XAS and RIXS: all-electron vs pseudo-potential many-body approaches

Francesco Sottile

ETSF and LSI, École Polytechnique (France)

HoW exciting! 2023

Christian Vorwerk's PhD Thesis (2020)

Laura Urquiza's Postdoc

What are the advantages of Rixs?

Resonant Inelastic X-ray Scattering (RIXS) spectroscopy offers several advantages in the field of materials science and condensed matter research:

1. **Element and Site Specificity**: RIXS can provide element-specific and even site-specific information about the electronic structure of a material. This allows researchers to study the behavior of specific atoms and their interactions within a sample.
2. **Soft X-rays and Core Excitations**: RIXS utilizes soft X-rays, which are well-suited for studying core-level excitations. This enables the investigation of electronic transitions that are not easily accessible by other techniques.
3. **Energy Resolution**: RIXS can achieve high energy resolution, allowing for the detailed characterization of energy levels and electronic states within a material. This makes it possible to distinguish subtle differences in electronic structure

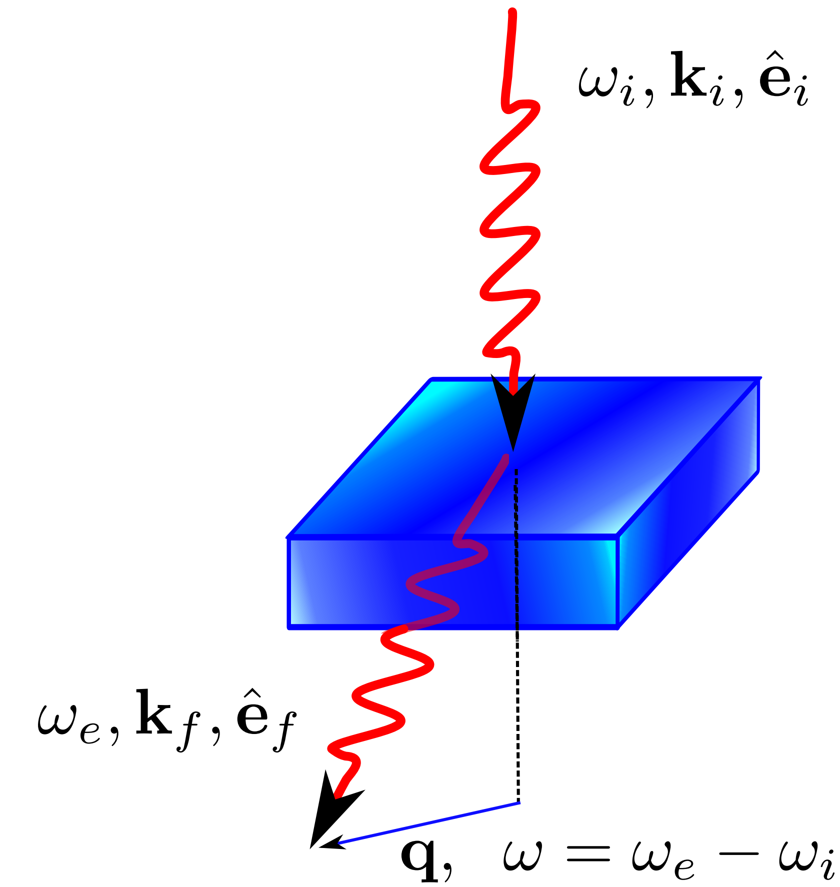
electronic properties of materials.

7. **Crystal Field Effects**: RIXS can probe crystal field effects and reveal details about the local symmetry and ligand environment around specific atoms.
8. **Materials Characterization**: RIXS is applicable to a wide range of materials, including complex oxides, molecular systems, transition metals, and more. It is particularly useful for studying strongly correlated electron systems.
9. **Complementary Technique**: RIXS complements other spectroscopic techniques like X-ray Absorption Spectroscopy (XAS) and X-ray Photoelectron Spectroscopy (XPS), providing a more comprehensive understanding of a material's electronic structure.
10. **Future Potential**: As technology advances, RIXS continues to evolve with improved instrumentation, energy resolution, and accessibility, enabling researchers to explore new frontiers in materials research.

Overall, RIXS spectroscopy is a powerful tool for probing electronic properties and excitations in materials, contributing to our understanding of complex materials and their behavior.

- RIXS scheme
- Derivation in terms of excitation pathways
- Example :: LiF
- Atomic Coherence in RIXS
- Towards shallow core excitations: pseudo-potentials vs all-electron approaches

X-ray scattering



non-Resonant IXS

Resonant IXS

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

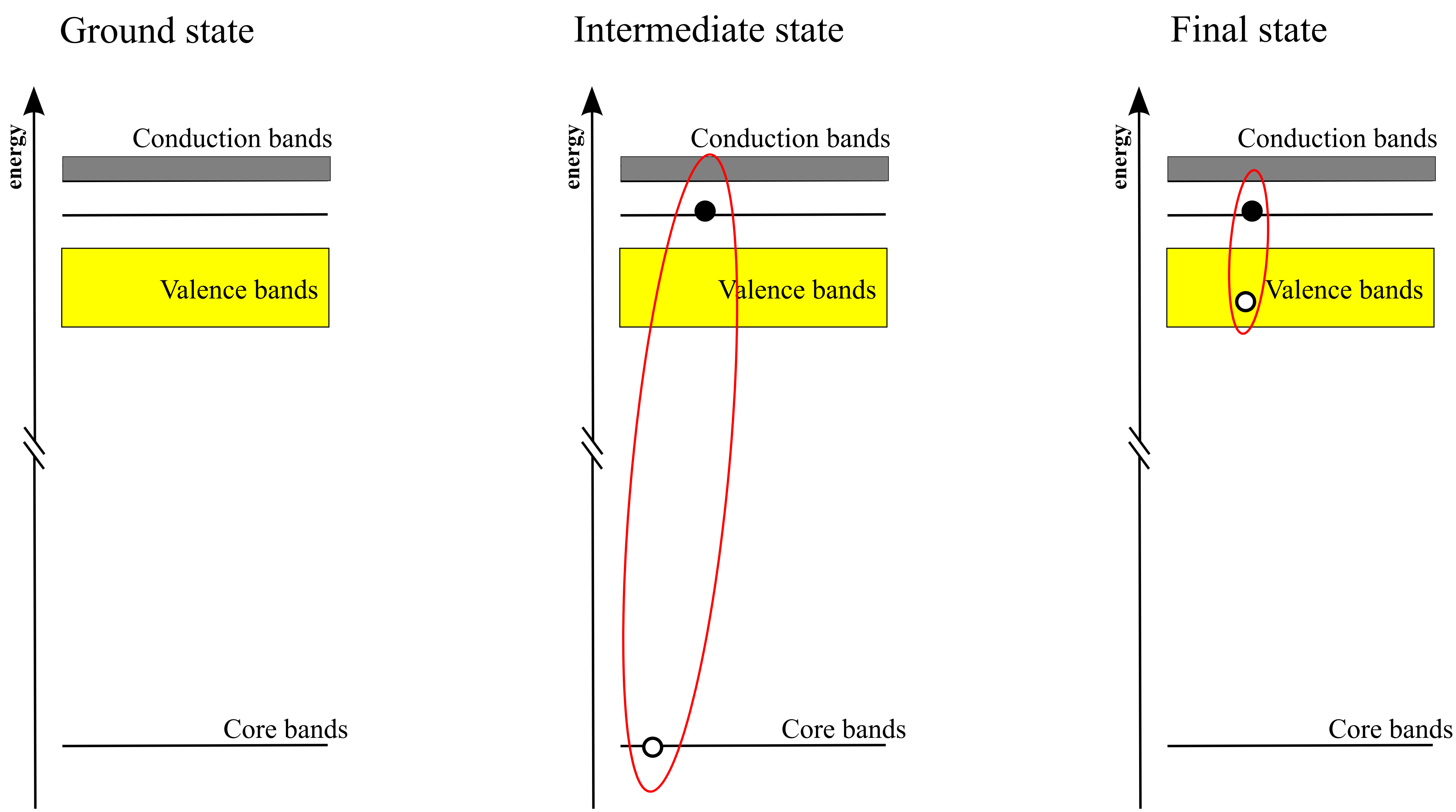
Resonant IXS

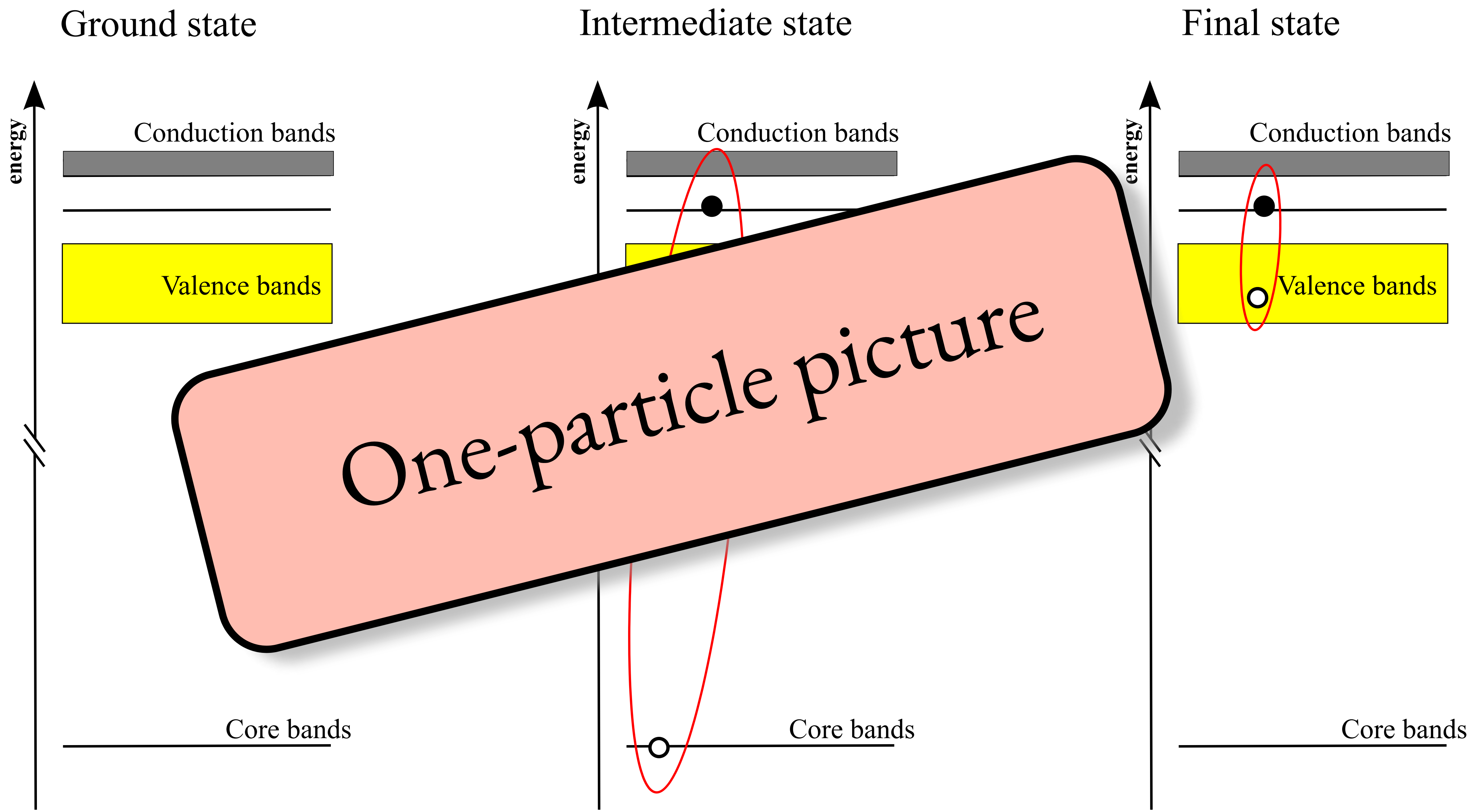
$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f|\hat{\mathbf{d}}|n\rangle \ \langle n|\hat{\mathbf{d}}|0\rangle}{\omega_i - (E_n - E_0) + i\eta} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

$\omega_i = (E_n - E_0)$ Resonance energy

$\omega = (E_f - E_0)$ Energy Loss

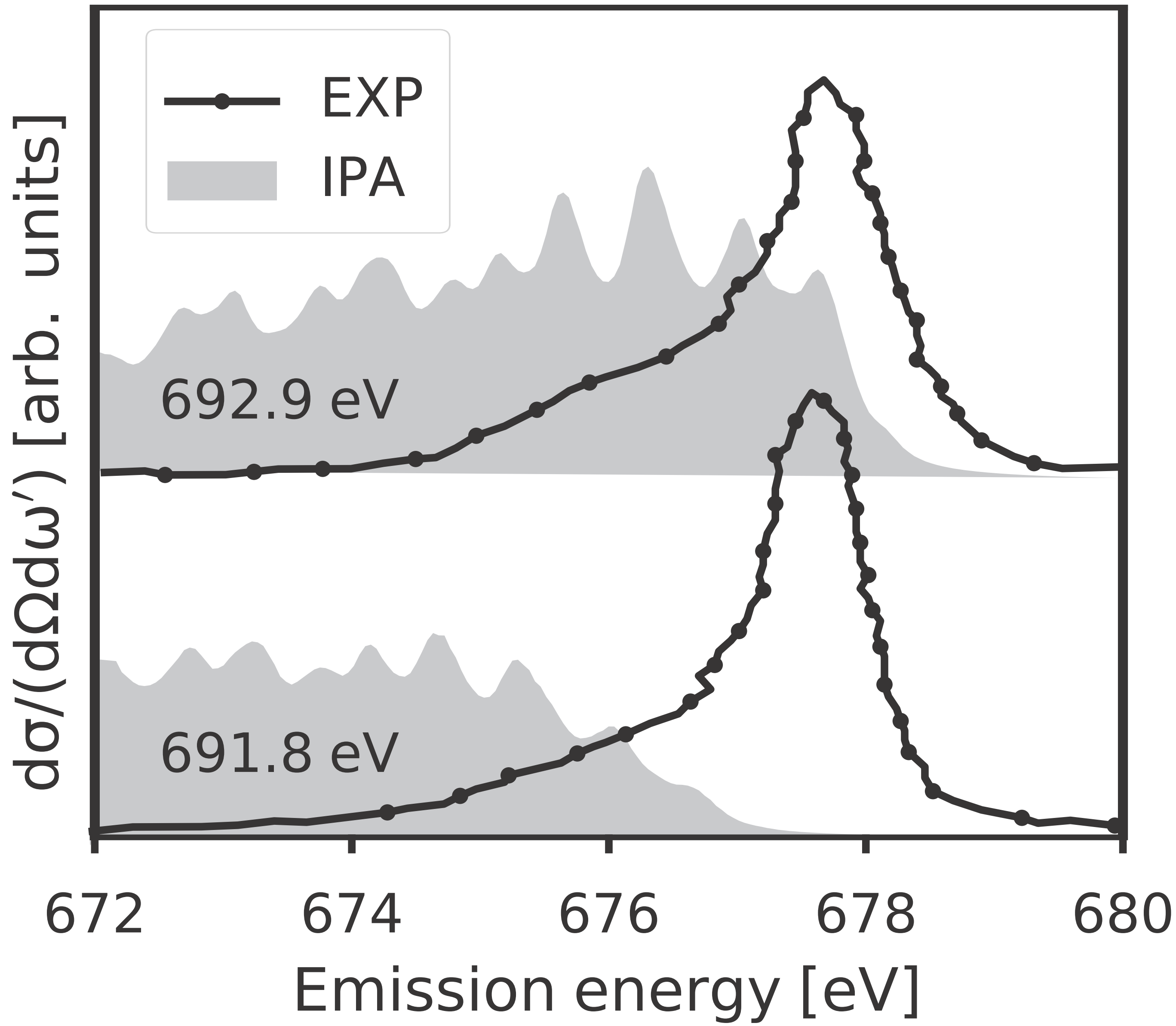
RIXS(ω_i, ω)


Ground 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


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

RIXS in IPA
LiF

$$\frac{d^2\sigma}{d\Omega_2 d\omega_e} \propto \sum_{vc\mu} \left| \frac{\langle \mu|\hat{\mathbf{d}}|v\rangle \ \langle c|\hat{\mathbf{d}}|\mu\rangle}{\omega_i - (\epsilon_c - \epsilon_\mu) + i\eta} \right|^2 \times \delta\left(\omega - (\epsilon_c - \epsilon_v)\right)$$

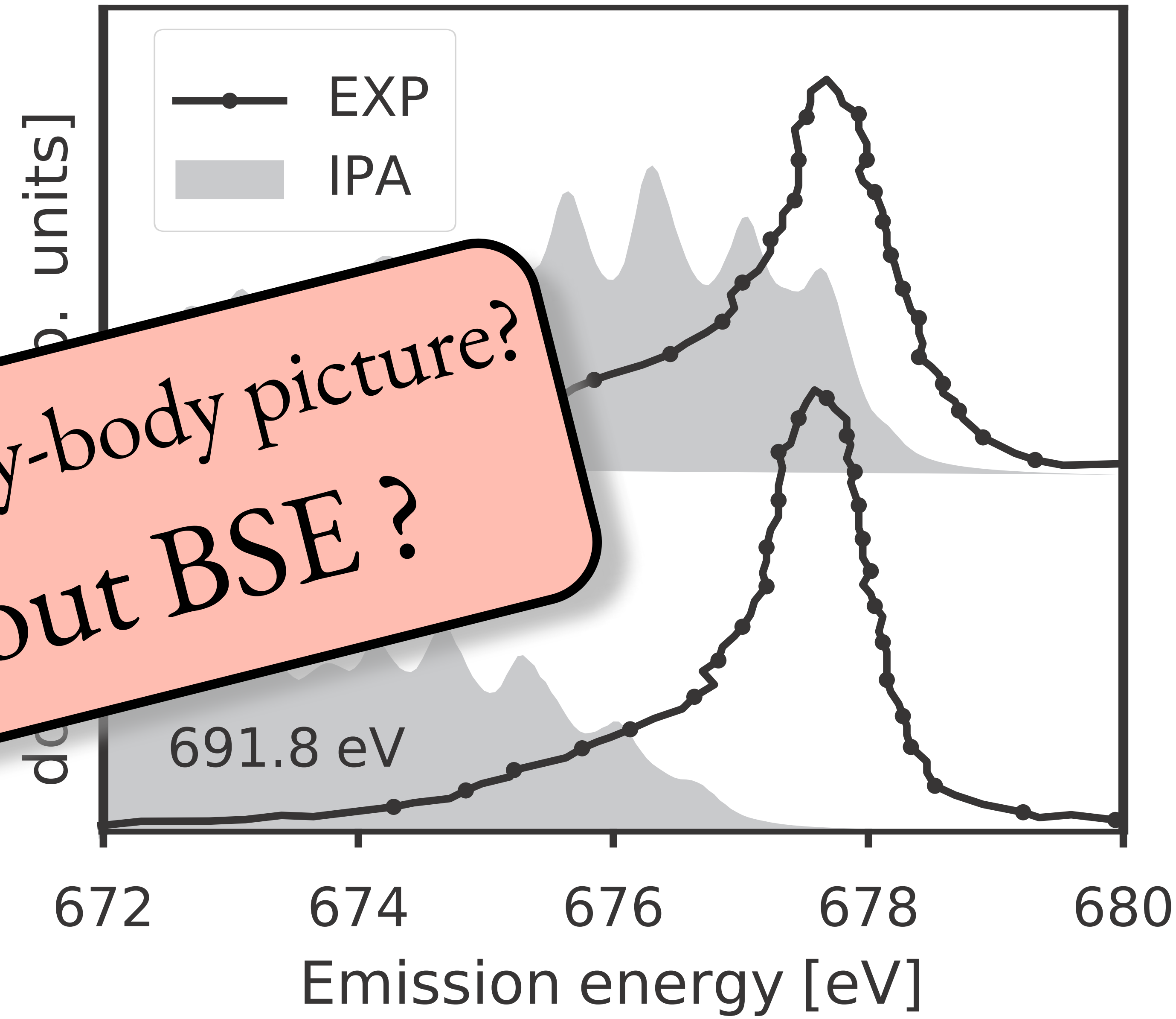


Kikas *et al.*, Phys. Rev. B **70**, 085102 (2004)

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

RIXS in IPA
LiF

$$\frac{\mathrm{d}^2\sigma}{\Omega_2 \mathrm{d}\omega_e} \propto \sum_{vc\mu} \left| \frac{\langle\mu|\hat{\mathbf{d}}|v\rangle \, \langle c|\hat{\mathbf{d}}|\mu\rangle}{\omega_i - (\epsilon_c - \epsilon_{\dots}) \dots} \right|^2$$



What about a many-body picture?
What about BSE ?

Kikas *et al.*, Phys. Rev. B **70**, 085102 (2004)

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

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 ?

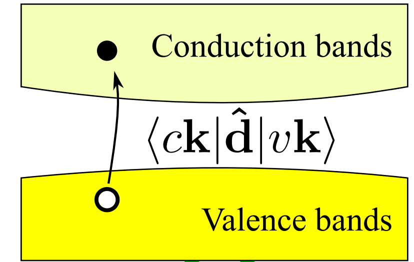
$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega_2 \mathrm{d}\omega_e} \propto \sum_f \left| \sum_n \frac{\langle f|\hat{\mathbf{d}}|n\rangle \ \langle n|\hat{\mathbf{d}}|0\rangle}{\omega_i - (E_n - E_0) + i\eta} \right|^2 \times \delta\left(\omega - (E_f - E_0)\right)$$

Absorption $\xrightarrow{\hspace{2em}}$ via BSE

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

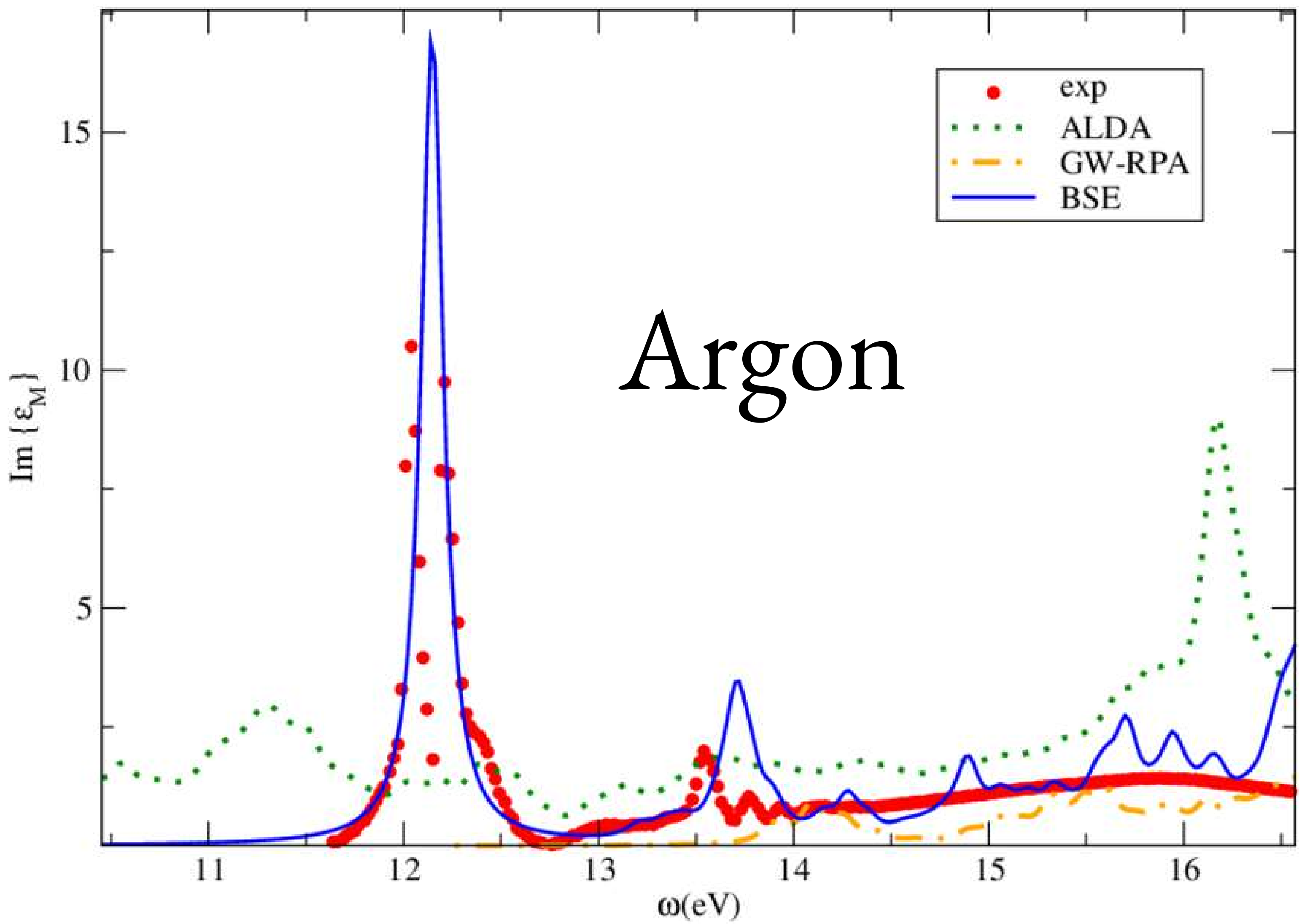
Absorption $\xrightarrow{\hspace{2em}}$ via BSE

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

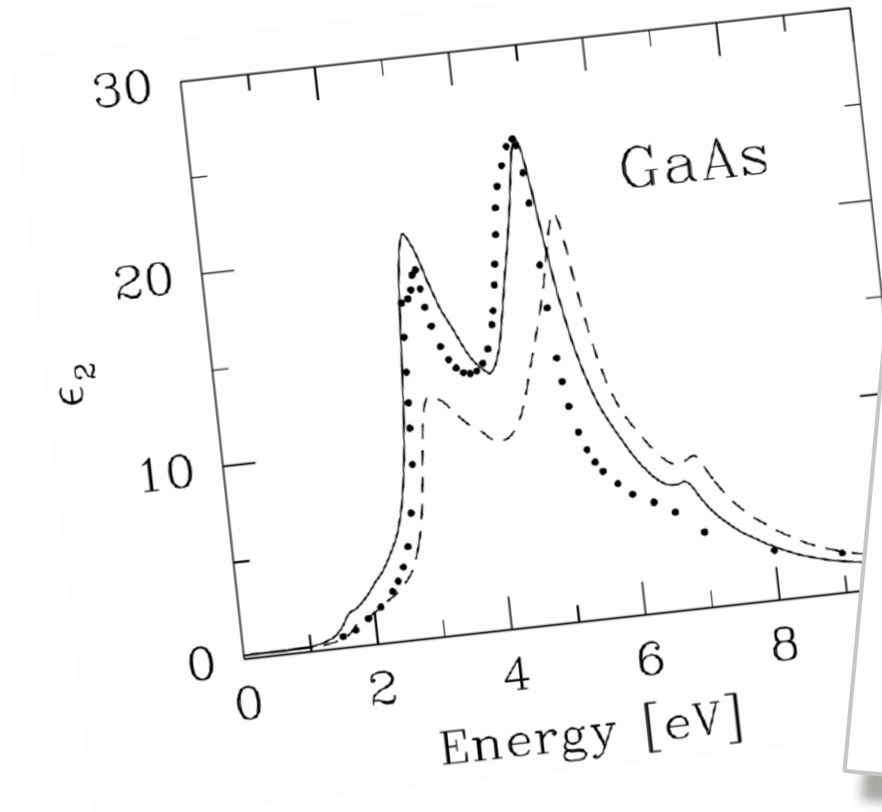


eigenvectors(values) of the exc Hamiltonian

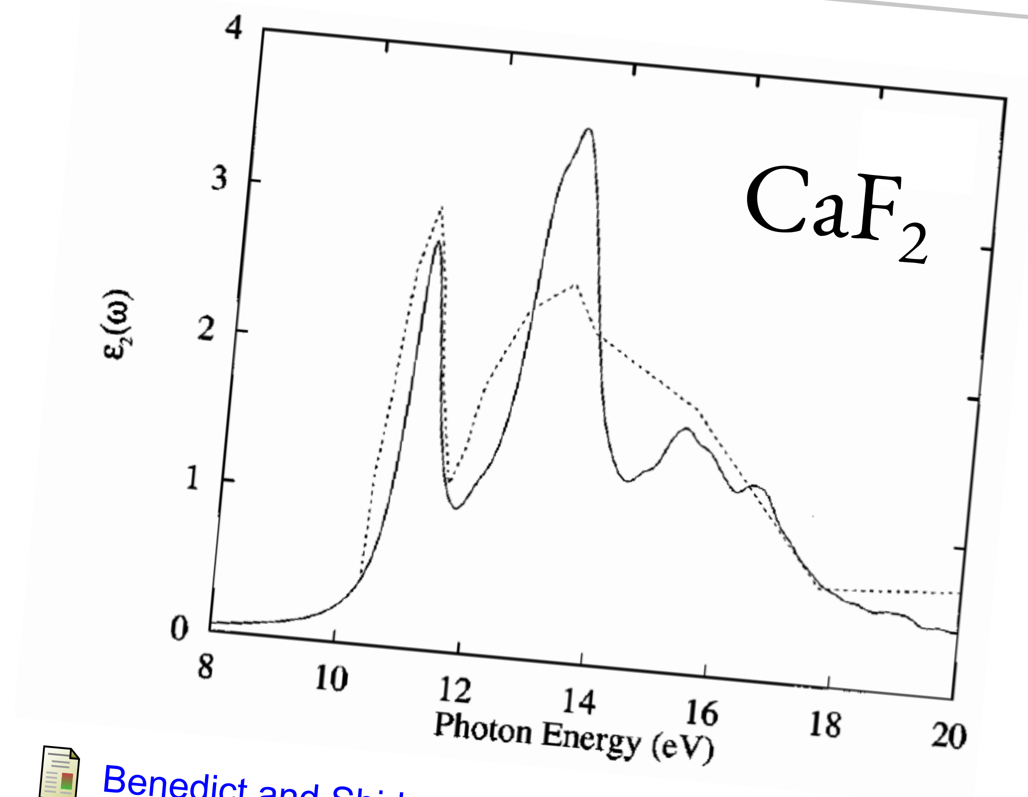
dipole matrix-elements
between one-particle states



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

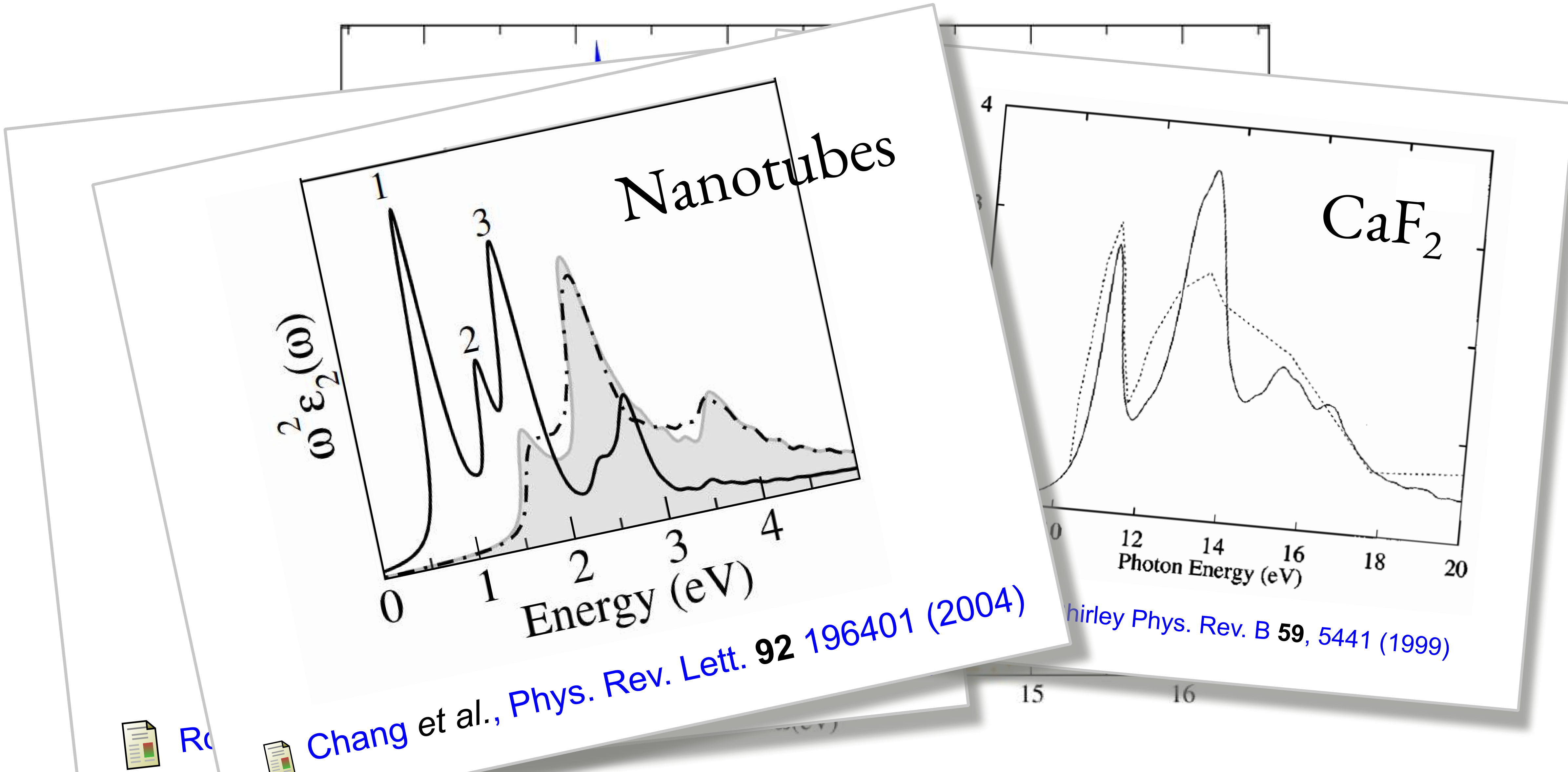


Rohlfing and Louie Phys. Rev. Lett. **81**, 2312 (1998)

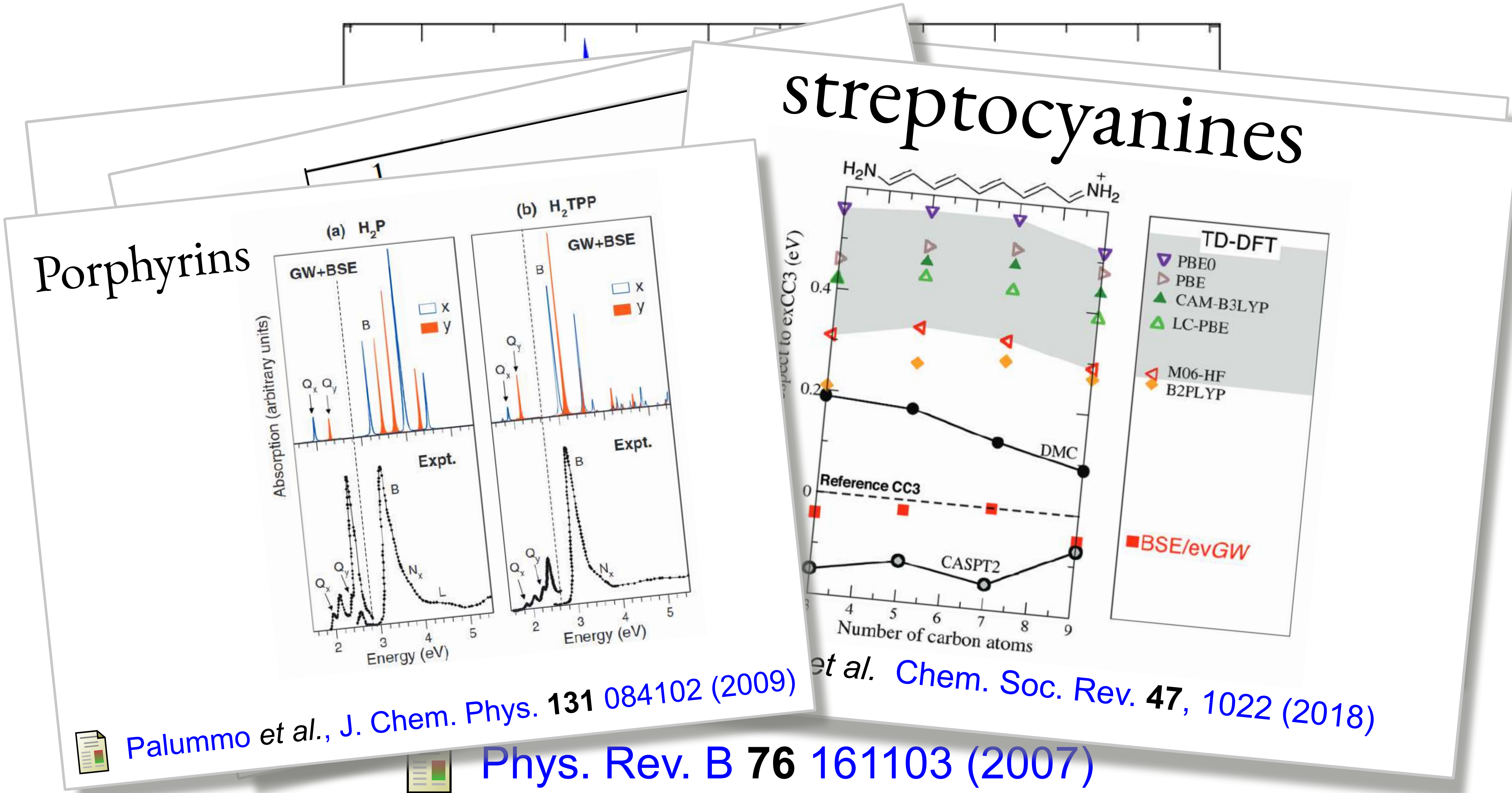


Benedict and Shirley Phys. Rev. B **59**, 5441 (1999)

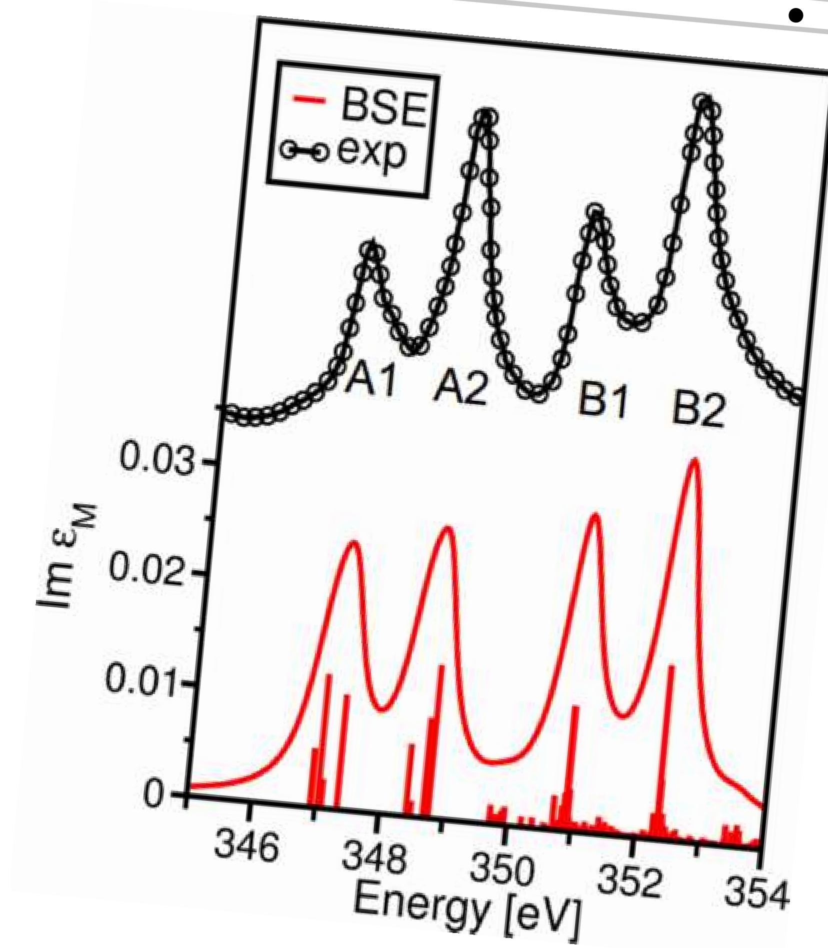
Phys. Rev. B **76** 161103 (2007)



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

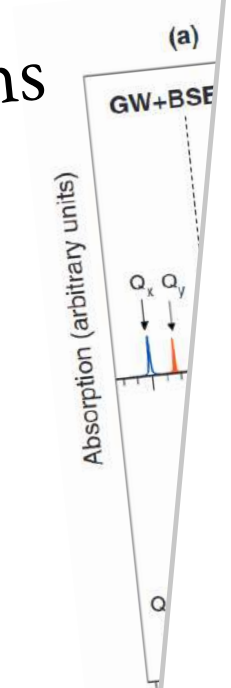

Porphyrins
(a) H_2P
(b) H_2TPP
GW+BSE
Expt.
x
y
B
Q_x
Q_y
N_x
L
Absorption (arbitrary units)
Energy (eV)
Palummo et al., J. Chem. Phys. 131 084102 (2009)
streptocyanines
TD-DFT
PBE0
PBE
CAM-B3LYP
LC-PBE
M06-HF
B2PLYP
DMC
Reference CC3
CASPT2
BSE/evGW
Number of carbon atoms
et al. Chem. Soc. Rev. 47, 1022 (2018)
Phys. Rev. B 76 161103 (2007)

CaO
Ca L-edge



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

Porphyrins



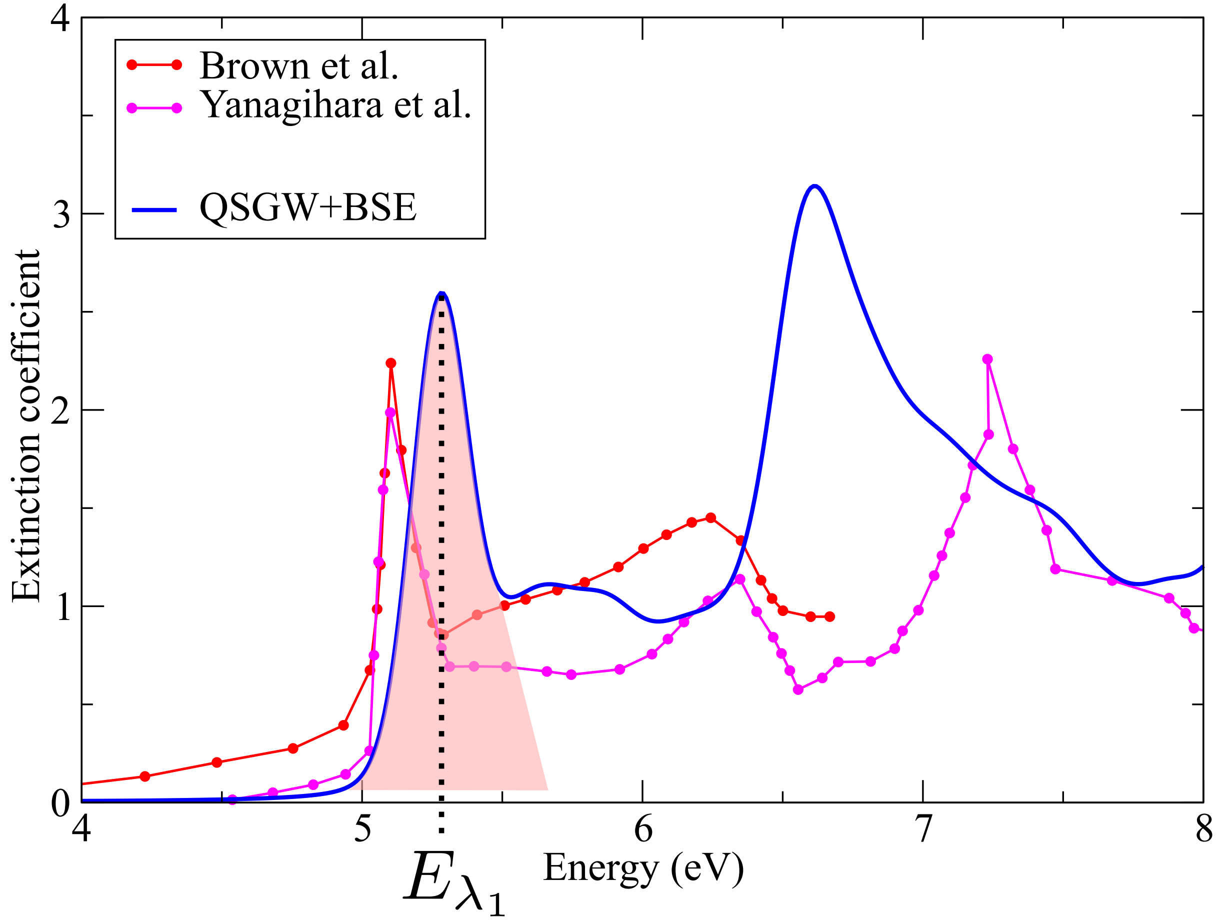
Palummo *et al.*, J. Chem.

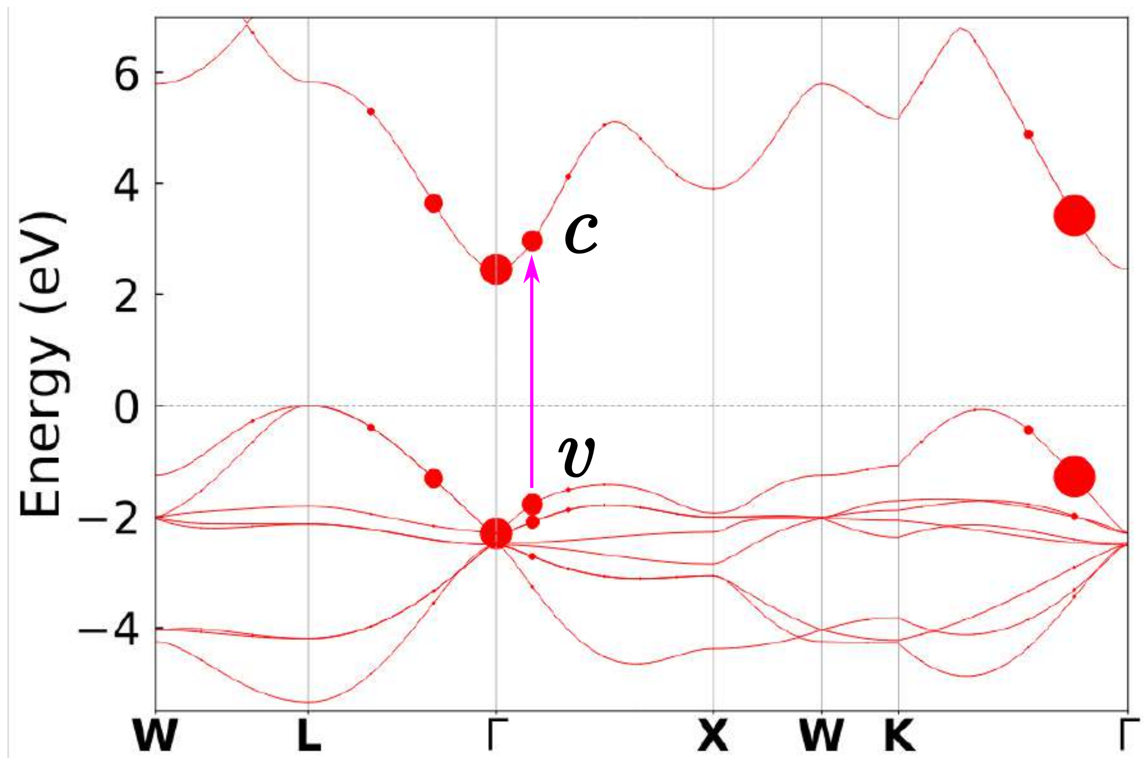
Phys. Rev. B **76** 1611

022 (2018)

AgCl absorption

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





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

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

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

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

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

$$\boldsymbol{\delta\left(\omega - (E_f - E_0)\right)}$$

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

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

$c \rightarrow$ conduction state

$v \rightarrow$ valence state

$\mu \rightarrow$ core state

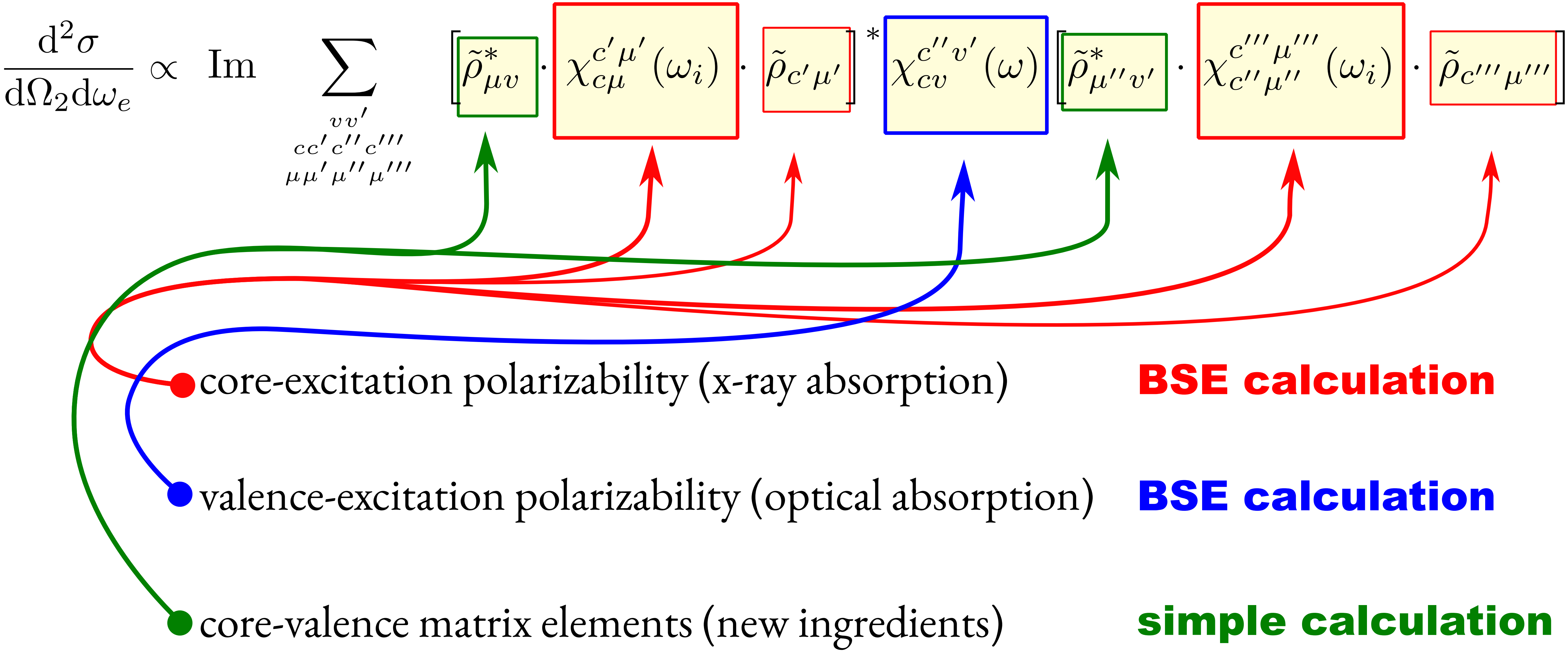
$$\chi^{v'c'}_{vc}(\omega) = \int d\mathbf{r} d\mathbf{r}' \ \psi^*_c(\mathbf{r})\psi_v(\mathbf{r}) \ \chi(\mathbf{r}, \mathbf{r}', \omega) \ \psi^*_{v'}(\mathbf{r})\psi_{c'}(\mathbf{r})$$

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

eigenvectors and eigenvalues of the BSE Hamiltonian

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

independent-particle (dipole) matrix elements



$$\frac{d^2\sigma}{d\Omega_2 d\omega_e} \propto \mathrm{Im} \sum_{\substack{vv' \\ cc'c''c''' \\ \mu\mu'\mu''\mu'''}} \left[\tilde{\rho}^*_{\mu v} \cdot \chi^{c'\mu'}_{c\mu}(\omega_i) \cdot \tilde{\rho}_{c'\mu'}\right]^* \chi^{c''v'}_{cv}(\omega) \left[\tilde{\rho}^*_{\mu''v'} \cdot \chi^{c'''\mu'''}_{c''\mu''}(\omega_i) \cdot \tilde{\rho}_{c'''\mu'''}\right]$$
core-excitation polarizability (x-ray absorption)
BSE calculation
valence-excitation polarizability (optical absorption)
BSE calculation
core-valence matrix elements (new ingredients)
simple calculation

- RIXS scheme
- **Derivation in terms of excitation pathways**
- Example :: LiF
- Atomic Coherence in RIXS
- Towards shallow core excitations:
  pseudo-potentials vs all-electron approaches

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

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

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

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

oscillator strength of the excitation

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

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

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

excitation pathway

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

oscillator strength of the excitation

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

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

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

oscillator strength of the excitation

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

← RIXS oscillator strength

BRIXS (and pyBRIXS) code on Gitlab

(C.Vorwerk, ..)

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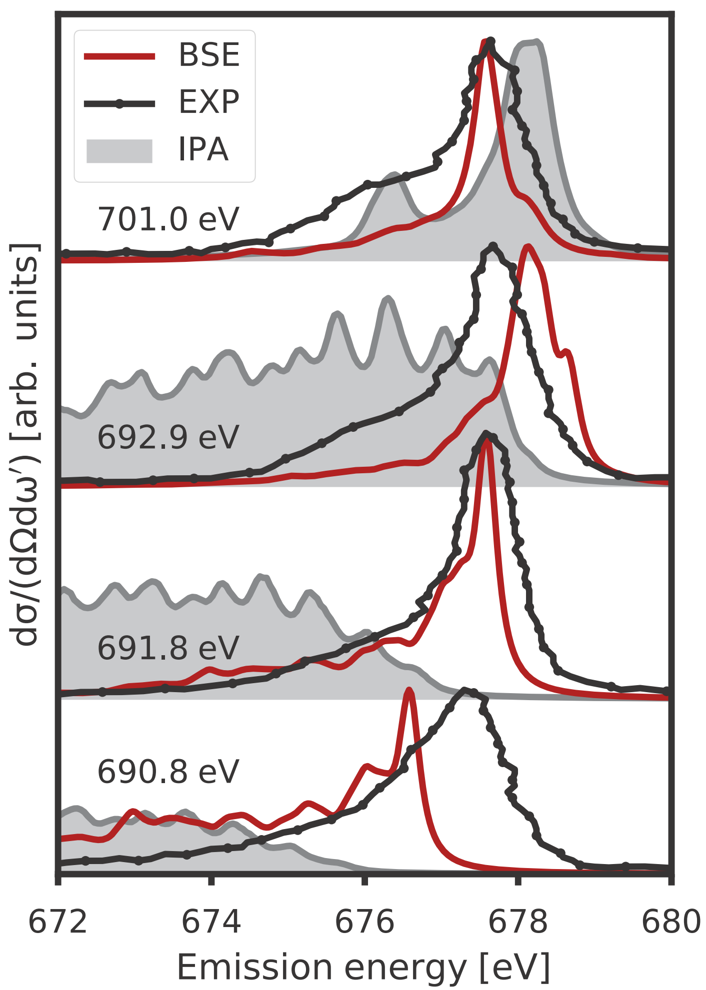
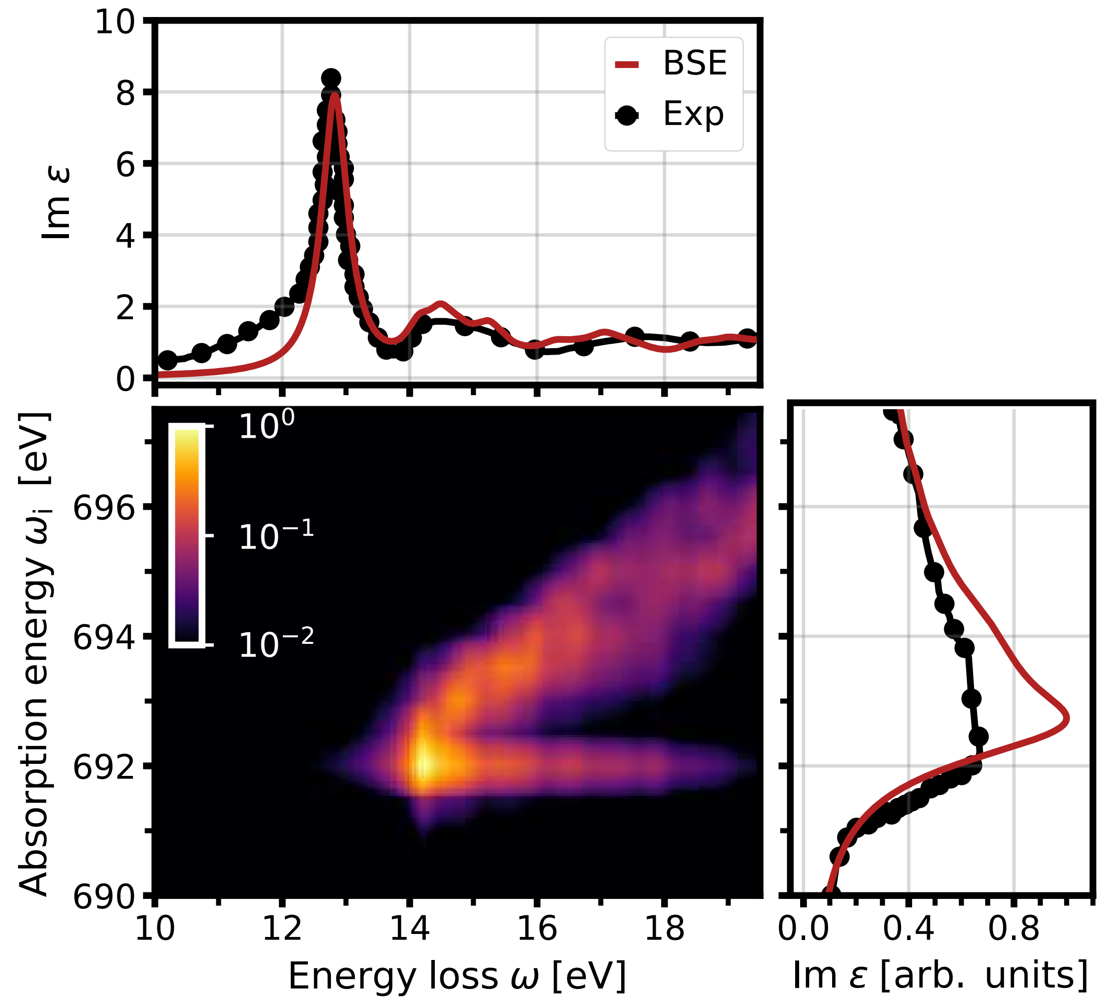
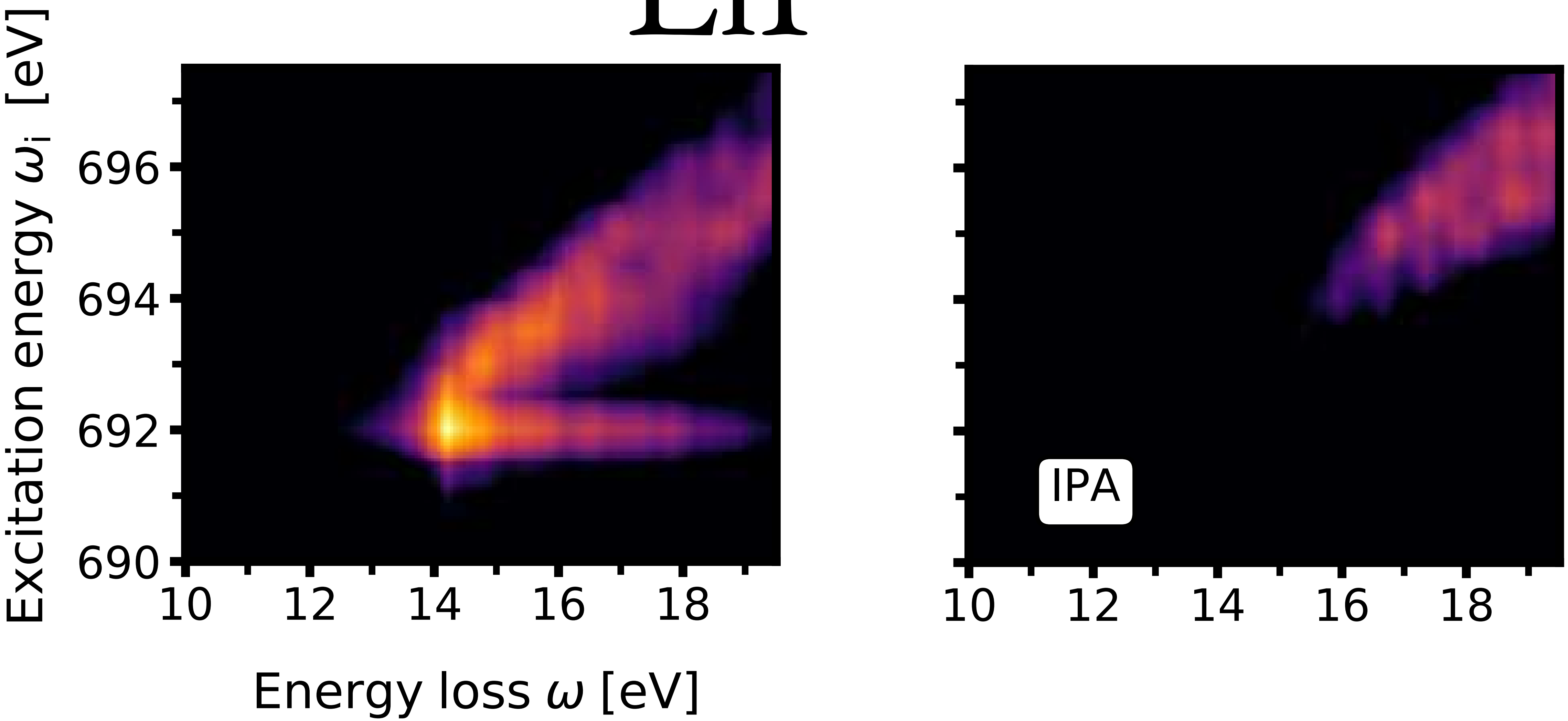
RIXS LiF at F K edge





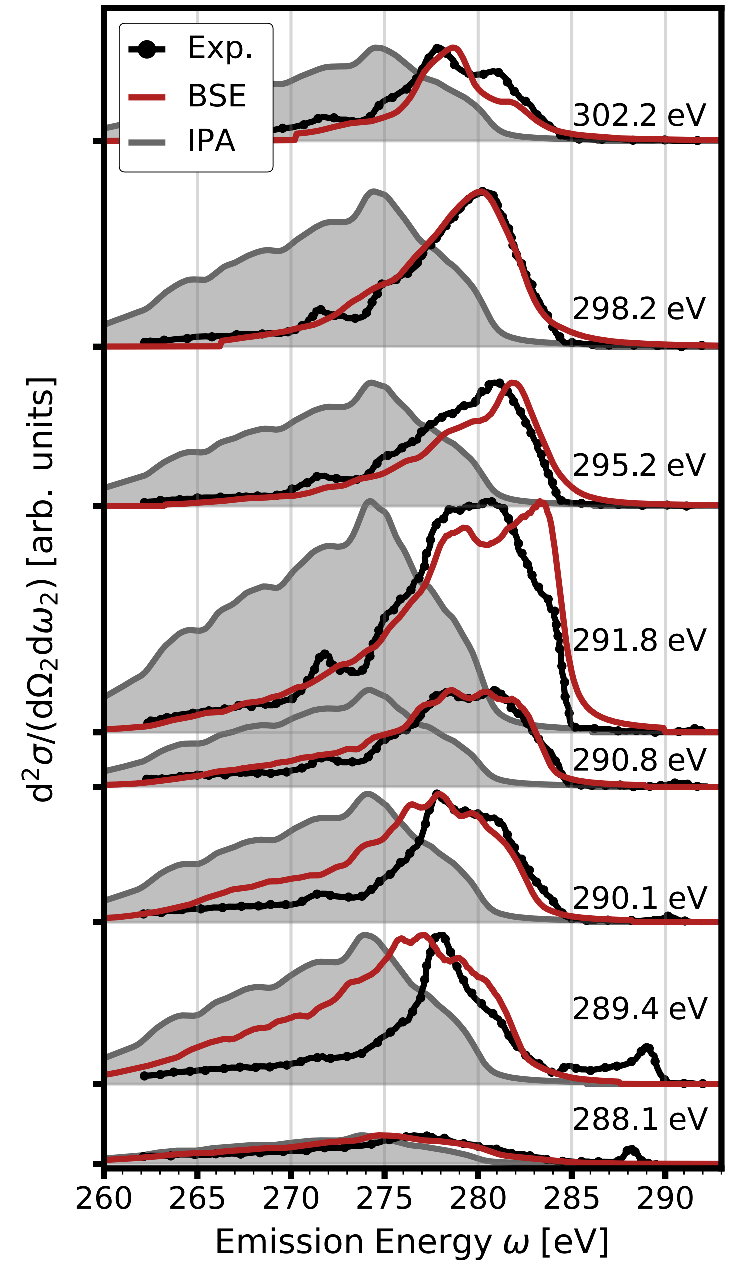
Vorwerk *et al.* Phys. Rev. Research **2**, 042003(R) (2020)

LiF



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

RIXS diamond
C K-edge



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

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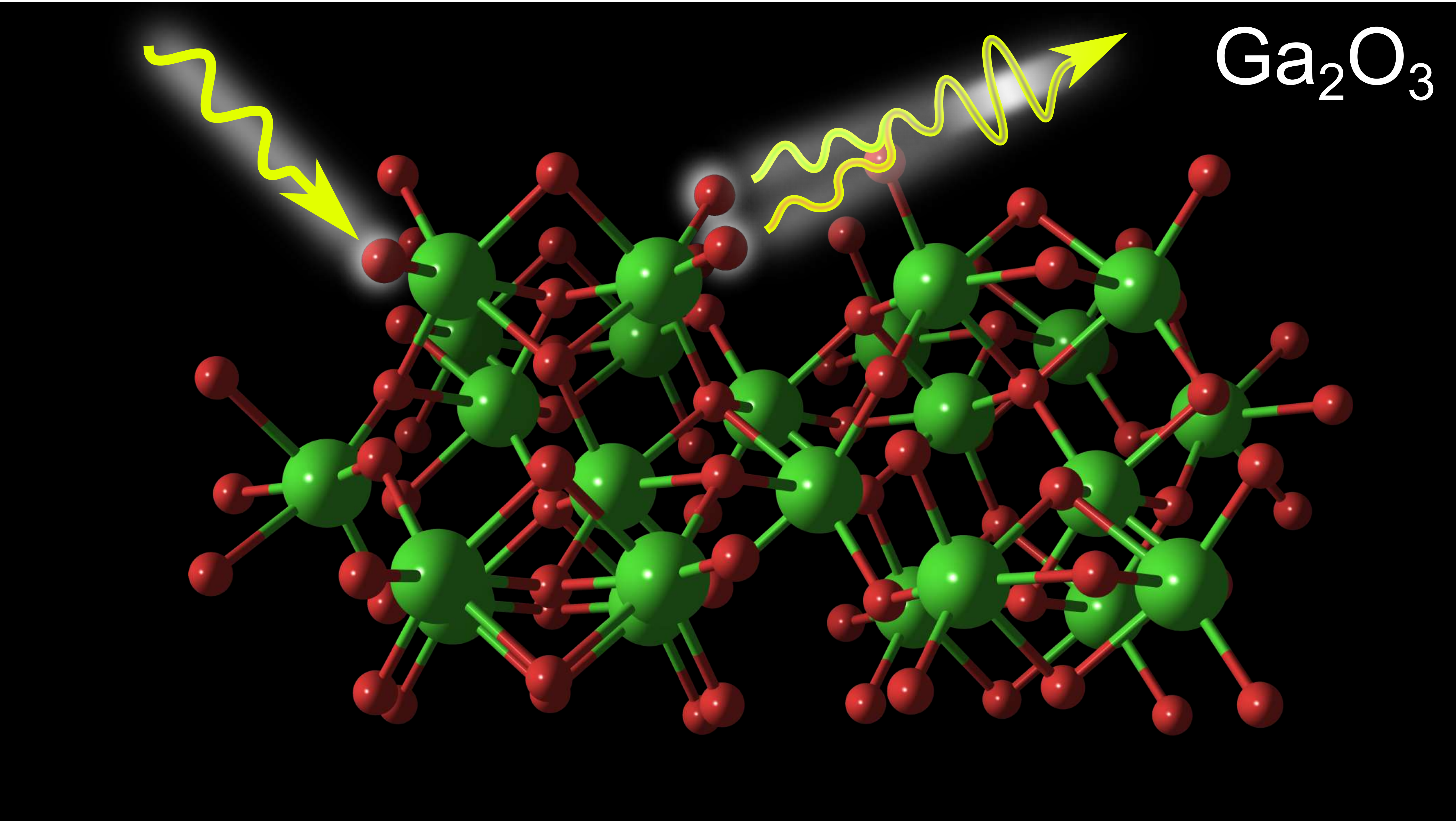
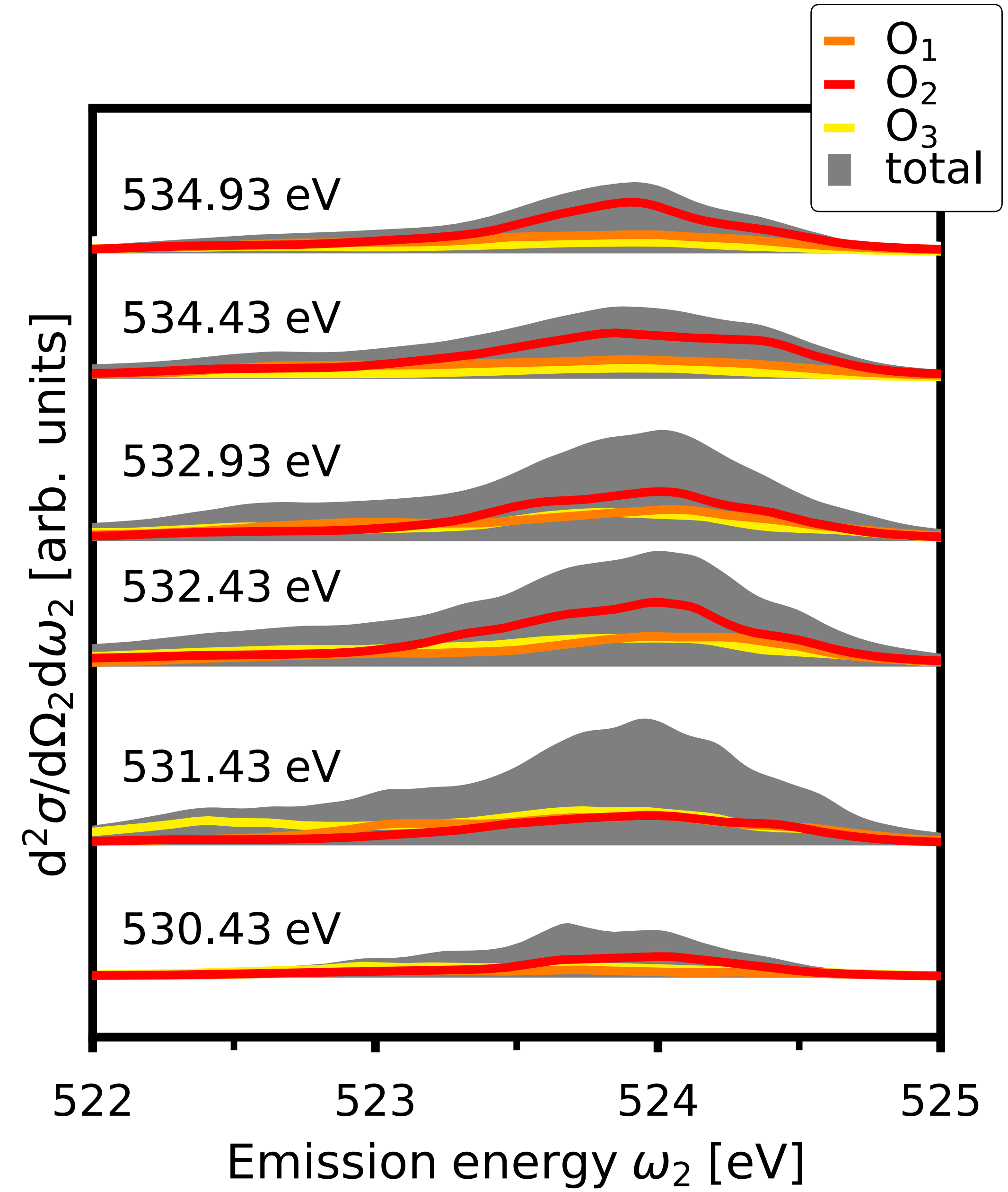
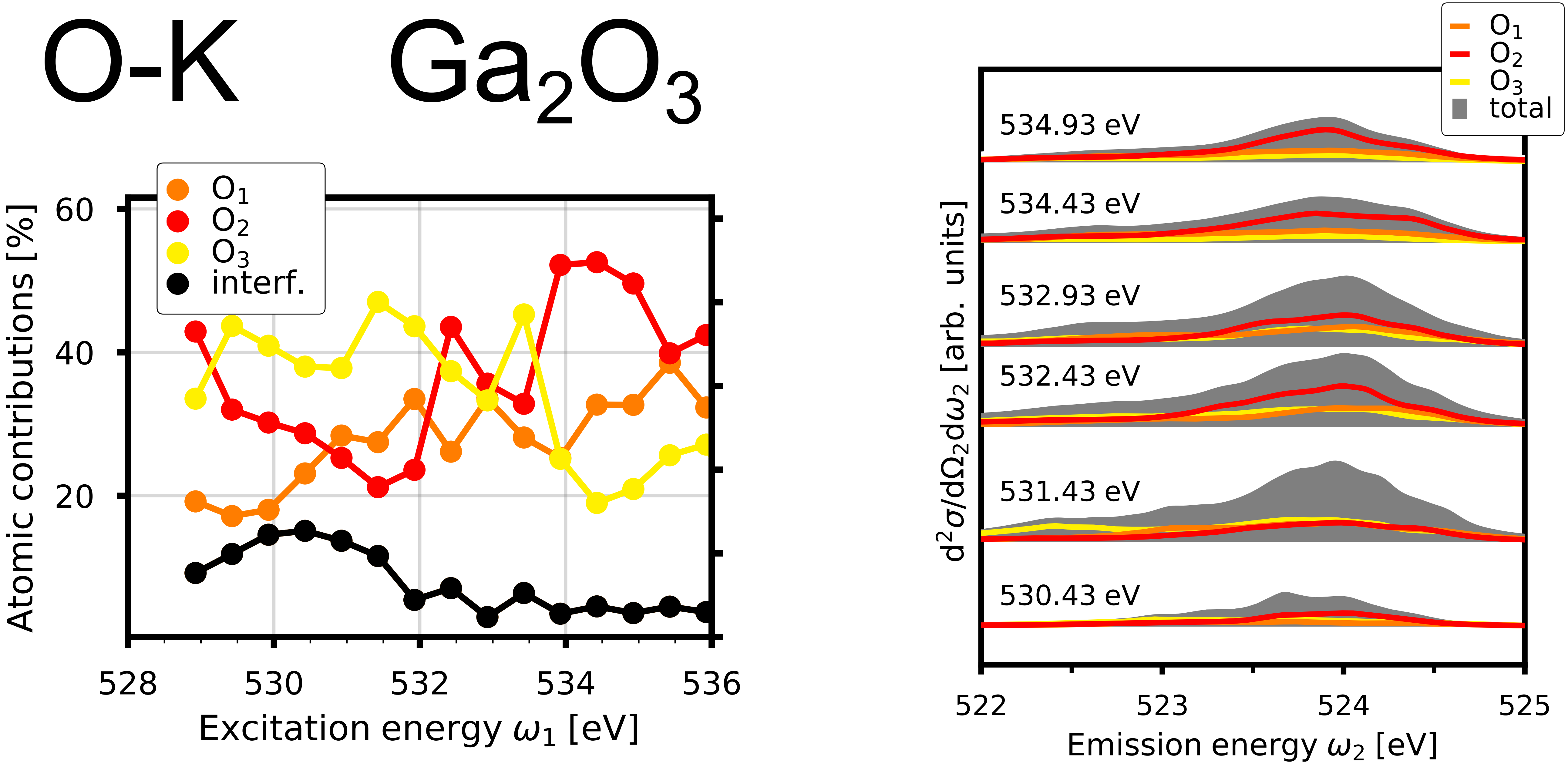

Ga_2O_3

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 Ga2O3
O1
O2
O3
interf.
Atomic contributions [%]
60
40
20
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]

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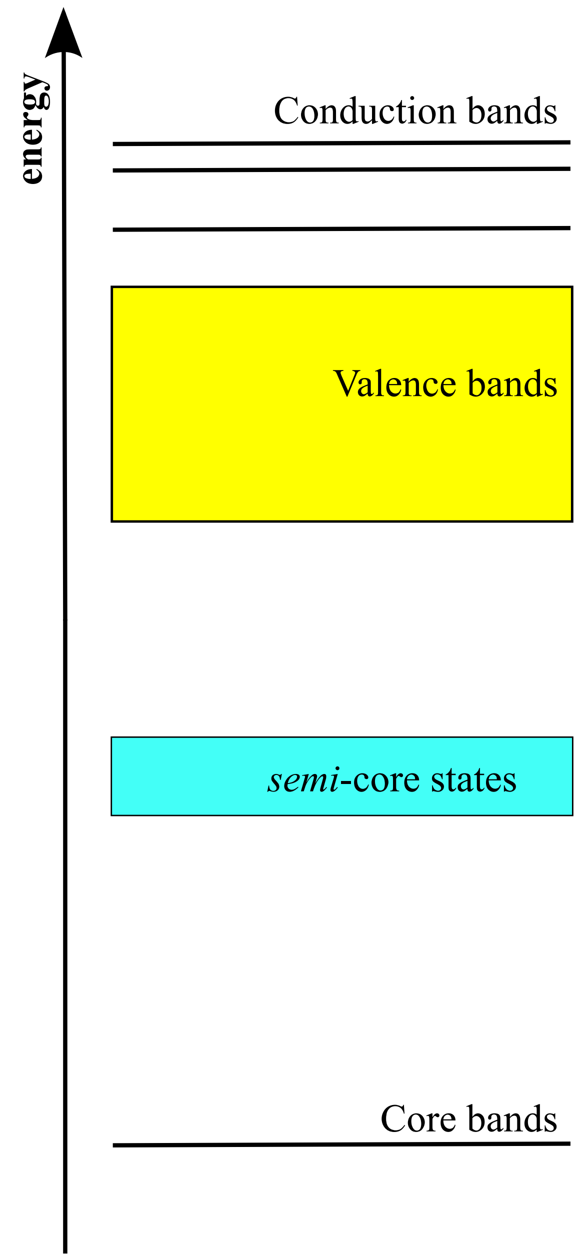
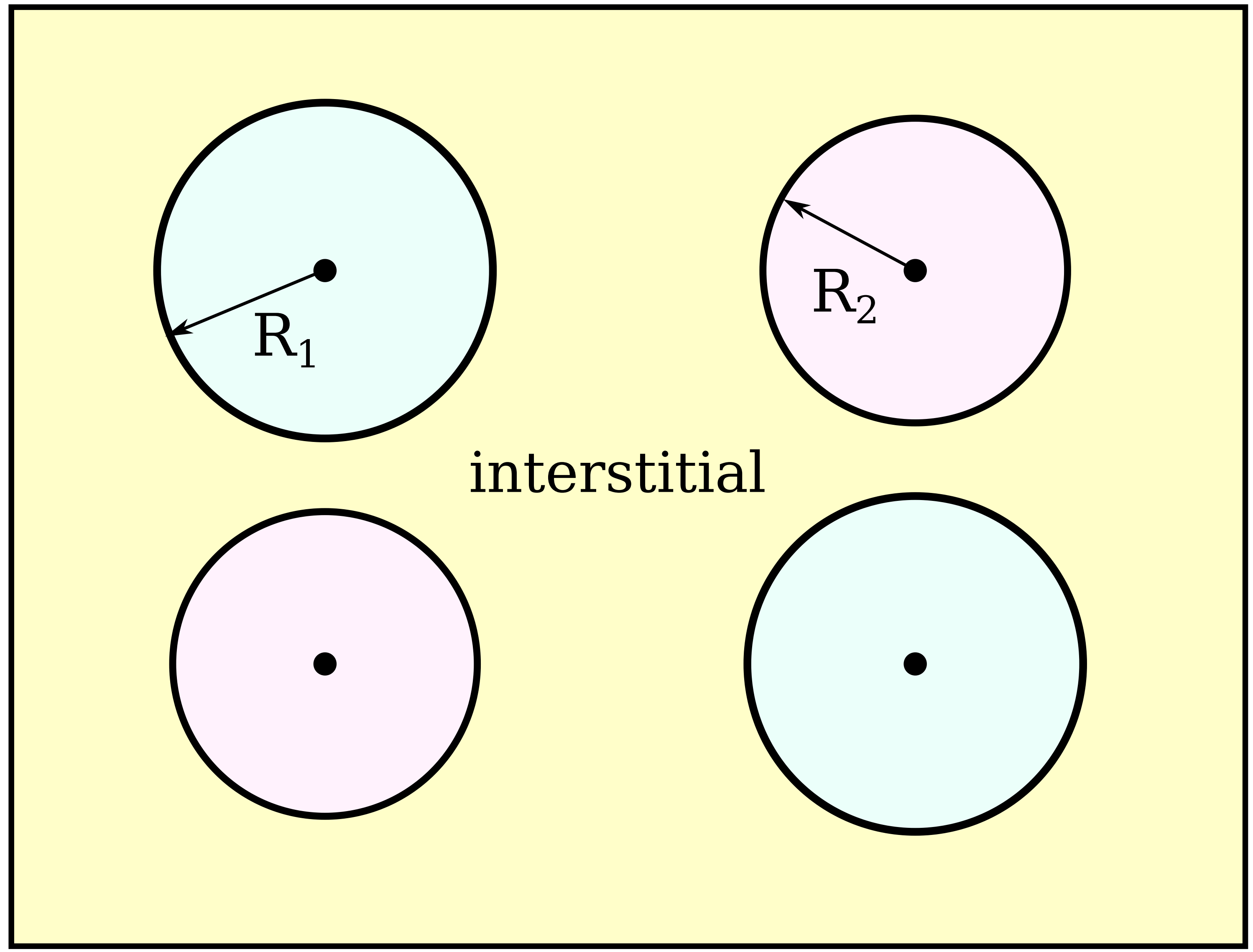
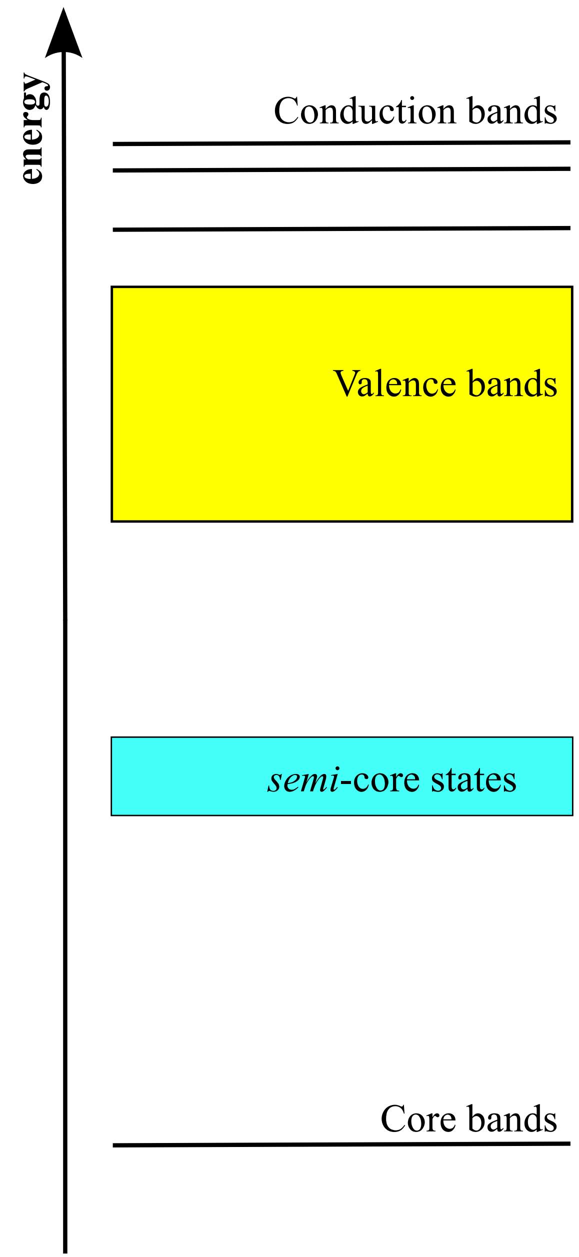
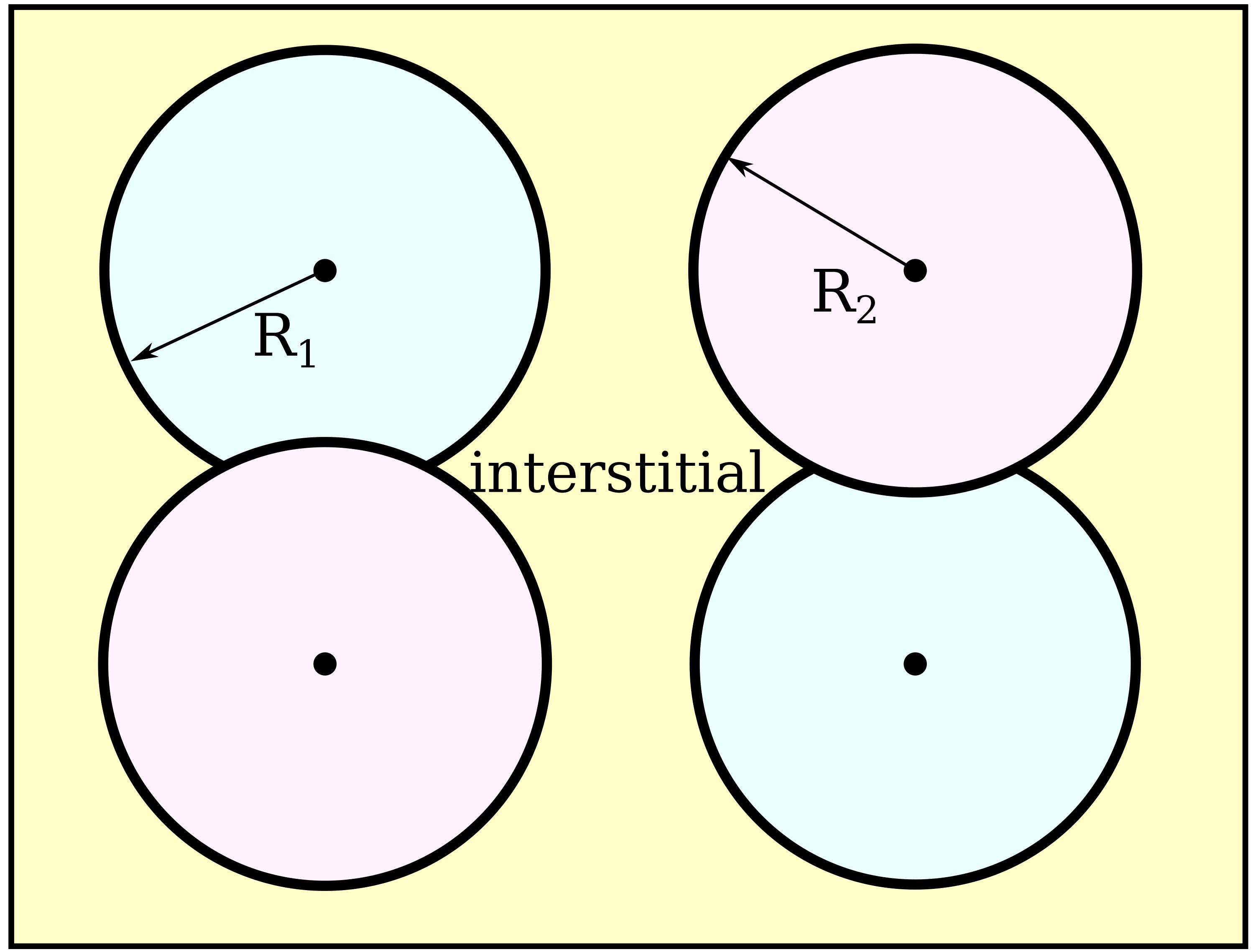


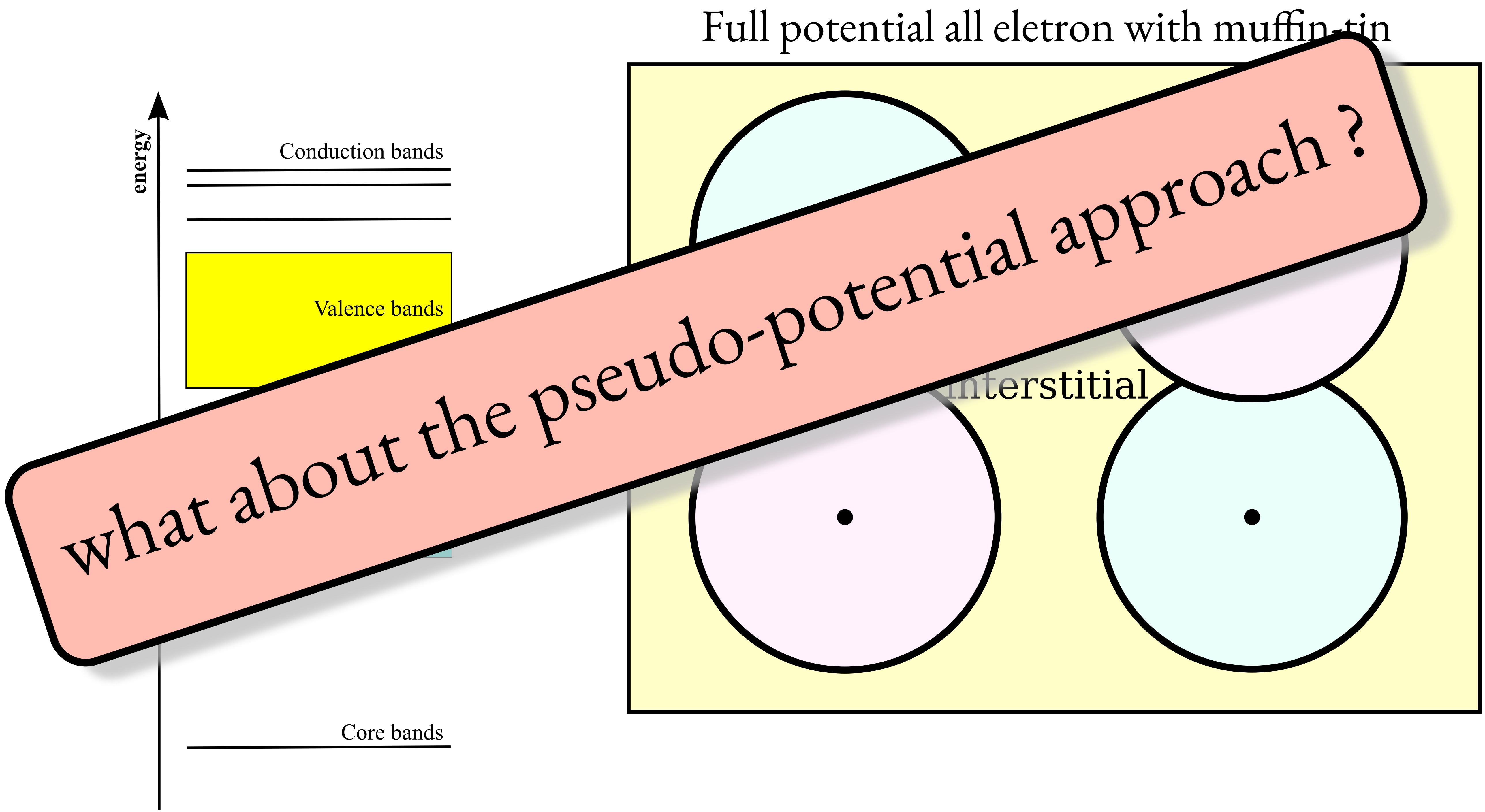
Full potential all eletron with muffin-tin



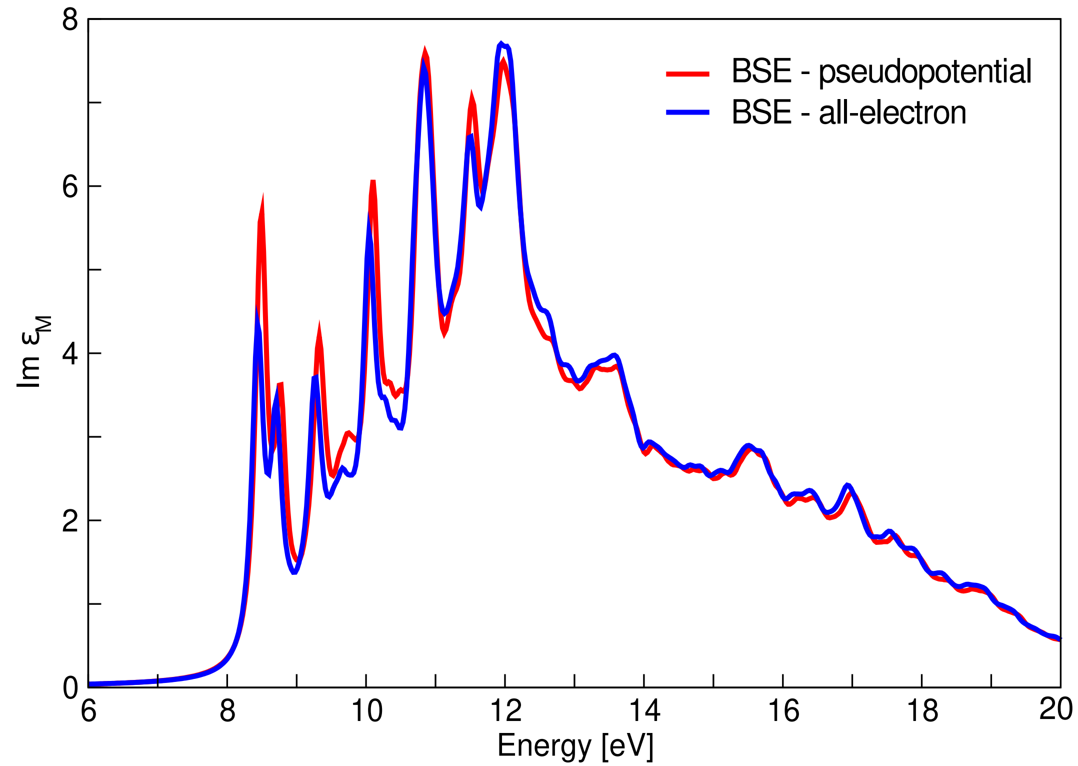


Full potential all eletron with muffin-tin




Full potential all eletron with muffin-tin
energy
Conduction bands
Valence bands
Core bands
interstitial
what about the pseudo-potential approach ?

optical absorption of Al_2O_3

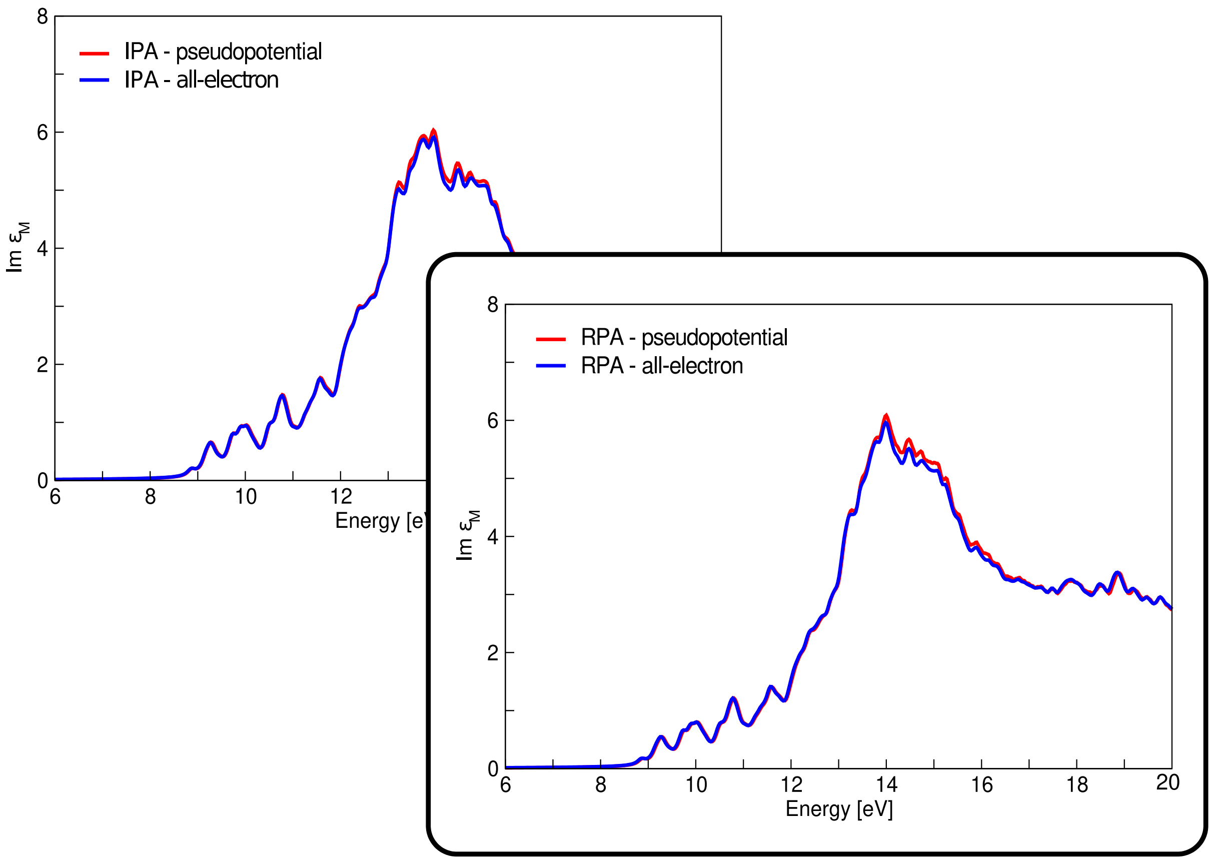


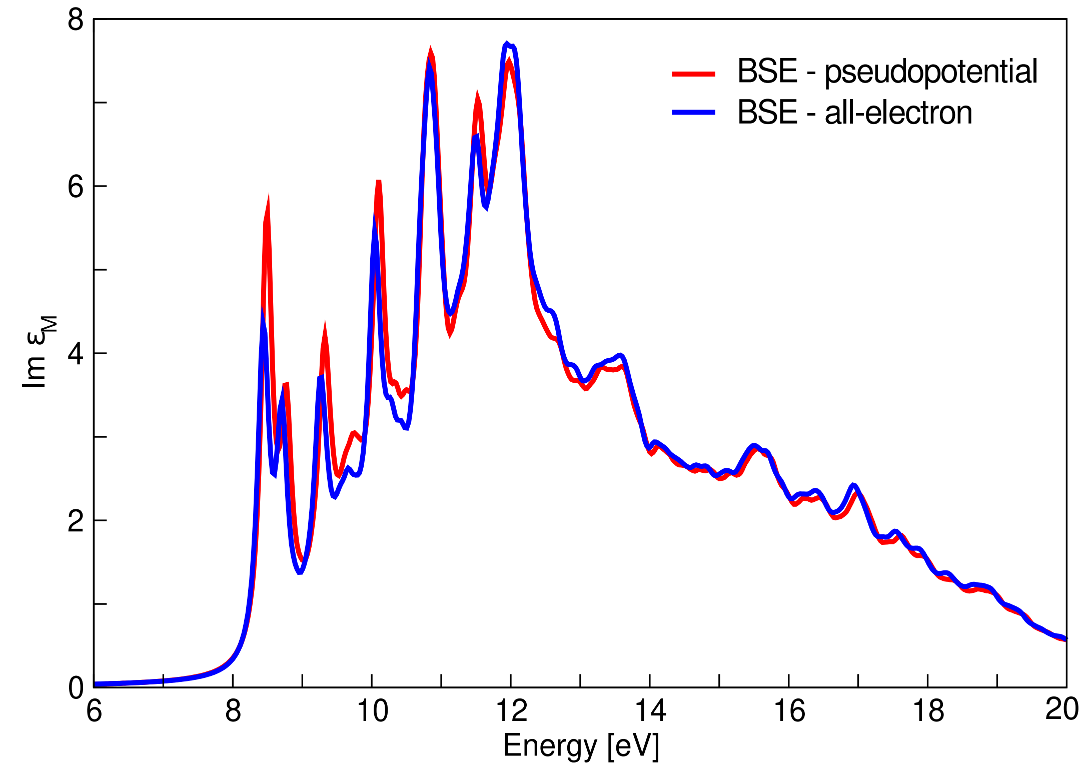
Exciting Code, A. Gulans *et al.*, J. Phys.: Condens. Matter **26**, 363202 (2014)

Abinit, X. Gonze *et al.*, Comput. Phys. Commun. 205, 106 (2016)

Exc code, L. Reining *et al.*, `https://etsf.polytechnique.fr/software/Ab_Initio/`

optical absorption of Al_2O_3





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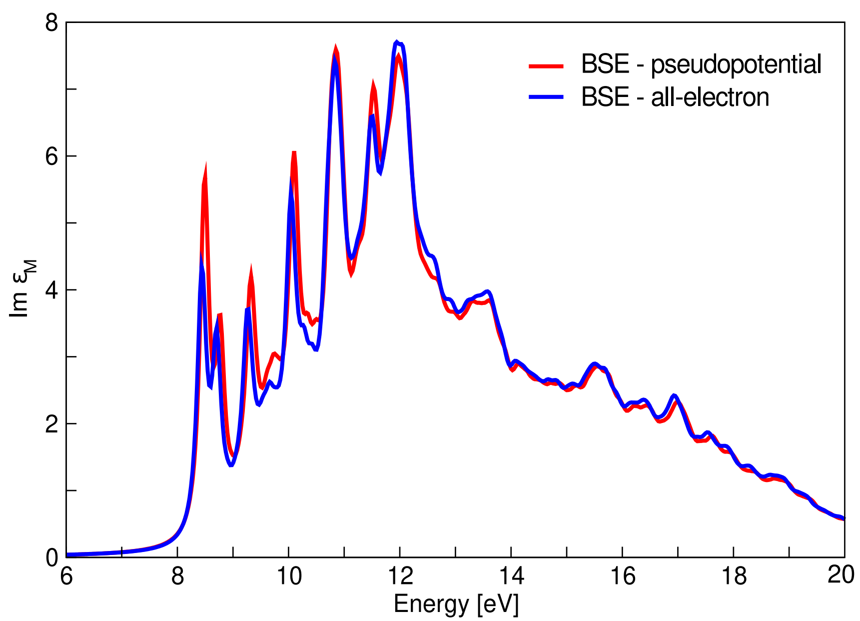
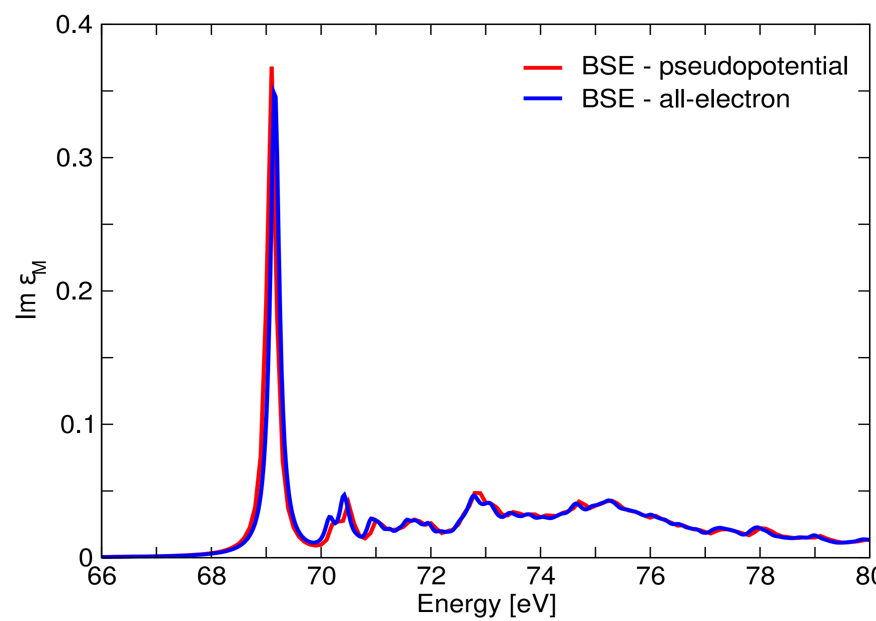
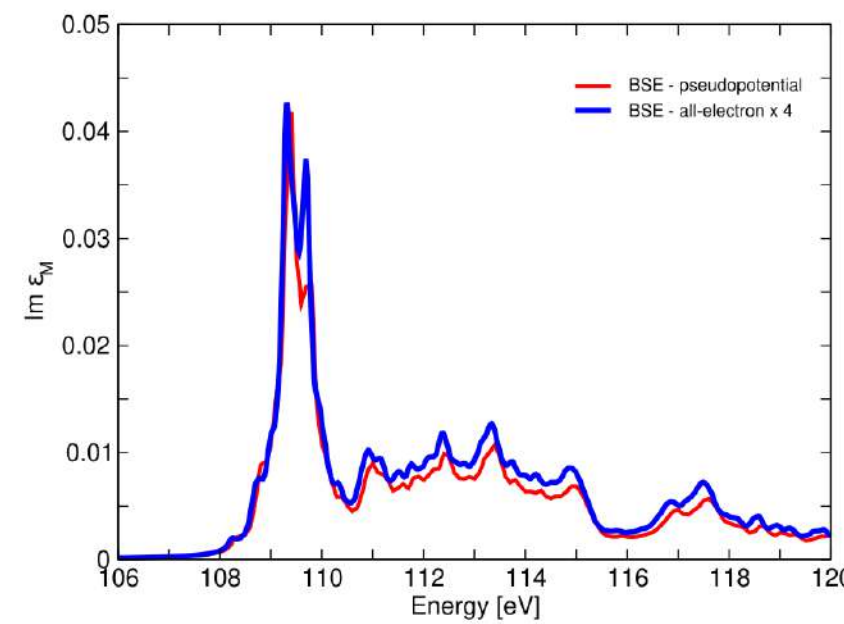
Optical and X-ray absorption of Al_2O_3
All-electron vs pseudo-potential



optical



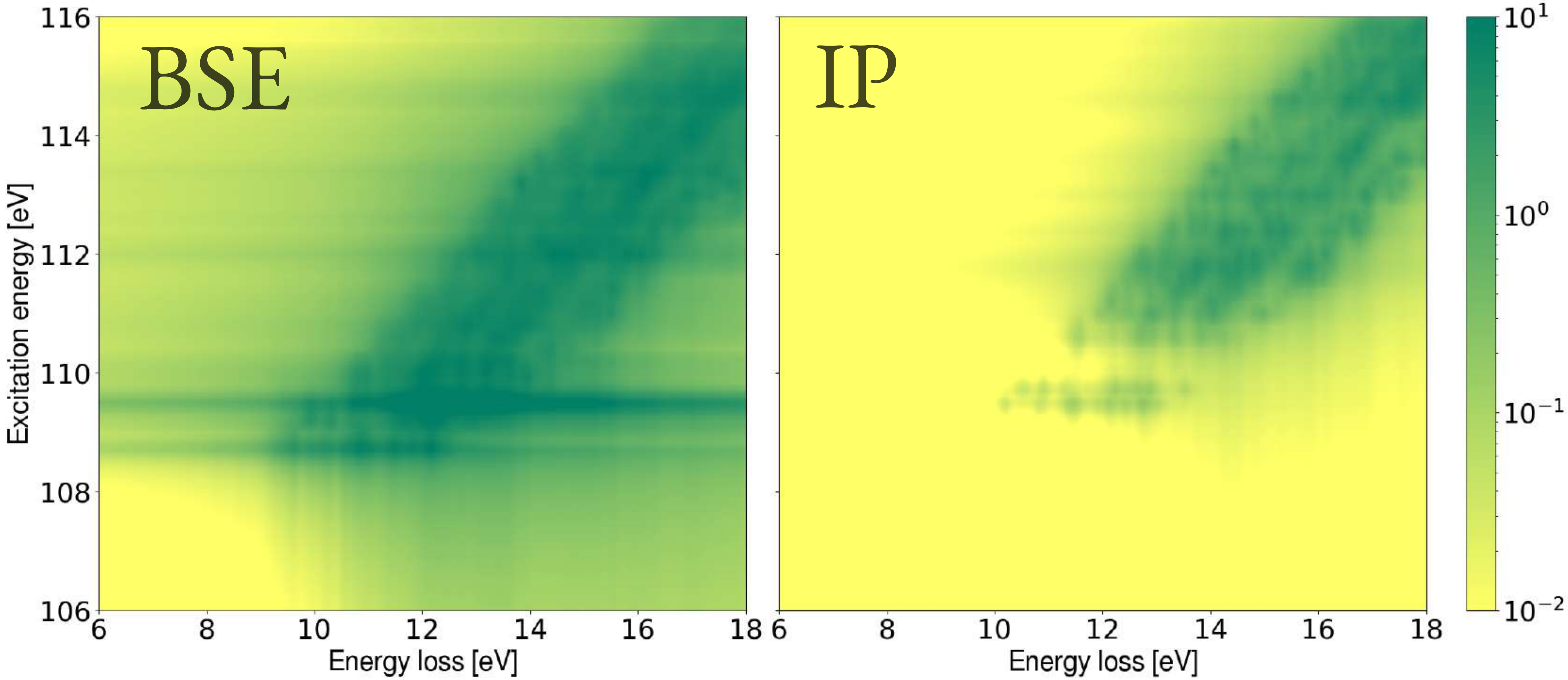
$L_{2,3}$



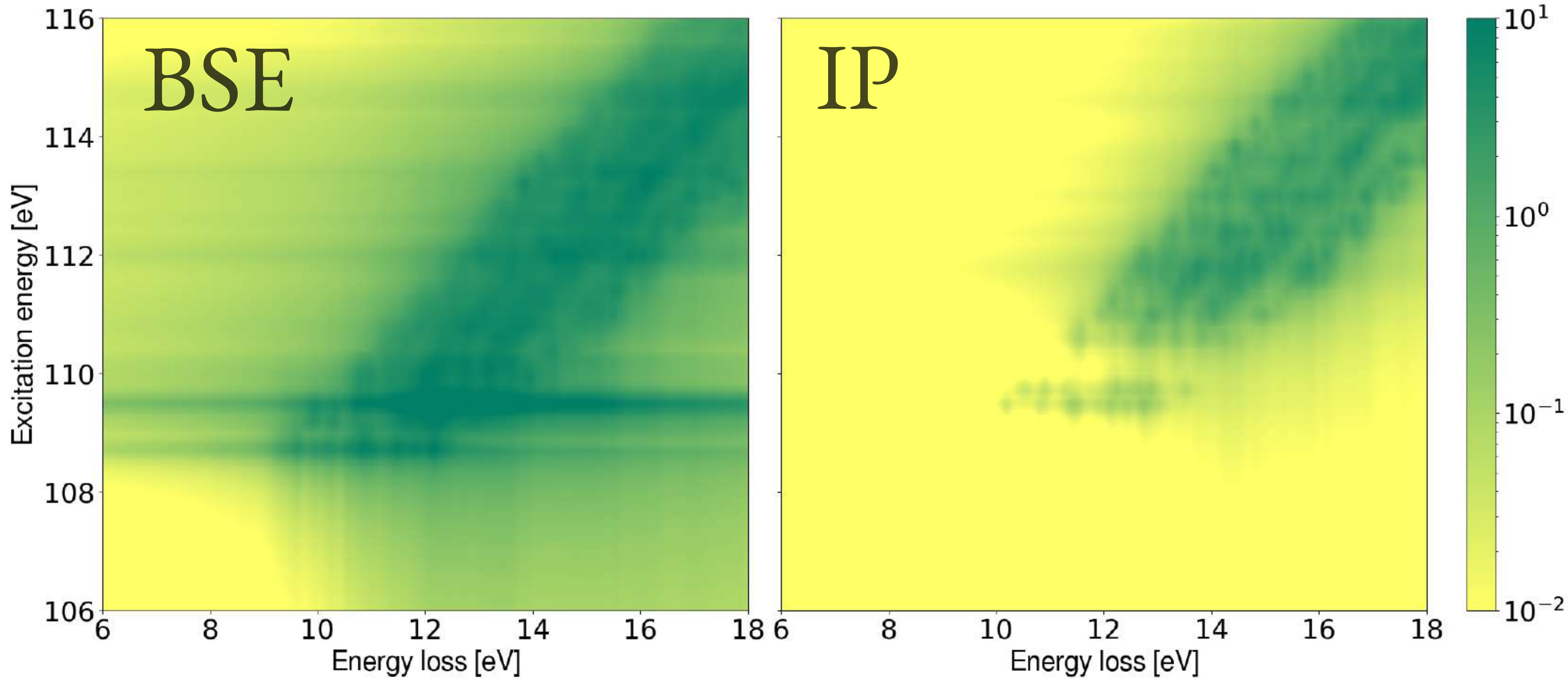
L_1

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

Preliminar RIXS of Al_2O_3 at $L_{2,3}$ edge of Al



M.L. Urquiza, M. Gatti, F. Sottile, working on it



- Beamtime for Abs and RIXS in L_1 and $L_{2,3}$ edge of Al at SOLEIL (A.Nicolau)
- Beamtime for time-dependent RIXS in hBN at FERMI (M.Malvestuto)

Conclusions

- RIXS within BSE
  in terms of excitation pathways
- Reliable results with LiF, Diamond, Ga_2O_3
- Interferences effects might play a role
- RIXS for shallow semi-core electrons
  (also) with pseudo-potentials approach
- New experiments on the way (Al_2O_3, hBN)