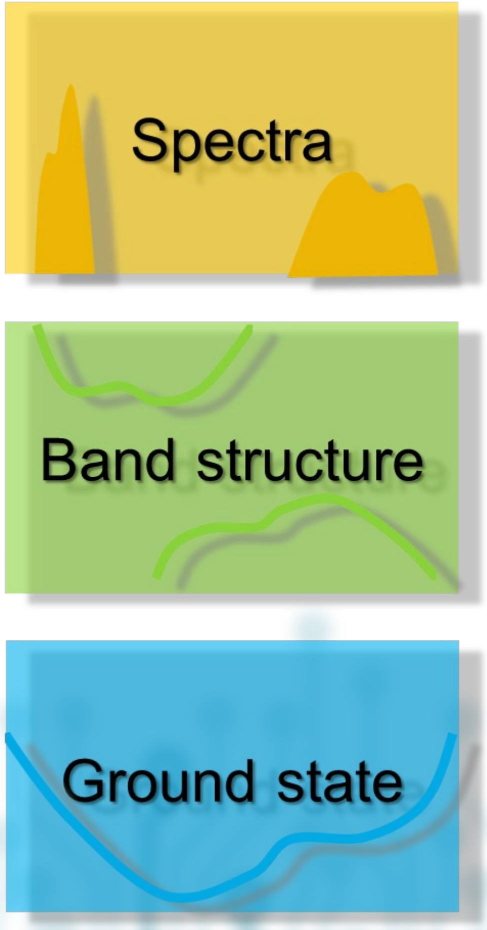
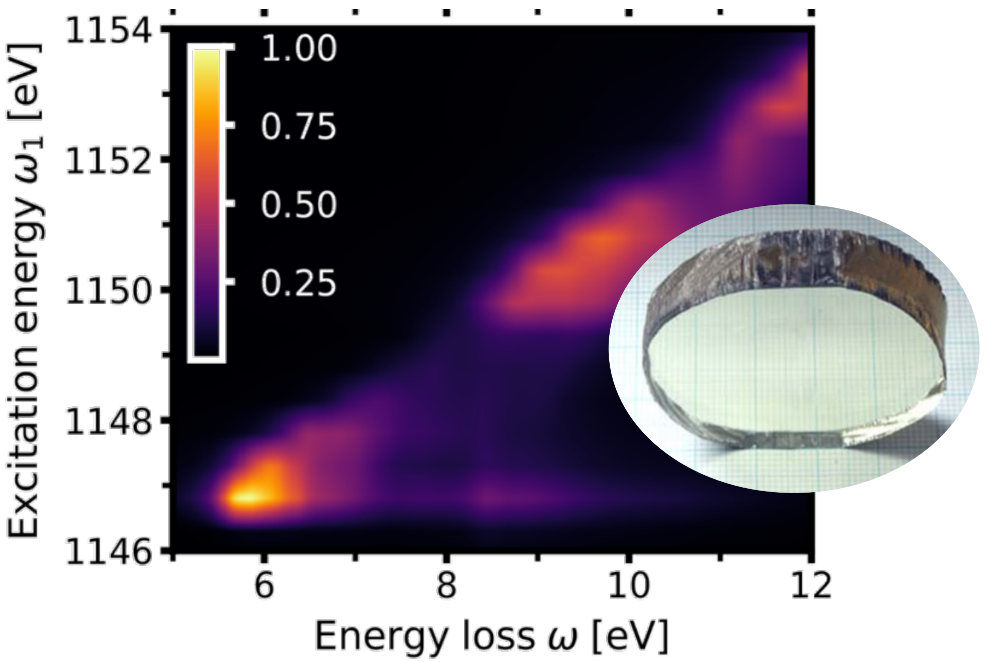
Theoretical spectroscopy of complex system: Fundamentals and challenges

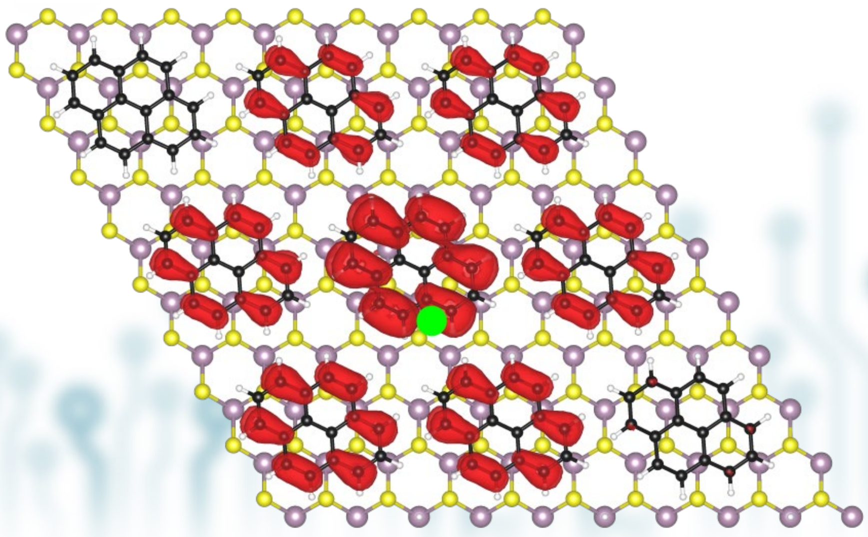
Claudia Draxl

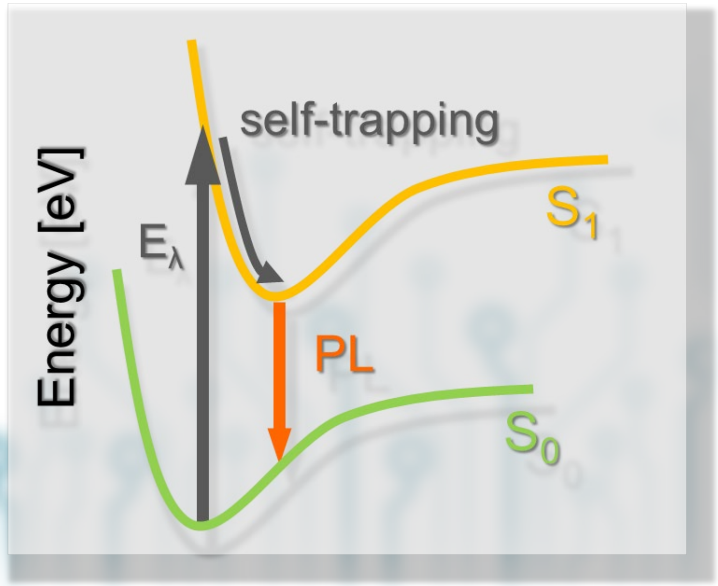
What is SMART-X?

A guided tour ...







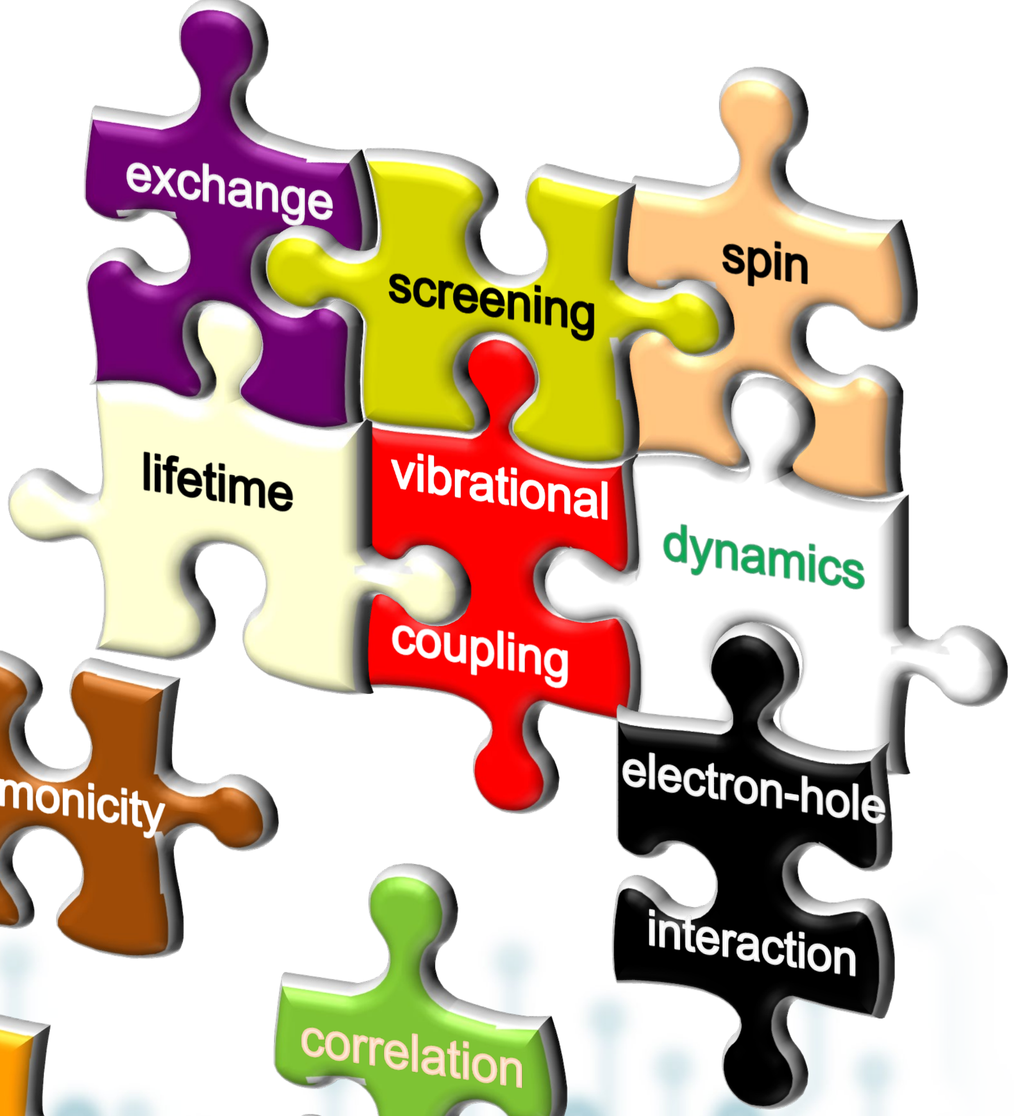


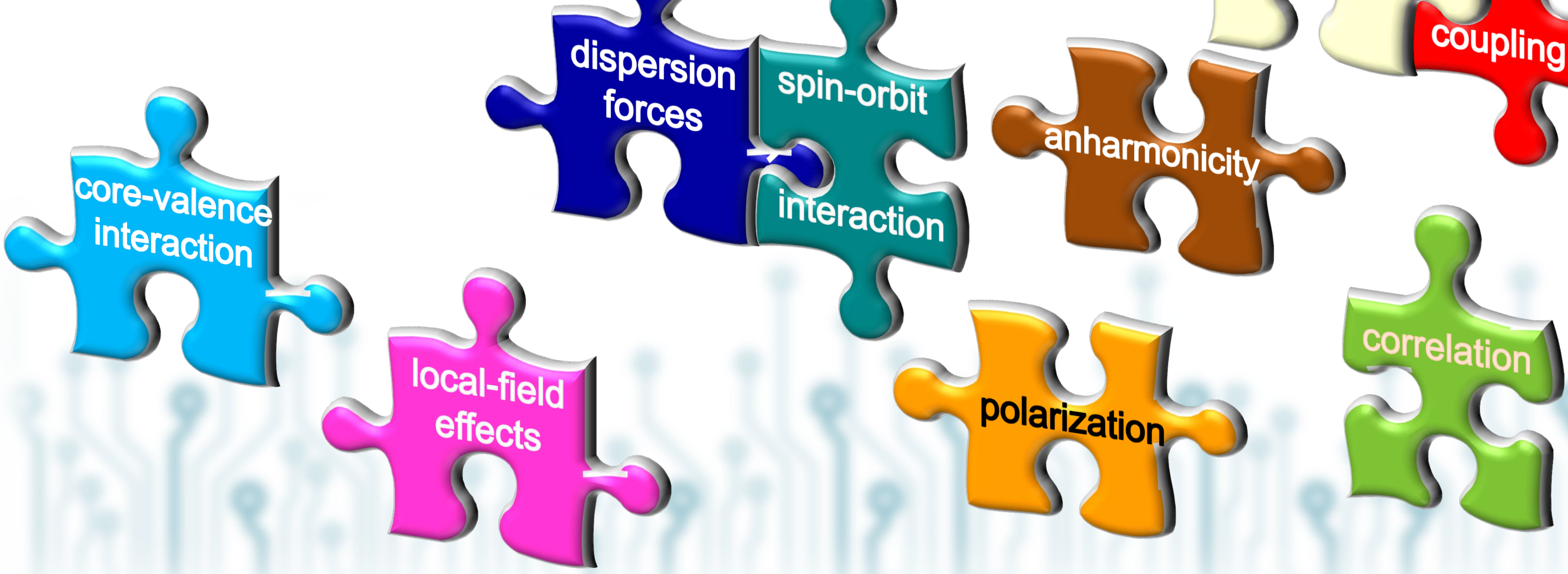
A quantum puzzle ...

In principle, a simple problem

Only one type of interaction – Coulomb

However, …





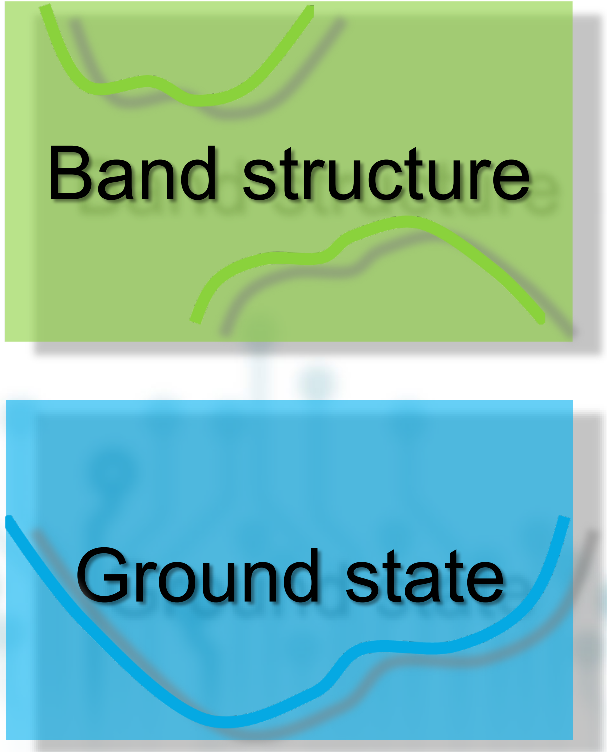
State-of-the-art methodology

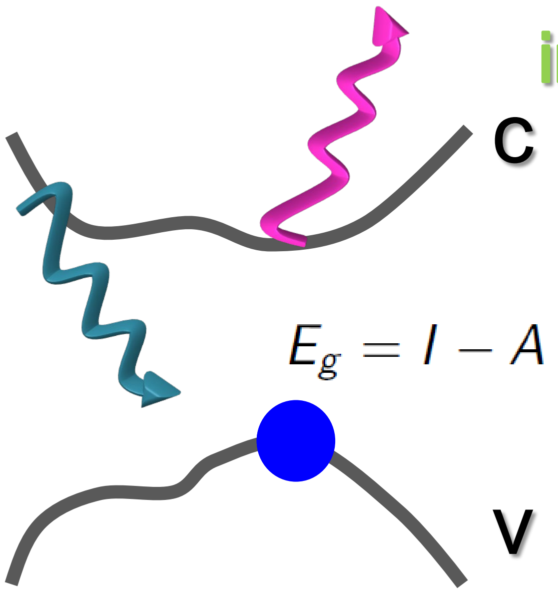
Density-functional theory

Kohn-Sham equation

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

State-of-the-art methodology





inverse photoemission

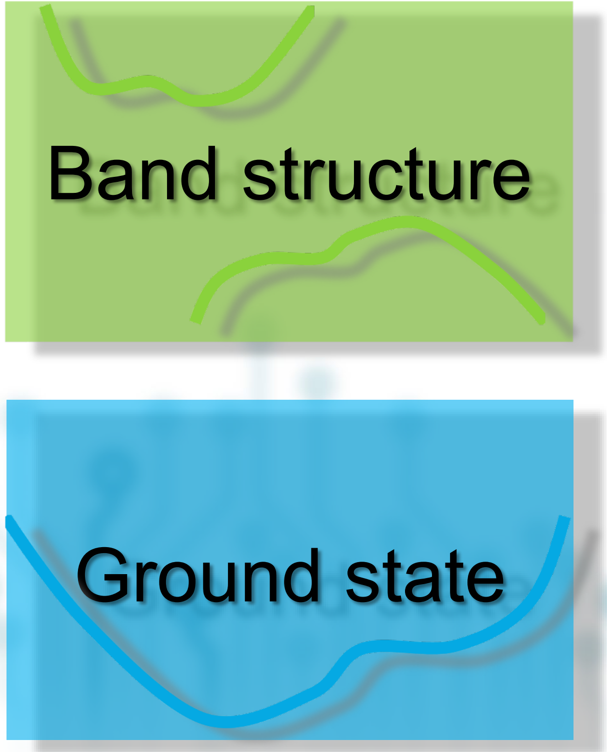
photoemission

Density-functional theory

Kohn-Sham equation

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

State-of-the-art methodology



Many-body perturbation theory

G_0W_0 approximation

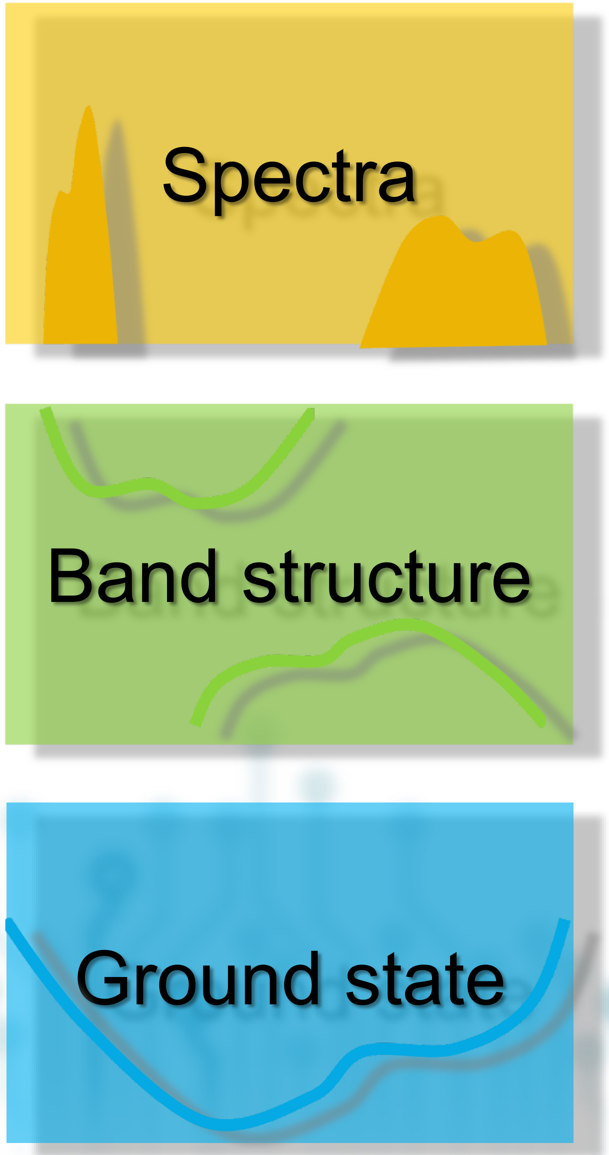
$$\epsilon_{n\mathbf{k}}^{QP} = \epsilon_{n\mathbf{k}}^{KS} + \left\langle n\mathbf{k} \middle| \Sigma - V_{xc}^{KS} \middle| n\mathbf{k} \right\rangle$$

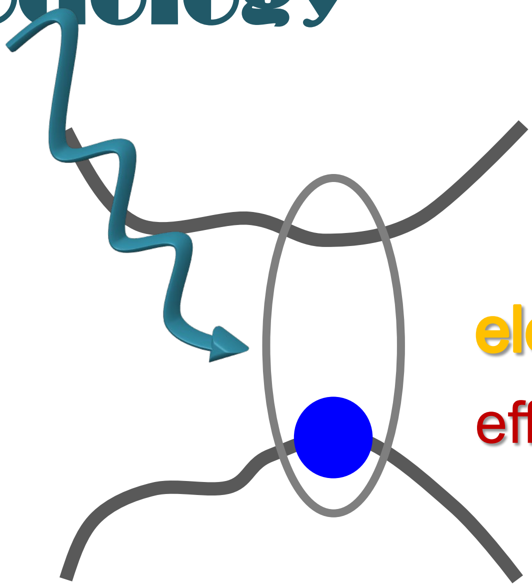
Density-functional theory

Kohn-Sham equation

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

State-of-the-art methodology





electron-hole pair = exciton

effective hydrogen atom

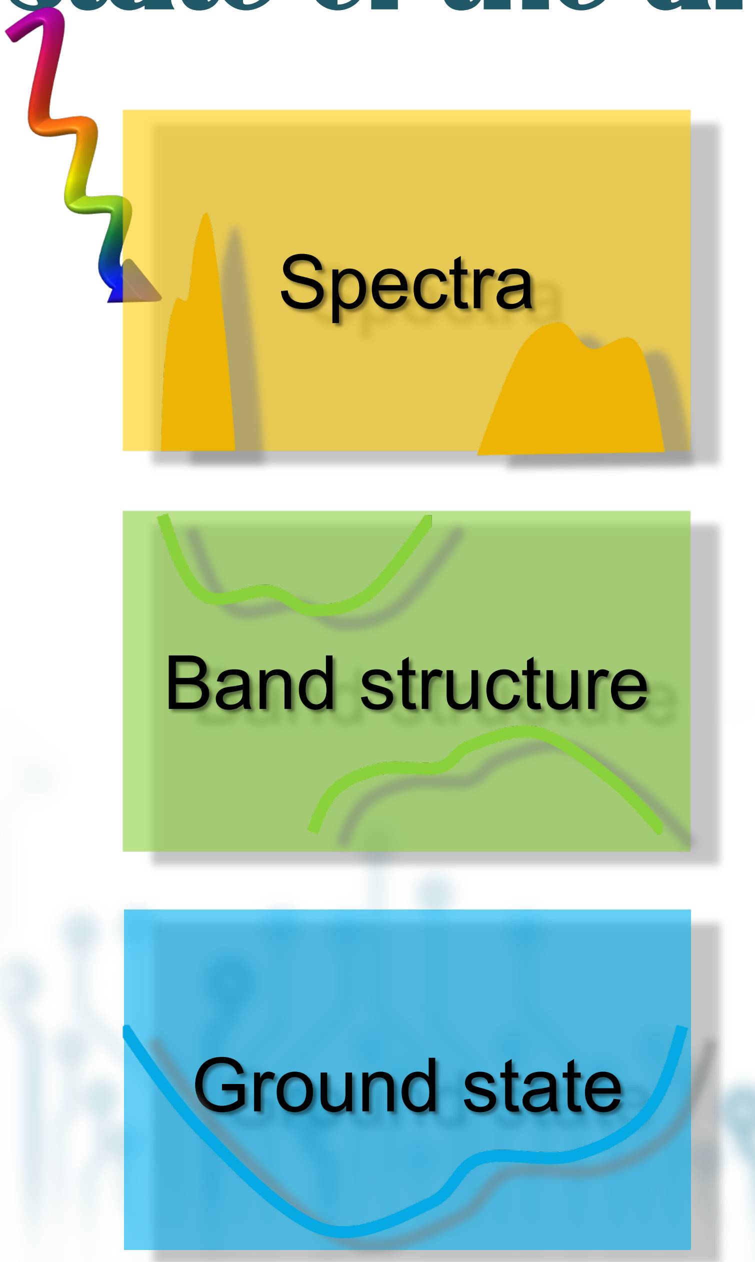
$$\epsilon^{QP}_{n\mathbf{k}} = \epsilon^{KS}_{n\mathbf{k}} + \left\langle n\mathbf{k} \middle| \Sigma - V^{KS}_{xc} \middle| n\mathbf{k} \right\rangle$$

Density-functional theory

Kohn-Sham equation

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

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

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

Density-functional theory

Kohn-Sham equation

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

Bethe-Salpeter equation

Two-particle eigenvalue problem

$$\sum_{v'c'\mathbf{k}'} H^{e-h}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E_{\lambda} A^{\lambda}_{vc\mathbf{k}}$$

Diagonal term

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

Direct term - attractive

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

Metals
Semiconductors
Insulators
Molecules

Exchange term - repulsive

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

Bethe-Salpeter equation

Spin singlets

$$H^{e-h} = H^{\text{diag}} + \gamma_c H^{\text{dir}} + 2\gamma_x H^{x}$$

Spin triplets

$$H^{e-h} = H^{\text{diag}} + \gamma_c H^{\text{dir}} + \cancel{2\gamma_x H^{x}}$$

Random-phase approximation

$$H^{e-h} = H^{\text{diag}} + \cancel{\gamma_c H^{\text{dir}}} + 2\gamma_x H^{x}$$

Independent-particle approximation

$$H^{e-h} = H^{\text{diag}} + \cancel{\gamma_c H^{\text{dir}}} + \cancel{2\gamma_x H^{x}}$$

Electron-hole pairs

$$\sum_{v'c'\mathbf{k}'} \hat{H}_{vc\mathbf{k},v'c'\mathbf{k}'} A^{\lambda}_{v'c'\mathbf{k}'} = E^{\lambda} A^{\lambda}_{vc\mathbf{k}}$$

Exciton wavefunction

Optical excitations

valence

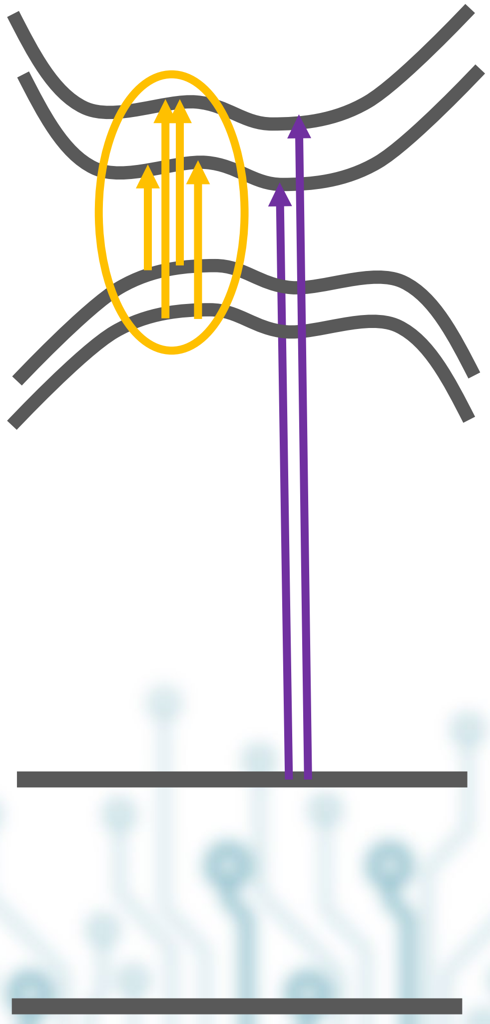
conduction

$$\phi^{\lambda}(\mathbf{r}_e, \mathbf{r}_h) = \sum_{\cancel{v}c\mathbf{k}} A^{\lambda}_{vc\mathbf{k}}\, \psi^{*}_{v\mathbf{k}}(\mathbf{r}_h)\, \psi_{c\mathbf{k}}(\mathbf{r}_e)$$

Core excitations

core

conduction



Spectra

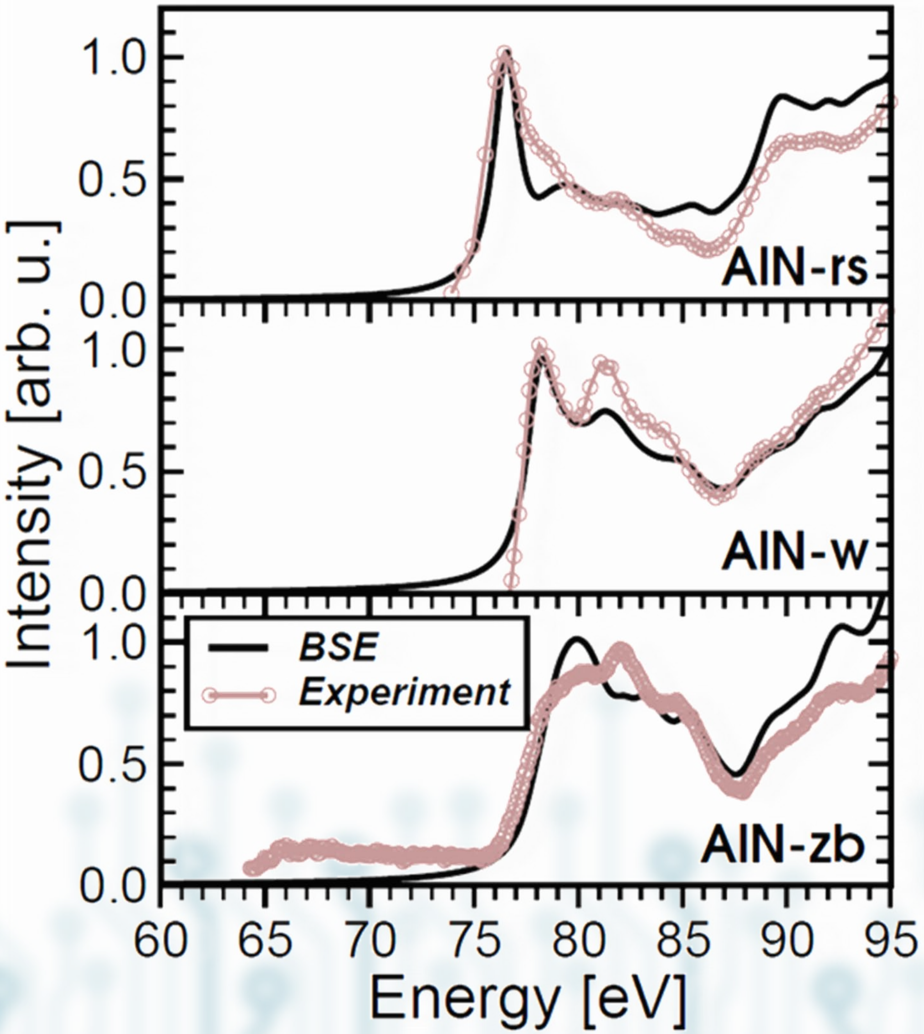
$$\mathrm{Im}\, \varepsilon_M(\omega) = \frac{8\pi^2}{\Omega} \sum_{\lambda} \left| \sum_{vc\mathbf{k}} \boxed{A^{\lambda}_{vc\mathbf{k}}} \frac{\langle v\mathbf{k}|\hat{\mathbf{p}}|c\mathbf{k}\rangle}{\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}}} \right|^2 \delta(\omega - \boxed{E_{\lambda}})$$

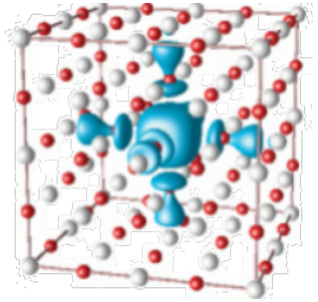
Examples ...

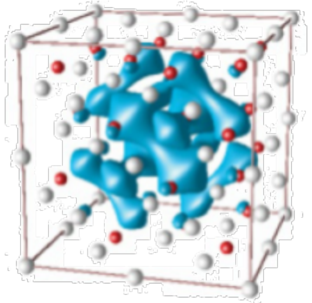
Structural fingerprints

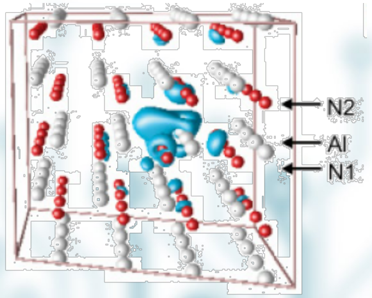
$$\phi_\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cv} A_\lambda^{cv} \psi_c(\mathbf{r}_e)\ \psi_v(\mathbf{r}_h)$$

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









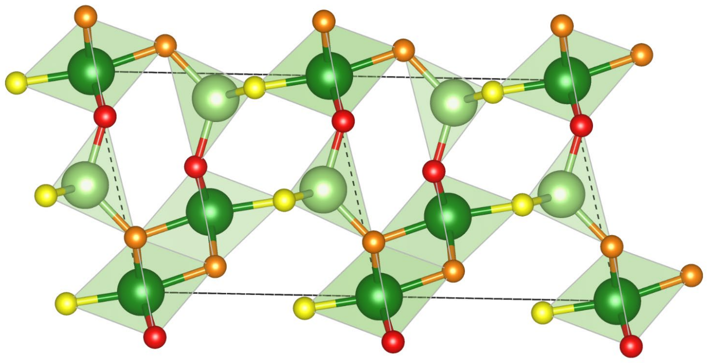
W. Olovsson et al., PRB **83**, 195206 (2011).

Experiment: T. Mizoguchi (2003), M. Sennour (2003).

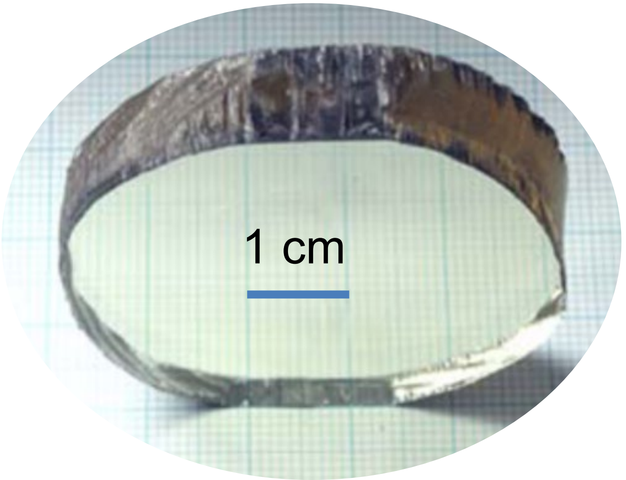
Crystal phases

Several polymorphs, e.g …

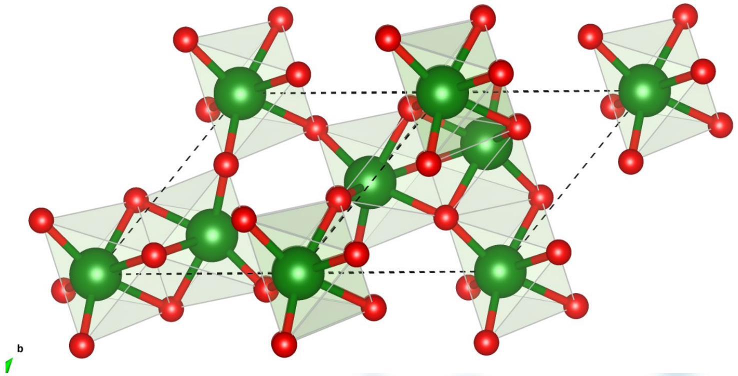
β-Ga_2O_3



monoclinic



α-Ga_2O_3



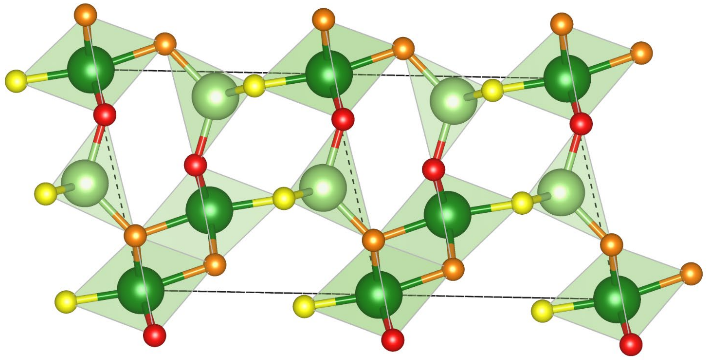
rhombohedral

Z. Galazka, Semicond. Sci. Technol. 33, 113001 (2018).

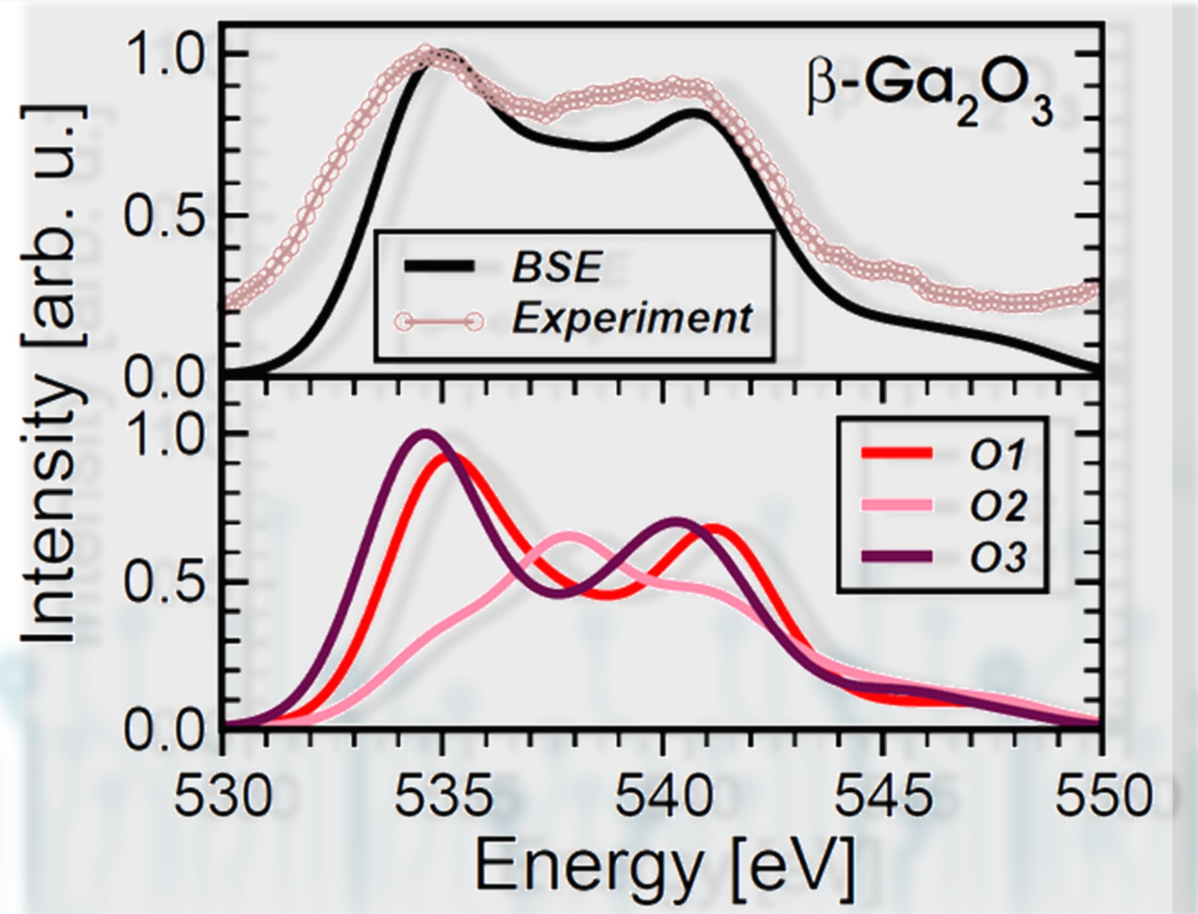
Structural fingerprints

O K edge in β-Ga_2O_3

Complementing ELNES experiments



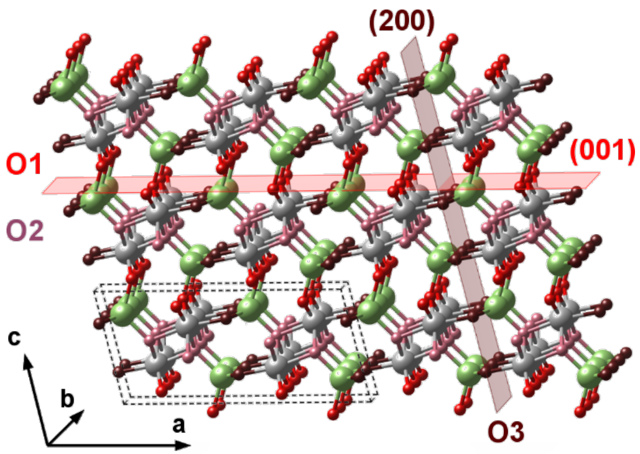
3 symmetrically inequivalent oxygen sites

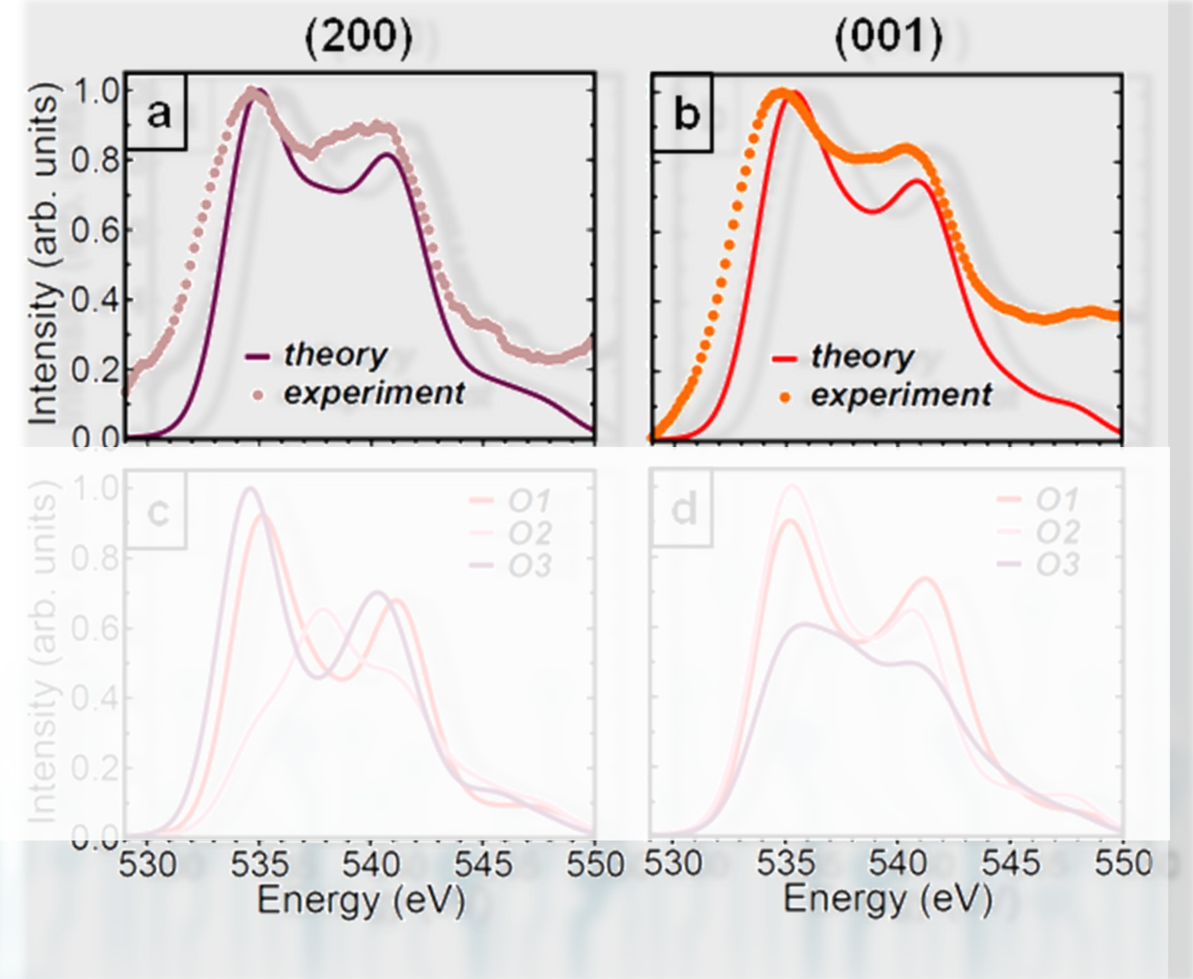


C. Cocchi C. Cocchi, H. Zschiesche, D. Nabok, A. Mogilatenko, M. Albrecht, Z. Galazka, H. Kirmse, C. Draxl, and C. T. Koch Phys. Rev. B **94**, 075147 (2016).

Structural fingerprints

O K edge in β-Ga_2O_3





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

C. Cocchi C. Cocchi, H. Zschiesche, D. Nabok, A. Mogilatenko, M. Albrecht, Z. Galazka, H. Kirmse, C. Draxl, and C. T. Koch
Phys. Rev. B **94**, 075147 (2016).

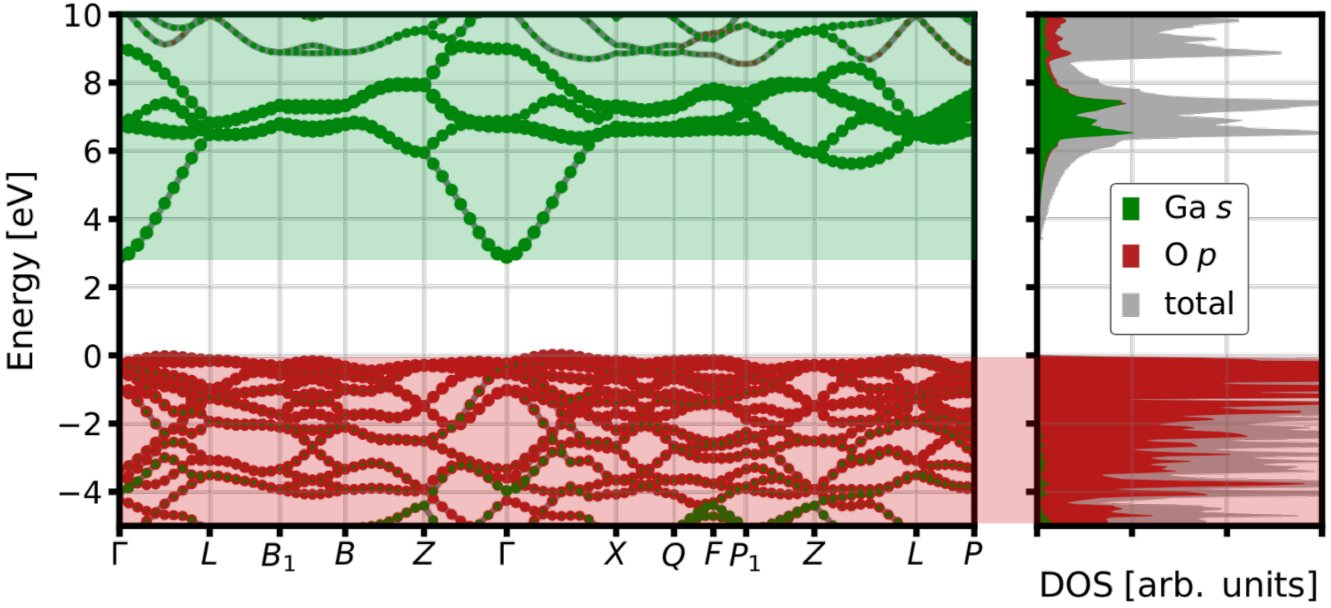
Electronic structure

Kohn-Sham bands

PBEsol functional

α-Ga_2O_3

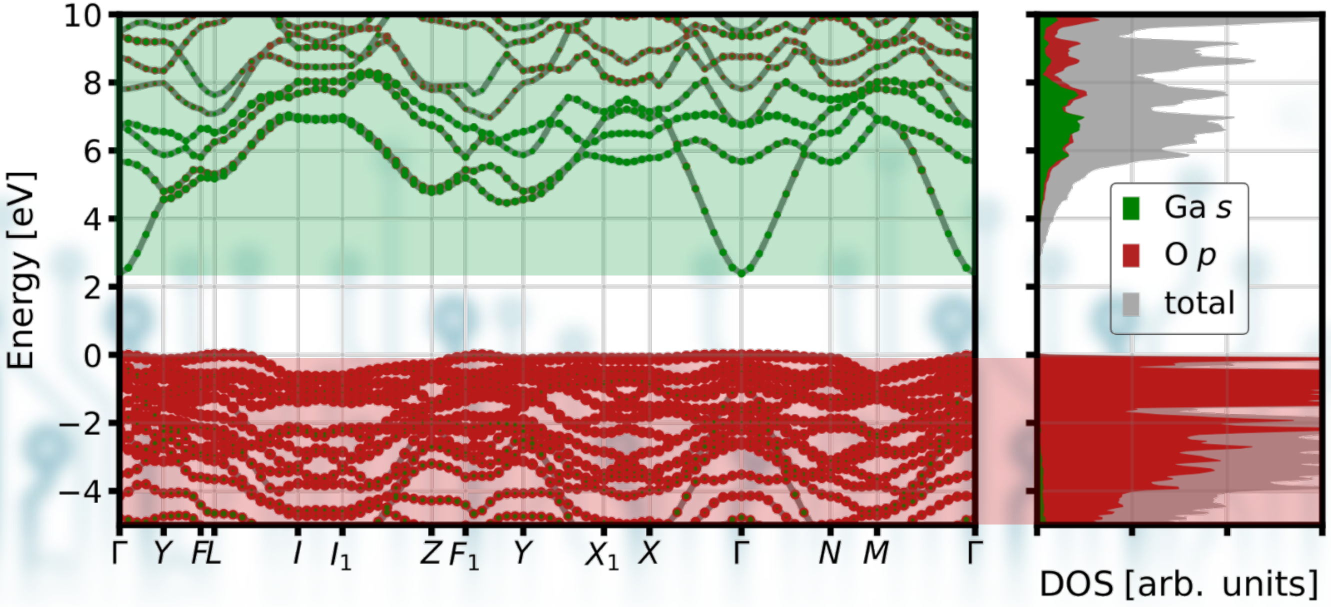
Mainly O *p* character
hybridized with Ga *s* and *p* states



Predominant Ga *s* and O *s* character

β-Ga_2O_3

Mainly O *p* character

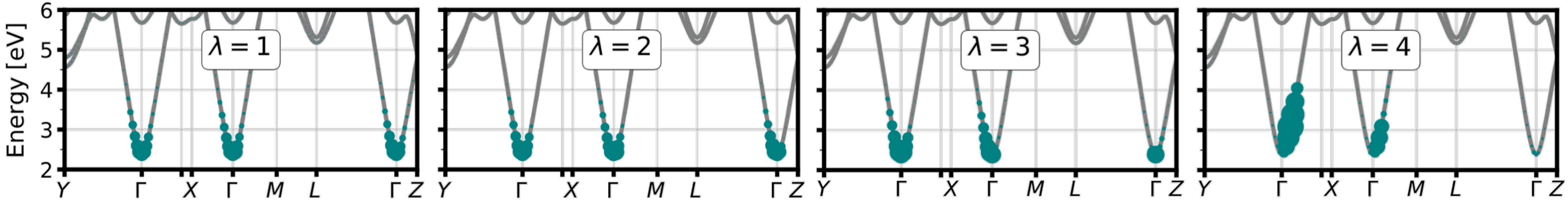


Core excitations

Exp. 1: V. L. Pool et al., J. Appl. Phys. 109, 07B529 (2001).
Exp. 2: K. I. Shimizu et al., Chem. Commun. 1827 (1996).

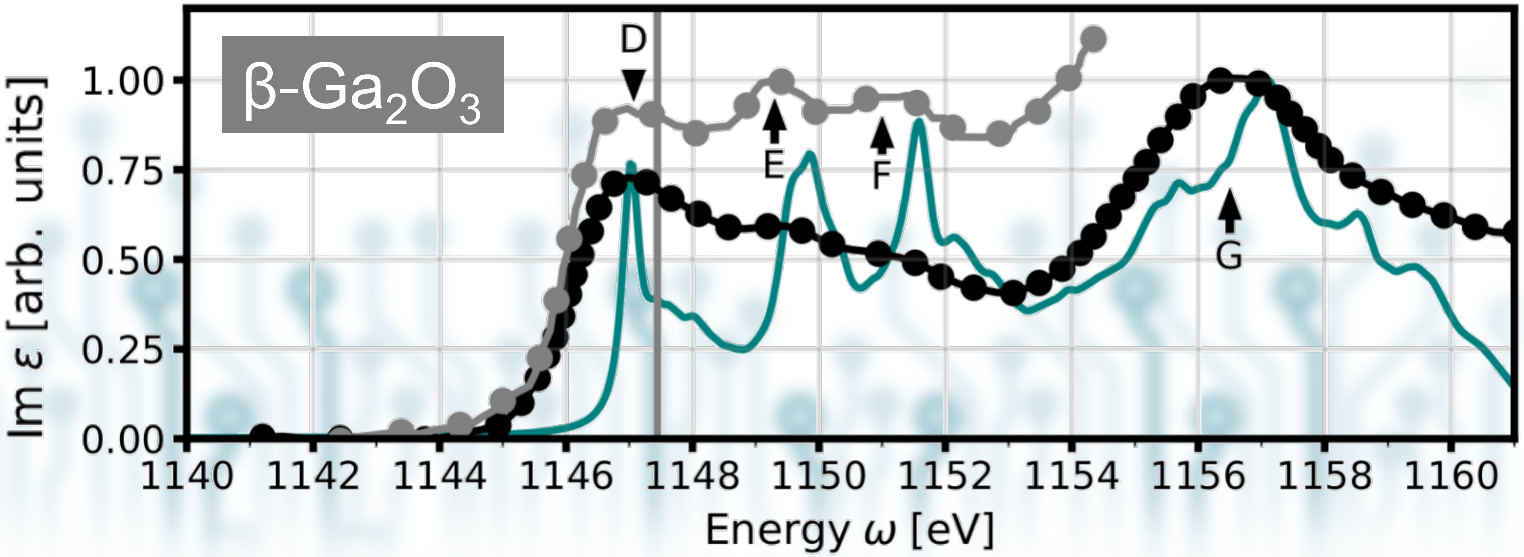
Ga L_2-edge

Electron-hole wavefunction $$\phi^\lambda(\mathbf{r}_e, \mathbf{r}_h) = \sum_{v c \mathbf{k}} A^\lambda_{vc\mathbf{k}}\, \psi^*_{v\mathbf{k}}(\mathbf{r}_h)\psi_{c\mathbf{k}}(\mathbf{r}_e)$$



Similar character of the 4 lowest excitons

Rydberg series



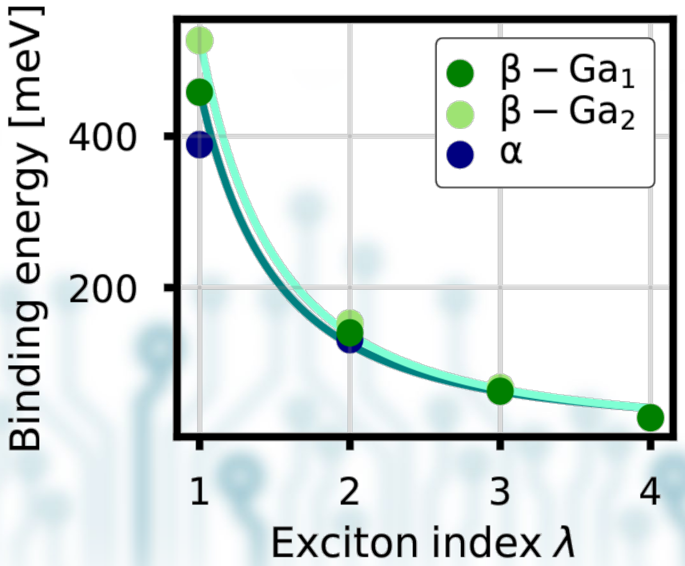
Core excitations

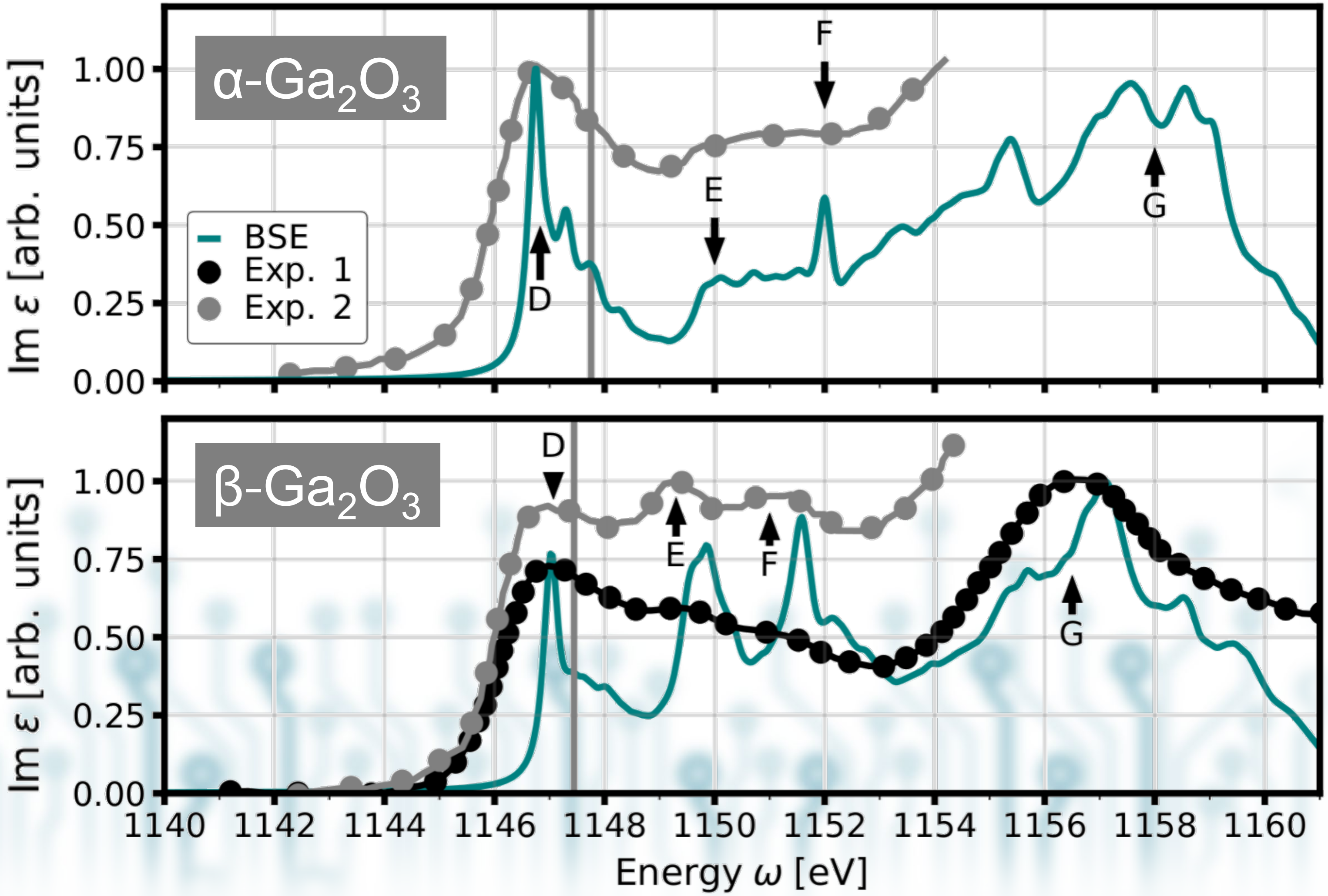
Exp. 1: V. L. Pool et al., J. Appl. Phys. 109, 07B529 (2001).
Exp. 2: K. I. Shimizu et al., Chem. Commun. 1827 (1996).

Hydrogenic Rydberg series for both polymorphs

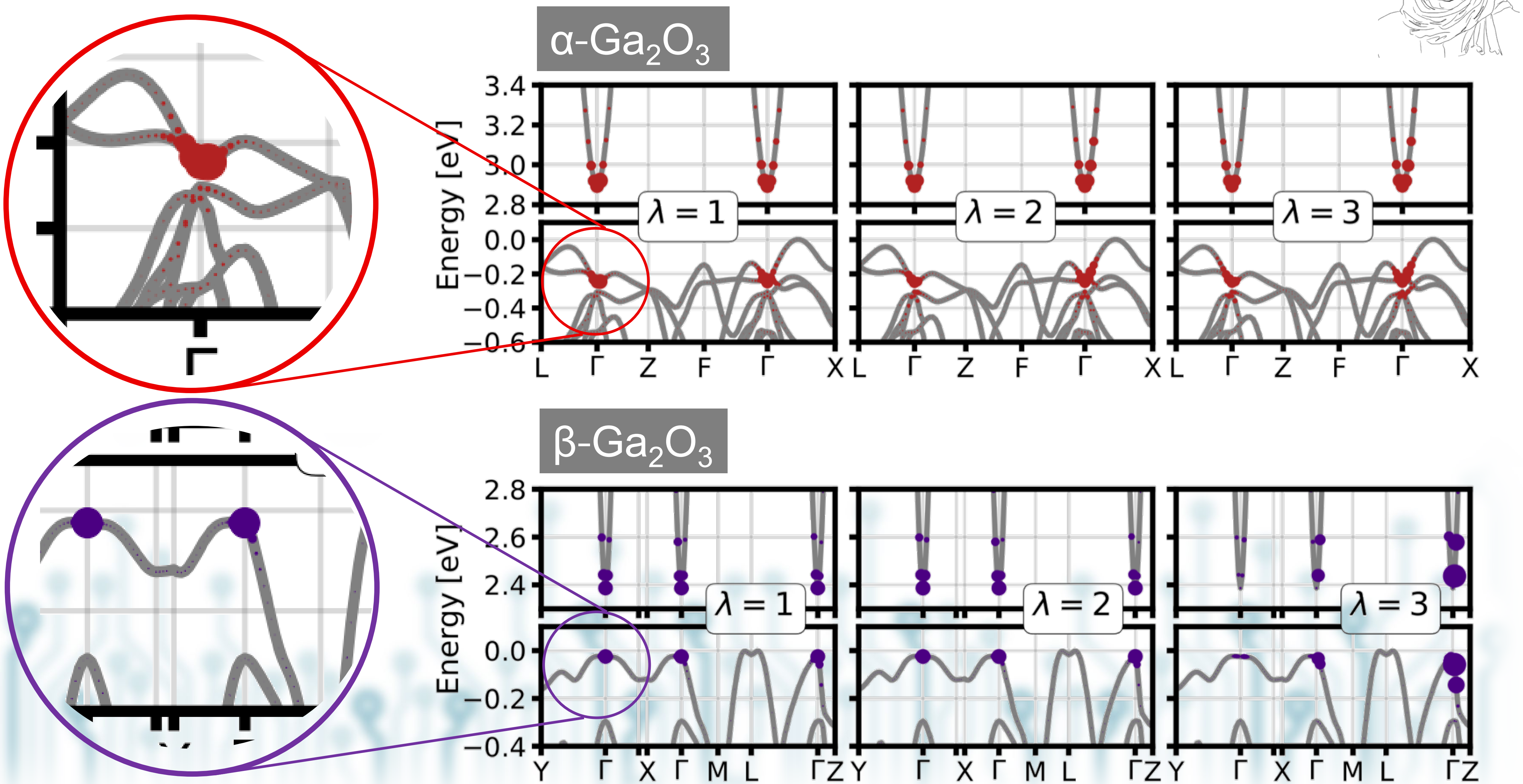
Similar distribution of Ga 2*p* hole and excited electron

$$E_b \sim \frac{1}{\lambda^2}$$



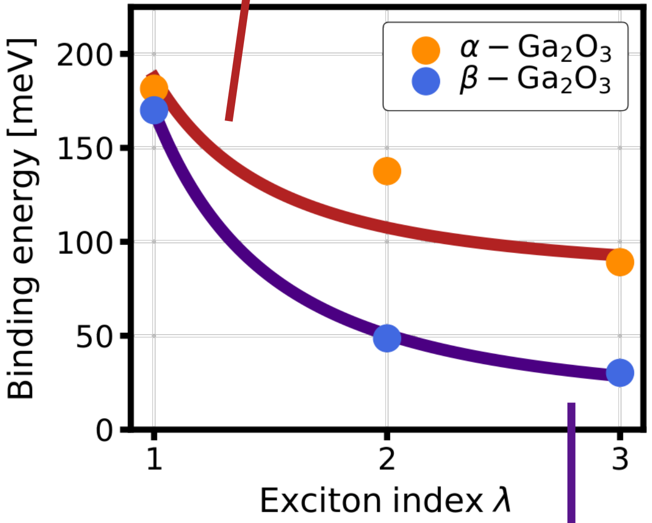


Optical excitations

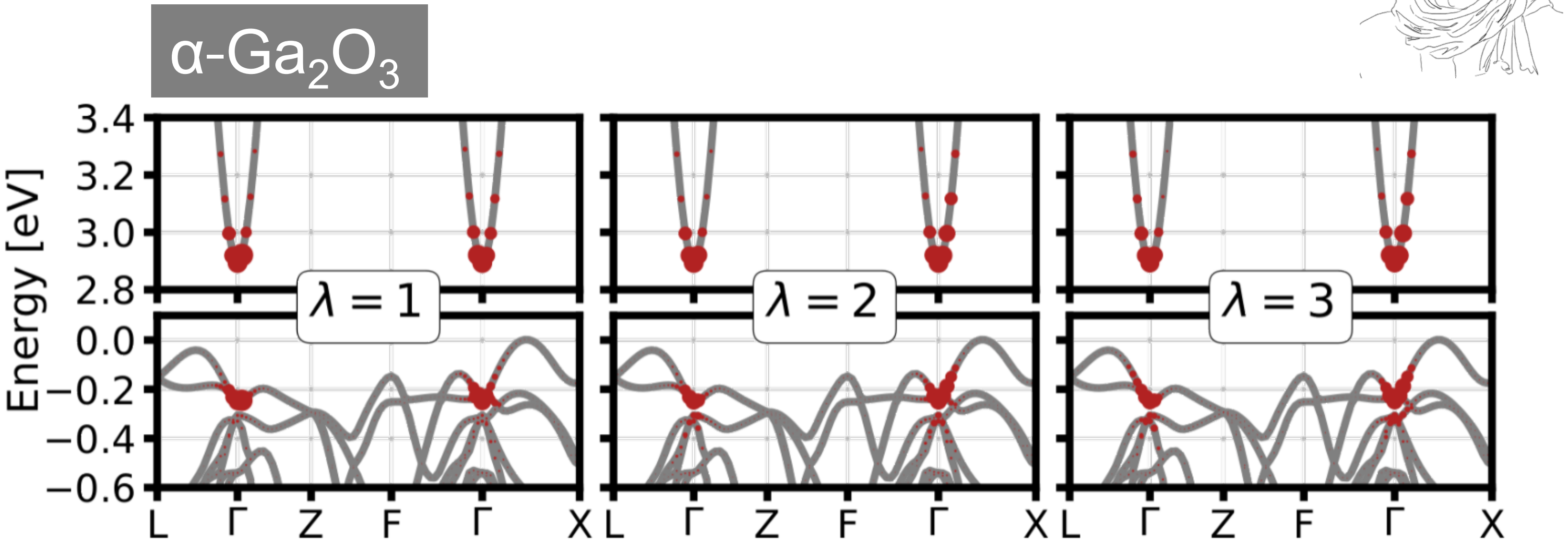


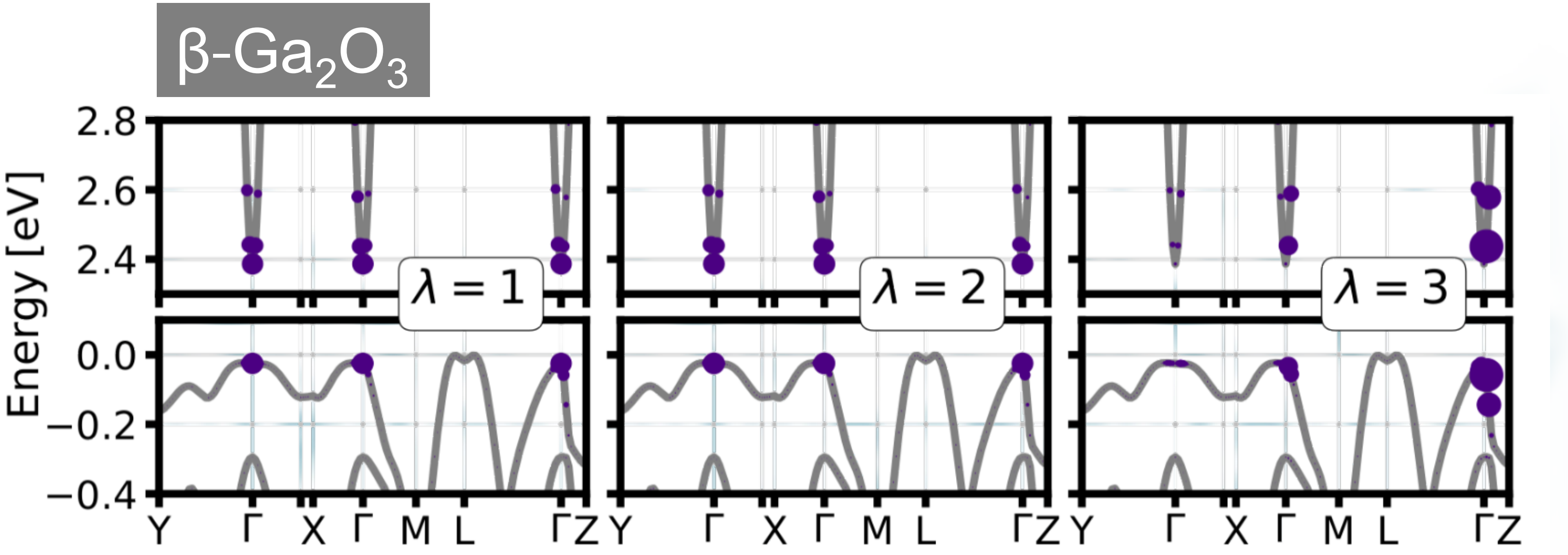
Optical excitations

Non-hydrogenic Rydberg series



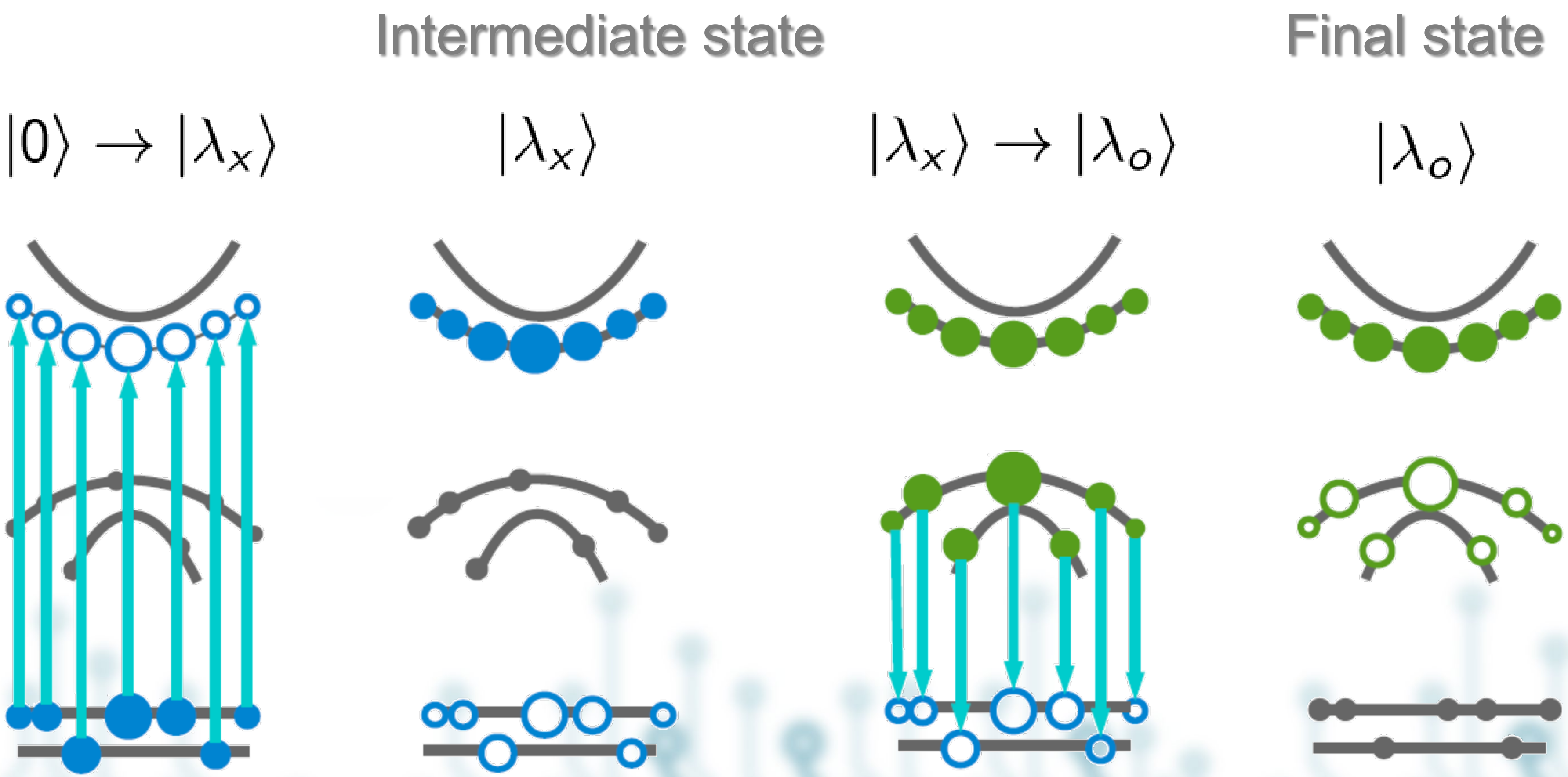
Hydrogenic Rydberg series





Interplay between core and valence excitations

Resonant inelastic x-ray scattering - RIXS



$$\boxed{t^{(1)}_{\lambda_x}} = \sum_{\mu c \mathbf{k}} \boxed{\left[A^{\lambda_x}_{\mu c \mathbf{k}}\right]^*} \boxed{\langle \mu \mathbf{k} | \mathbf{p} | c \mathbf{k} \rangle}$$

$$\boxed{t^{(2)}_{\lambda_x \lambda_o}} = \sum_{v c \mathbf{k}} \sum_{\mu} \boxed{A^{\lambda_o}_{v c \mathbf{k}}} \boxed{\langle v \mathbf{k} | \mathbf{p} | \mu \mathbf{k} \rangle} \boxed{\left[A^{\lambda_x}_{\mu c \mathbf{k}}\right]^*}$$

Resonant inelastic x-ray scattering - RIXS

Double differential cross section

excitation energy

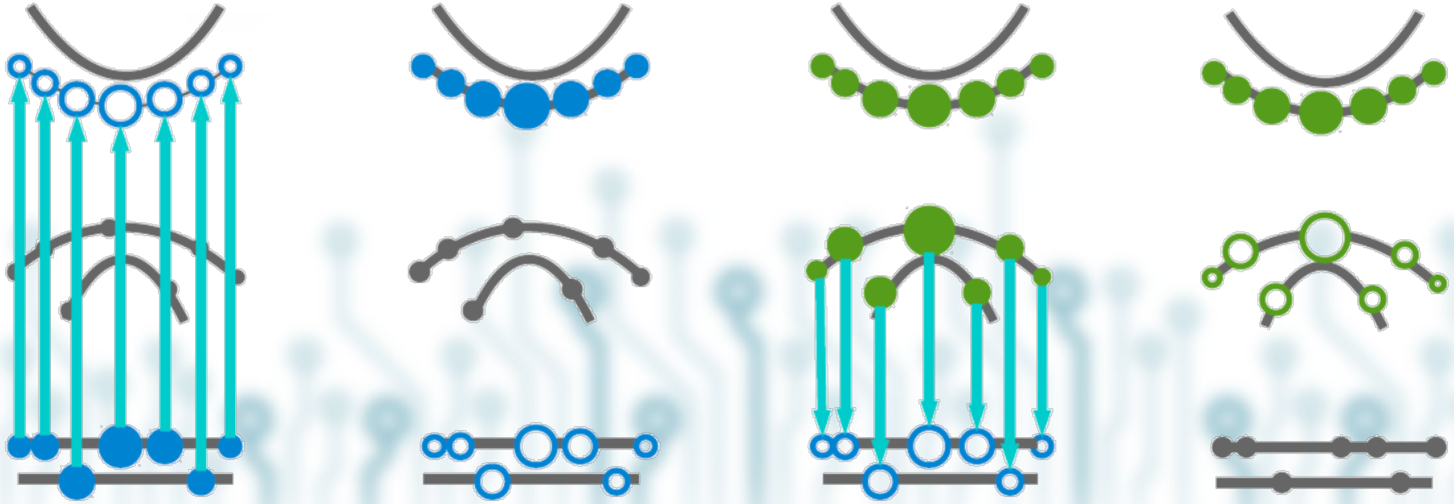
$$\frac{d^2\sigma}{d\Omega_2 d\omega_2} \propto \mathrm{Im}\sum_{\lambda_o} \frac{\left|t^{(3)}_{\lambda_o}(\omega_1)\right|^2}{E^{\lambda_o} - \omega + i\eta}$$

energy loss

frequency independent

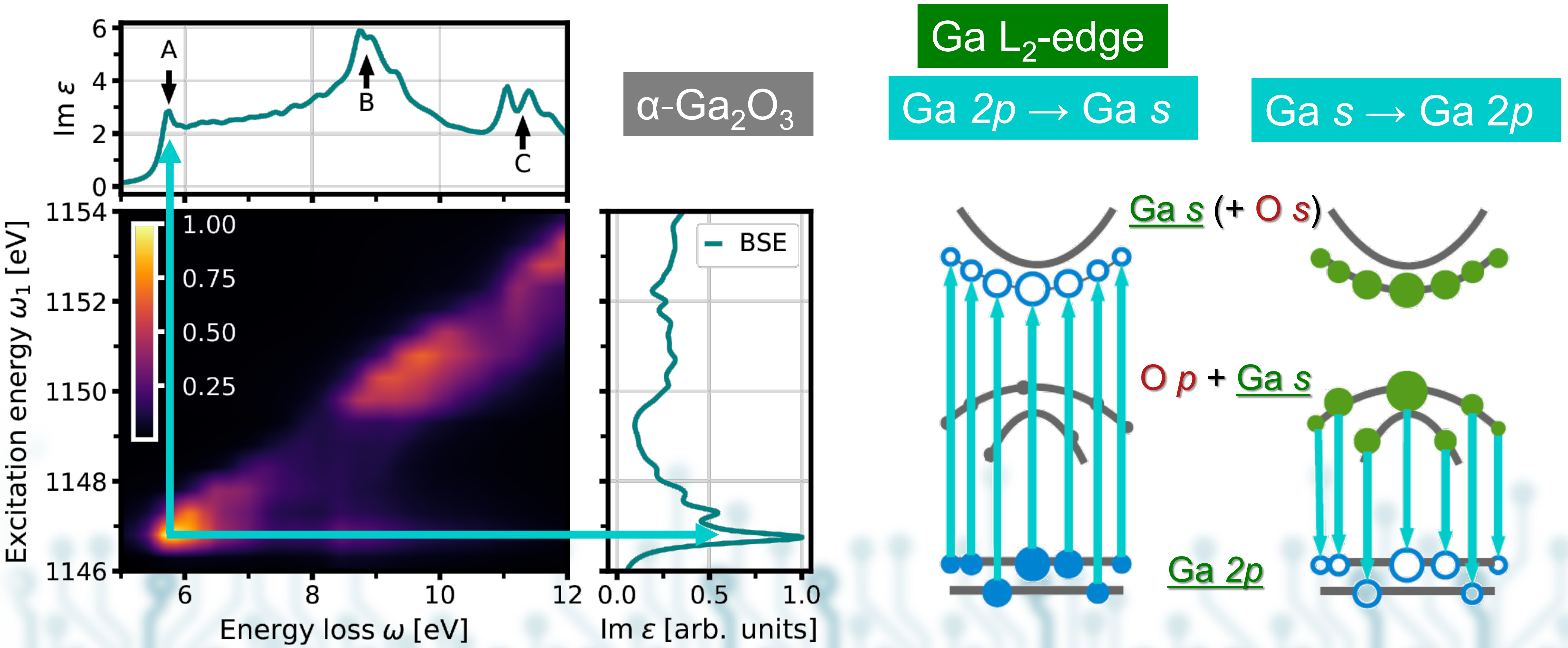
excitation energy

$$\boxed{t^{(3)}_{\lambda_o}(\omega_1)} = \sum_{\lambda_x} \frac{\boxed{t^{(2)}_{\lambda_o\lambda_x}}\,\boxed{t^{(1)}_{\lambda_x}}}{E^{\lambda_x} - \omega_1 + i\eta}$$



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

RIXS in Ga_2O_3



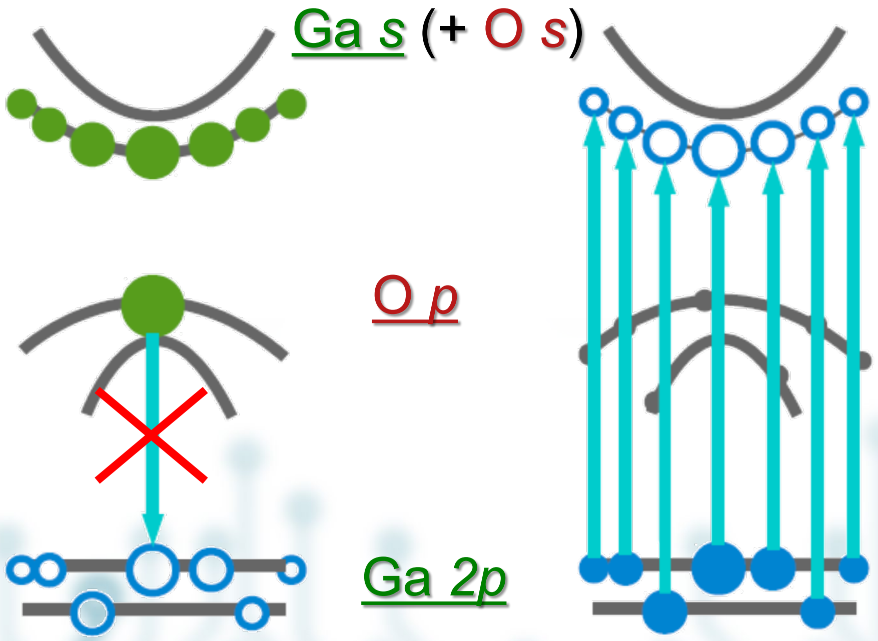
Pronounced exciton-exciton scattering due to hybridization of valence bands

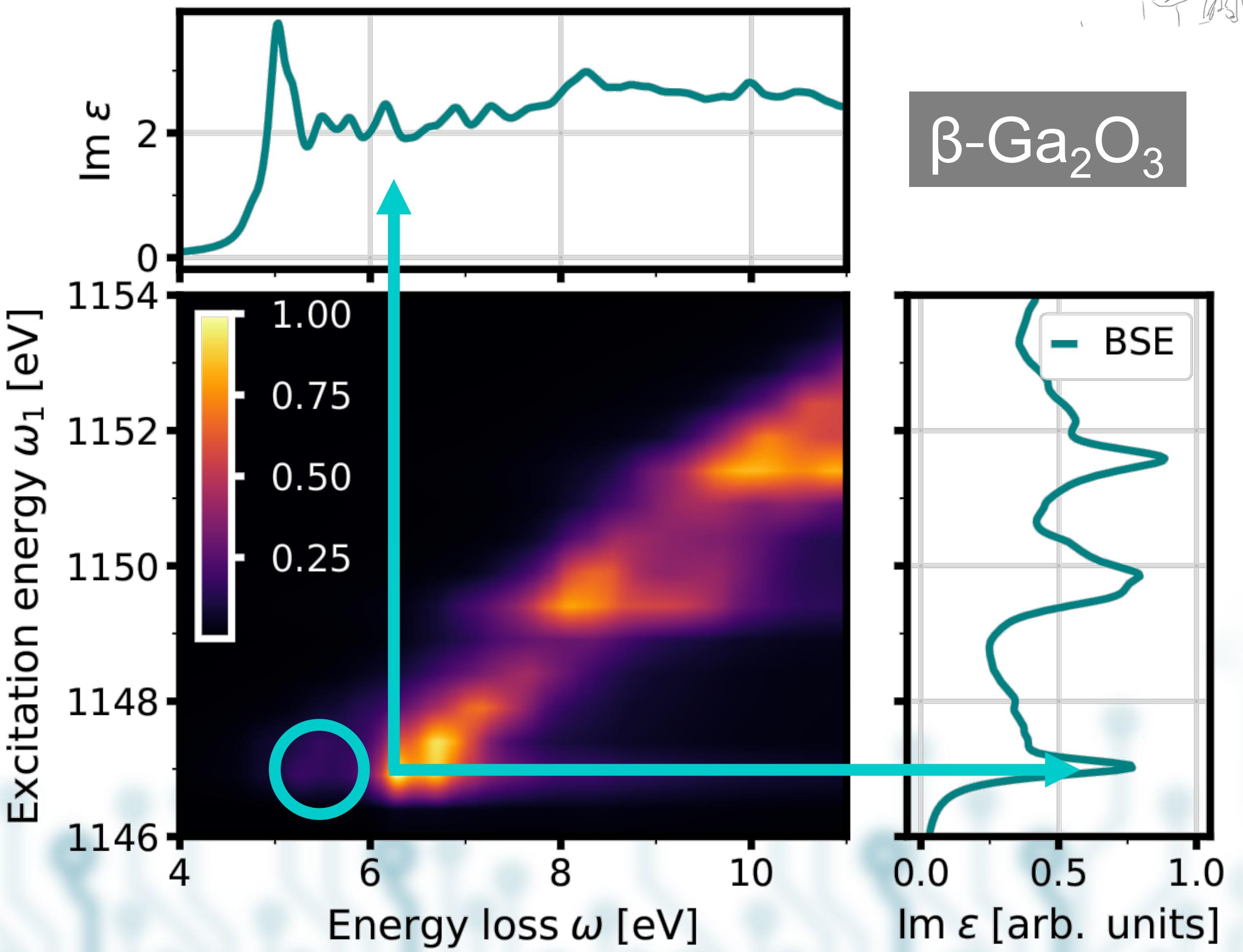
C. Vorwerk, D. Nabok, C. Draxl, preprint.

RIXS in Ga_2O_3

~~O p → Ga $2p$~~

Ga $2p$ → Ga s





β-Ga_2O_3

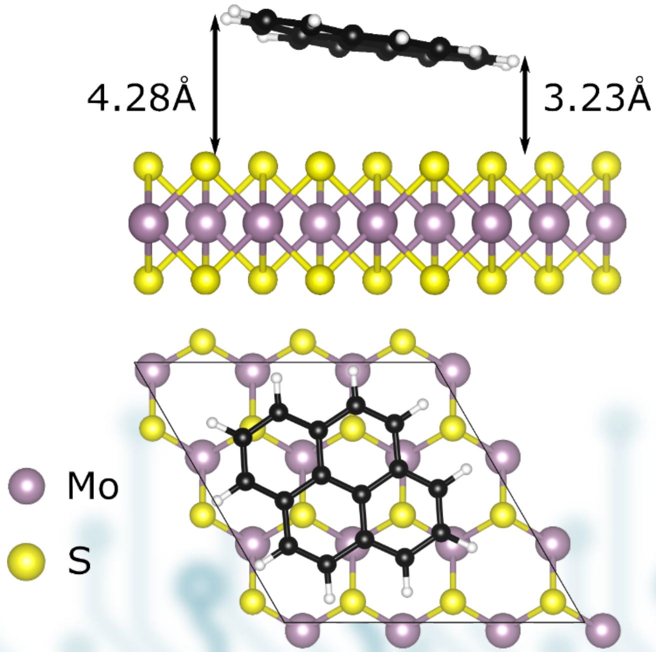
Dark valence excitons in Ga L_2 RIXS
due to strong O contribution to valence hole

C. Vorwerk, D. Nabok, C. Draxl, preprint.

Organic molecules on 2D materials ...

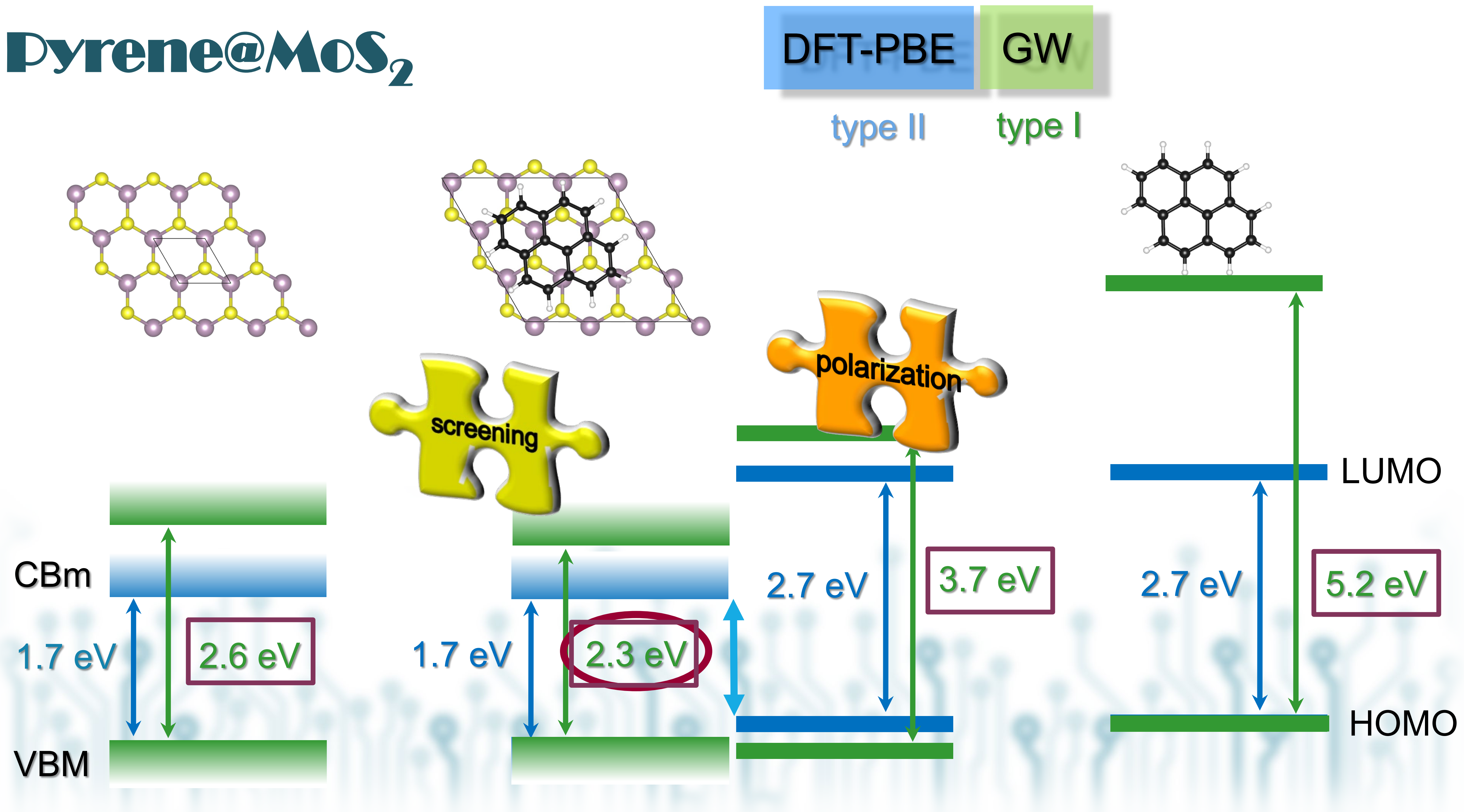
Nature of excitons

Pyrene@MoS_2

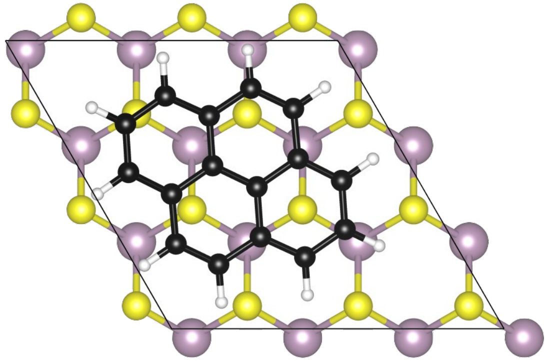


I. Gonzales, F. Caruso, P. Pavone, and C. Draxl, Phys. Rev. Materials 6, 054004 (2022).

Pyrene@MoS$_2$


DFT-PBE
GW
type II
type I
screening
polarization
CBm
VBM
1.7 eV
2.6 eV
1.7 eV
2.3 eV
2.7 eV
3.7 eV
2.7 eV
5.2 eV
LUMO
HOMO

Optical excitations

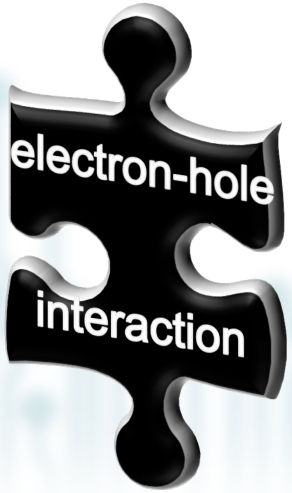


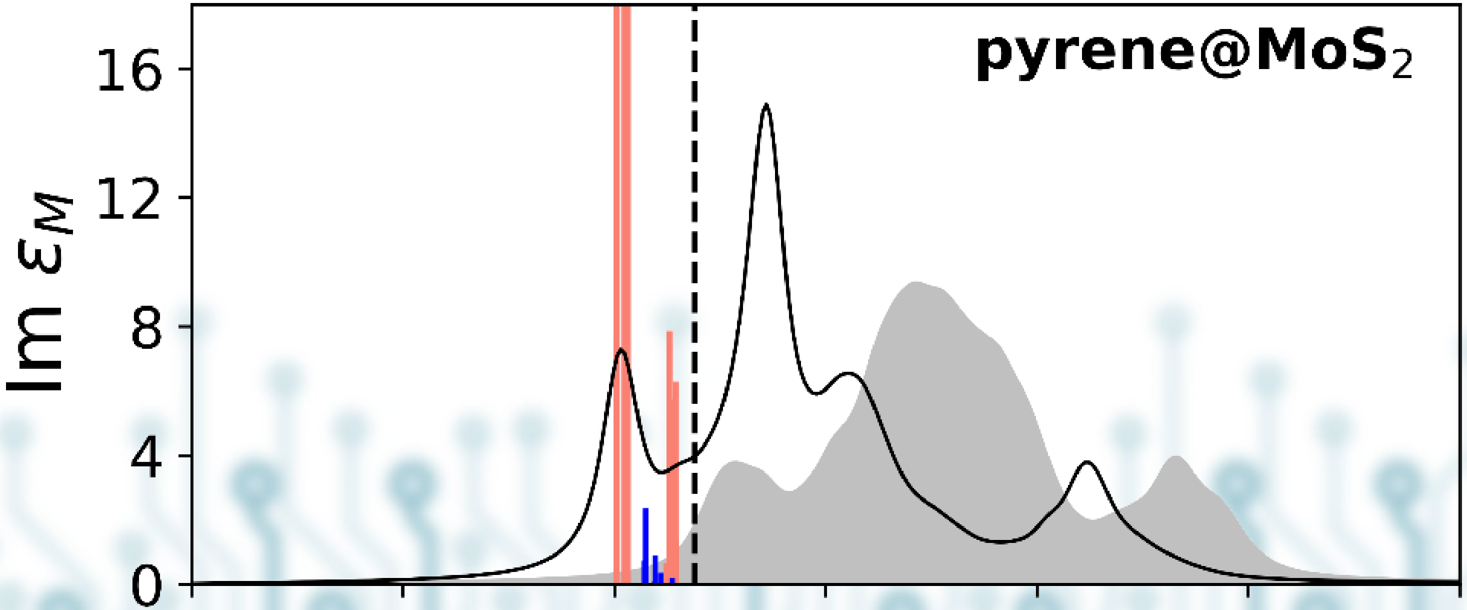
Nature of excitons

Bethe-Salpeter equation

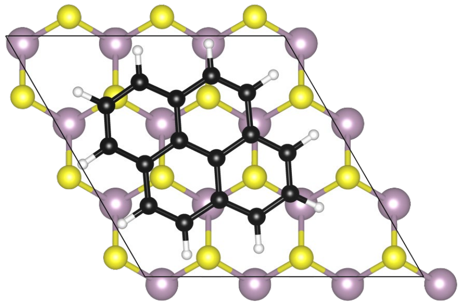
In the **visible** range:

Charge-transfer excitons





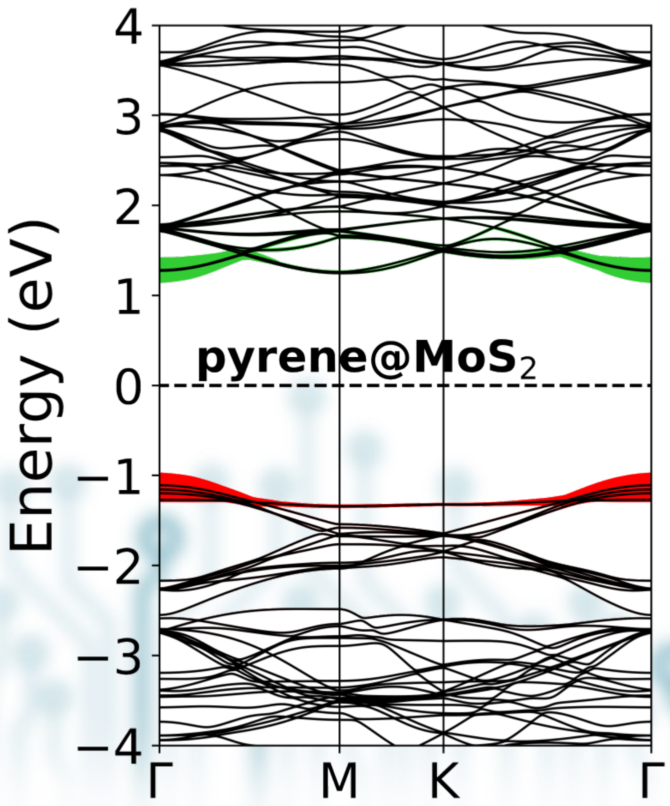
Optical excitations

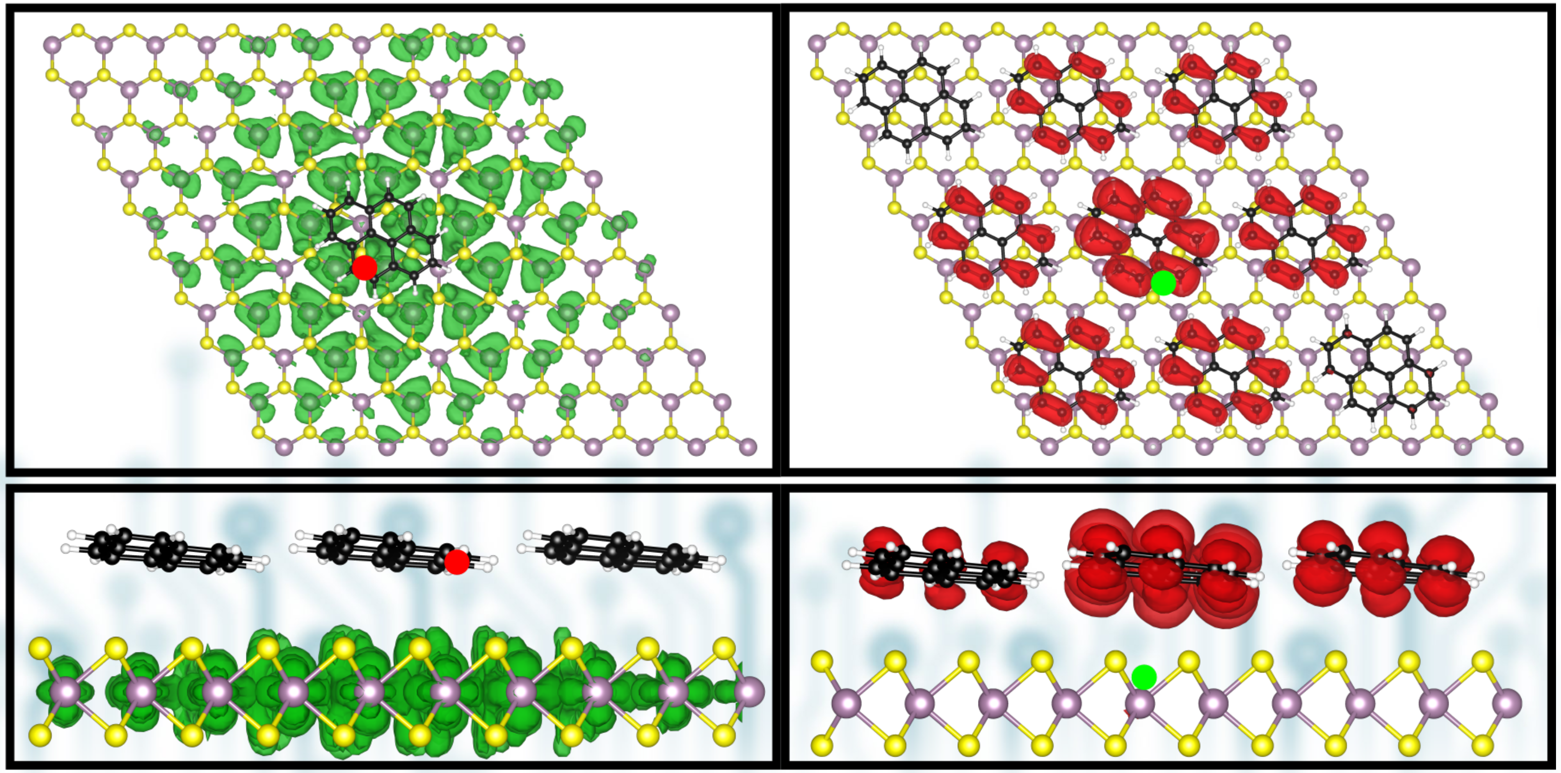


Example: CT exciton in pyrene@MoS_2

Exciton wavefunction

$$\phi^{\lambda}(\mathbf{r}_e, \mathbf{r}_h) = \sum_{vc\mathbf{k}} A^{\lambda}_{vc\mathbf{k}} \psi^{*}_{v\mathbf{k}}(\mathbf{r}_h) \psi_{c\mathbf{k}}(\mathbf{r}_e)$$





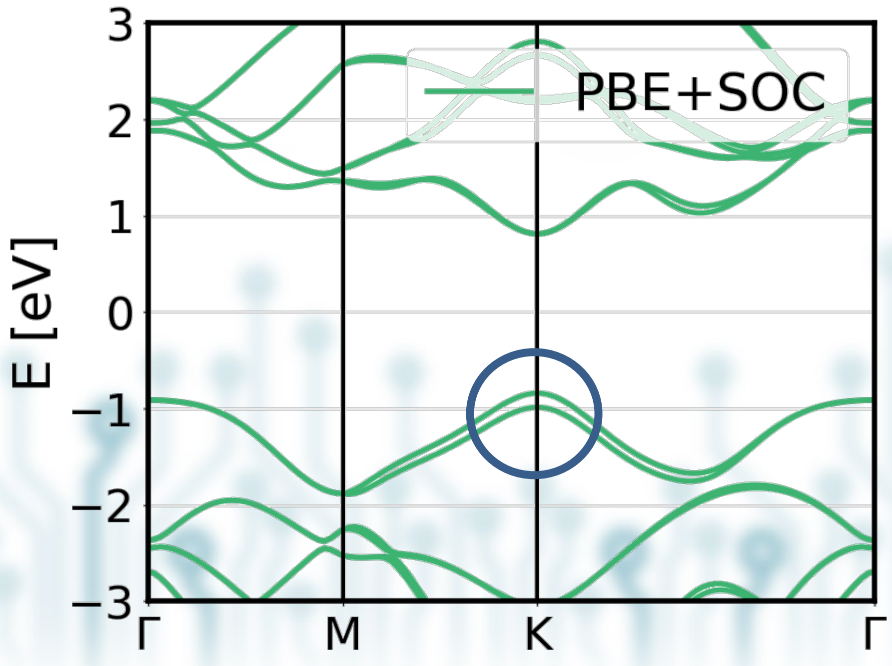
An elephant in the room ...

Type-I alignment

Lowest excitations are MoS_2-like

Band structure

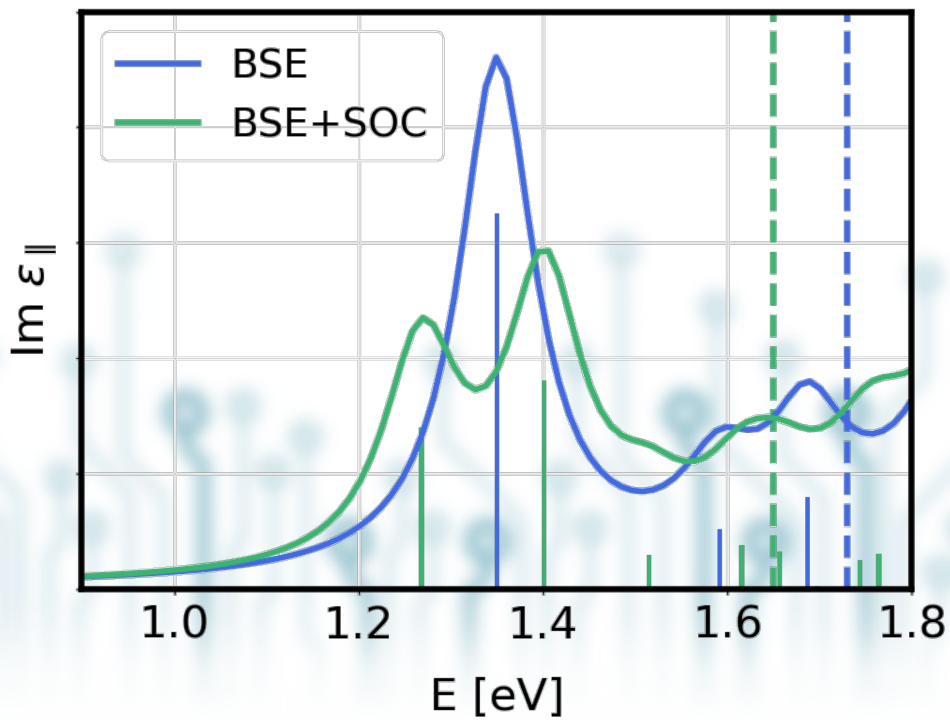
Not dramatic



Spectra

Significant

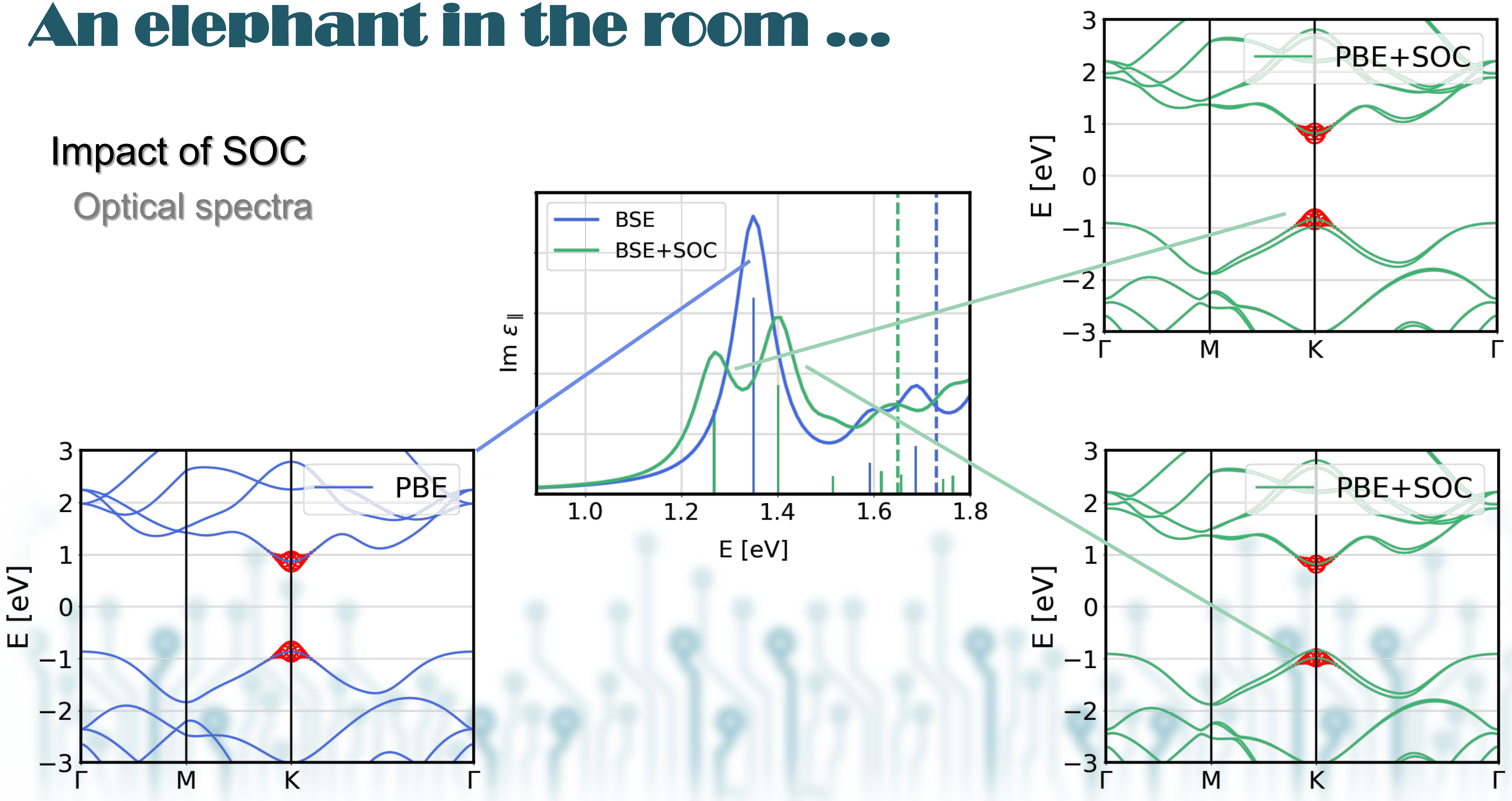
see also A. Marini et al.



An elephant in the room ...

Impact of SOC

Optical spectra

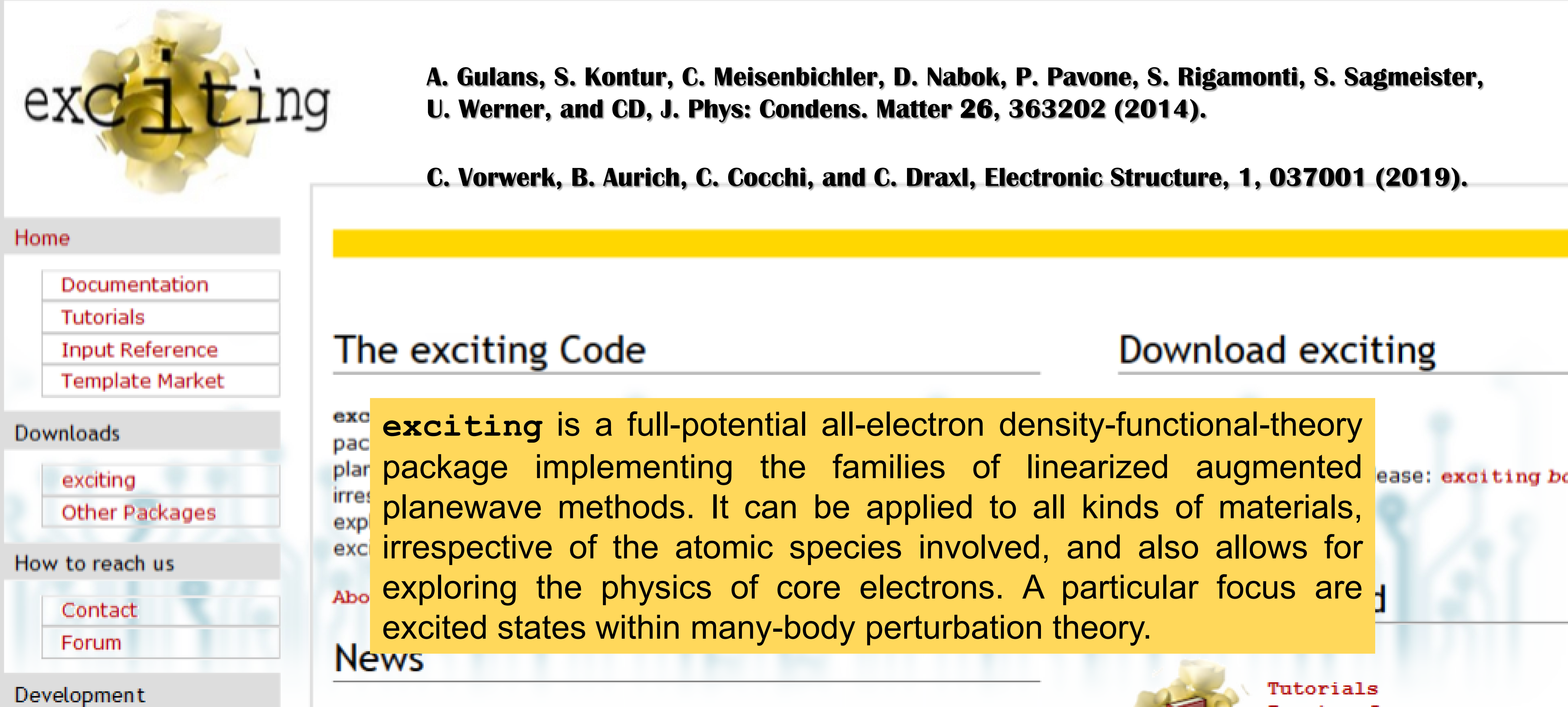


Our instrument

http://exciting-code.org

A. Gulans, S. Kontur, C. Meisenbichler, D. Nabok, P. Pavone, S. Rigamonti, S. Sagmeister, U. Werner, and CD, J. Phys: Condens. Matter 26, 363202 (2014).

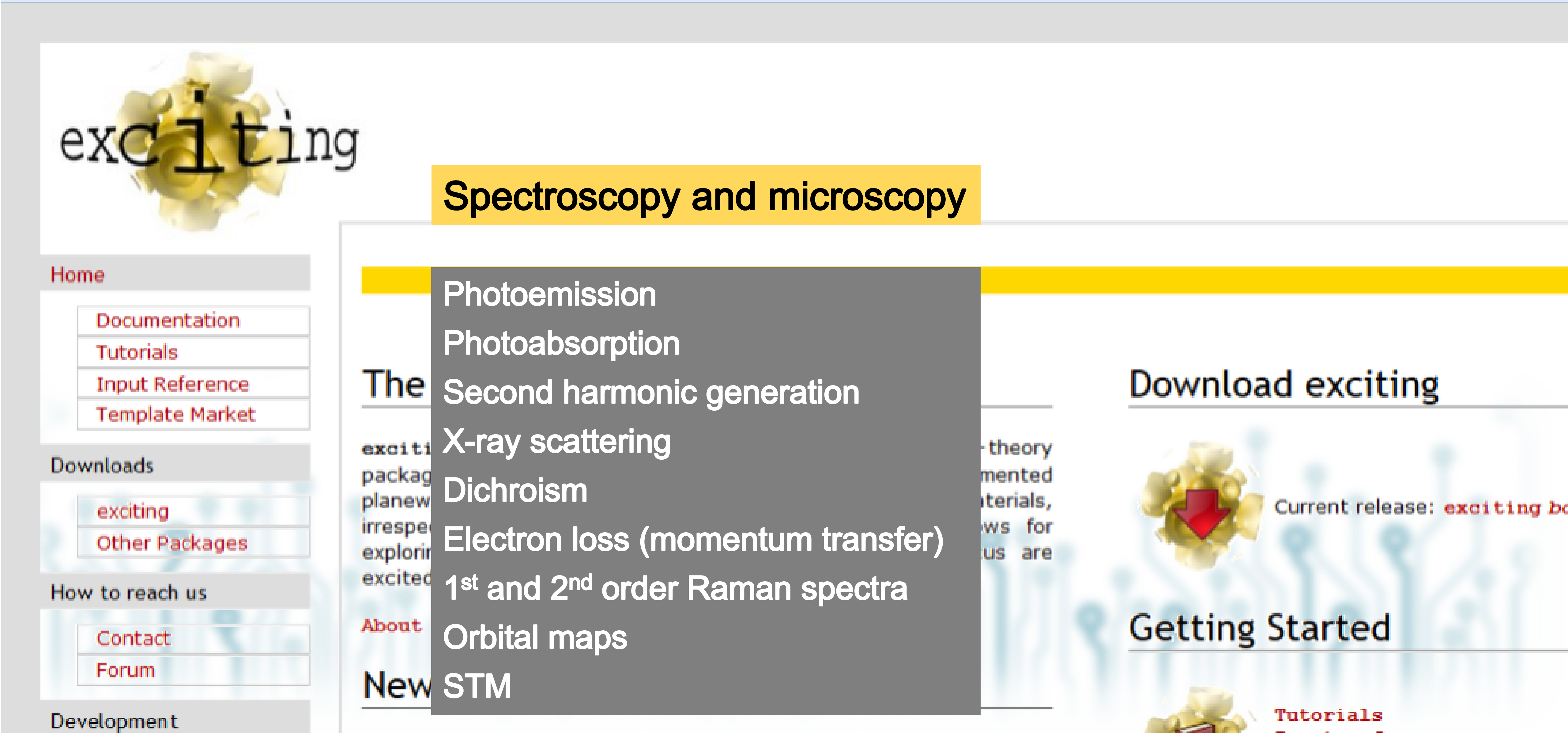
C. Vorwerk, B. Aurich, C. Cocchi, and C. Draxl, Electronic Structure, 1, 037001 (2019).



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.

Our instrument

http://exciting-code.org

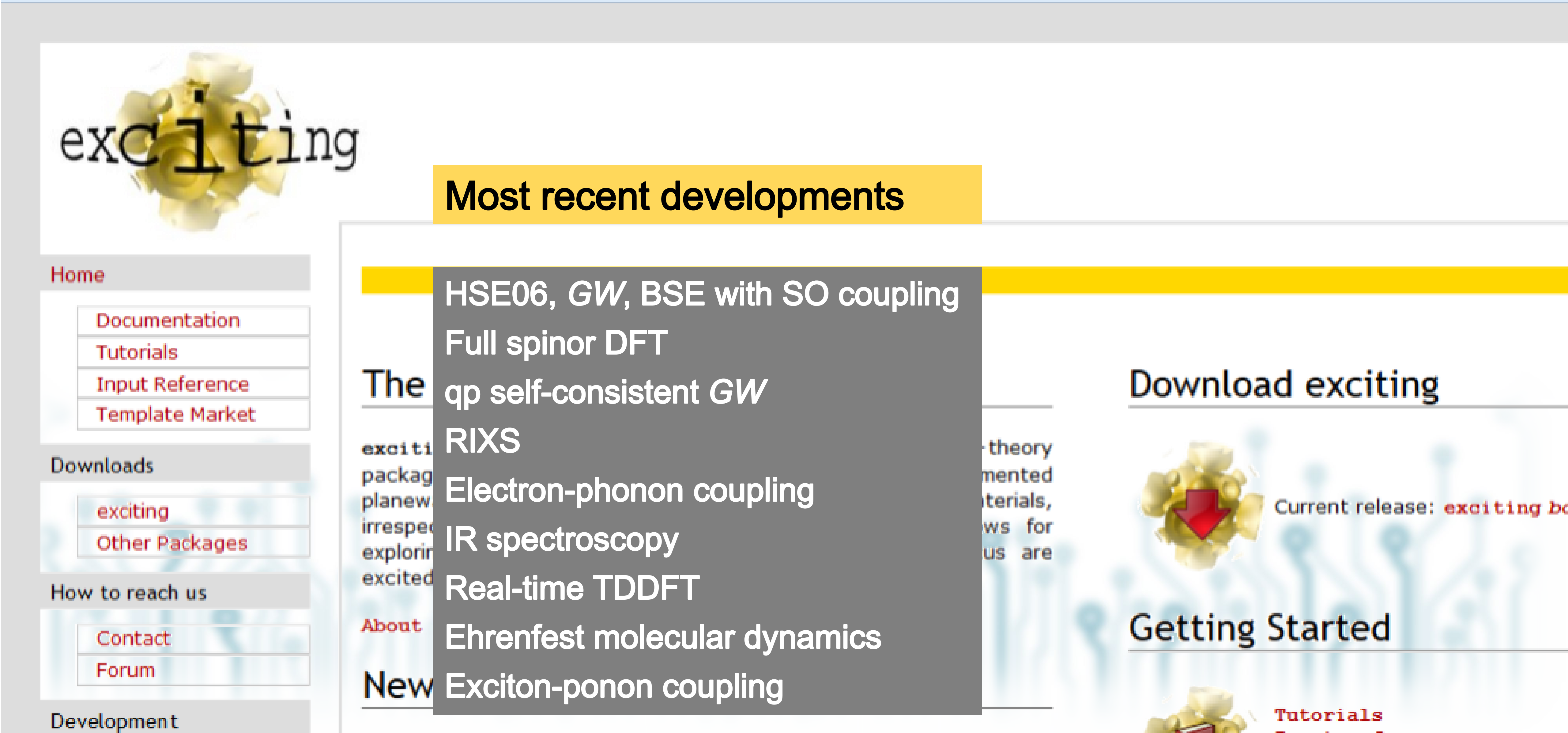


Spectroscopy and microscopy

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

Our instrument

http://exciting-code.org



Most recent developments

- HSE06, *GW*, BSE with SO coupling
- Full spinor DFT
- qp self-consistent *GW*
- RIXS
- Electron-phonon coupling
- IR spectroscopy
- Real-time TDDFT
- Ehrenfest molecular dynamics
- Exciton-ponon coupling

From electron-hole interaction …

… to exciton-phonon coupling

Polarons and self-trapping

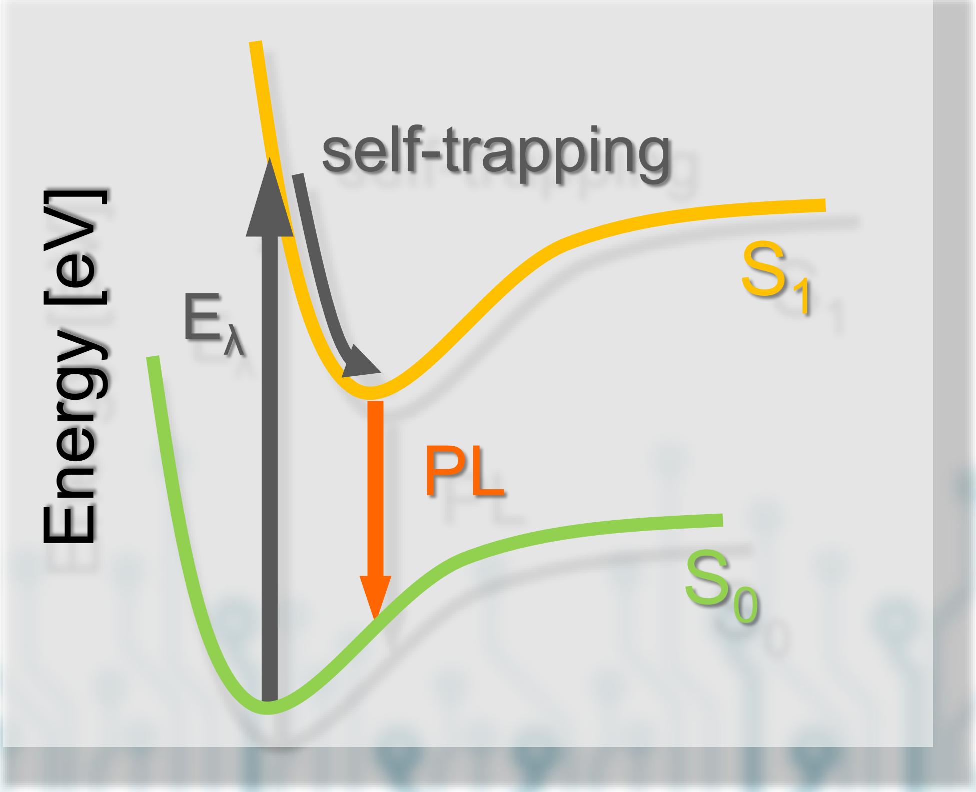
Structural relaxation in excited state

Coupled equations for

- exciton wavefunction
- atomic displacement

Input

- Solution of BSE
  - momentum transfer
- Electron-phonon coupling

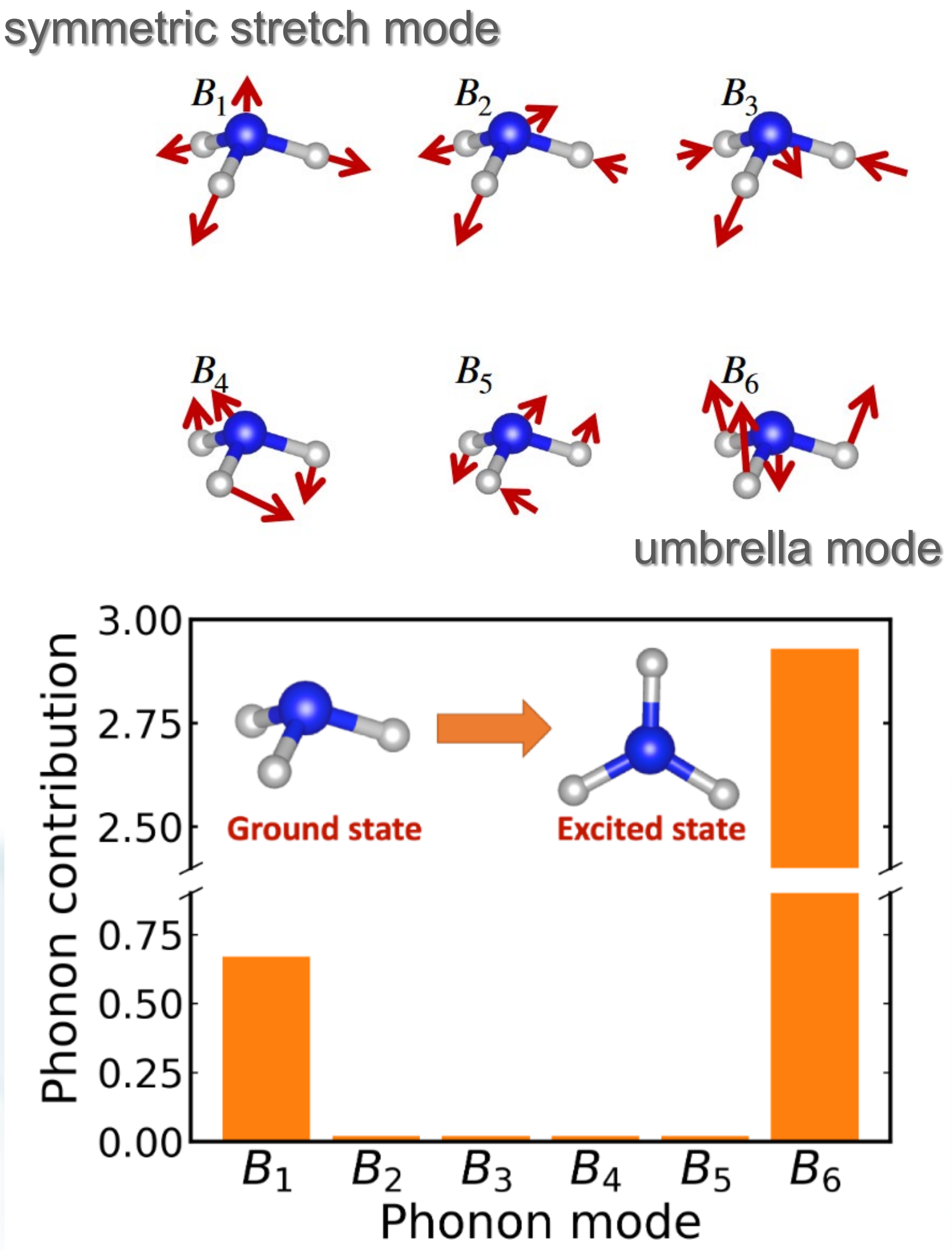


M. Yang ad CD, preprint.

Self-trapping

Results

Method	CO	H_2O		NH_3	
	d	d	α	d	α
This work	1.22	0.99	108.5	1.07	119.7
CDFT [22]	1.21	-	-	1.08	120
BSE-ESF [22]	1.26	-	-	1.08	120
QC [8, 23, 24]	1.21-1.22	0.96	109	1.06	120
Experiment [23]	1.24	1.02	107	1.08	120



M. Yang ad CD, preprint.

Teamwork

exciting

FAIRmat

DFG

HIOS

NOMAD

Leibniz GraFOx ScienceCampus

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