscillator strength

BRIXS (and pyBRIXS) code on Gitlab

RIXS LiF at F K edge

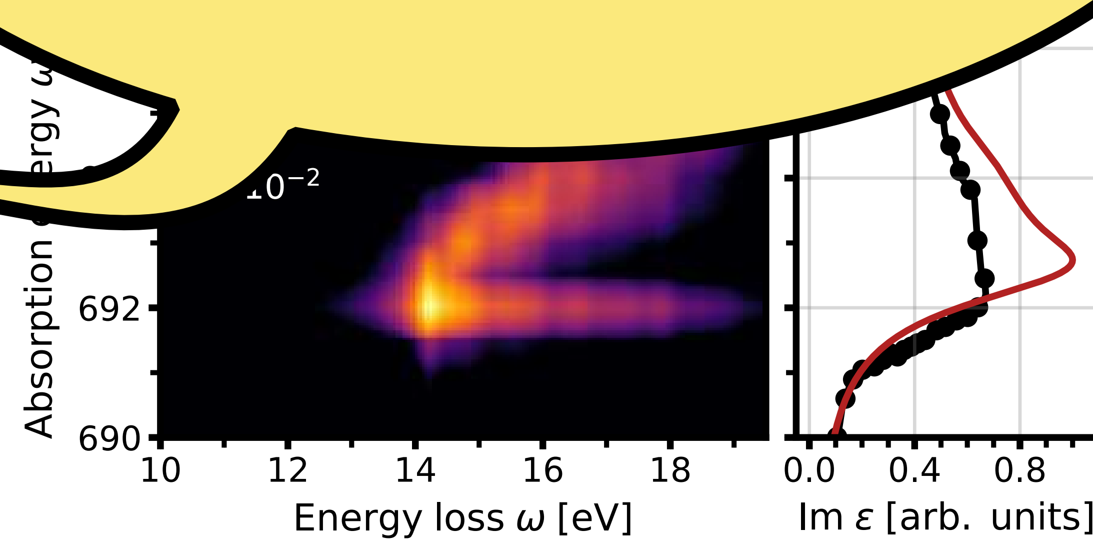


Vorwerk *et al.* Phys. Rev. Research **2**, 042003(R) (2020)

RIXS LiF at F K edge

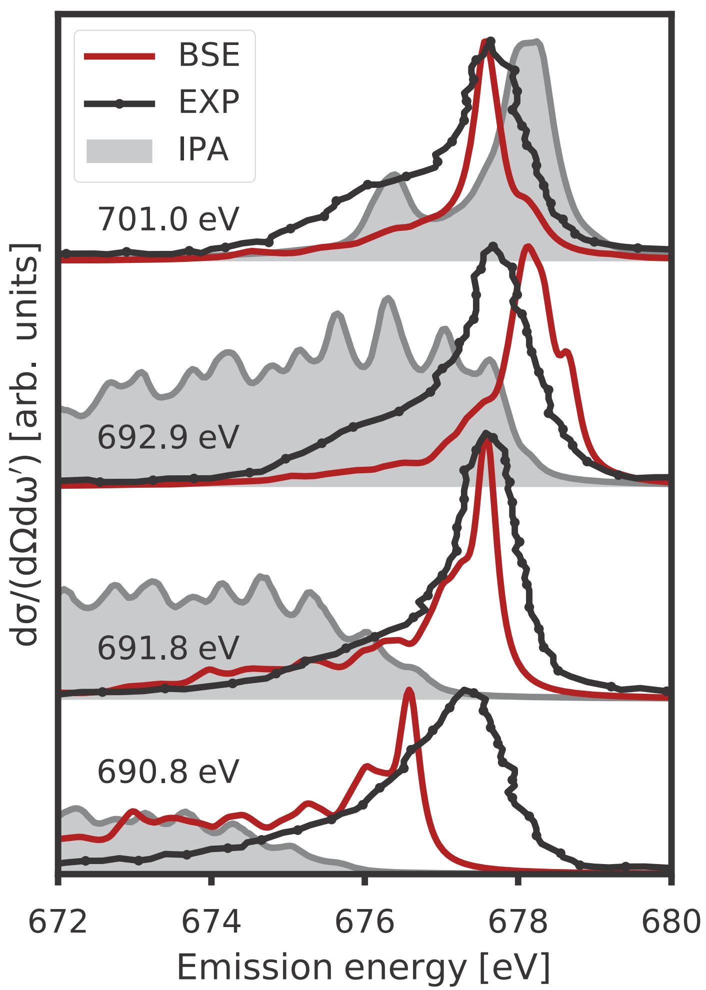
It is called FLUORESCENCE

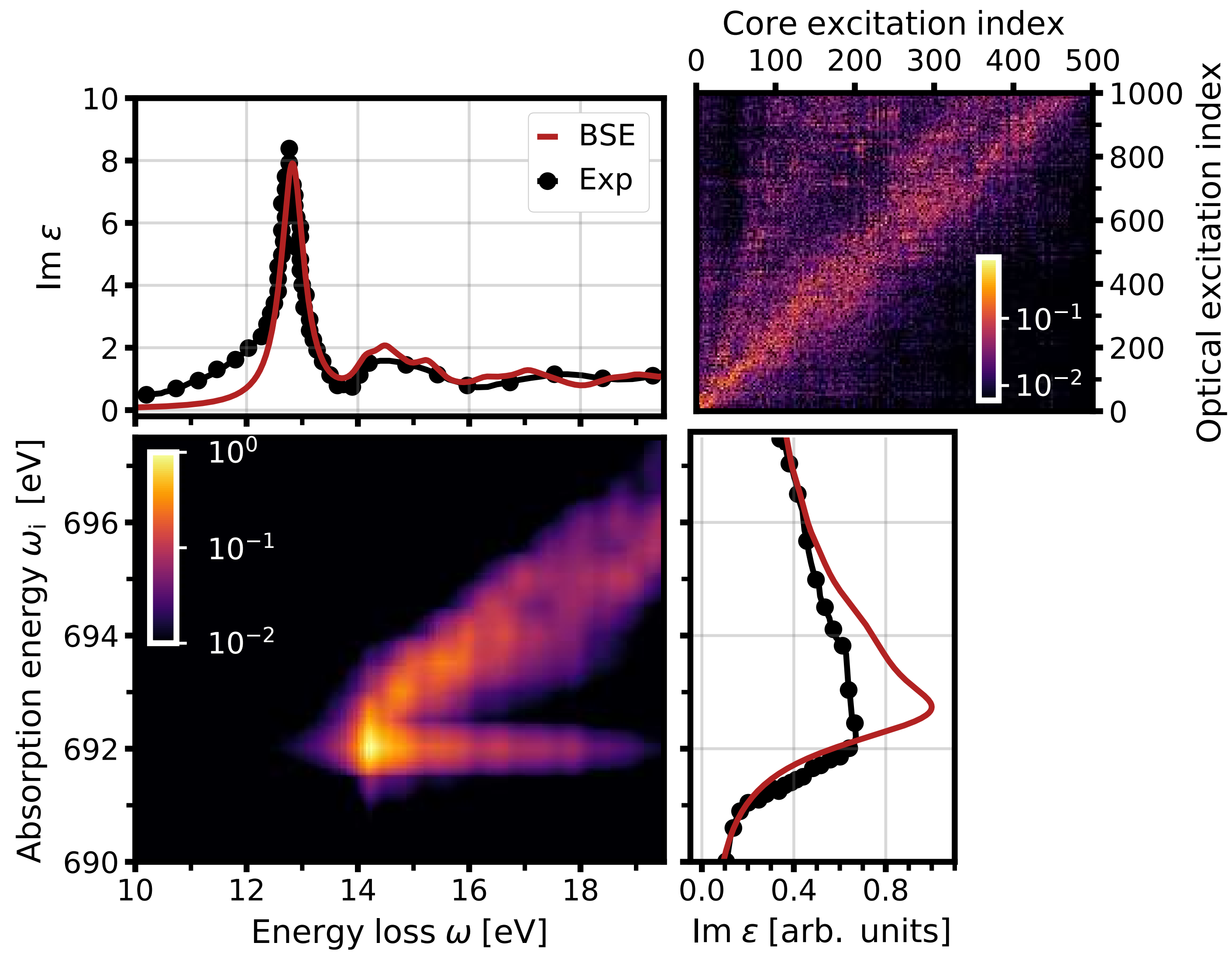
Speak clearly, come on!



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

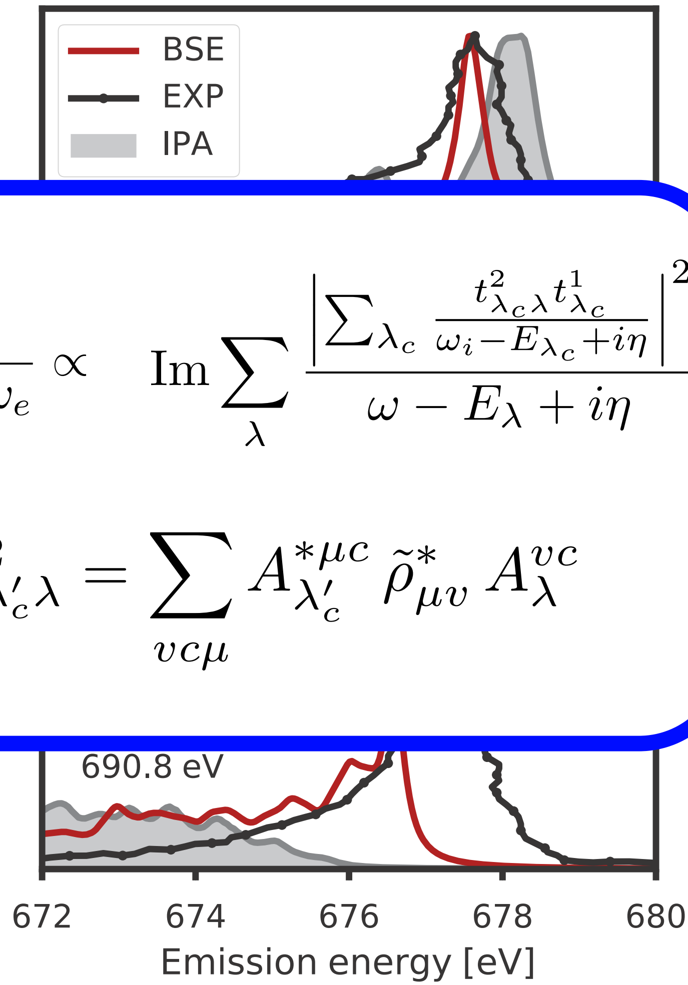
RIXS LiF at F K edge





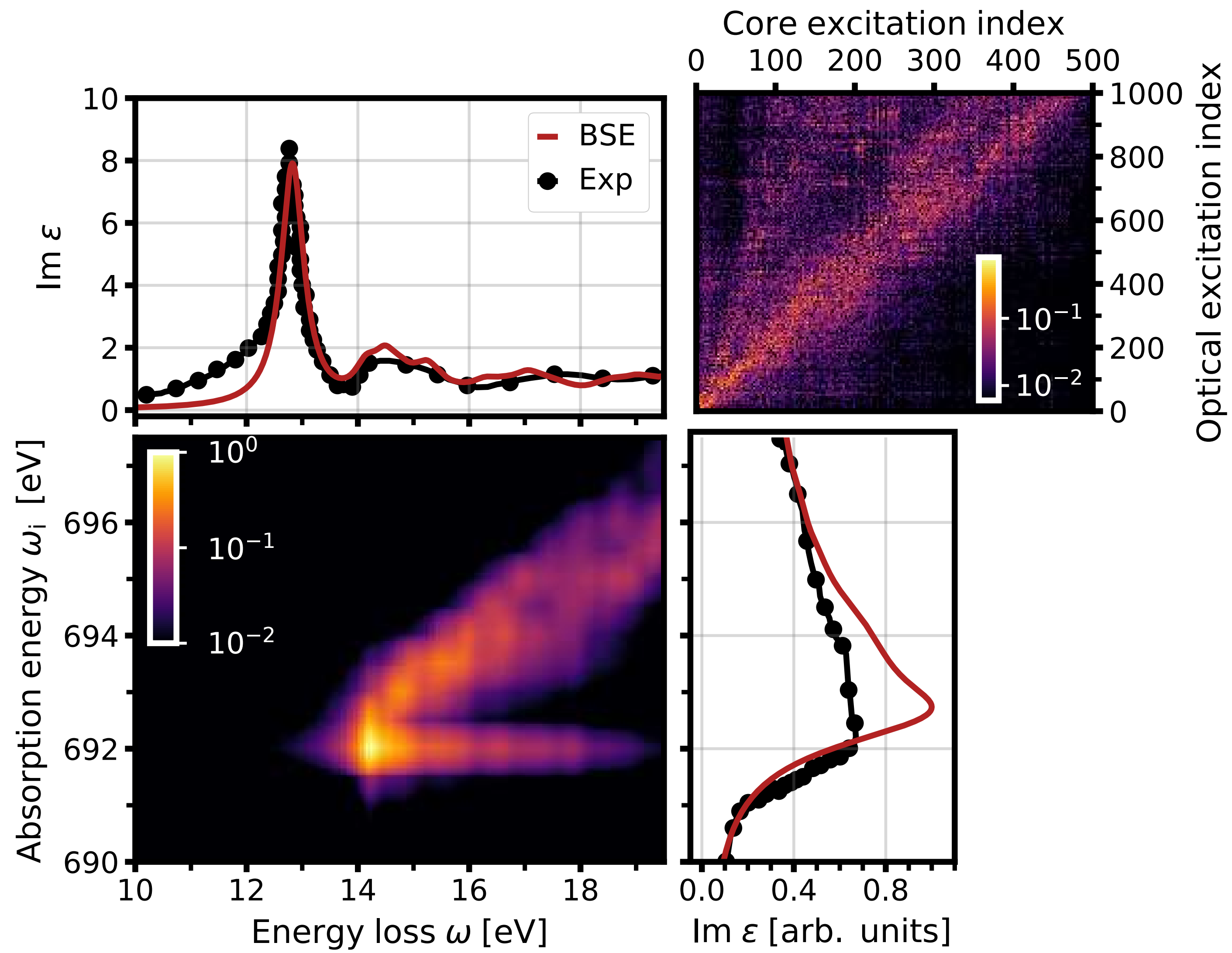
Vorwerk *et al.* Phys. Rev. Research **2**, 042003(R) (2020)

RIXS LiF at F K edge



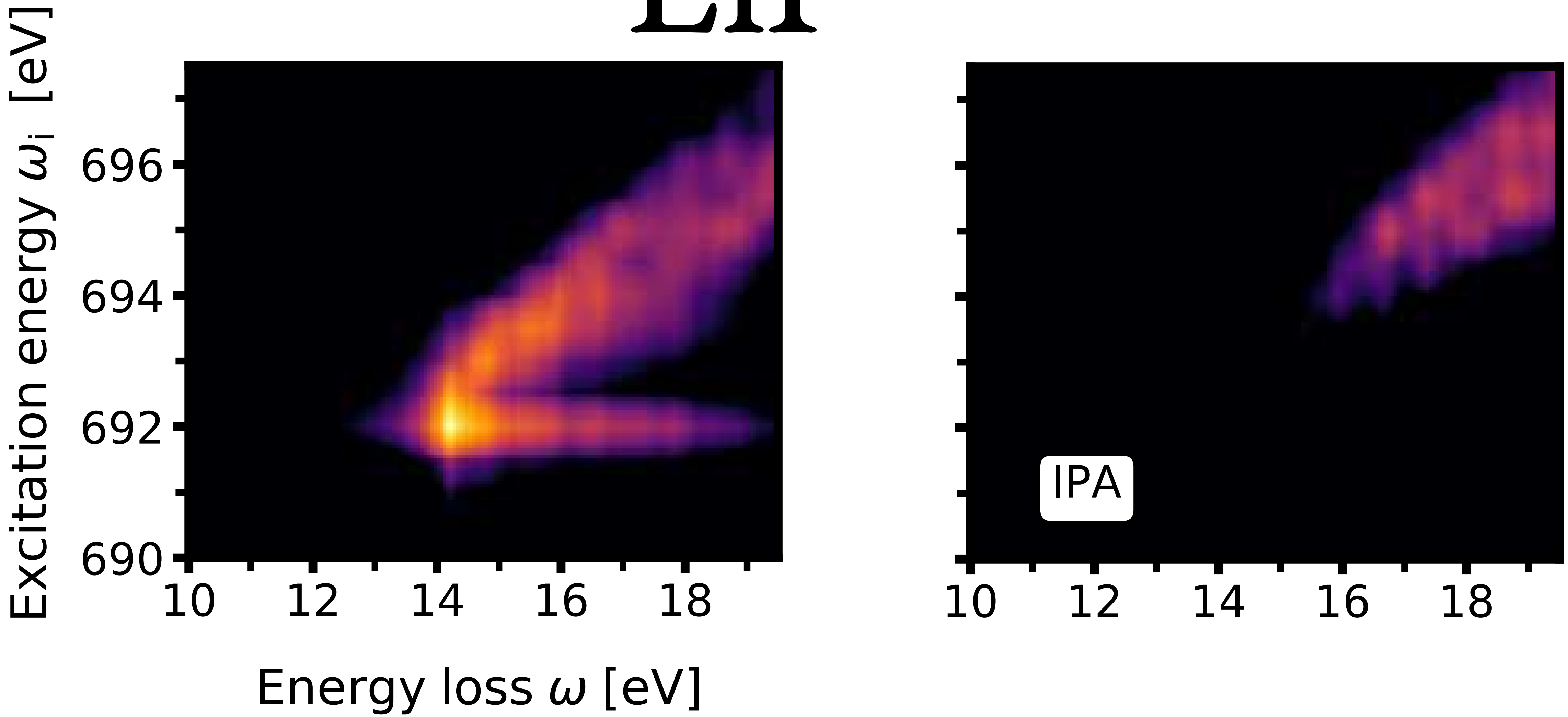
$$\frac{d^2\sigma}{d\Omega_2 d\omega_e} \propto \quad \mathrm{Im} \sum_{\lambda} \frac{\left| \sum_{\lambda_c} \frac{t^2_{\lambda_c \lambda} t^1_{\lambda_c}}{\omega_i - E_{\lambda_c} + i\eta} \right|^2}{\omega - E_\lambda + i\eta}$$

$$t^2_{\lambda'_c \lambda} = \sum_{vc\mu} A^{*\mu c}_{\lambda'_c} \, \tilde{\rho}^*_{\mu v} \, A^{vc}_{\lambda}$$



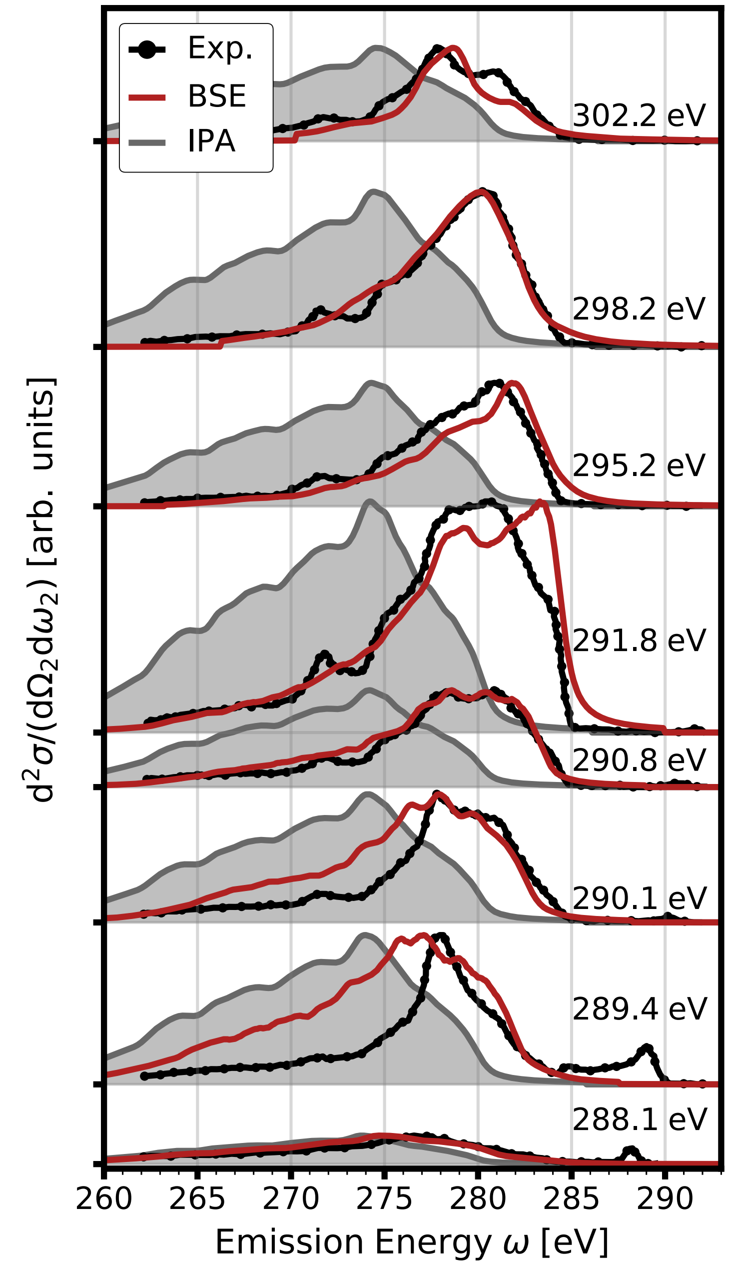
Vorwerk *et al.* Phys. Rev. Research **2**, 042003(R) (2020)

LiF



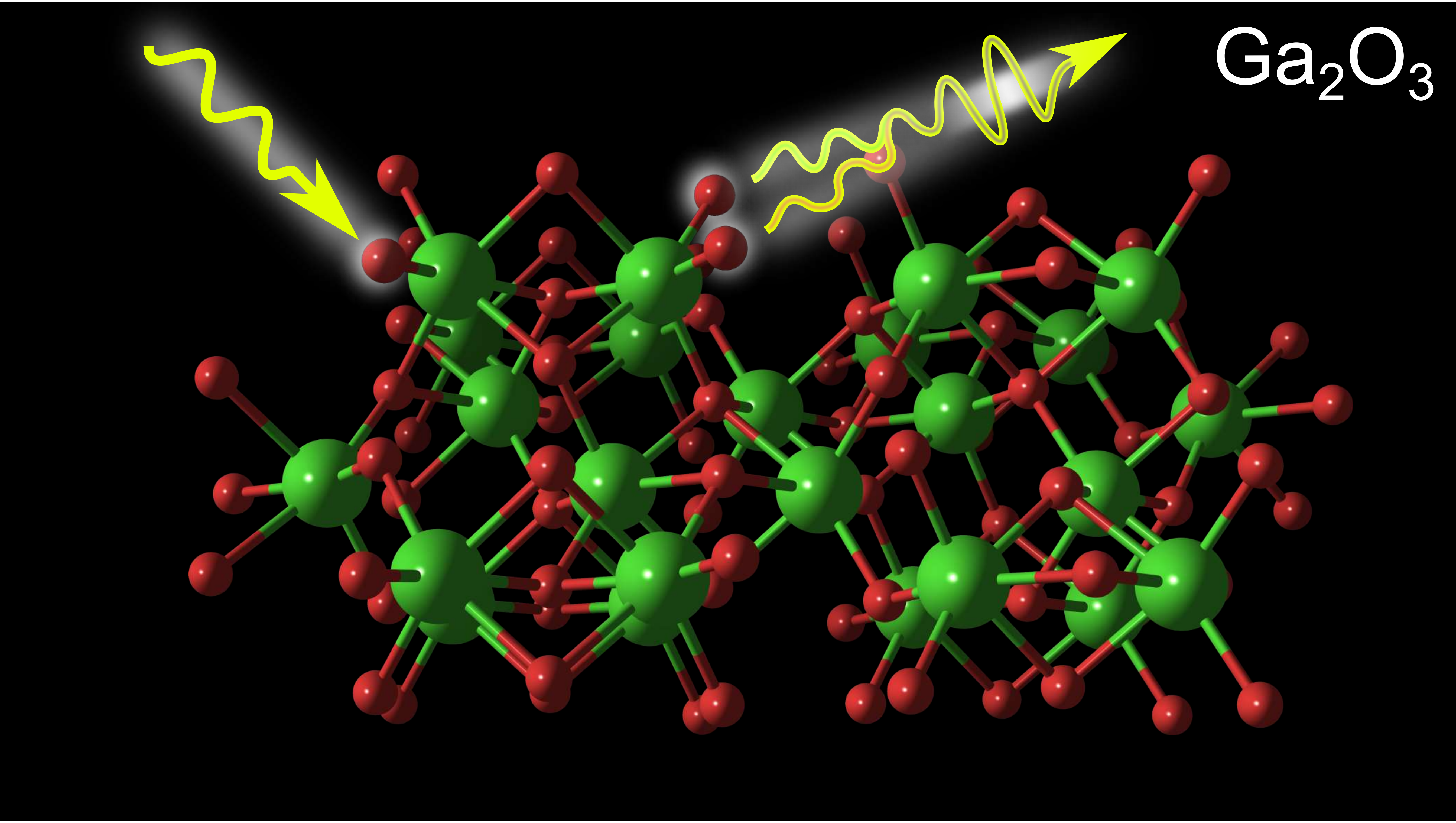
Vorwerk *et al.* Phys. Rev. Research **2**, 042003(R) (2020)

RIXS diamond
C K-edge



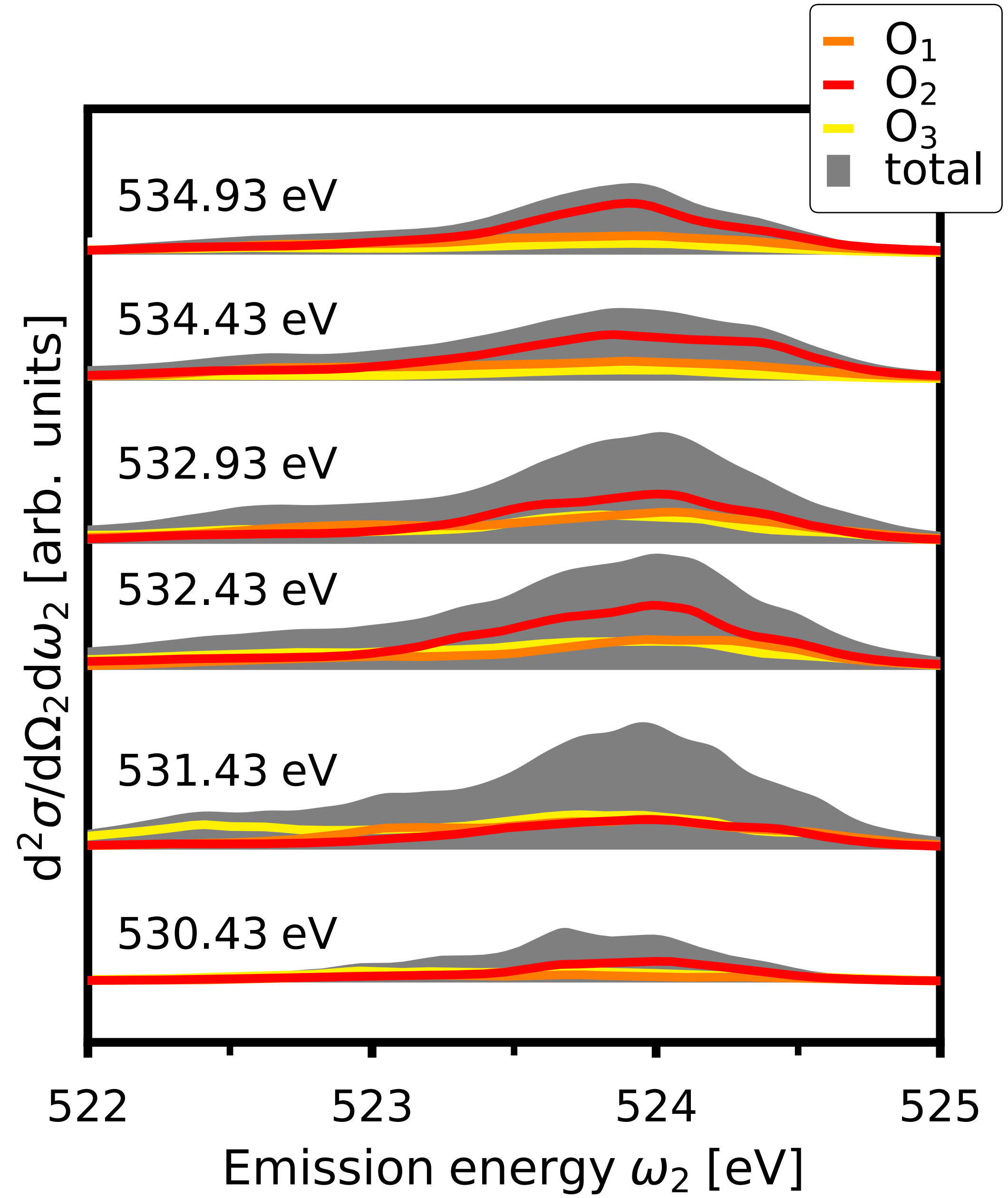
Vorwerk *et al.* Phys. Chem. Chem. Phys. (2022), accepted.

- RIXS scheme
- Derivation in terms of excitation pathways
- Example :: LiF
- Atomic Coherence in RIXS


Ga_2O_3

O-K Ga_2O_3

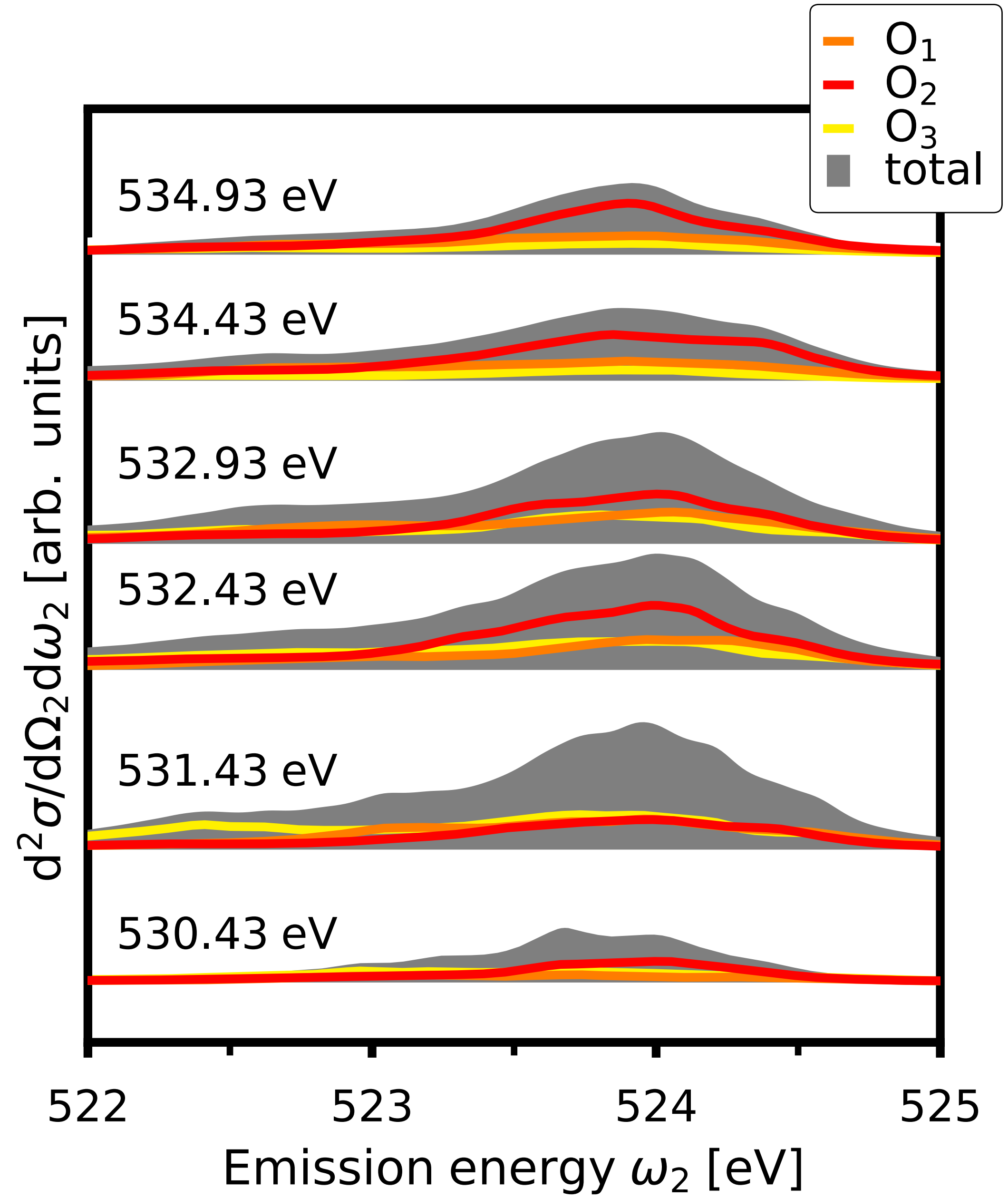
3 inequivalent oxigens



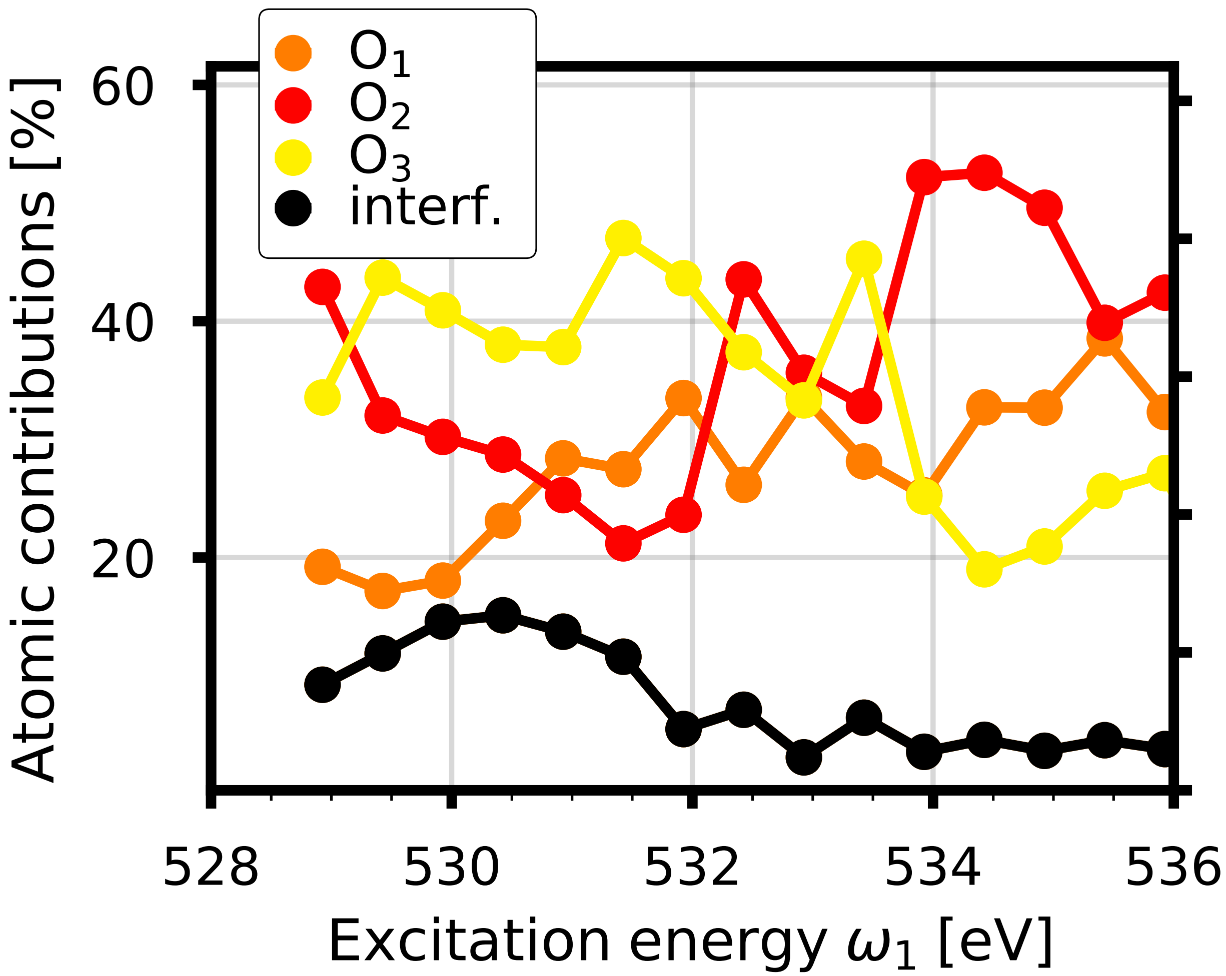
O-K Ga_2O_3

3 inequivalent oxigens

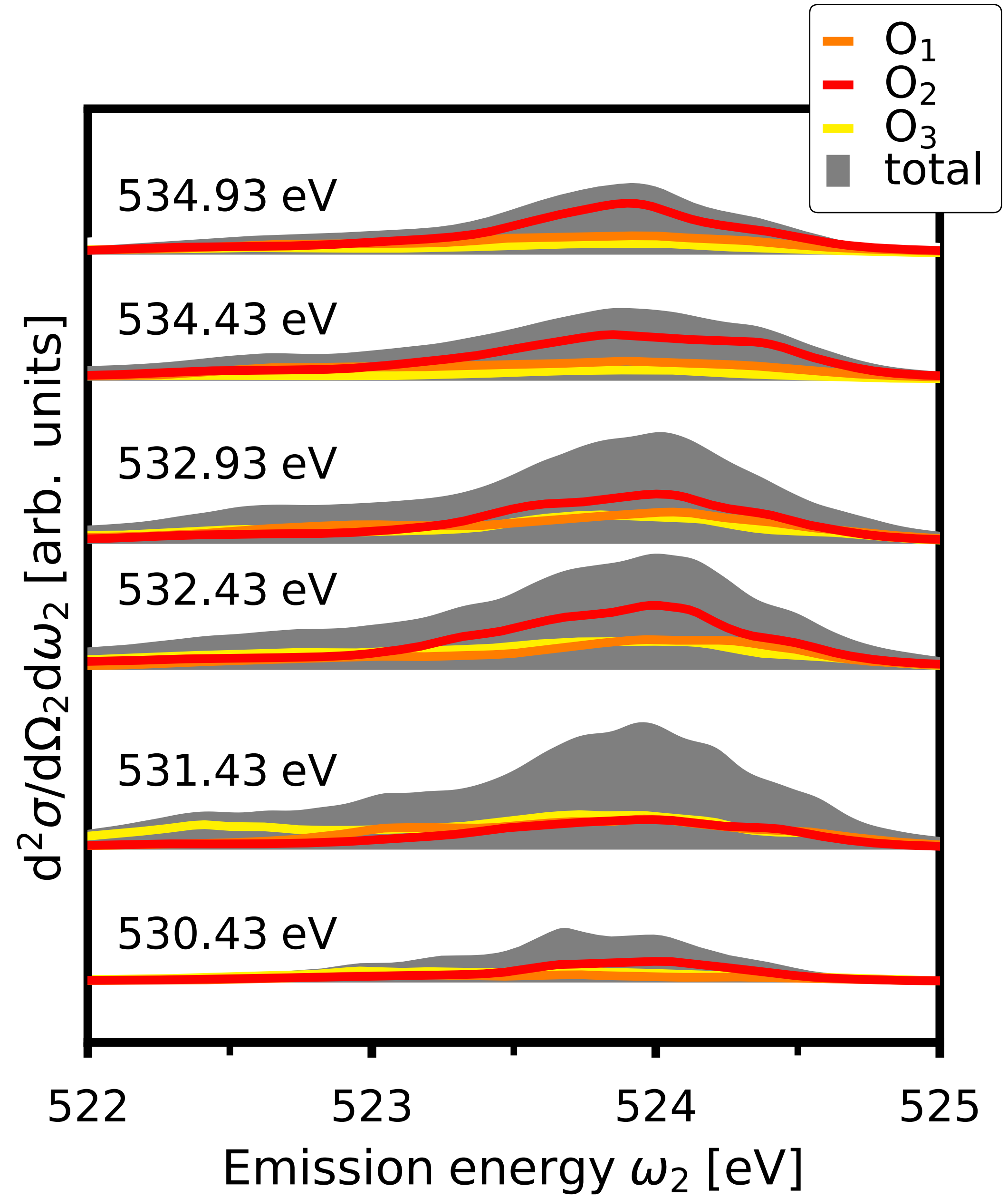
$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2\mathrm{d}\omega_e} \propto \mathrm{Im}\sum_{\lambda} \frac{\left|\sum_{\lambda_c} \frac{t^{(2)}_{\lambda_c\lambda} t^{(1)}_{\lambda_c}}{\omega_i - E_{\lambda_c} + i\eta}\right|^2}{\omega - E_\lambda + i\eta}$$



O-K Ga_2O_3



O1
O2
O3
interf.
60
40
20
Atomic contributions [%]
528
530
532
534
536
Excitation energy ω1 [eV]



O1
O2
O3
total
534.93 eV
534.43 eV
532.93 eV
532.43 eV
531.43 eV
530.43 eV
d2σ/dΩ2dω2 [arb. units]
522
523
524
525
Emission energy ω2 [eV]

- RIXS within BSE
  in terms of excitation pathways
- Example :: LiF, Diamond
- Towards semi-core RIXS :: Al_2O_3
- Coherence in RIXS :: interferences