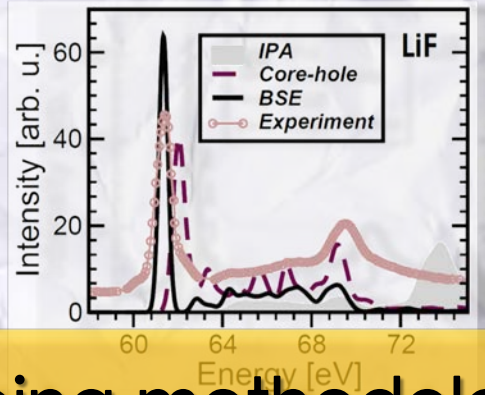
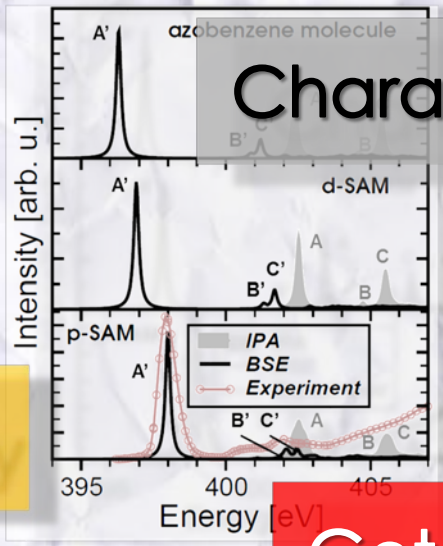
Many-body approach to core-level excitations

CLAUDIA DRAXL

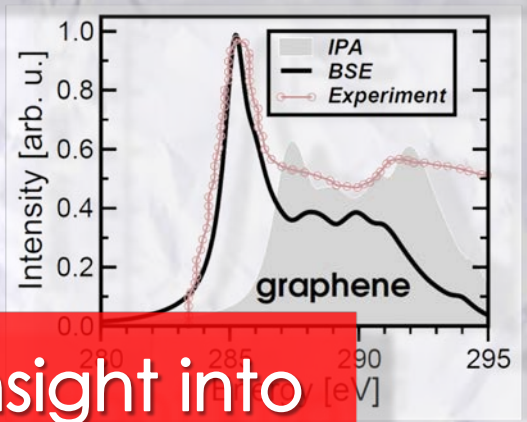
Why core spectroscopy?

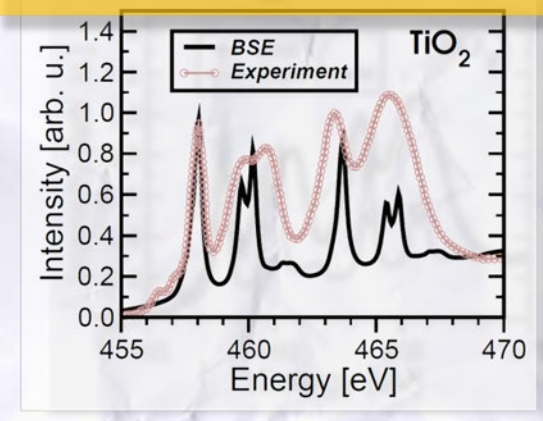


Probing methodology

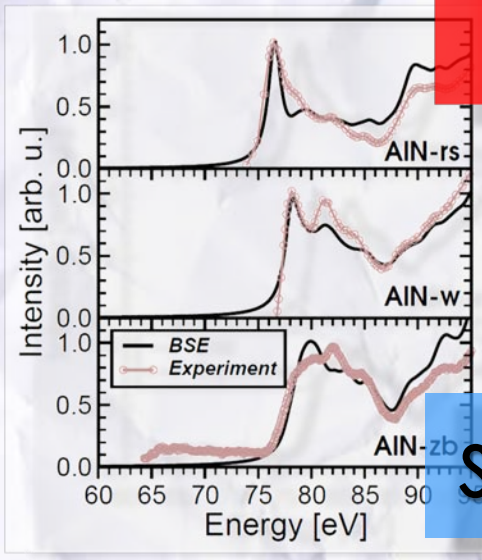


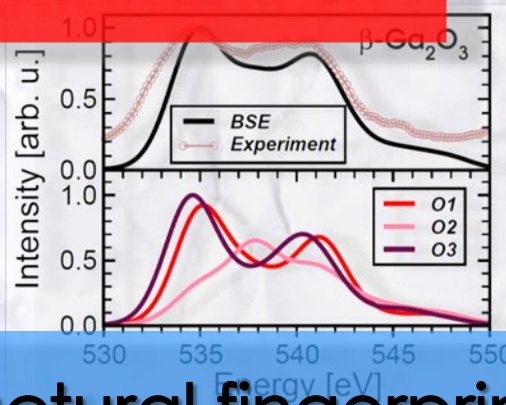
Characterize materials





Get insight into interactions





Structural fingerprints

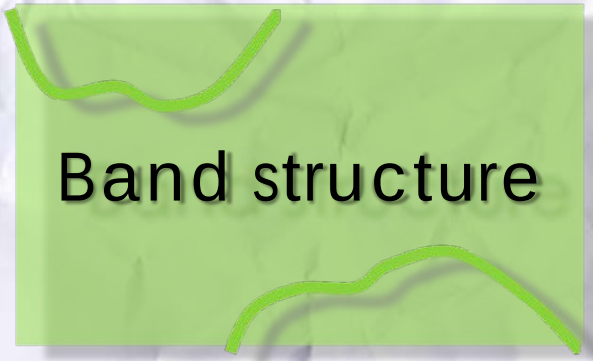
State of the art methodology

$$\left[H_{el} + H_{hole} + H_{el-hole}\right] A_\lambda = E_\lambda A_\lambda$$

Bethe-Salpeter equation

Many-body perturbation theory

G_0W_0 approximation



$$\epsilon_{n\mathbf{k}}^{QP} = \epsilon_{n\mathbf{k}}^{KS} + \left\langle n\mathbf{k} \middle| \Sigma - V_{xc}^{KS} \middle| n\mathbf{k} \right\rangle$$

Density-functional theory

Kohn-Sham equation

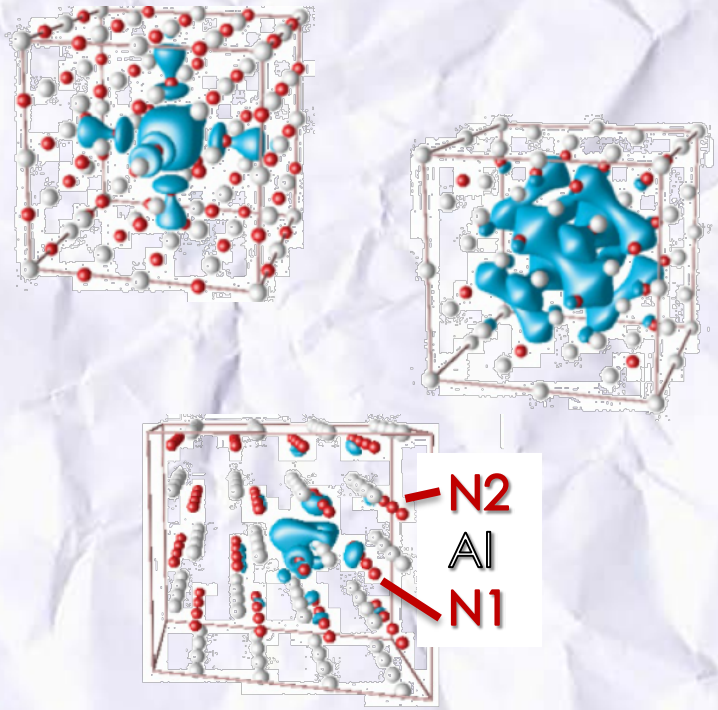
$$\left[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r})\right] \psi_i^{KS}(\mathbf{r}) = \epsilon_i^{KS} \psi_i^{KS}(\mathbf{r})$$

Structural fingerprints

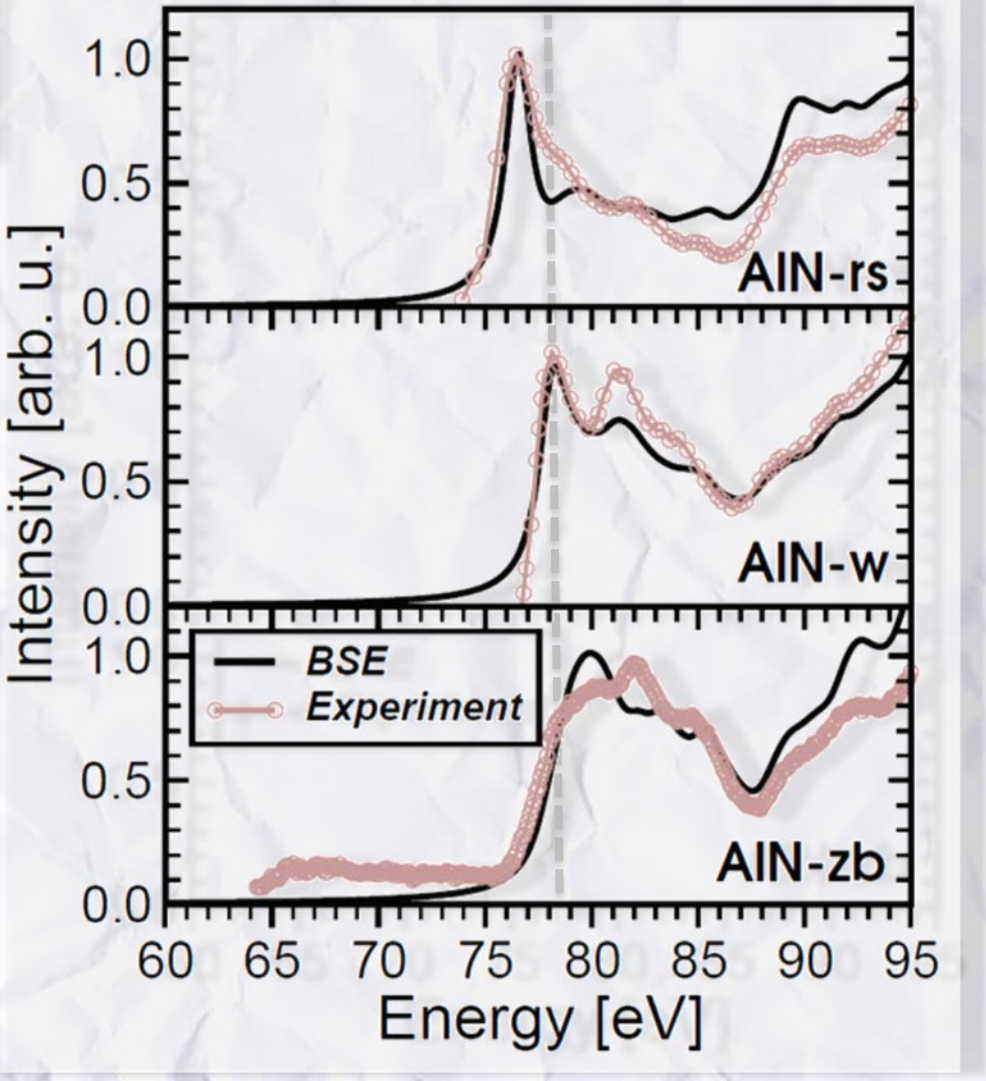
Exciton wavefunction

Bound states

$$\phi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cv} A_\lambda^{cv} \psi_c(\mathbf{r}_e)\, \psi_v(\mathbf{r}_h)$$



Al $L_{2,3}$ edge in AlN

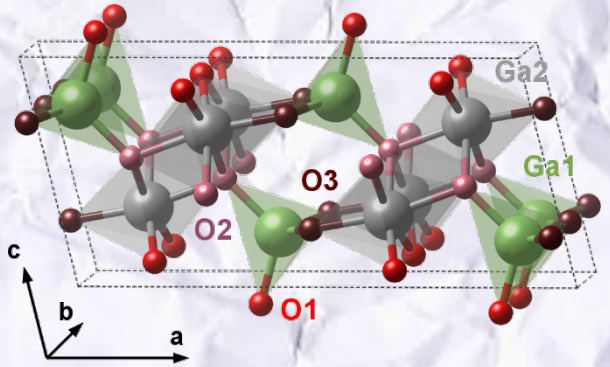


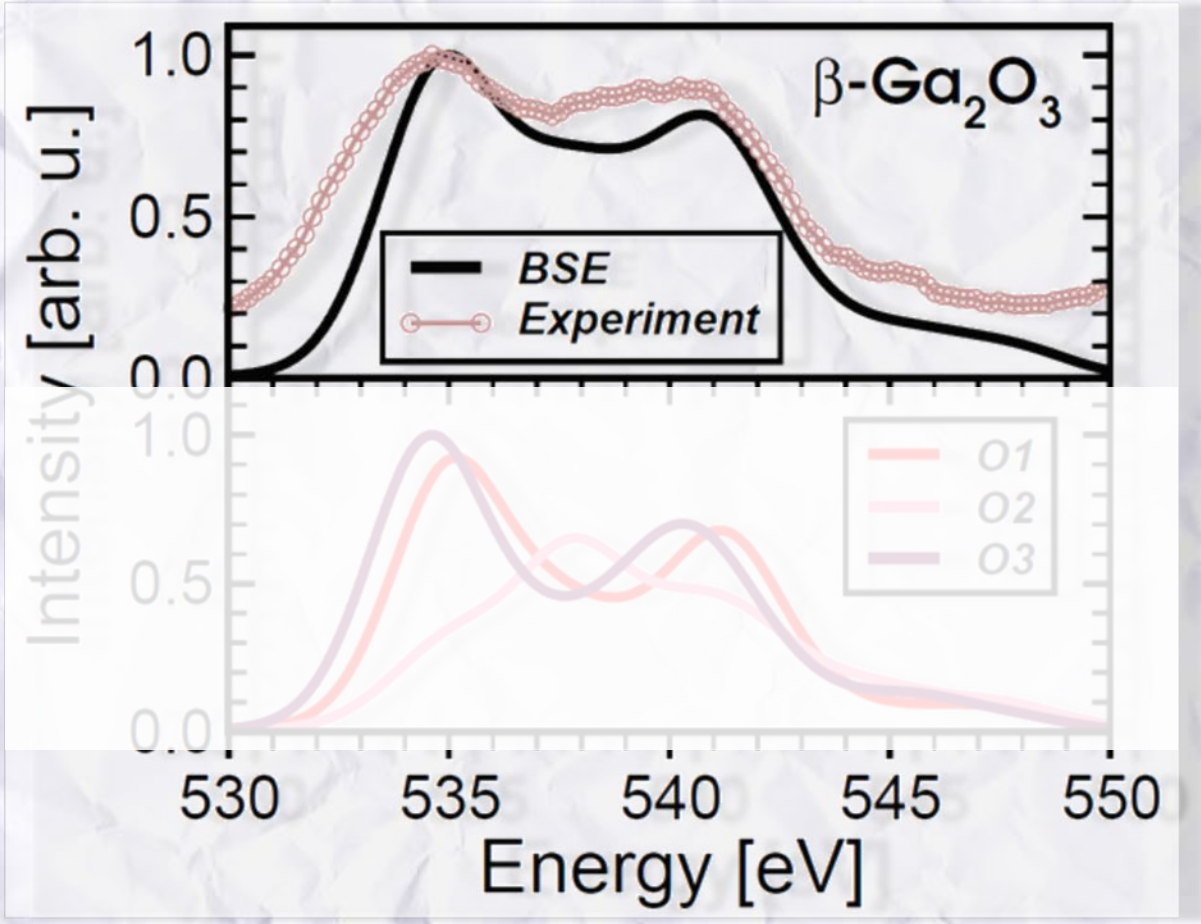
W. Olovsson et al., PRB **83**, 195206 (2011).

Structural fingerprints

O K edge in β-Ga_2O_3

Complementing ELNES experiments



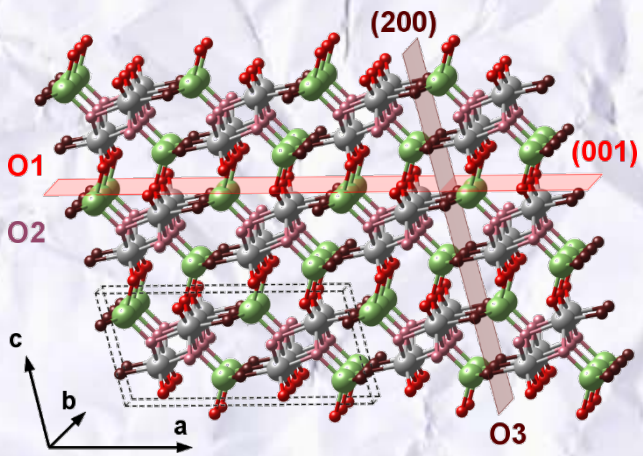


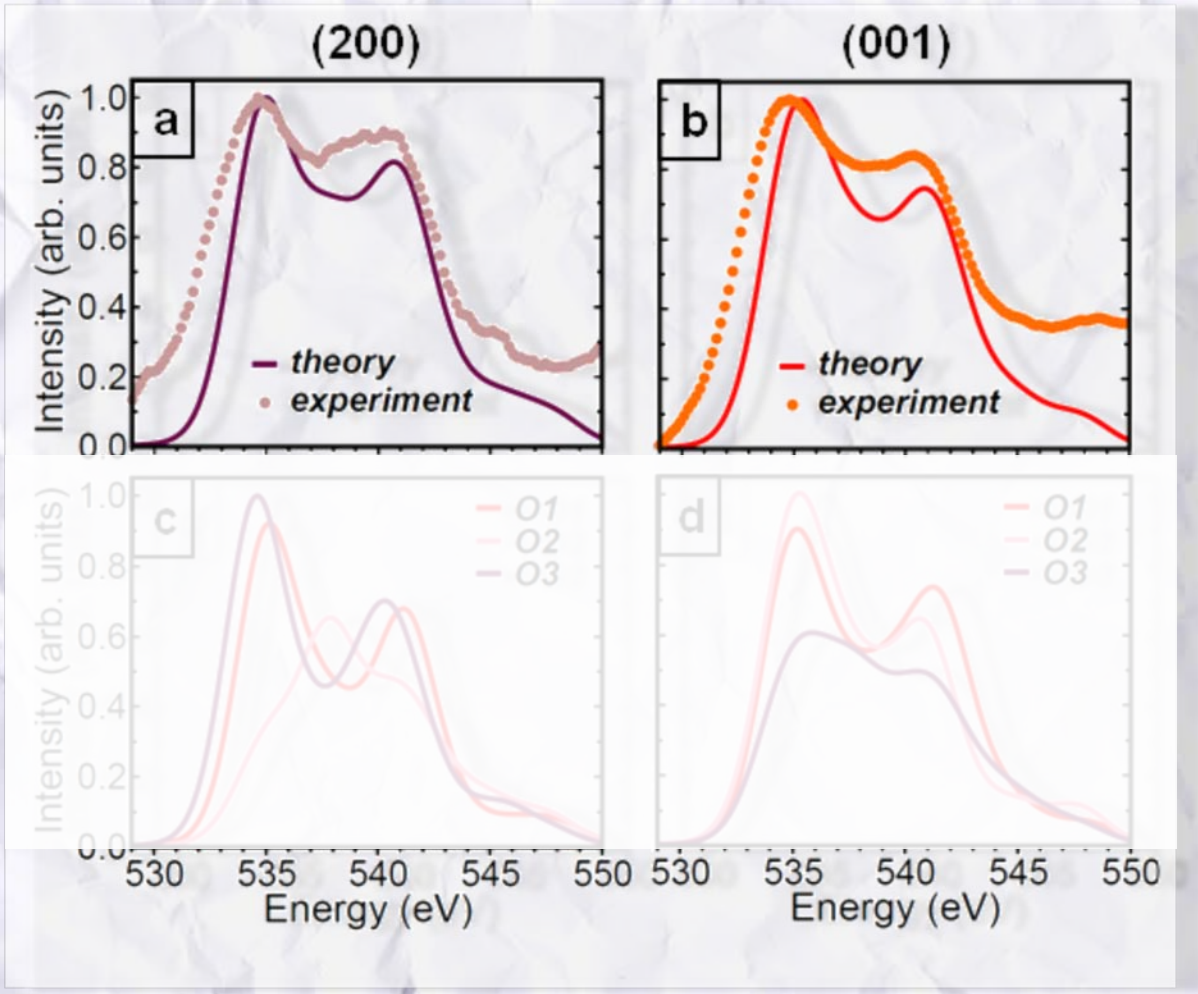
C. Cocchi et al., PRB (2016).

Structural fingerprints

O K edge in β-Ga_2O_3

Probing different index planes





C. Vorwerk, C. Cocchi, and CD **Layer Optics**: Microscopic modeling of optical coeffcients in layered materials Comp. Phys. Commun. **201**, 119 (2016).

C. Cocchi et al., PRB (2016).

Bethe-Salpeter equation

Valence vs core excitations !!

$$H^{e-h} = H^{diag} + H^{dir} + H^{x}$$

Diagonal term

$$H^{\text{diag}}_{vc\mathbf{k},v'c'\mathbf{k}'} = (\varepsilon_{c\mathbf{k}} - \varepsilon_{v\mathbf{k}})\delta_{vv'}\delta_{cc'}\delta_{\mathbf{k}\mathbf{k}'}$$

Metals
Semiconductors
Insulators
Molecules

Direct term - attractive

$$H^{\text{dir}}_{cv\mathbf{k},c'v'\mathbf{k}'} = \int \mathrm{d}^3r\,\mathrm{d}^3r'\,\frac{\psi_{v\mathbf{k}}(\mathbf{r})\psi^*_{c\mathbf{k}}(\mathbf{r}')\,\epsilon^{-1}(\mathbf{r},\mathbf{r}')\,\psi^*_{v'\mathbf{k}'}(\mathbf{r})\psi_{c'\mathbf{k}'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Exchange term - repulsive

Local field effects

$$H^{\text{x}}_{vc\mathbf{k},v'c'\mathbf{k}'} = \int \mathrm{d}^3r\,\mathrm{d}^3r'\,\psi_{v\mathbf{k}}(\mathbf{r})\psi^*_{c\mathbf{k}}(\mathbf{r})\,\bar{v}(\mathbf{r},\mathbf{r}')\,\psi^*_{v'\mathbf{k}'}(\mathbf{r}')\psi_{c'\mathbf{k}'}(\mathbf{r}')$$

Bethe-Salpeter equation

for core excitations

$$\sum_{c'u'\mathbf{k}'} H^{e-h}_{cu\mathbf{k},c'u'\mathbf{k}'} A^{\lambda}_{c'u'\mathbf{k}'} = E^{\lambda} A^{\lambda}_{cu\mathbf{k}}$$

$$t^{\lambda}_{\alpha} = \sum_{cu\mathbf{k}} A^{\lambda}_{cu\mathbf{k}} \frac{\langle c\mathbf{k}|\hat{p}_{\alpha}|u\mathbf{k}\rangle}{\epsilon_{u\mathbf{k}} - \epsilon_{c}}$$

$$\epsilon^{\alpha\beta}_{M}(\omega) = \delta_{\alpha\beta} + \frac{4\pi}{V} \sum_{\lambda} \frac{t^{\lambda}_{\alpha} \left[t^{\lambda}_{\beta}\right]^{*}}{\omega - E^{\lambda} + \mathrm{i}\delta}$$

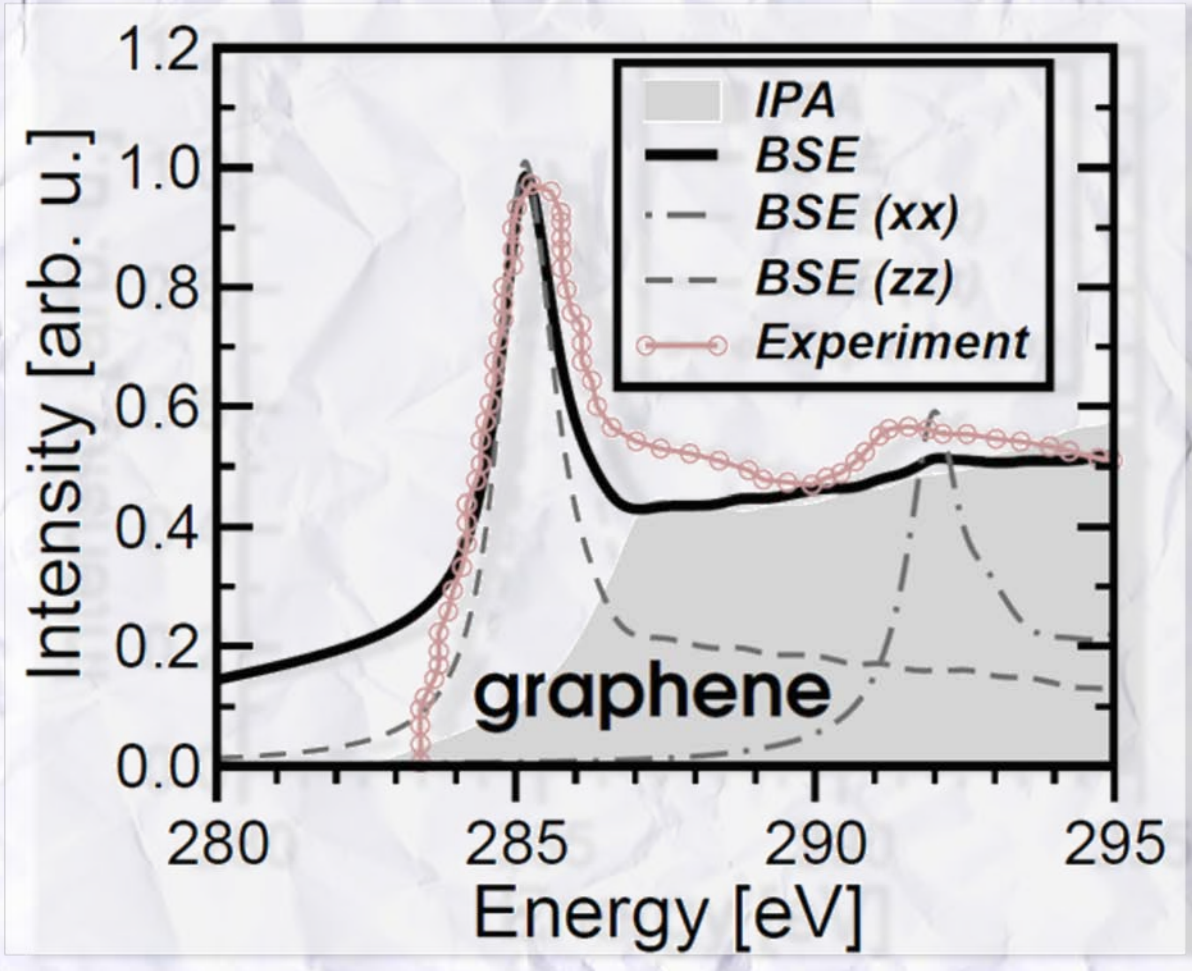
Transition coefficients

Dielectric tensor

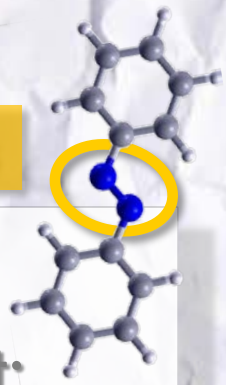
Carbon-based materials

C K edge in graphene

Sharp near-edge peak

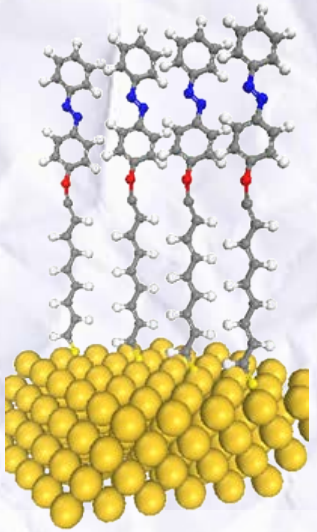


Organic molecules

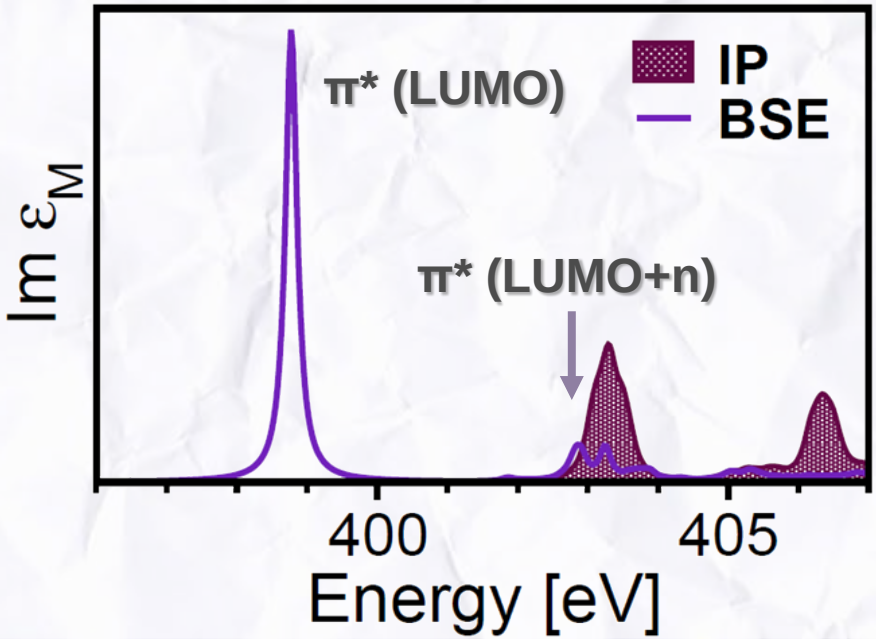


Azobenzene SAMs

Excellent agreement with experiment:
exciton character and realitve intensities

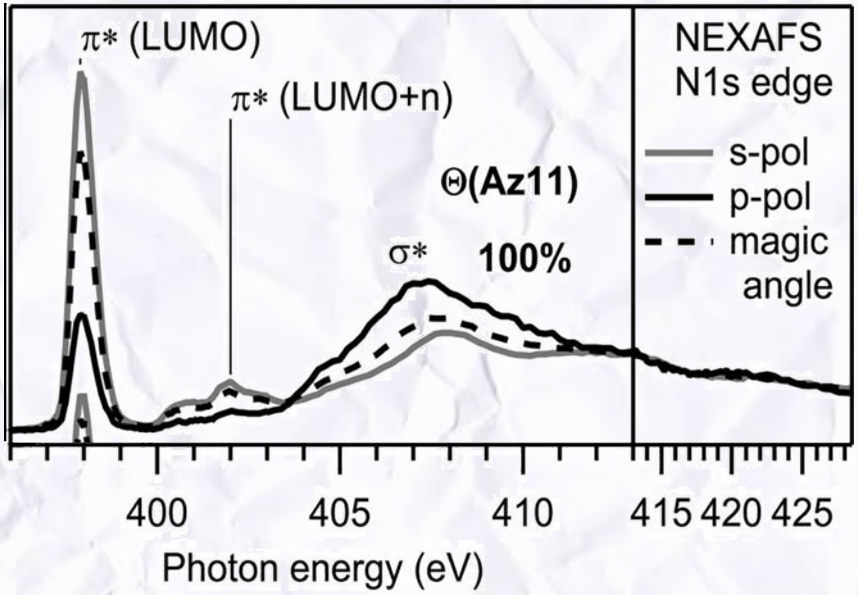


Theory



C. Cocchi & CD, PRB **92**, 205105 (2015).

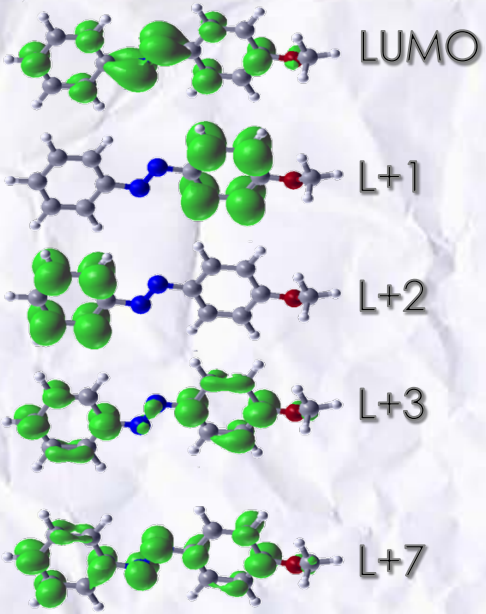
Experiment

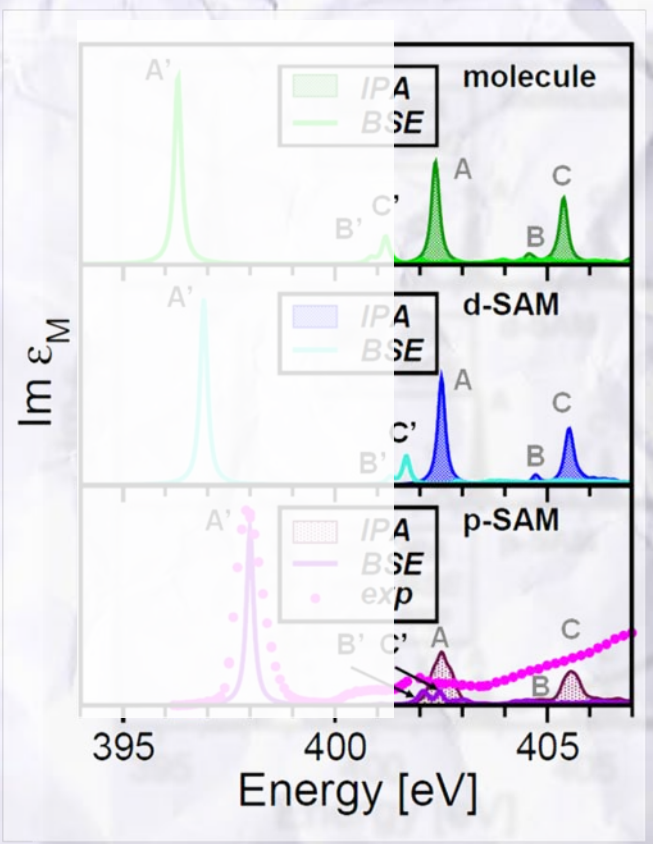


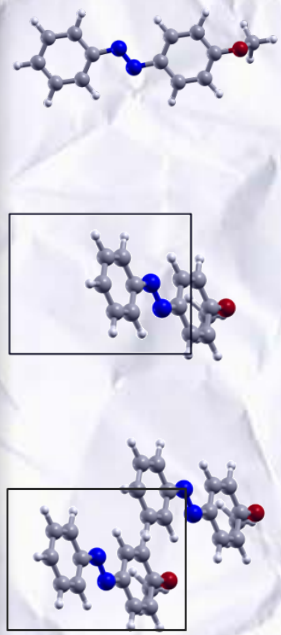
Moldt et al. Langmuir 31, 1048 (2015)

XAS of molecules & SAMs

Impact of packing







Independent particle picture

3 transitions

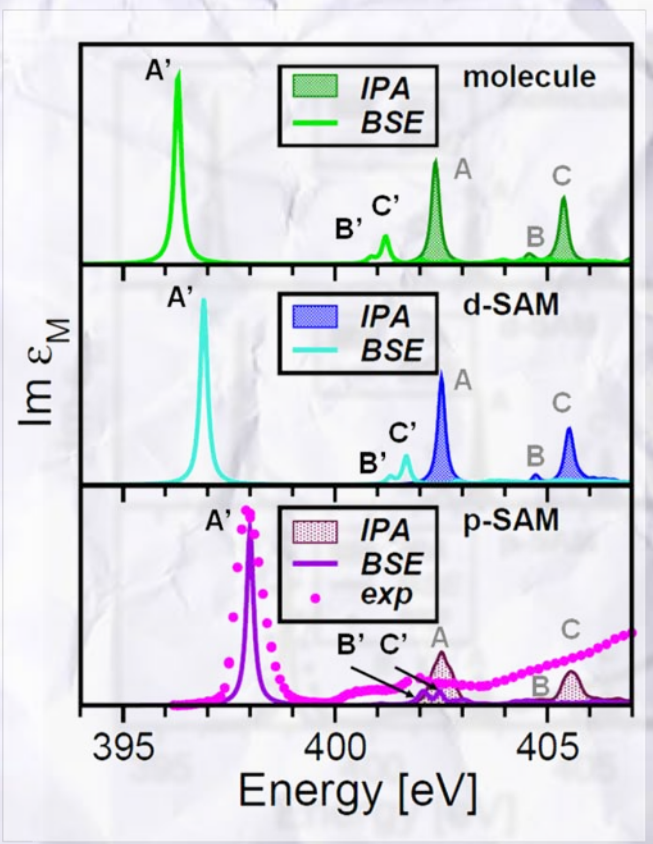
- A: 1s → LUMO (π*)
- B: 1s → LUMO+3 (π*)
- C: 1s → LUMO+7 (π*)

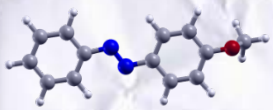
Peak positions unchanged

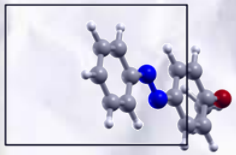
Similar intensities of A & C

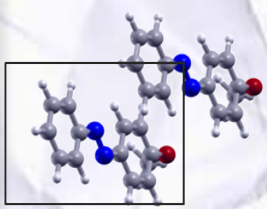
XAS of molecules & SAMs

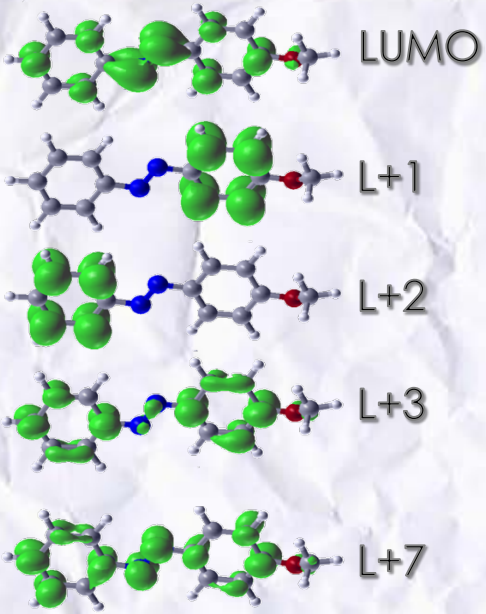
Impact of packing











Inclusion of excitonic effects

Mixing of transitions

Molecule

A': E_b ~ 6 eV

B' / C': E_b ~ 3.7 / 4.2 eV

p-SAM

A': E_b ~ 4 eV

Alternatives?

Core-hole approach

Spectra

BSE

IPA

Band structure

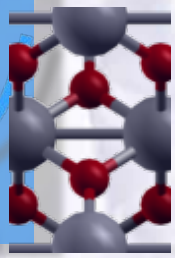
G_0W_0

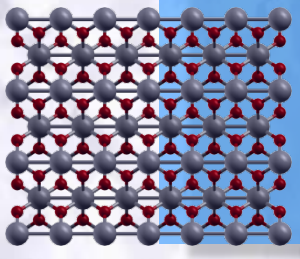
Ground state

constrained

DFT

supercell

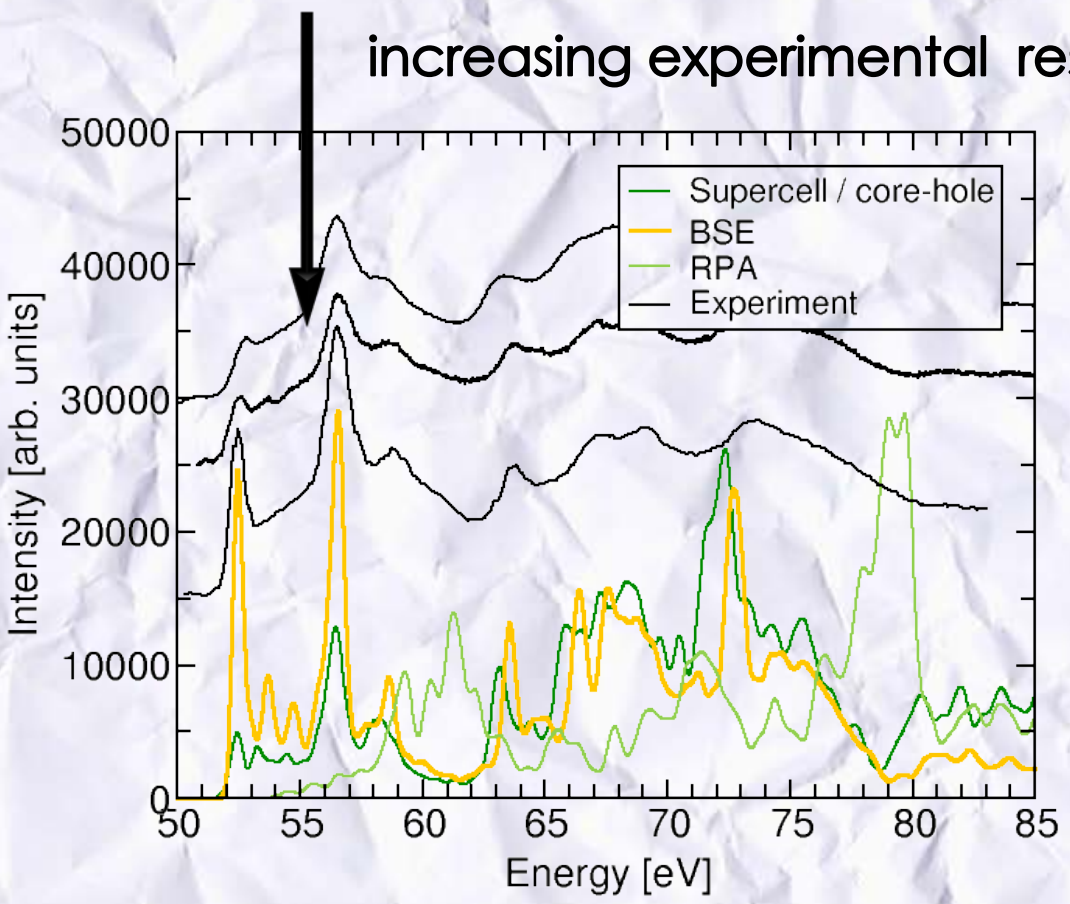




Core-hole vs BSE

Mg $L_{2,3}$ edge in MgO

Constrained DFT underestimates excitonic effects
Role of xc functional in electron-hole binding



T. Mizoguchi, et al.,
Ultramicroscopy **106**, 1120 (2006) .

W. L. O'Brien, et al.,
Phys. Rev. B **44** , 1013 (1991) .

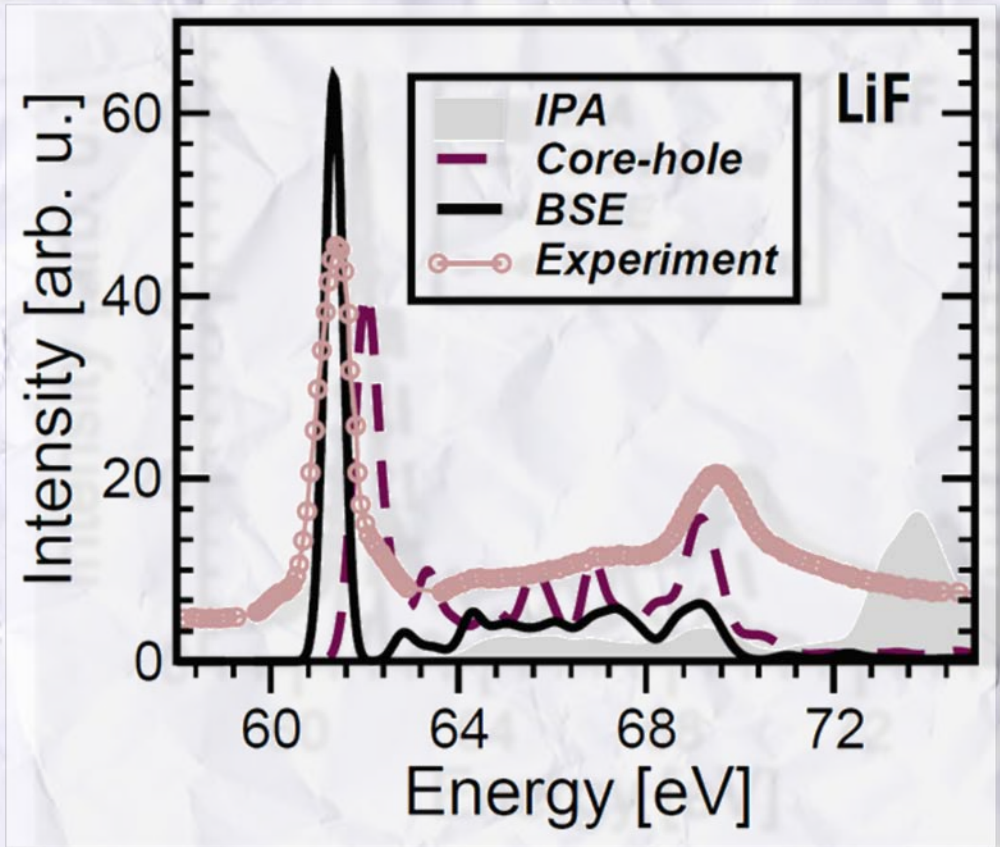
W. Olovsson, et al.,
PRB **79**, 041102(R) (2009).

Core-hole vs BSE

Li K edge in LiF

Absorption onset unknown

Spectra are typically aligned to some peak



W. Olovsson, I. Tanaka, T. Mizoguchi, P. Puschnig, and CAD, PRB 79, 041102(R) (2009).

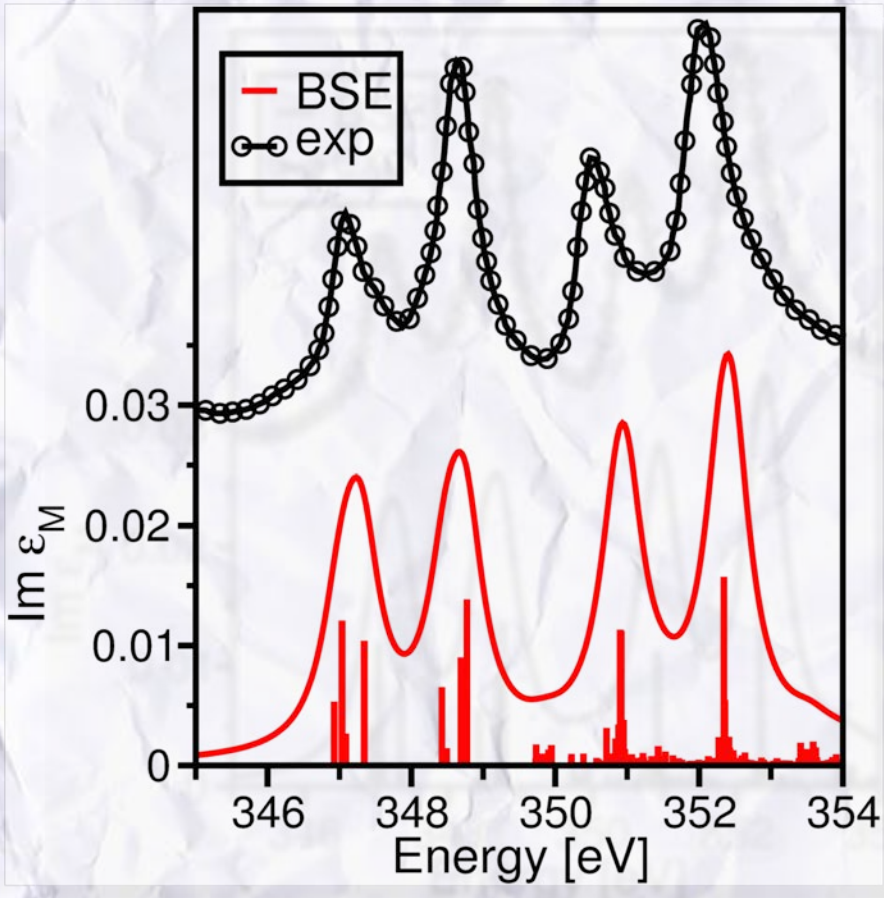
Back to BSE ...

Implementing fully relativistic treatment

Probing electron-hole correlation

Ca $L_{2,3}$ edge in CaO

- SO splitting of 3.7 eV
- Pronounced exchange interaction
  - Localized Ca 3d states
- Strong local-field effects

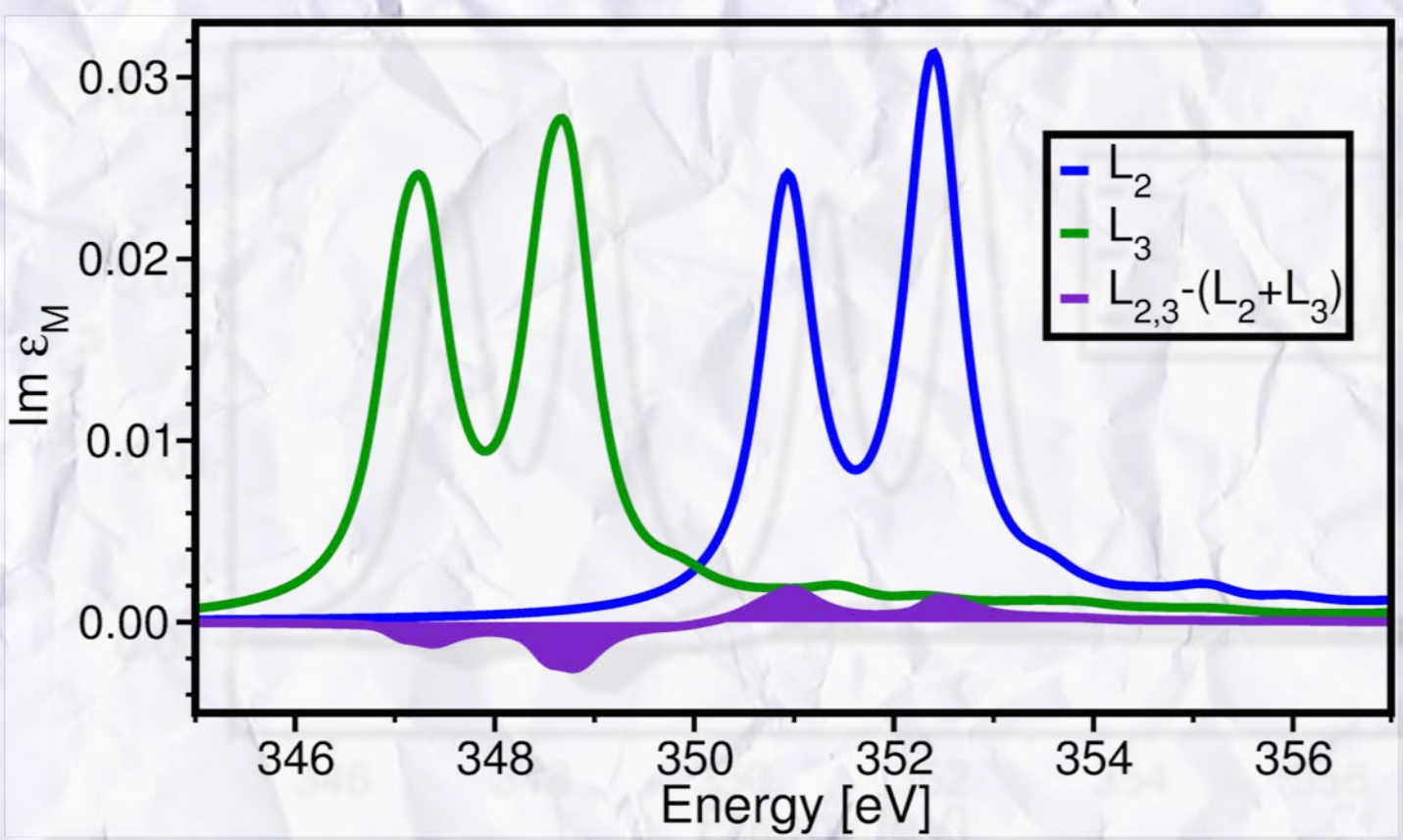


C. Vorwerk, C. Cocchi and CD, Phys. Rev. B. **95**, 155121 (2017).

Probing electron-hole correlation

Ca $L_{2,3}$ edge in CaO

Ca $2p_{3/2} \rightarrow$ Ca $3d$ Ca $2p_{1/2} \rightarrow$ Ca $3d$



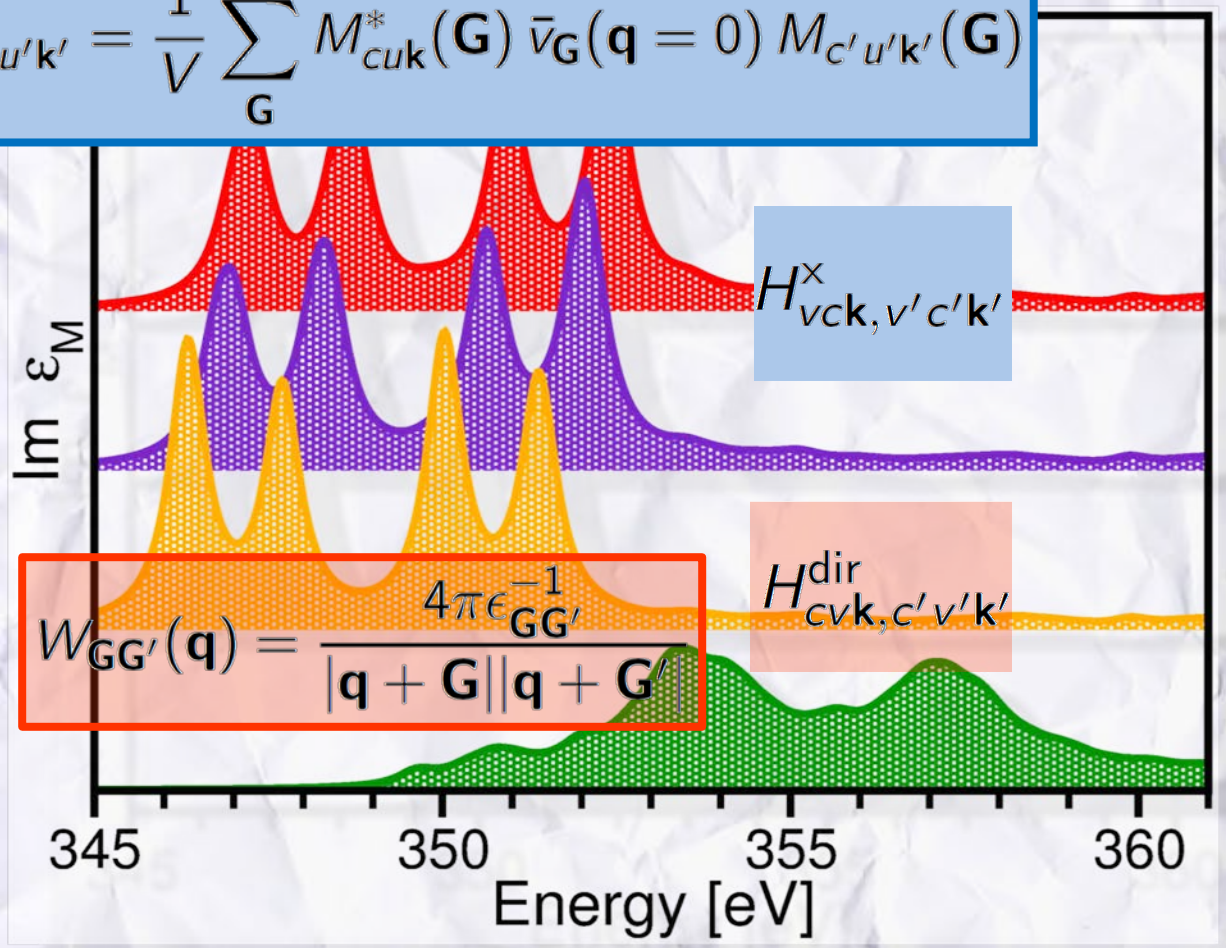
Local-field effects

Ca $L_{2,3}$ edge in CaO

Both aspects of LFE crucial!

$$H^{x}_{cu\mathbf{k},c'u'\mathbf{k}'} = \frac{1}{V}\sum_{\mathbf{G}} M^{*}_{cu\mathbf{k}}(\mathbf{G})\,\bar{v}_{\mathbf{G}}(\mathbf{q}=0)\,M_{c'u'\mathbf{k}'}(\mathbf{G})$$

$$W_{\mathbf{G}\mathbf{G}'}(\mathbf{q}) = \frac{4\pi\epsilon^{-1}_{\mathbf{G}\mathbf{G}'}}{|\mathbf{q}+\mathbf{G}||\mathbf{q}+\mathbf{G}'|}$$

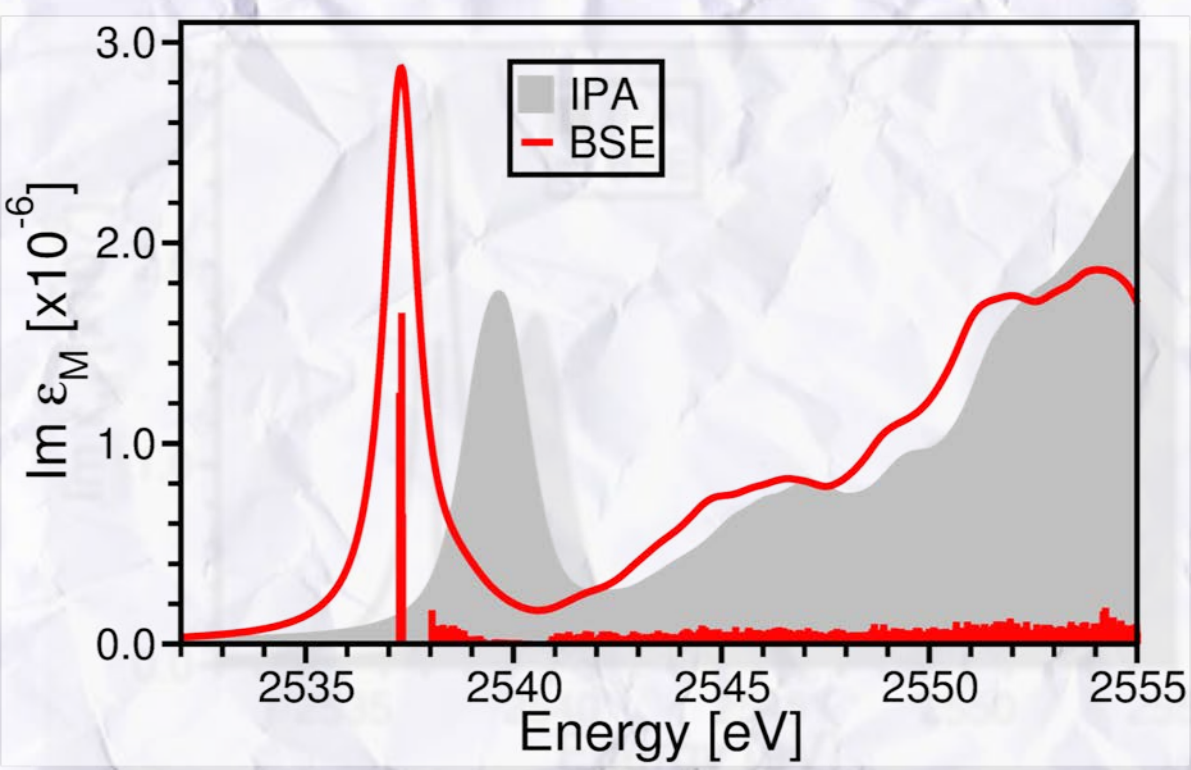


Solar-cell materials

Including relativity

Pb M_4 edge in PbI_2

Transitions to Pb *f* states



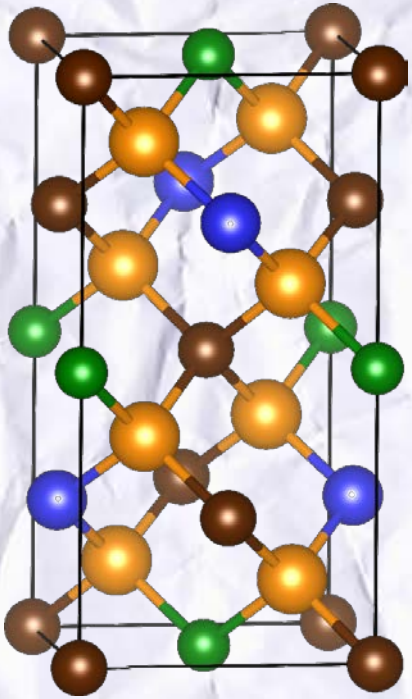
C. Vorwerk, C. Cocchi and CD, Phys. Rev. B. **95**, 155121 (2017).

Kesterites

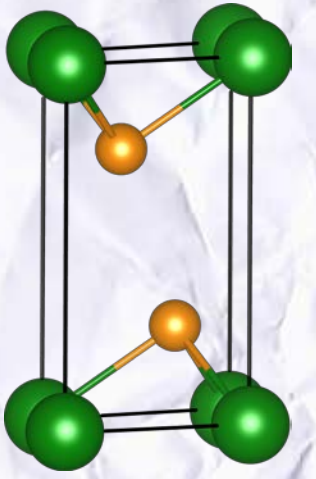
S $L_{2,3}$ edge in CZTS

Promising candidates for solar-cell absorbers

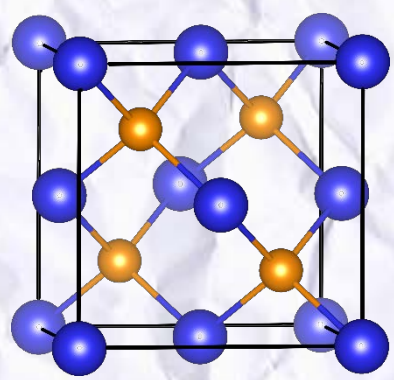
- Non-toxic
- Cheap ingredients



Cu_2ZnSnS_4



SnS_2

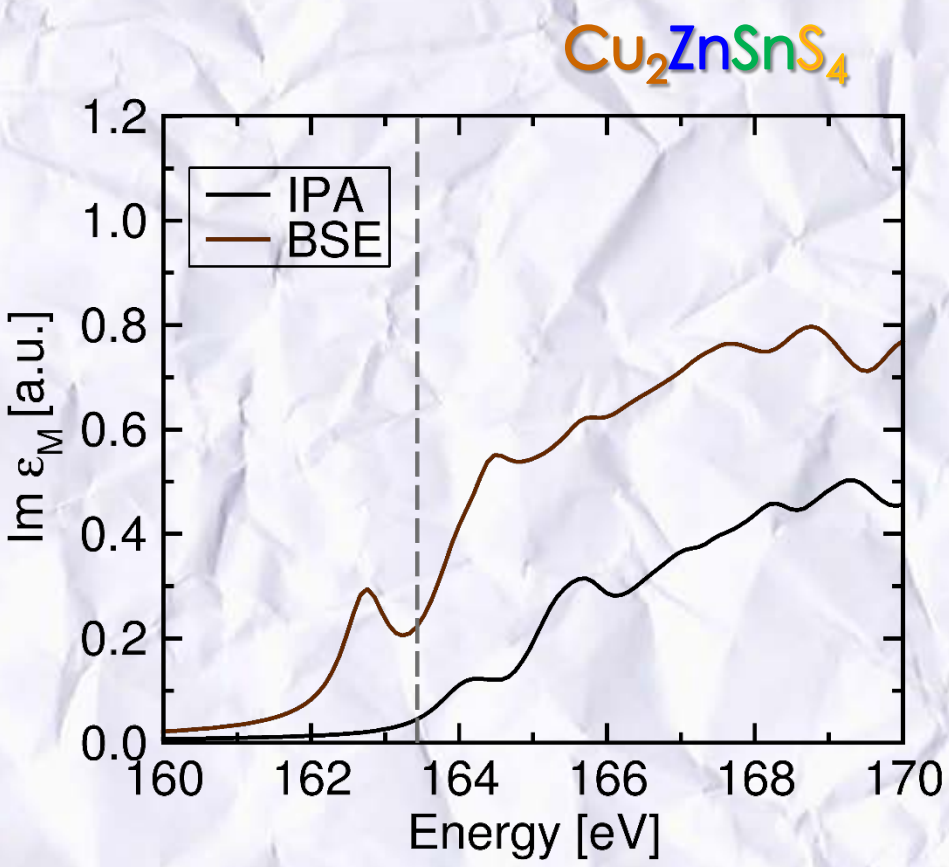


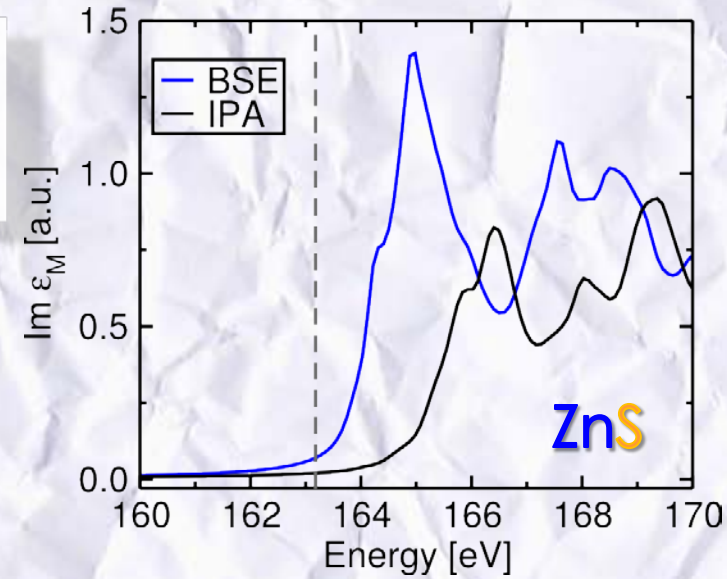
ZnS

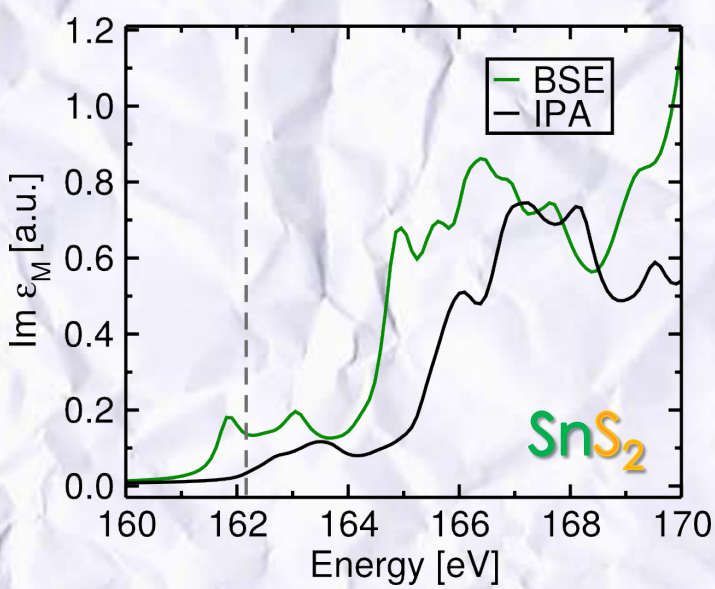
A. Manoharan et al., in preparation

Sulfur $L_{2,3}$ edge

Bound excitons in CZTS and SnS_2 but not in ZnS

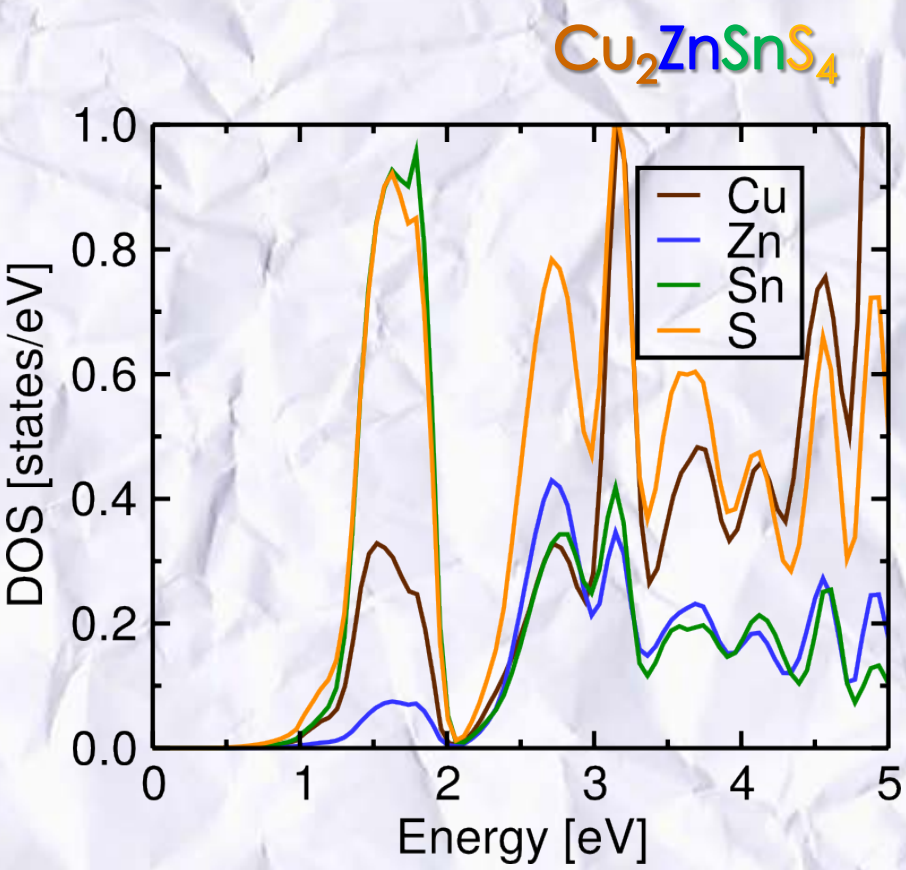


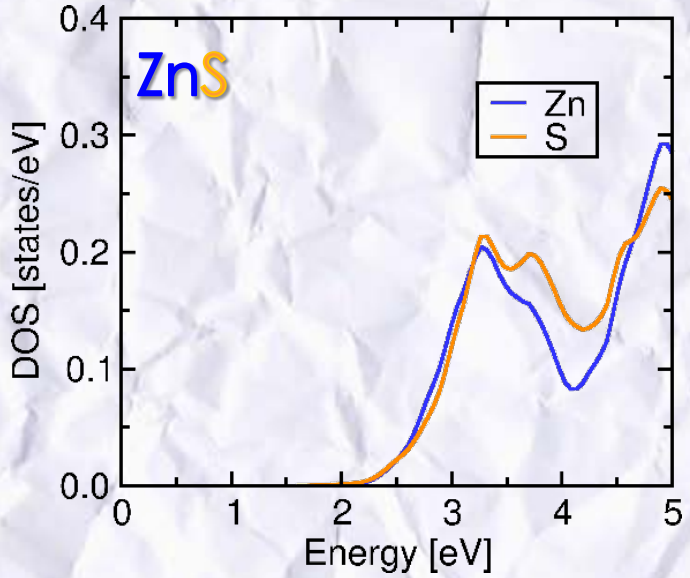


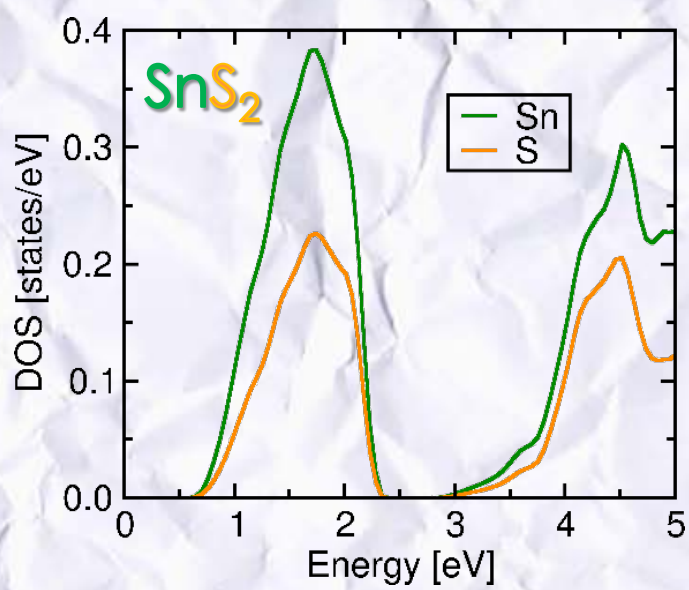


Densities of states

Hybridization of Sn and S

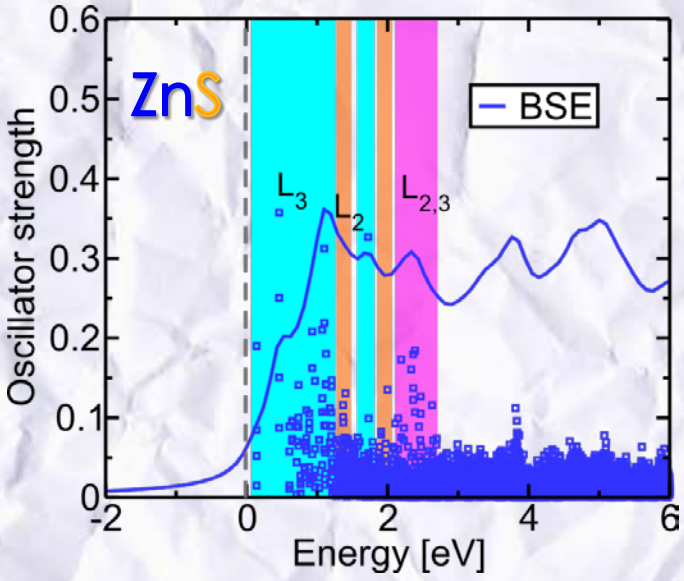




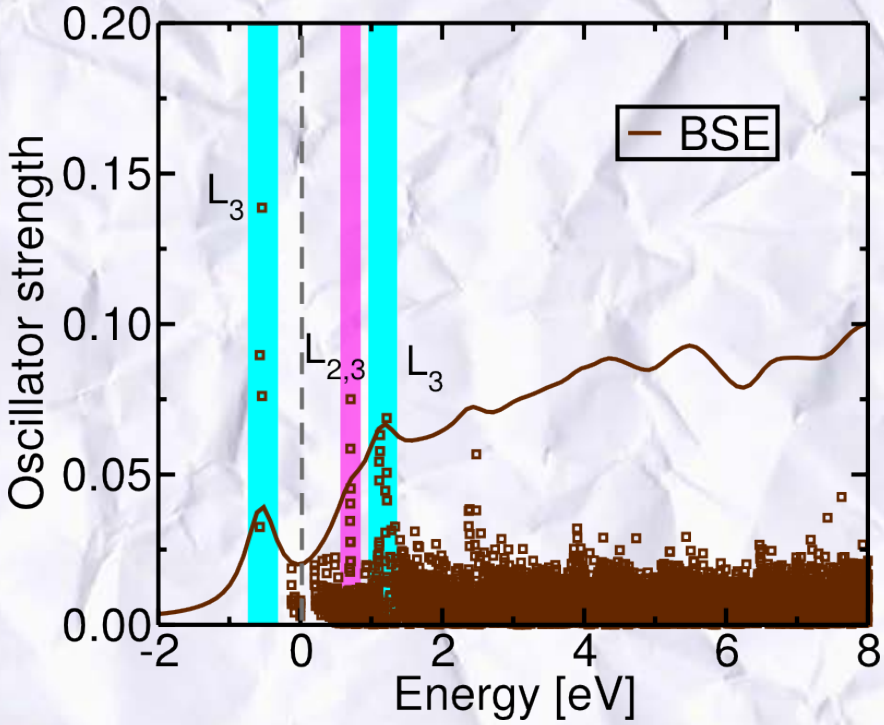


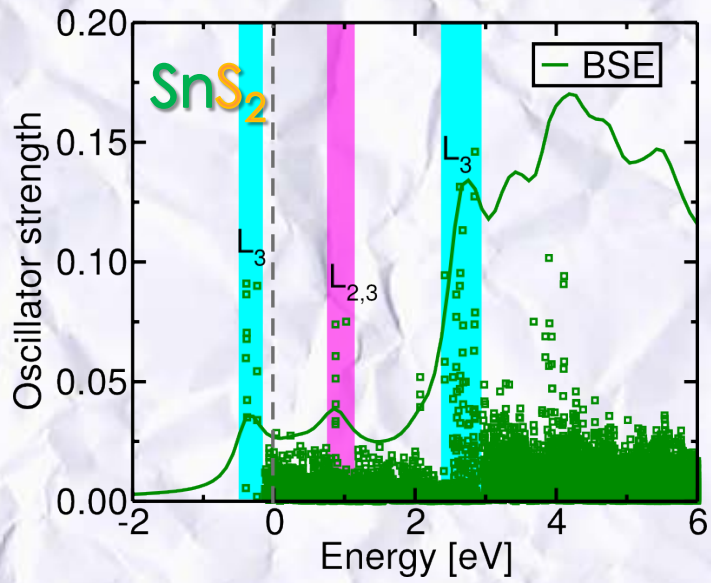
Exciton character

$L_{2,3}$ splitting of 1.22 eV
Bound states from L_3 edge



Cu_2ZnSnS_4

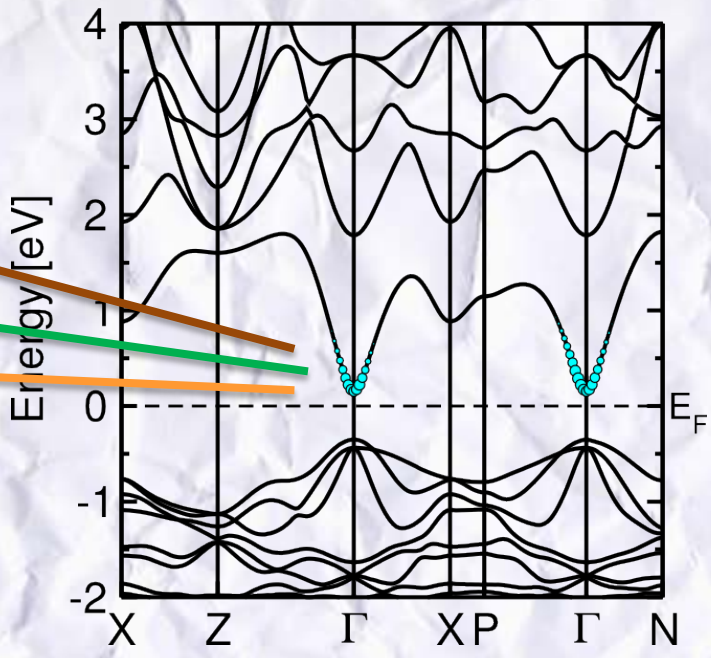




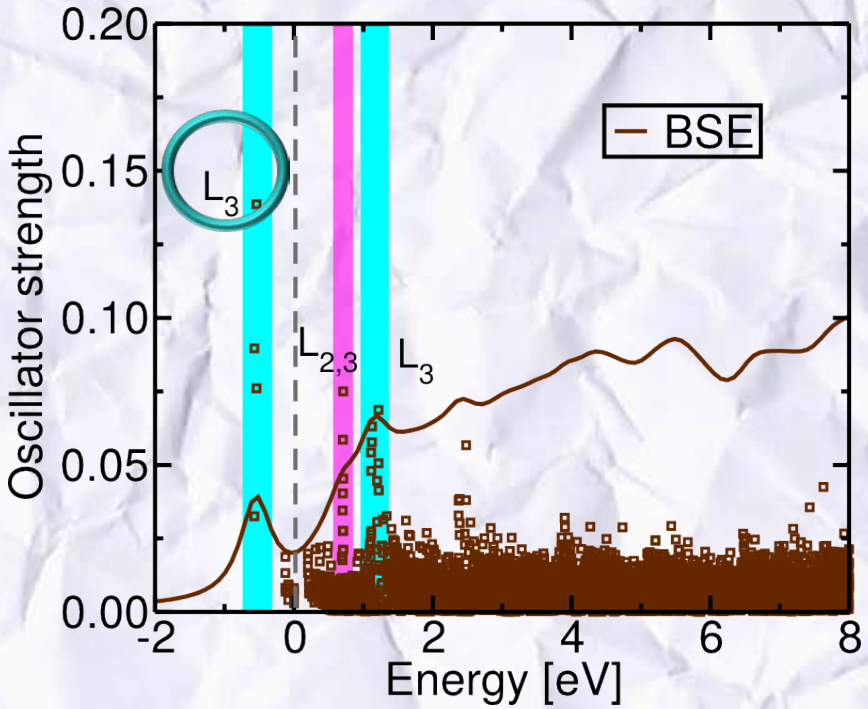
Exciton character

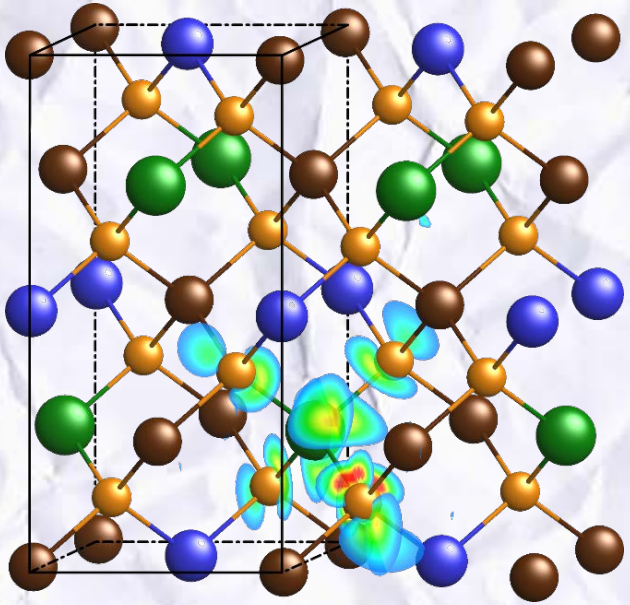
S $L_{2,3}$ edge

Cu-d
Sn-s,d
S-s,d



Cu_2ZnSnS_4

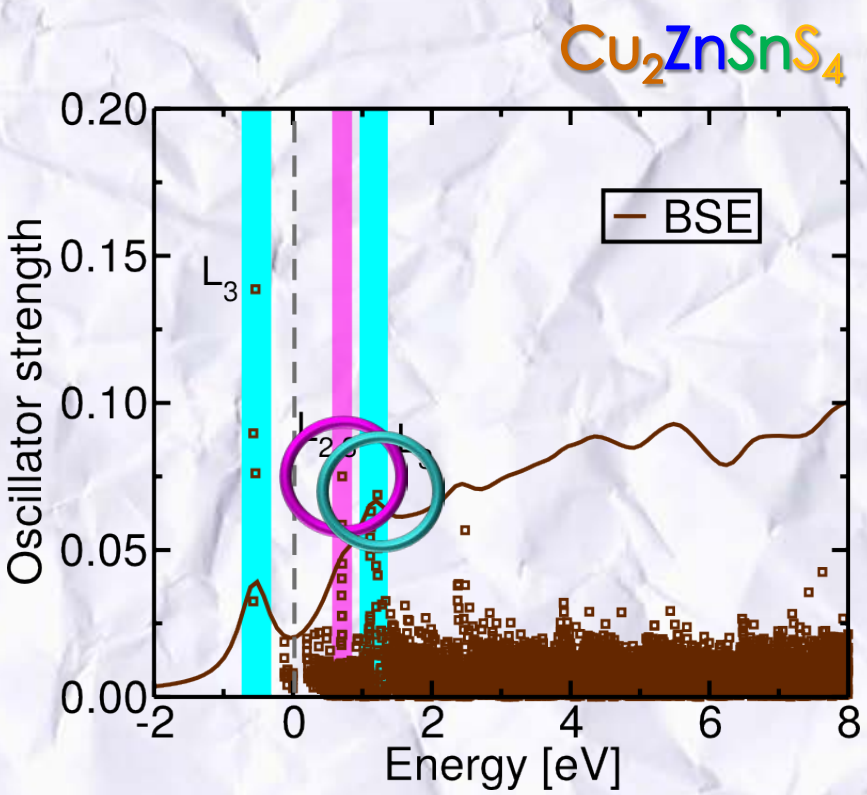


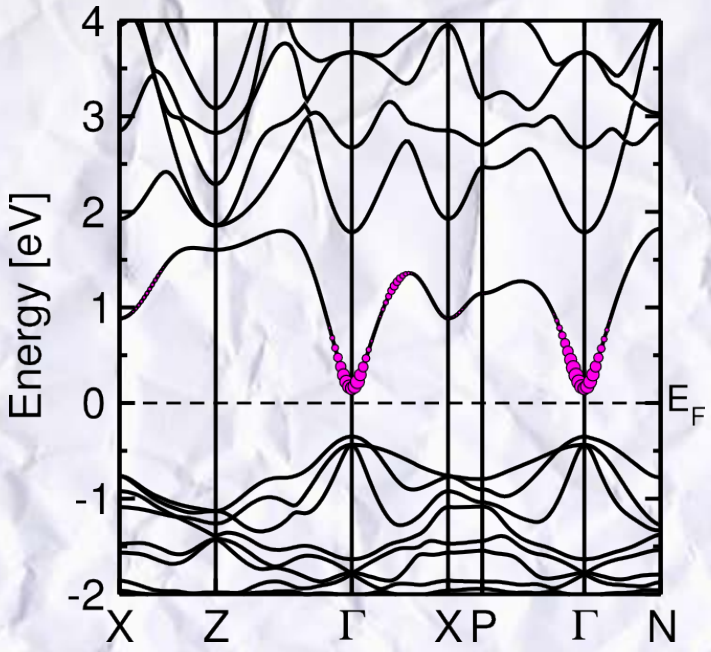


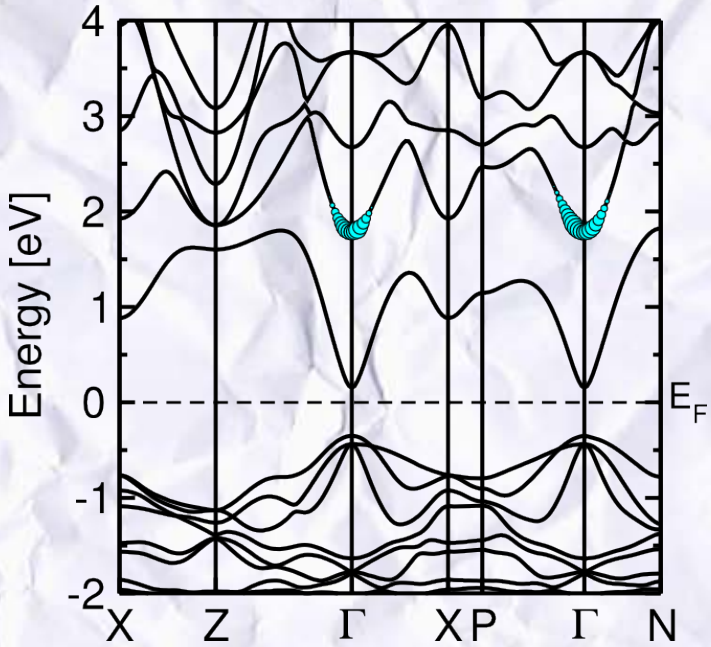
Min Max

Exciton character

S $L_{2,3}$ edge







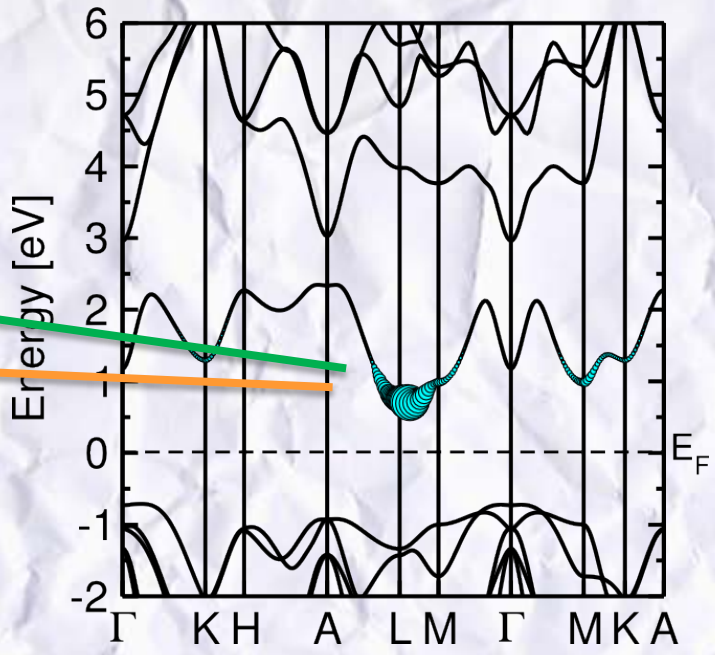
Exciton character

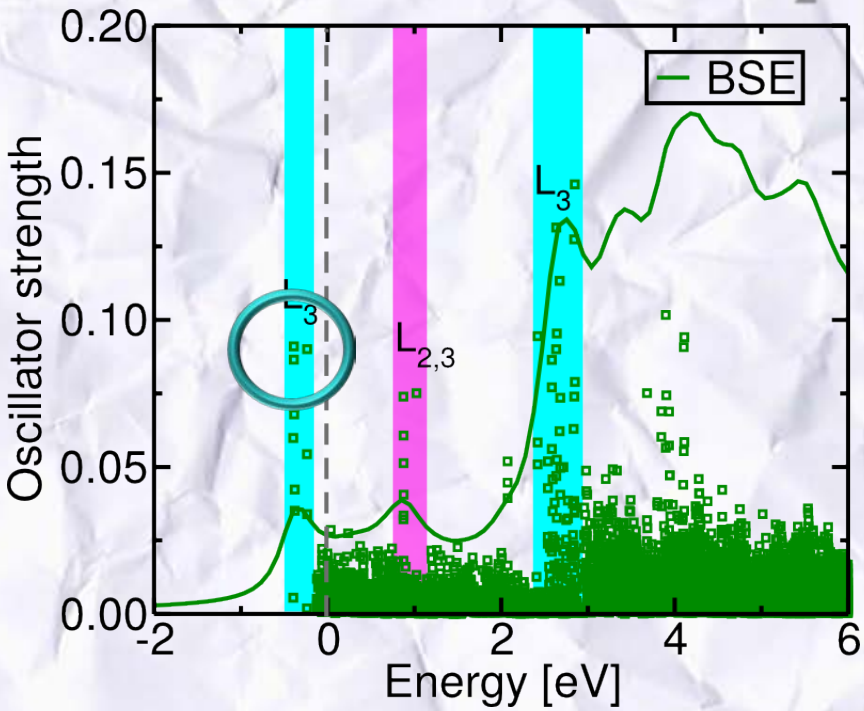
S $L_{2,3}$ edge

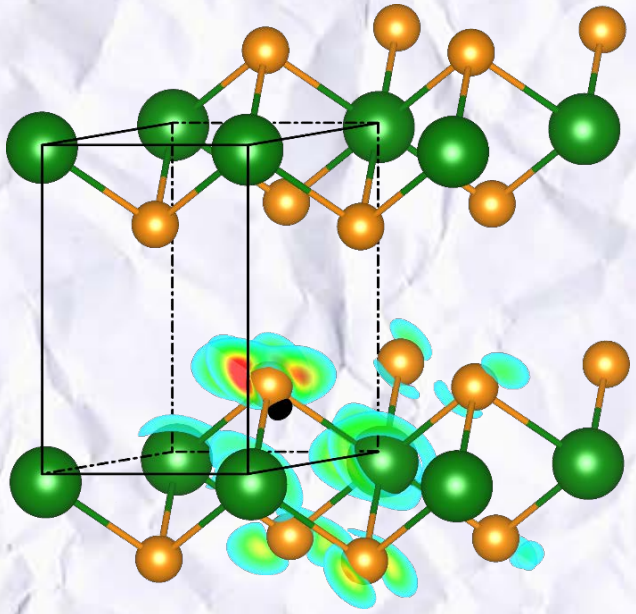
Sn-s,d

S-s,d

SnS_2





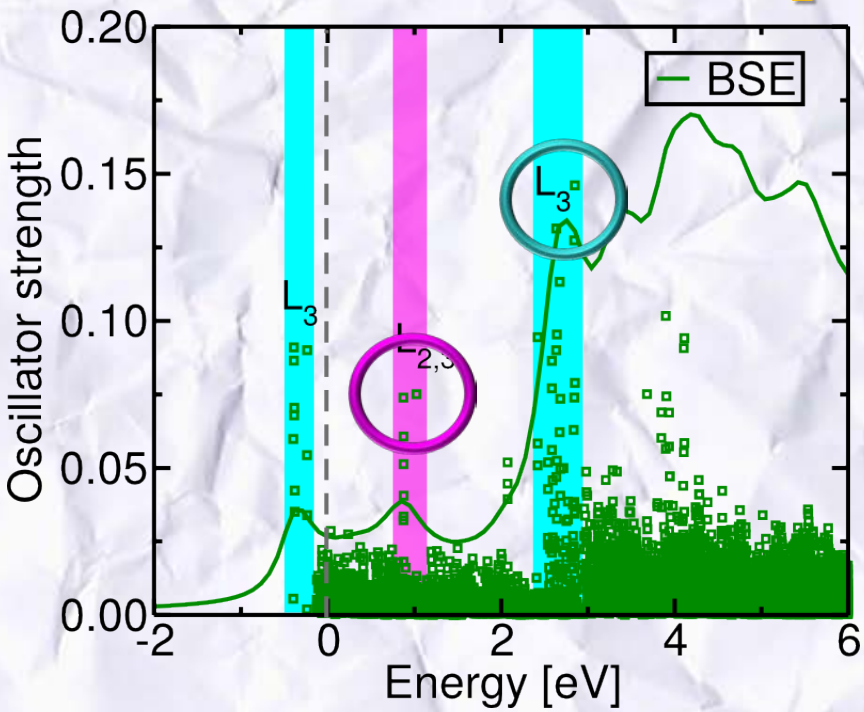


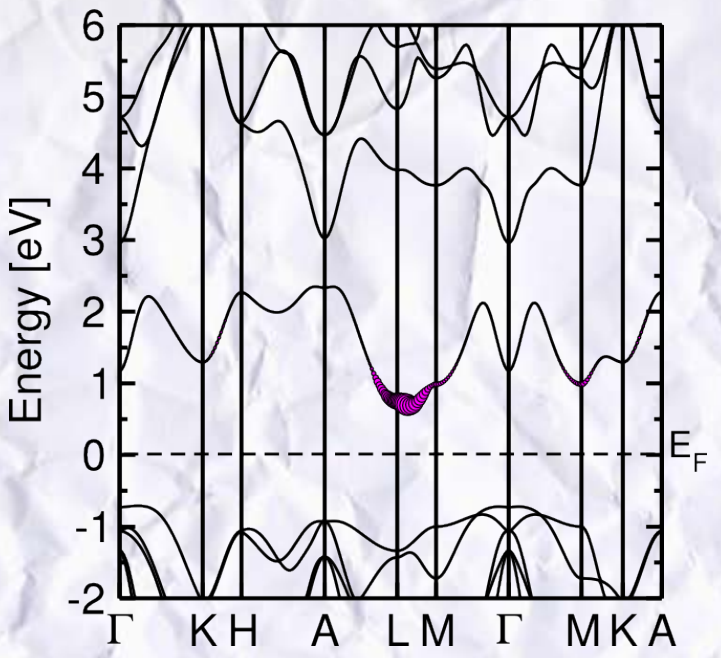
Min — Max

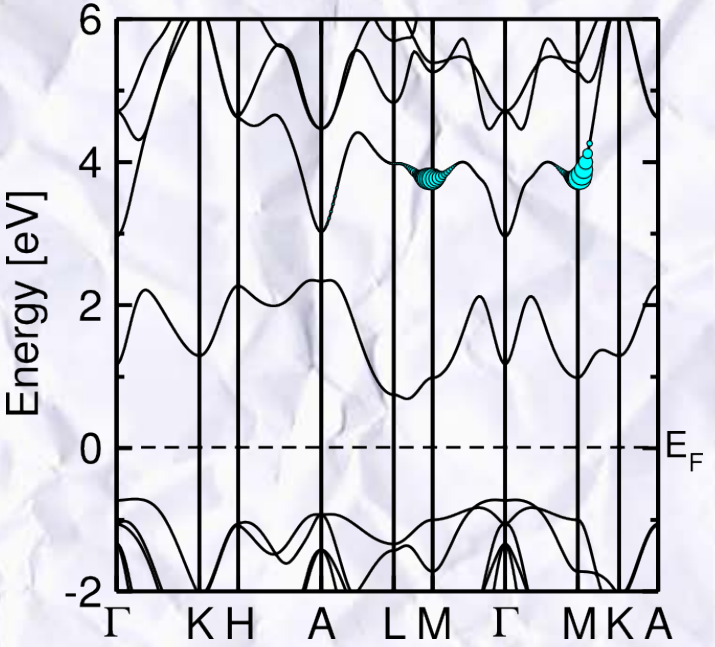
Exciton character

S $L_{2,3}$ edge

SnS_2

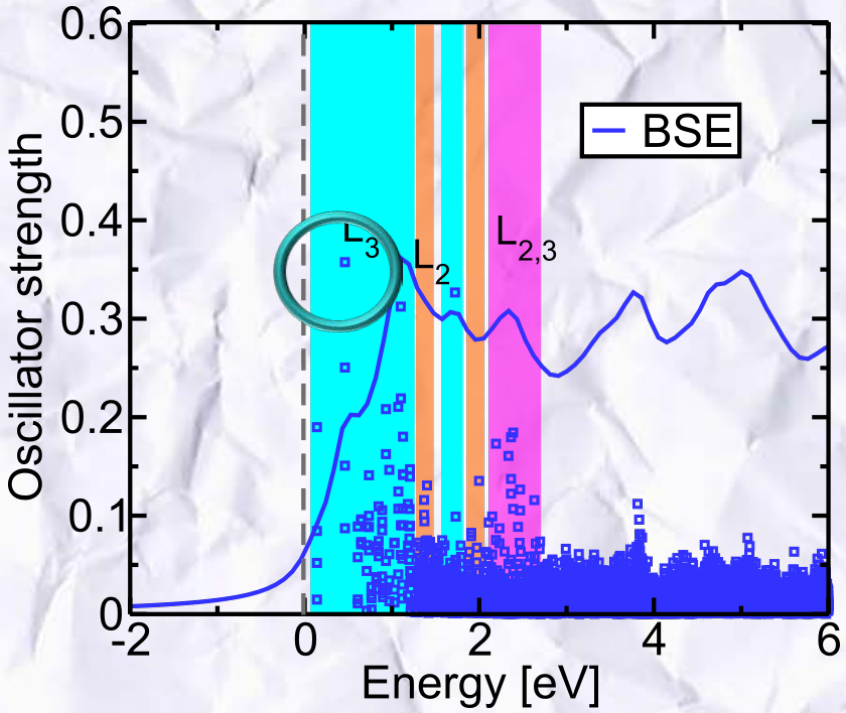


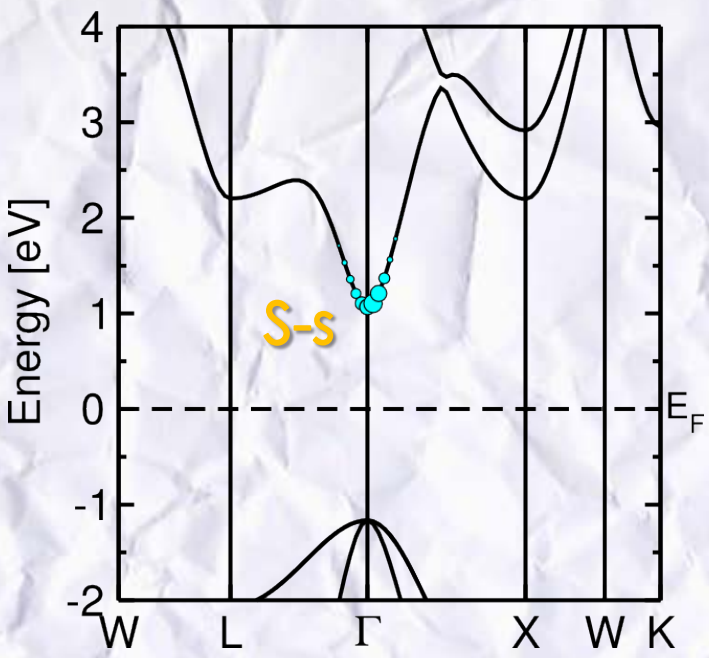


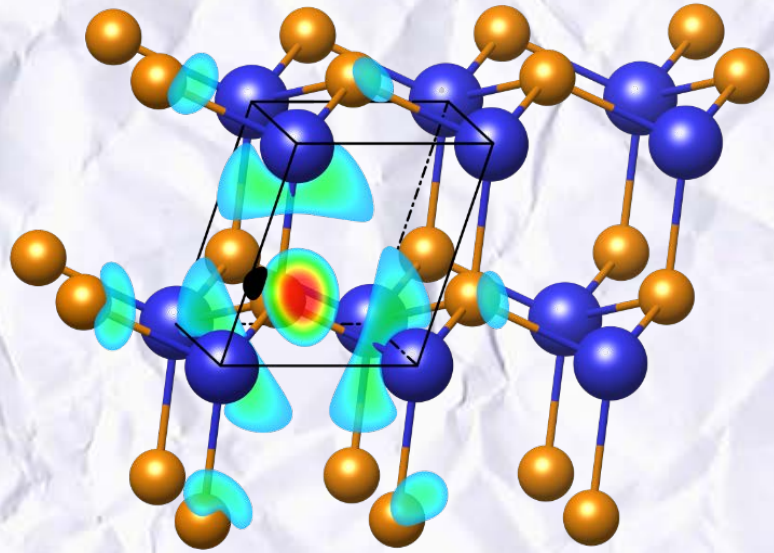


Exciton character

S $L_{2,3}$ edge



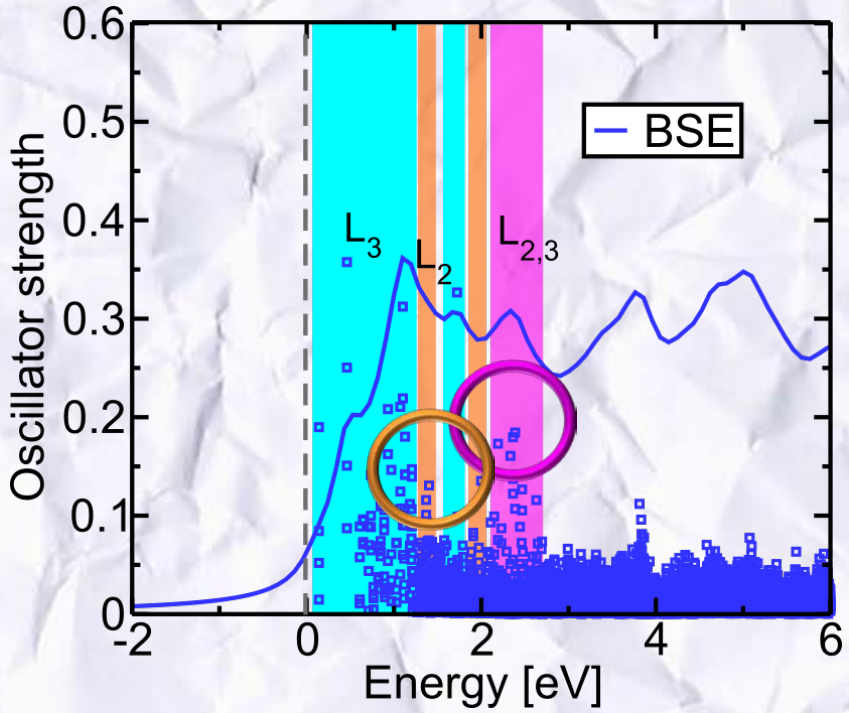


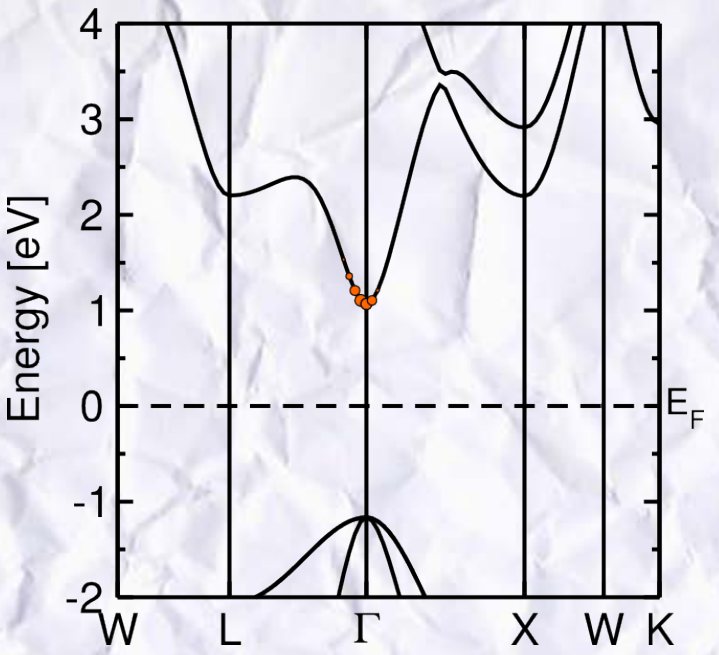


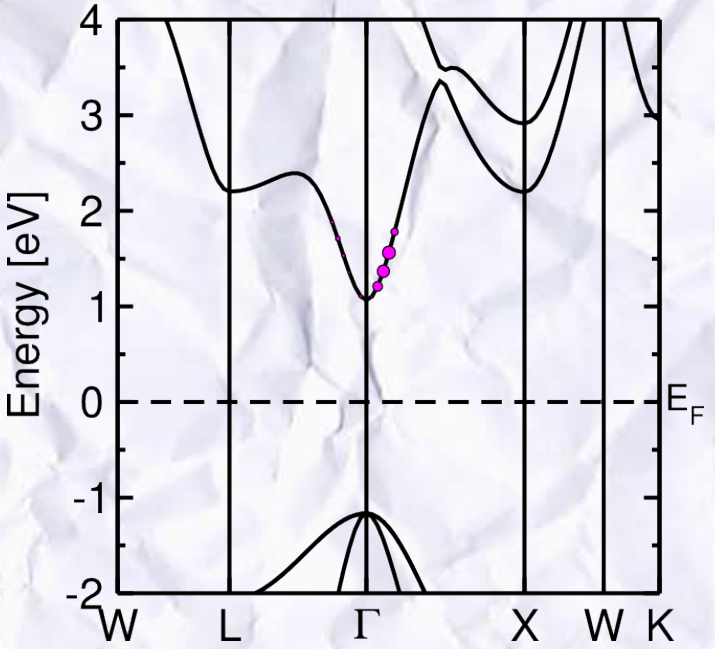
Exciton character

S $L_{2,3}$ edge

ZnS



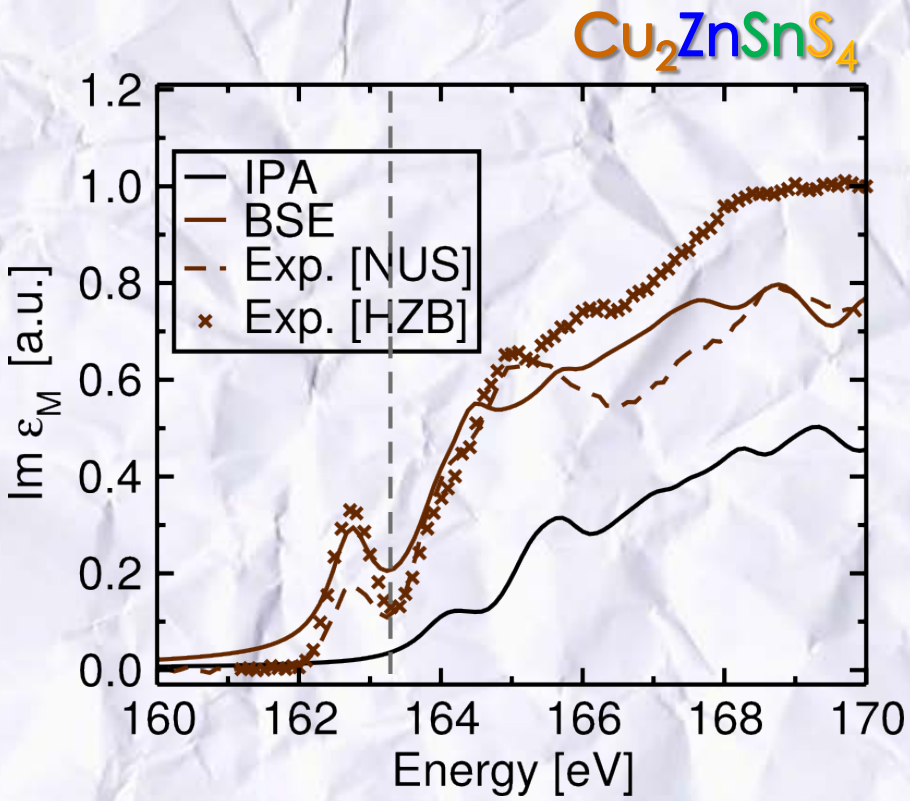


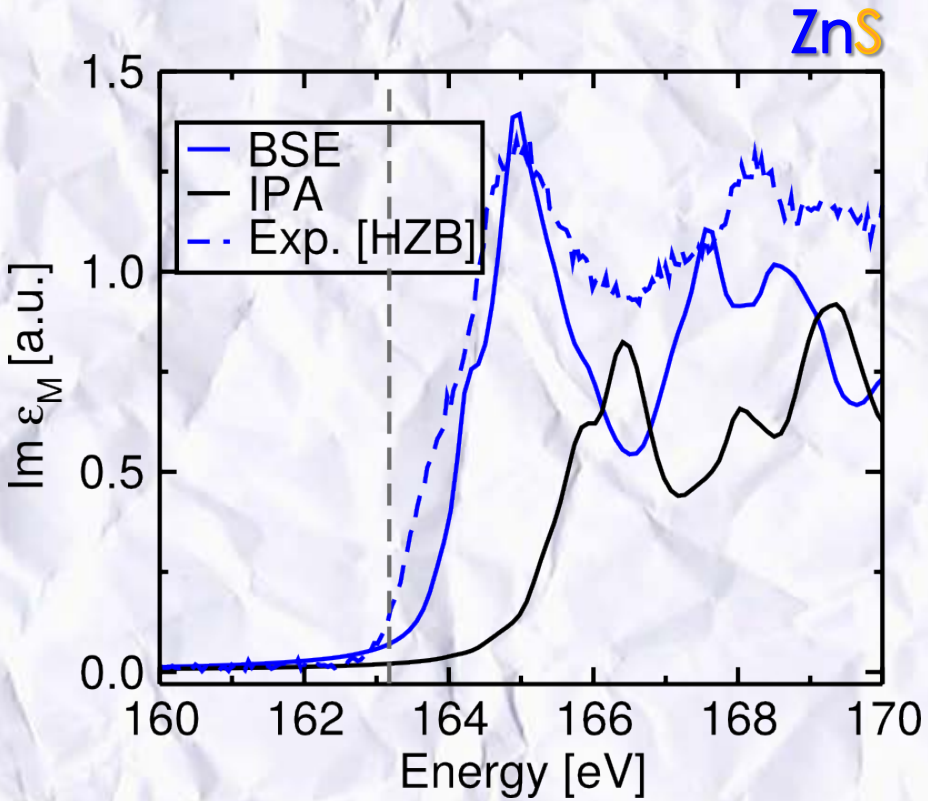


Theory vs experiment

A. Manoharan et al., in preparation

Theoretical spectra aligned with experiment





[HZB] J. H. Alsmeier & M. Bär, Helmholtz Zentrum Berlin

[NUS] A. Rusydi, National University of Singapore

Our instrument ...

http://exciting-code.org

A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl

exciting: a full-potential all-electron package implementing density-functional theory and many-body perturbation theory
J. Phys: Condens. Matter 26, 363202 (2014).

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exciting is a full-potential all-electron density-functional-theory package implementing the families of linearized augmented planewave methods. It can be applied to all kinds of materials, irrespective of the atomic species involved, and also allows for exploring the physics of core electrons. A particular focus are excited states within many-body perturbation theory.

The exciting Code

A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl, "**exciting** — a full-potential all-electron package implementing density-functional theory and many-body perturbation theory", J. Phys.: Condens. Matter **26**, 363202 (2014)

Events

Download exciting

HoW exciting! Hands-on w

Developers Team

- exciting hub at the Humboldt Uni
- Current developers

Our instrument ...

A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and C. Draxl

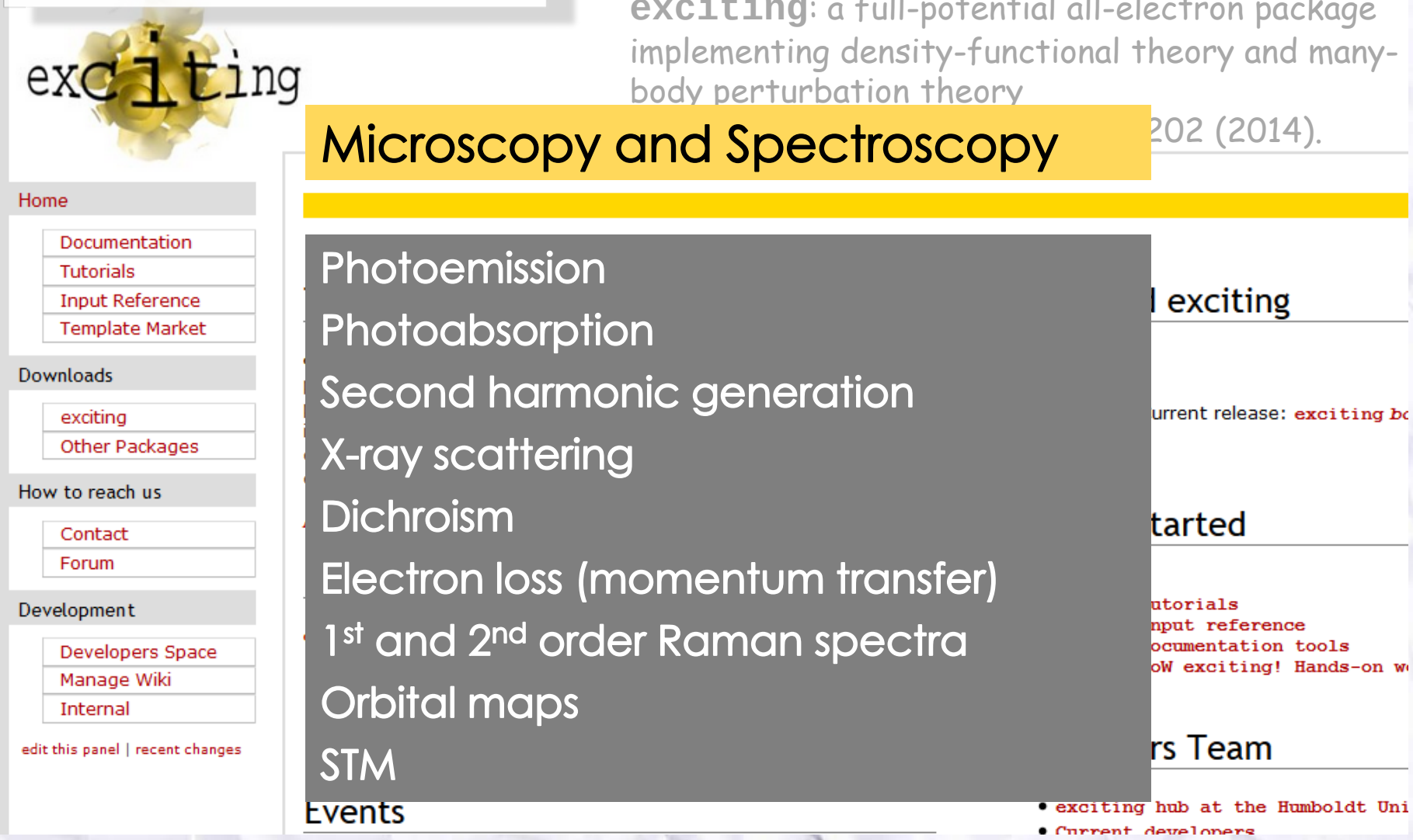
http://exciting-code.org

exciting: a full-potential all-electron package implementing density-functional theory and many-body perturbation theory

202 (2014).

Microscopy and Spectroscopy

- Photoemission
- Photoabsorption
- Second harmonic generation
- X-ray scattering
- Dichroism
- Electron loss (momentum transfer)
- 1st and 2nd order Raman spectra
- Orbital maps
- STM



Teamwork

Archana Manoharan

Andris Gulans

Thanks!

Christian Vorwerk

Dmitrii Nabok

Caterina Cocchi