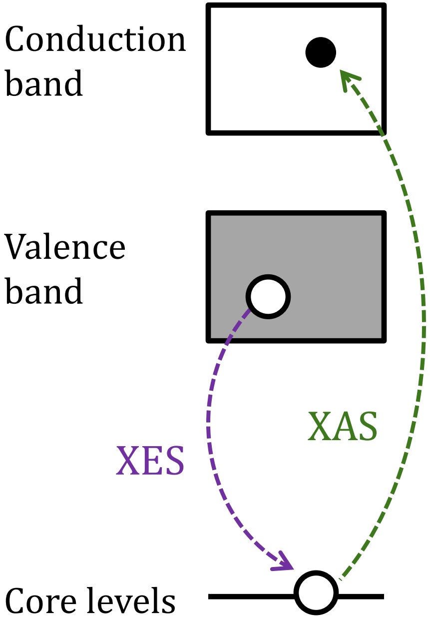
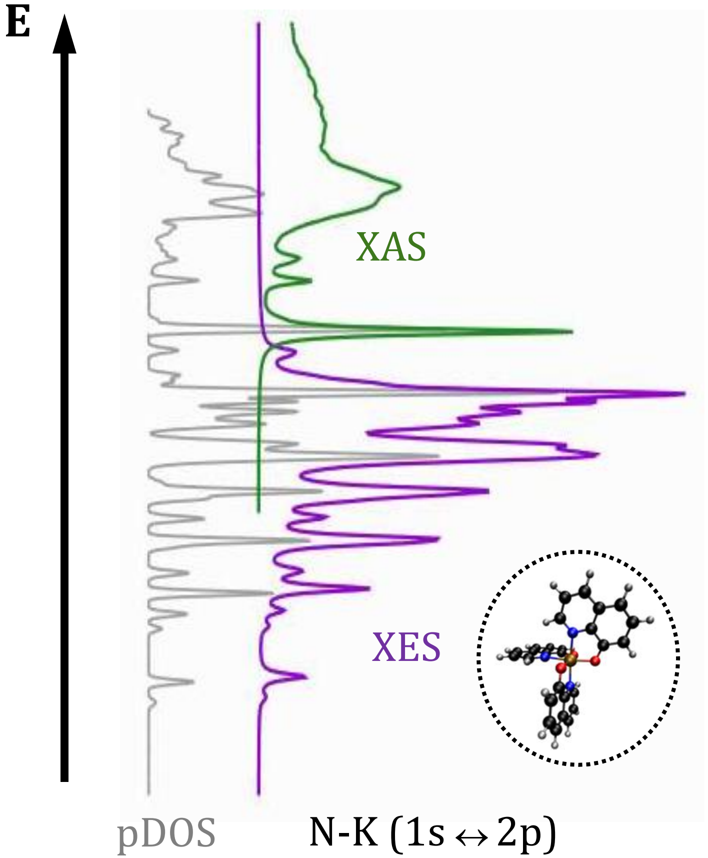
Introduction to x-ray spectroscopy and computational approaches

Keith Gilmore

Core-level spectroscopy probes pDOS

exciting !





Simplified picture:

- XES probes occupied pDOS
- XAS probes unoccupied pDOS

Advantages:

- Element selective
- Orbital selective
- Site selective

Complications:

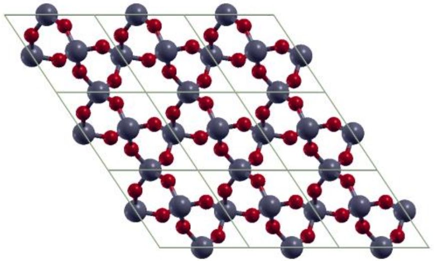
- Local correlations in excited state
- Charge transfer in excited state
- ➢ Deviations from pDOS

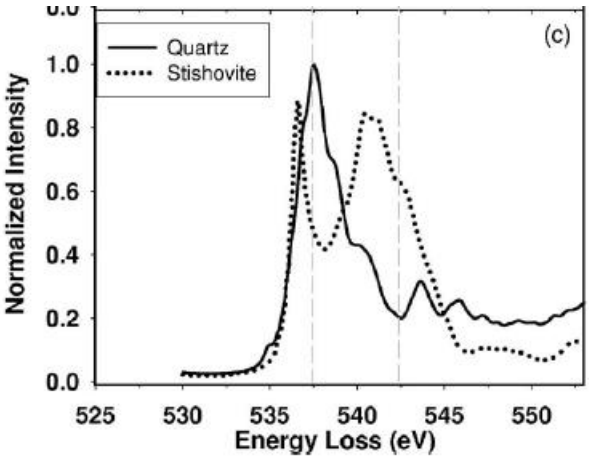
XAS finger-printing for structural determination

exciting !

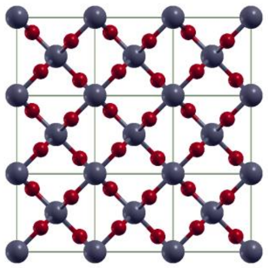
SiO_2

Quartz (4-fold)





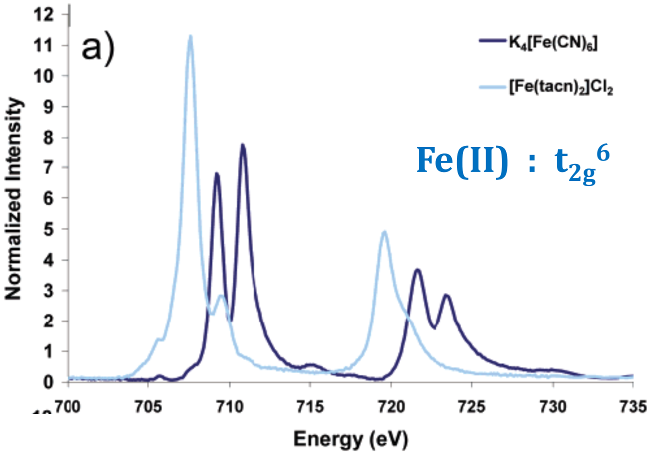
Stishovite (6-fold)



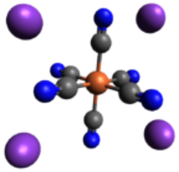
Lin *et al., Phys. Rev. B* ***75****, 012201* (2007)

XAS determination of oxidation state

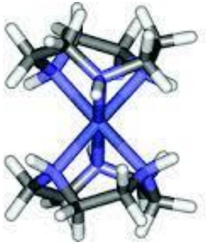
exciting !



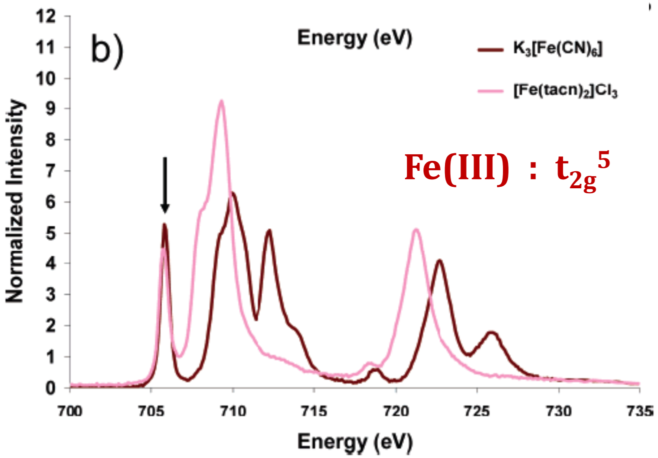
Fe(II) : t_{2g}^6



$Fe(CN)_6$



$Fe(tacn)_2$

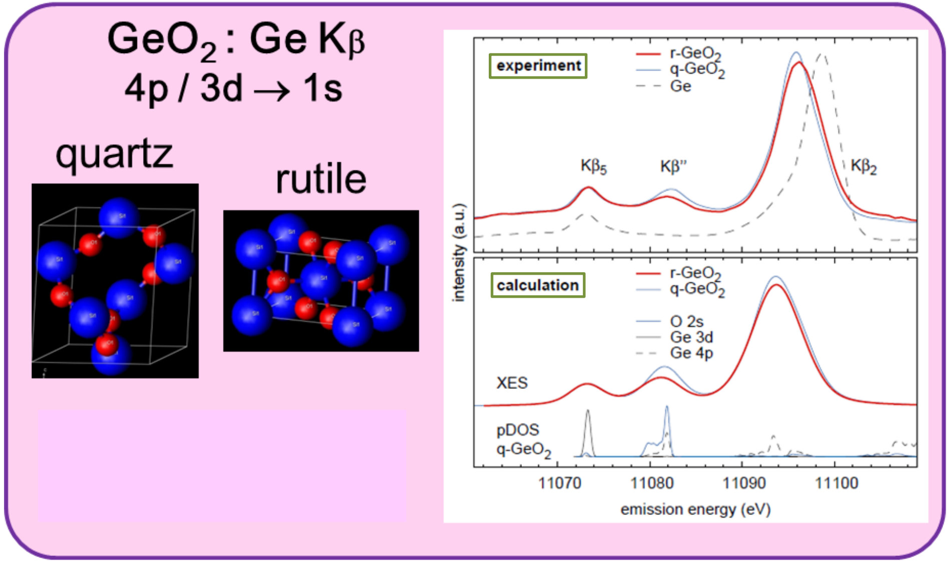


Fe(III) : t_{2g}^5

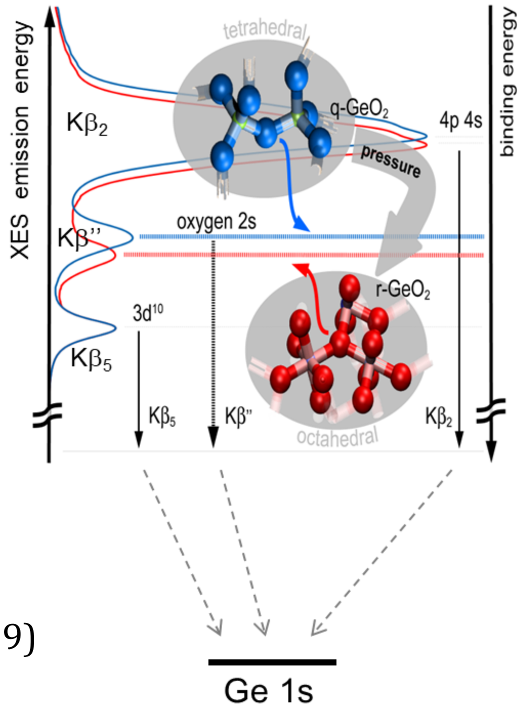
Hocking *et al.*, *JACS* **128**, 10442 (2006)

Benefit of combining experiment & calculations

exciting !



X-ray emission spectrum



Spiekermann, Harder, Gilmore, *et al.*, *Phys Rev X* **9**, 011025 (2019)

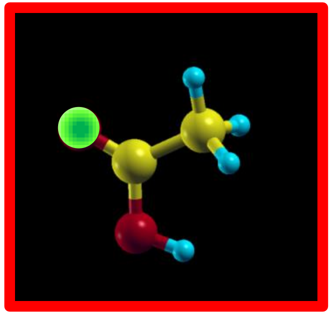
1-particle approaches: core-hole DFT

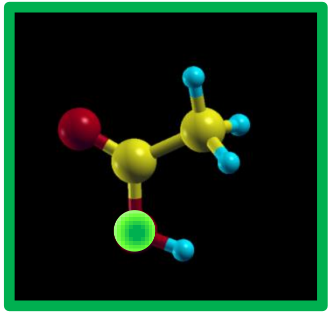
exciting !

$$\mu(\omega) = 2\pi \sum_f |\langle f|d|0\rangle|^2 \delta(\omega - \epsilon_{f0})$$

- $\langle f|$: final-state orbitals
- d: dipole matrix elements
- $|0\rangle$: atomic orbital
- ϵ_{f0}: final-state energies

Acetate





Site with core-hole

<u>Constrained DFT calculation:</u>

- DFT calculation with core-hole and extra electron in LUMO / CBM level
  - ➢ Final-state orbitals & energies
- Evaluation of dipole matrix elements
- Sample each unique site of a selected element

1-particle approaches: core-hole DFT

exciting !

$$\mu(\omega) = 2\pi \sum_f |\langle f|d|0\rangle|^2 \delta(\omega - \epsilon_{f0})$$

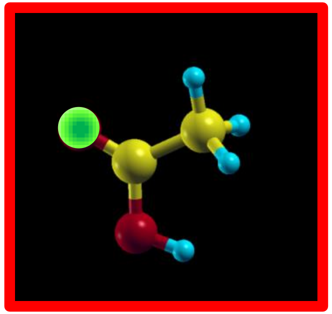
final-state energies

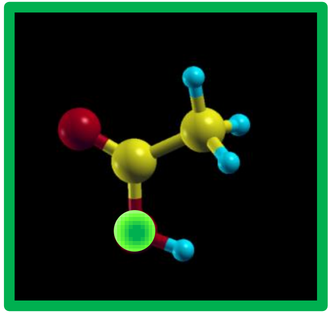
atomic orbital

dipole matrix elements

final-state orbitals

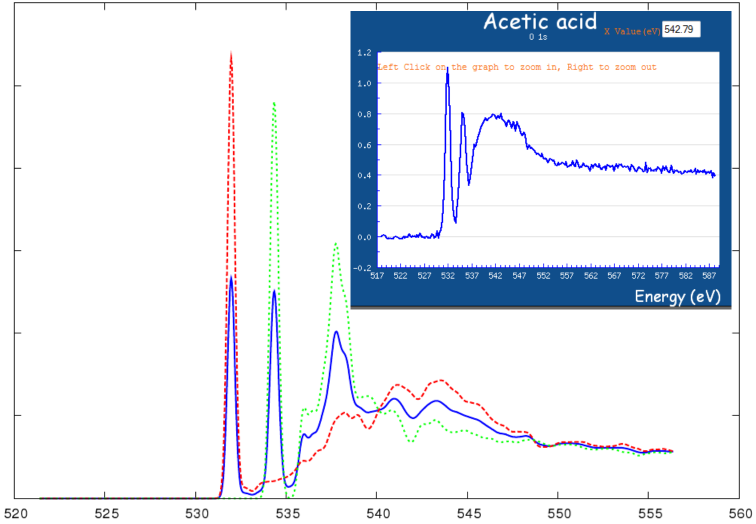
Acetate





 Site with core-hole

Acetate O-K XAS



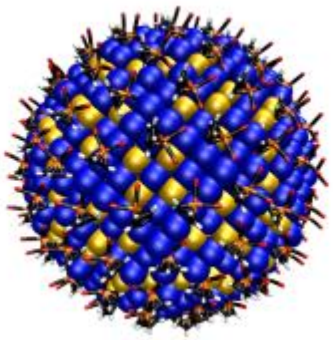
Photon Energy (eV)

Experimental reference spectrum from
Adam Hitchcock, McMaster University, Ontario, CA
unicorn.mcmaster.ca/corex/name-list.html

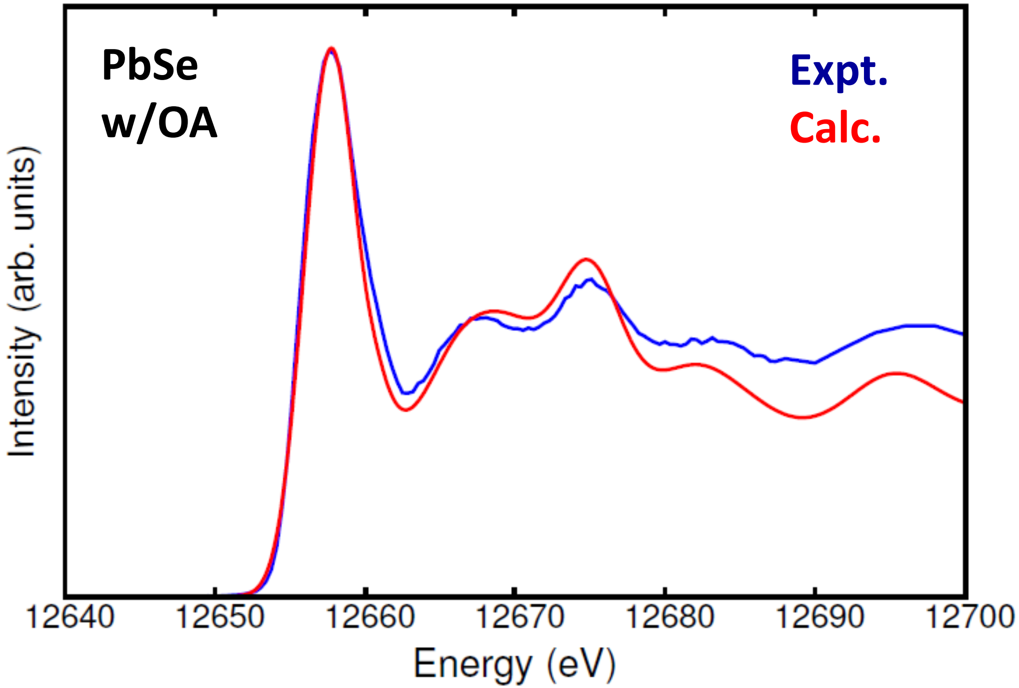
Core-hole DFT is efficient & predictive

exciting !

Coated PbSe nanocrystal



Se K-edge



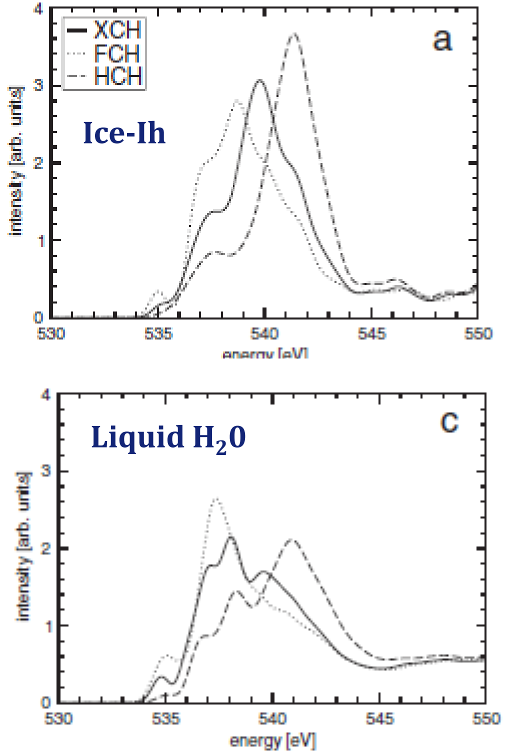
Rosen, Gilmore *et al.*, *Chemical Science* (2015)

Problem 1: non-unique treatment of core-hole

exciting !

Flavors of core-hole treatment

- Half core-hole (HCH)
- Full core-hole (FCH)
- Excited-electron core-hole (XCH)



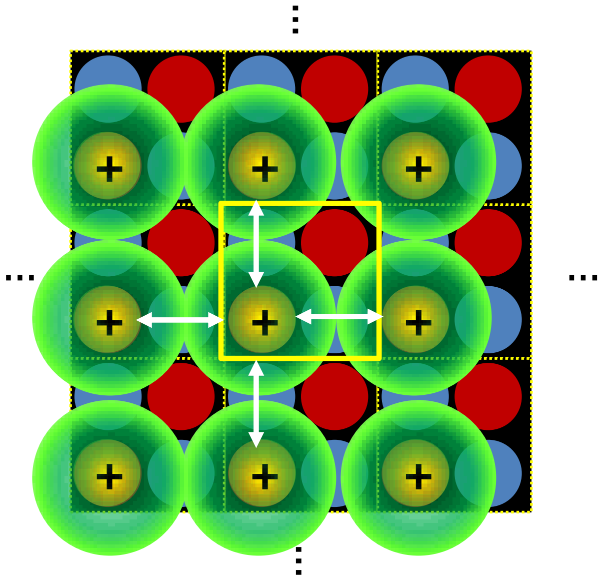
Prendergast & Galli, *Phys. Rev. Lett.* **96,** 215502 (2006)

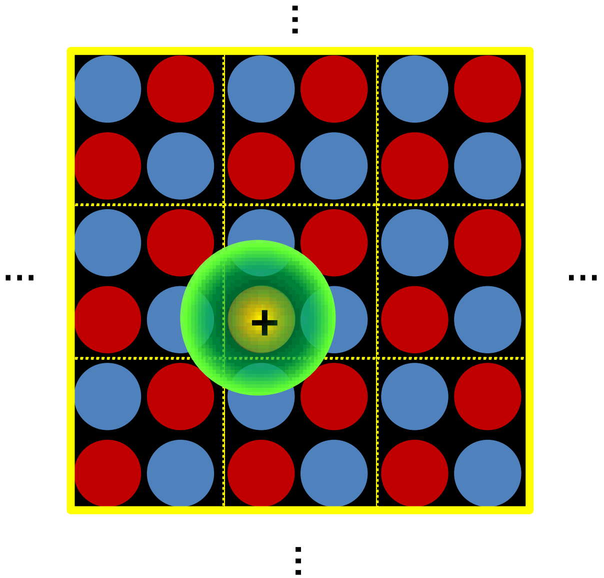
Problem 2: periodic image effects

Problem :

– excitons become delocalized
– image charge interactions

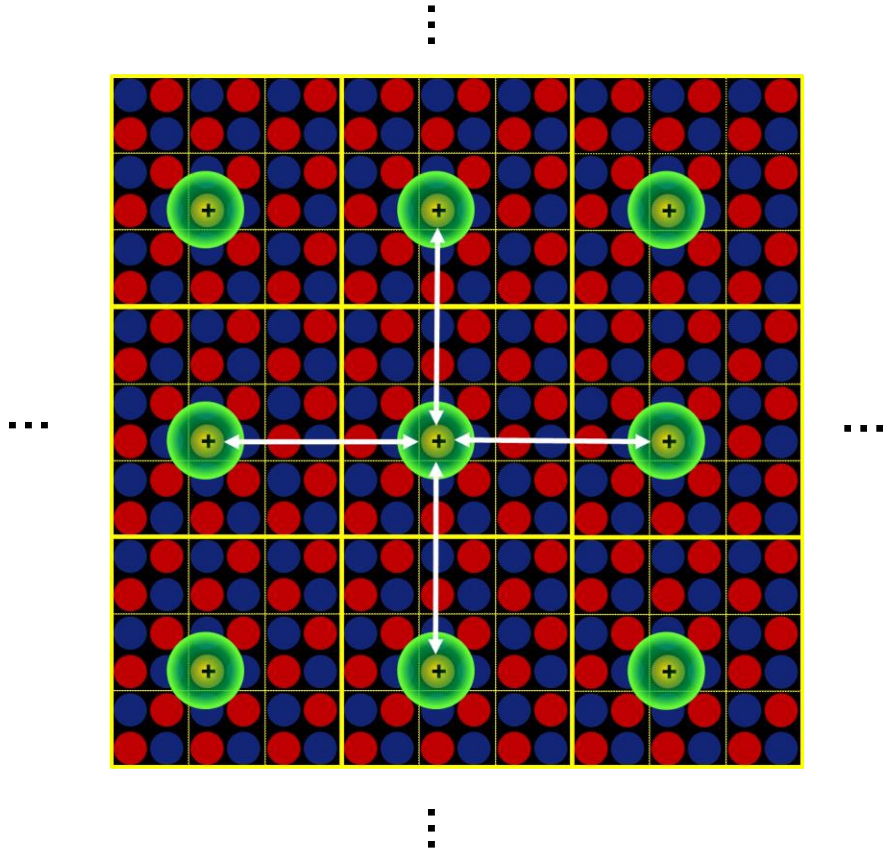
“Solution” : supercells





Problem 2: periodic image effects

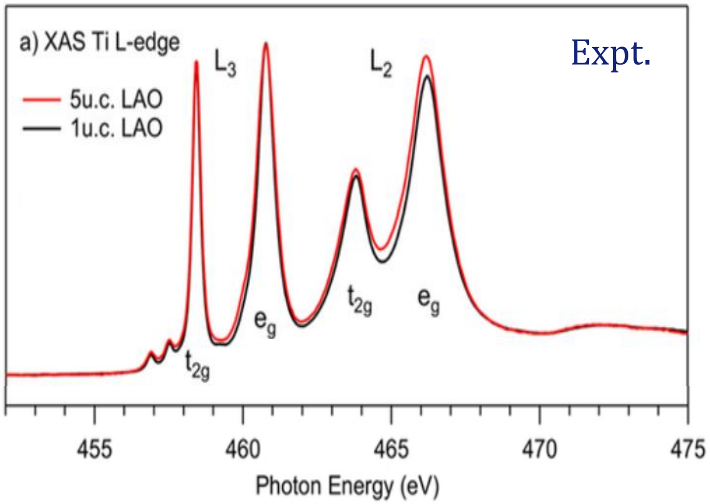
- ✓ Significant improvement in spectra
- ✗ Significant increase in computational cost

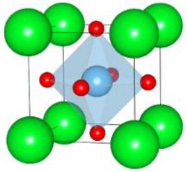


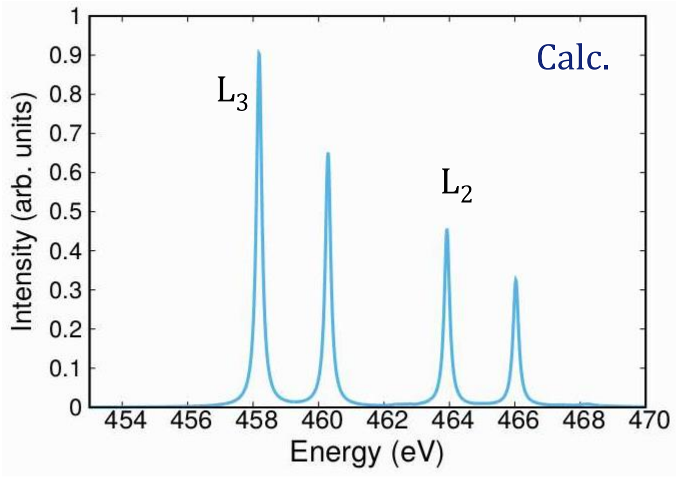
Problem 3: no multiplet effects

exciting !

Ti L-edge of $SrTiO_3$







Treske *et al.*, *Sci. Rep.* ***5***, *14506* (2015)

Core-hole DFT limited to 2:1 (L_3:L_2) branching ratio

1-particle approach: convenient but limited

exciting !

Advantages of core-hole DFT calculations

1. Predictive (no free parameters)
2. Arbitrary structures (symmetry, disorder, liquids)
3. Chemical selectivity (chemical shifts, etc.)
4. Easy to implement / use

Limitations of core-hole DFT calculations

1. Disputed core-hole treatment
2. Computationally intensive (supercells & new calc for each site)
3. Incorrect L-edge branching ratio (no multipet effects)

2-particle Bethe-Salpeter equation (BSE)

exciting !

$$\mu(\omega) = 2\pi \sum_F \left|\langle F|\hat{\Delta}|0\rangle\right|^2 \delta[\omega - (E_F - E_0)]$$

$$\hat{\Delta} = \sum_k \langle k|\hat{d}|\alpha\rangle \hat{c}_k^+ \hat{a} + h.c.$$

$$\mu(\omega) = -\frac{1}{\pi} \mathrm{Im} \sum_F \frac{\langle 0|\hat{\Delta}^+|F\rangle\langle F|\hat{\Delta}|0\rangle}{(\omega - E_{F0}) - i\gamma}$$

$$\mu(\omega) = -\frac{1}{\pi} \mathrm{Im} \, \langle 0|\hat{\Delta}^+ G(\omega - E_0)\hat{\Delta}\,|0\rangle$$

$$G(\omega) = \frac{1}{\omega - H}$$

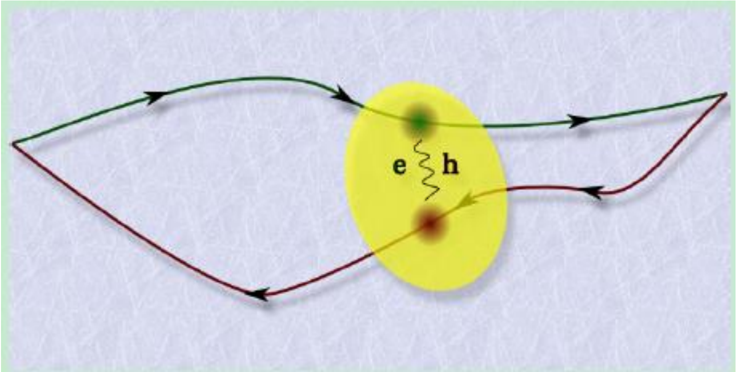


Image credit: Francesco Sottile, Ecole Polytechnique

H is the full many-body Hamiltonian

→ Reduce to a hole–photoelectron Hamiltonian $G \rightarrow G_{eh}$

2-particle Bethe-Salpeter equation (BSE)

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$$\mu(\omega) = -\frac{1}{\pi}\mathrm{Im}\,\langle 0|\hat{\Delta}^+ G(\omega - E_0)\hat{\Delta}\,|0\rangle$$

2-particle basis →

h : core atomic orbital φ_α

e : Kohn-Sham wfcn. ψ_{nk}

(GW corrections)

$$\mu(\omega) = -\frac{1}{\pi}\mathrm{Im}\sum_{e',h'}\sum_{e,h}\langle 0|\hat{d}^+|e',h'\rangle\left\langle e',h'\left|\frac{1}{\omega - H_{BSE} + i\eta}\right|e,h\right\rangle\langle e,h\,|\hat{d}|0\rangle$$

Bethe-Salpeter Hamiltonian

$$H_{BSE} = H_e - H_h + V_X - W_D$$

Excitonic eigenstates of Bethe-Salpeter Hamiltonian

$$|\xi\rangle = \sum_{\alpha nk} A^{\xi}_{\alpha nk}|\psi_{nk},\varphi_\alpha\rangle$$

2-particle Bethe-Salpeter equation (BSE)

exciting !

$$H_{\mathbf{eff}} \approx H_{\mathbf{h}} + H_{\mathbf{e}} + H_{\mathbf{eh}}$$

$$H_{\mathrm{h}} = -\varepsilon_{\alpha} + \mathbf{L}\cdot\mathbf{S}(p)$$

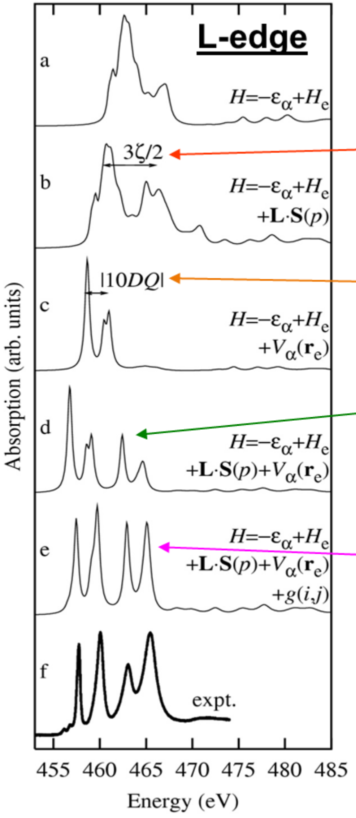
$$H_{\mathrm{e}} = \frac{p_{\mathrm{e}}^{2}}{2m} + V_{\mathrm{KS}}^{\mathrm{xtal}} + \mathbf{L}\cdot\mathbf{S}(d)$$

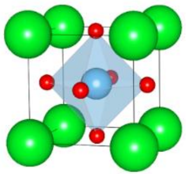
$$H_{\mathrm{eh}} = V_{\alpha}(\mathbf{r}_{\mathrm{e}}) + g(i,j)$$

$V_{\alpha}(\mathbf{r}_{\mathrm{e}})$: central part screened by RPA

$g(i,j)$: Slater-type integrals, scaled by × 0.83

Ti L-edge of $SrTiO_3$





spin-orbit splitting

crystal-field splitting

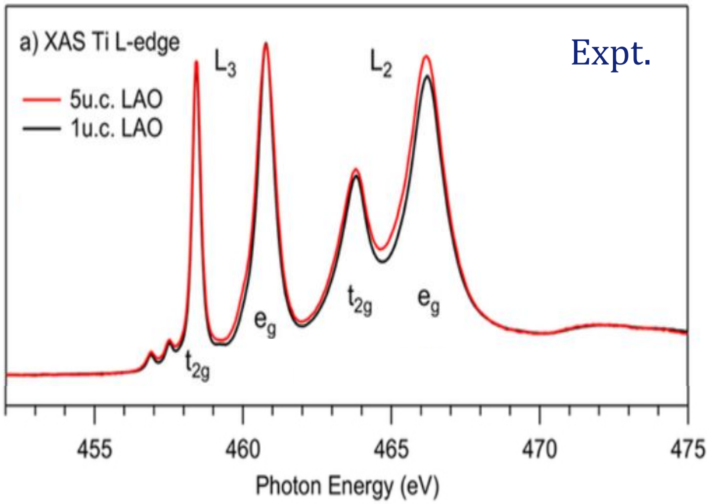
spin-orbit and crystal-field splittings evident

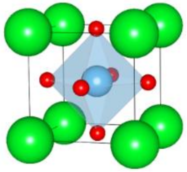
re-arranged oscillator strength

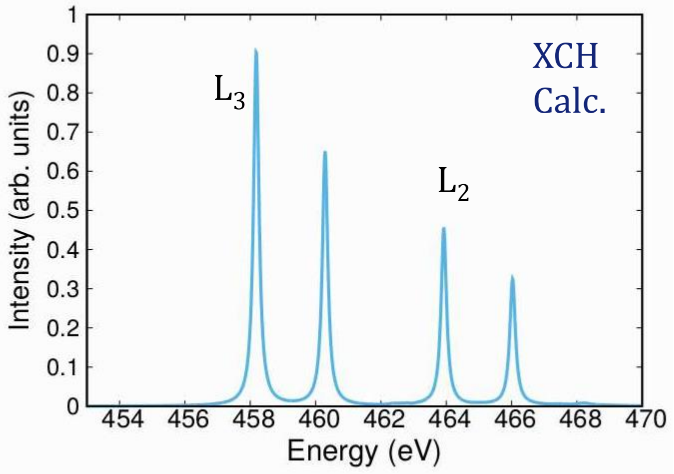
BSE includes (partial) multiplet effects

exciting !

Ti L-edge of $SrTiO_3$







Treske *et al.*, *Sci. Rep.* ***5***, *14506* (2015)

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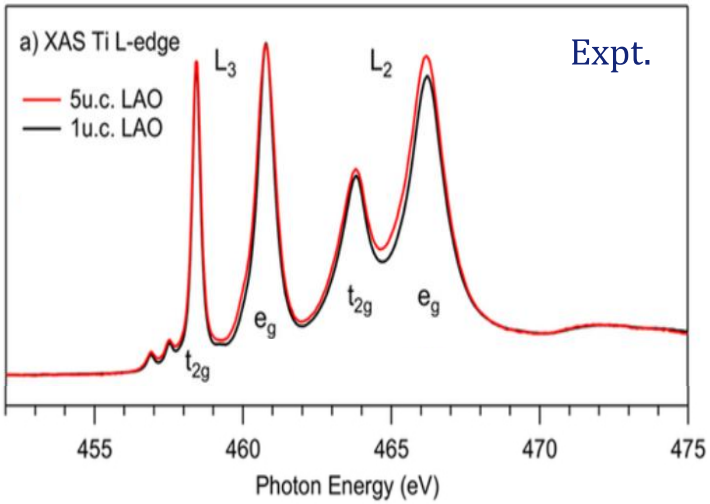
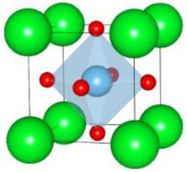
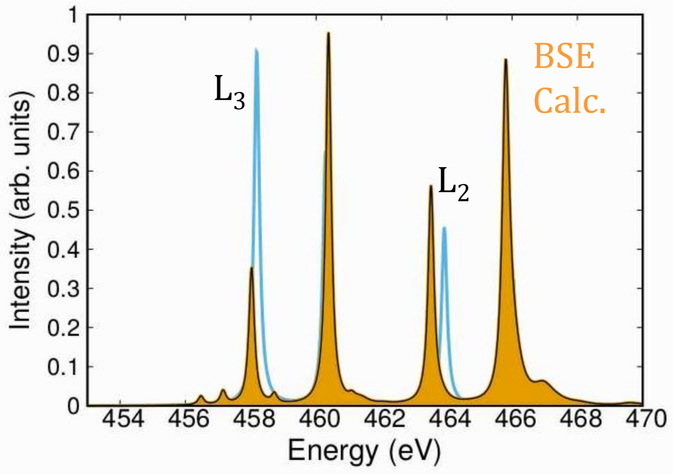






Treske *et al.*, *Sci. Rep.* ***5***, *14506* (2015)

BSE recovers correct (L_3:L_2) branching ratio

BSE does not need supercells

exciting !

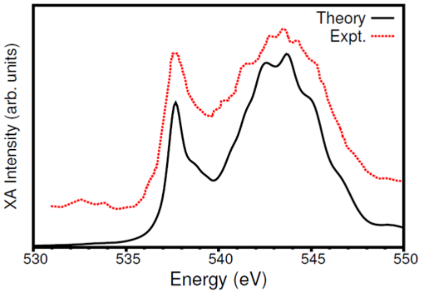
BSE results with unit cells

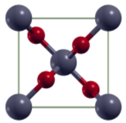
SiO_2

XCH results with supercells

O K-edge

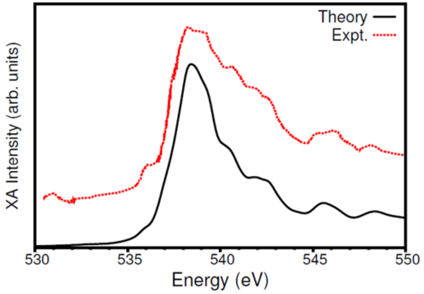
Stishovite

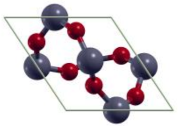




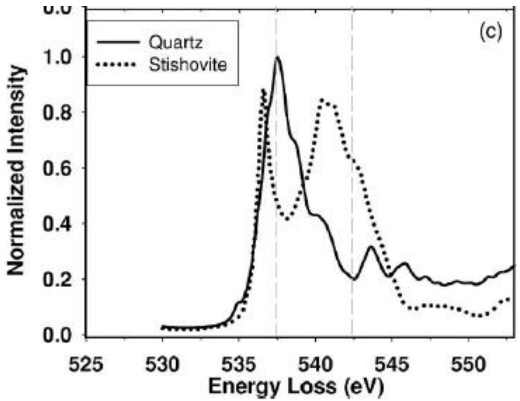
6 atoms

α-Quartz



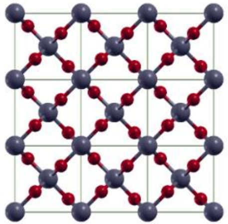


9 atoms

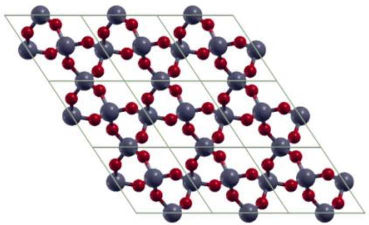


Lin *et al., Phys. Rev. B* ***75****, 012201* (2007)

Stishovite 3x3x4
(216 atoms)



Quartz 3x3x3
(243 atoms)



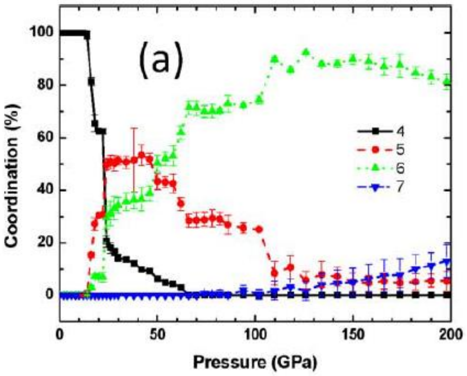
BSE does not need supercells

exciting !

Silica glass pressurized up to ~100 GPa

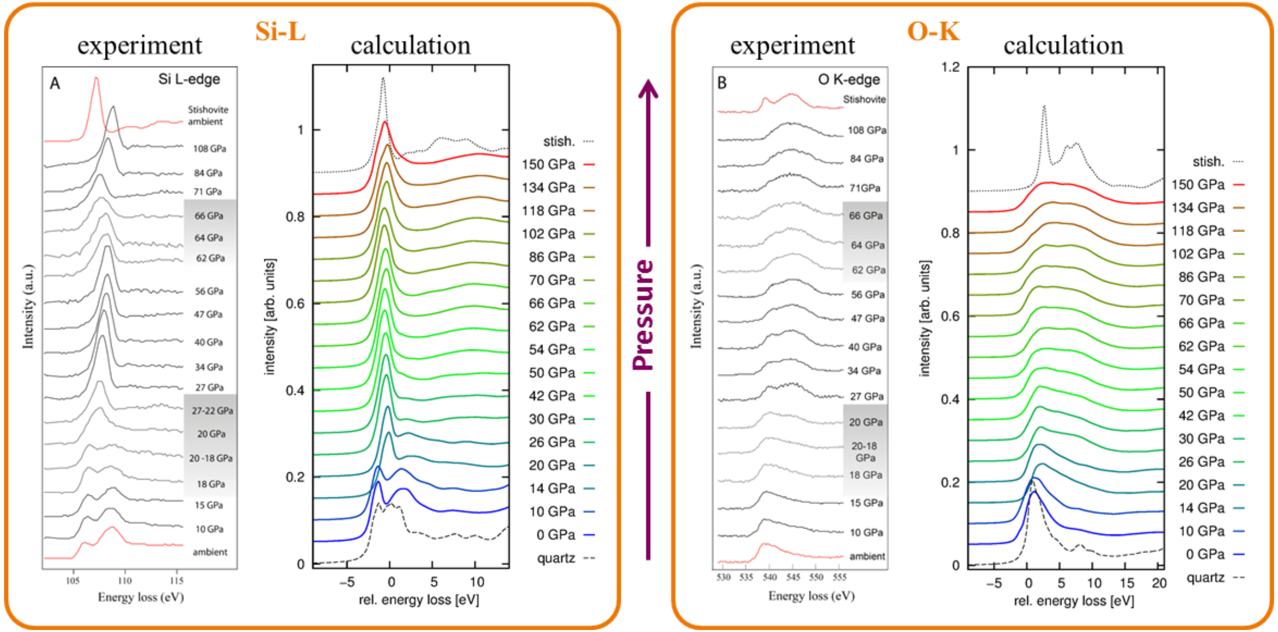
- Disordered structures obtained by *ab initio* molecular dynamics (AIMD)
- 72 atoms / MD cell × 10 MD samples × 17 pressures = 12,240 spectra
- In-house computing resources sufficient

Only one DFT calc per MD cell



AIMD calculations Si-O coordination vs pressure

Wu *et al.*, *Sci Reps* (2012)

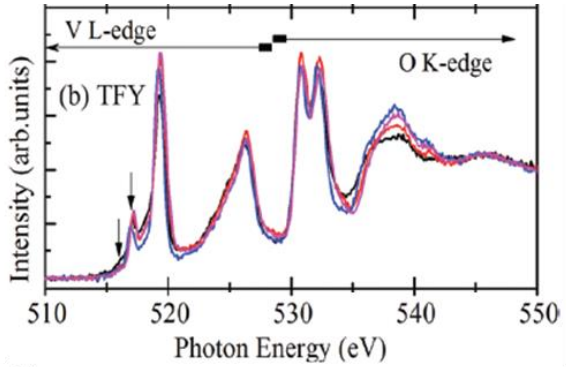


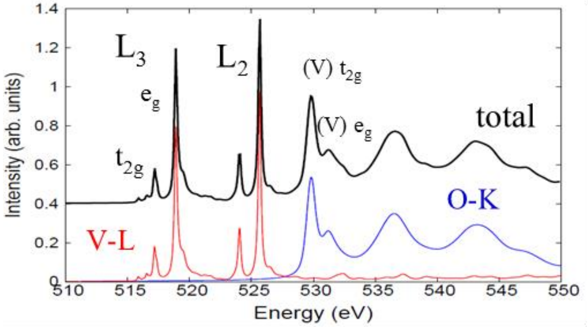
Petitgirard, Sahle, Weis, Gilmore *et al.*, Geochemical Perspectives Letters **9**, 32 (2019)

BSE treats different edges on equal footing

exciting !

- Metal L & oxygen K edges treated equally
- Local multiplet effects & long-range screening
- Optical excitations in addition to core-level excitations



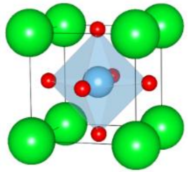


Calc.: Gilmore; *unpublished*

Expt.: Sharma *et al*; *Phys Chem Chem Phys* (2017)

V L-edge and O K-edge

$SrVO_3$



Bethe-Salpeter approach:

exciting !

Advantages of BSE calculations

1. Predictive (no free parameters)
2. No final states or supercells
3. Beyond K-edges
4. Valence and core excitations with same formalism

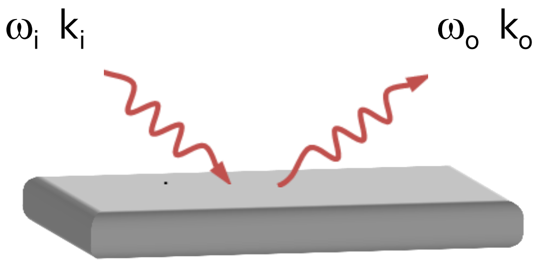
Limitations of BSE calculations

1. Computationally demanding
2. Only partial multiplet effects
3. Limited treatment of additional many-body effects

RIXS: resonant inelastic x-ray scattering

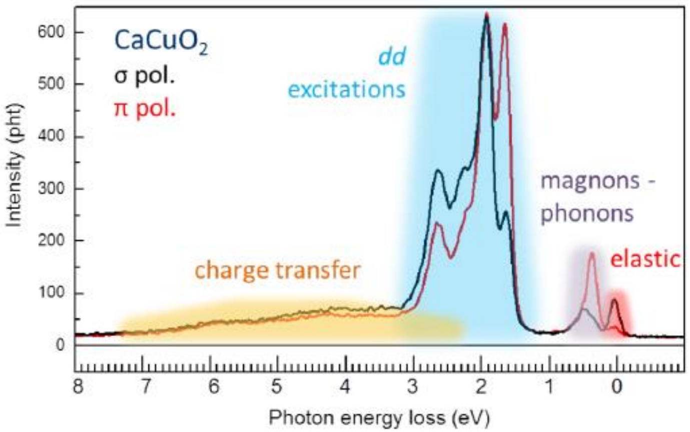
exciting !

➢ **New probe of low energy excitations in correlated materials**



- Incident photon tuned to core level resonance
- Inelastic scattering: $\omega_{loss} = \omega_{in} - \omega_{out}$
- Momentum transfer: $\Delta q = k_{in} - k_{out}$
- Couples to all degrees of freedom
- Sensitive to small sample volumes

Experimental observation of excitations

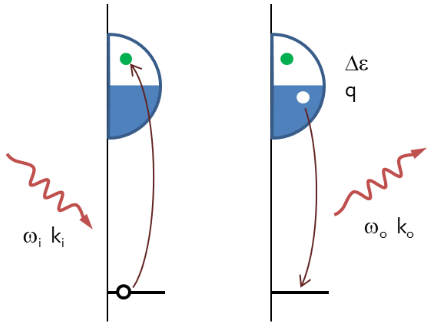


Example data from ESRF, ID32 *N Brookes et al.*

RIXS: Fluorescence versus Raman features

exciting !

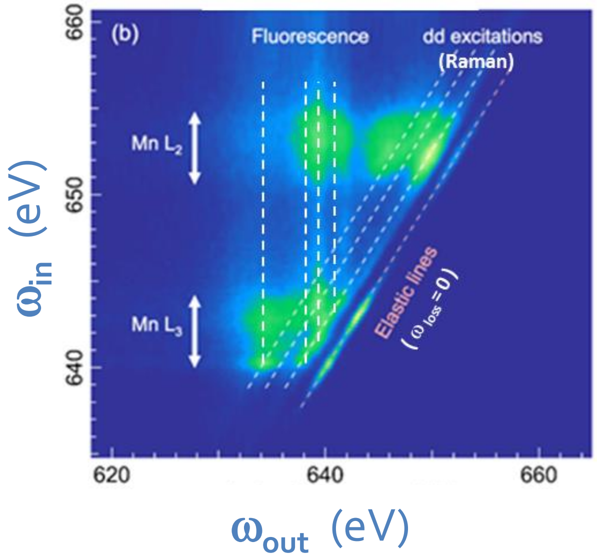
Direct RIXS (fluorescence)



➢ **Constant ω_{out}**

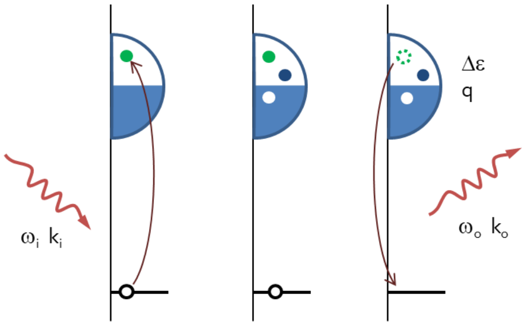
Example data

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$



Y.-D. Chuang *et al.*, *Review of Scientific Instruments* **88**, 013110 (2017)

Indirect RIXS (Raman)



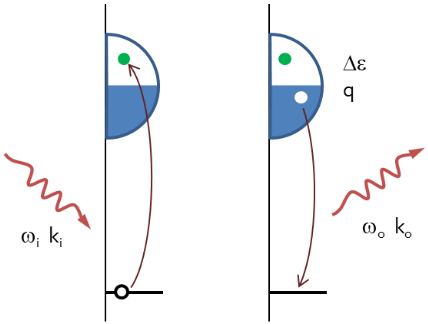
➢ **Constant ω_{loss}**

RIXS: Fluorescence versus Raman features

exciting !

BSE for RIXS

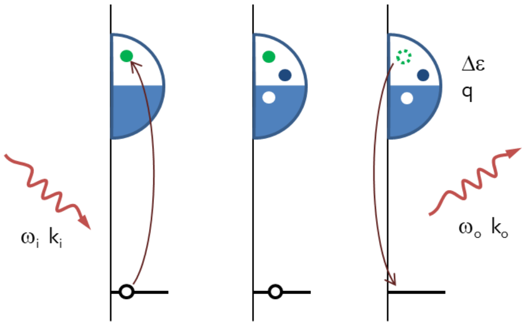
Direct RIXS (fluorescence)



- **Constant ω_{out}**

- Direct contributions only
- No indirect terms
  - e-h only
  - no secondary excitations
- Indirect features are most interesting

Indirect RIXS (Raman)



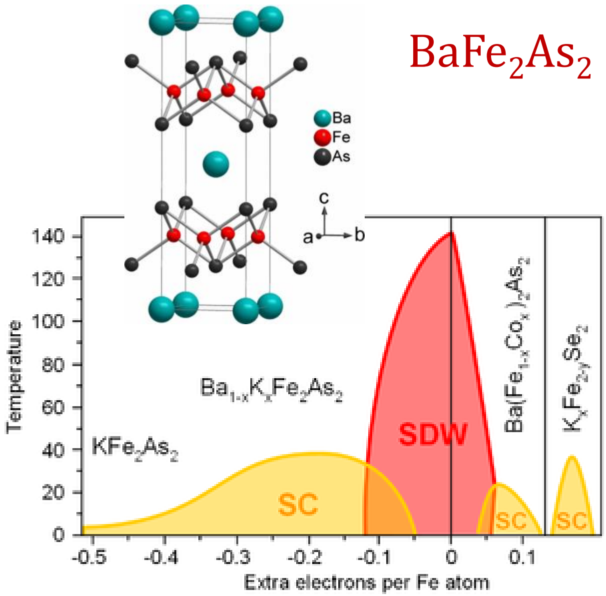
- **Constant ω_{loss}**

Iron-pnictides & -chalcogenides

exciting !

- 2D square lattice of Fe atoms
- AF ground state of parent compound
- SC phase with hole/electron doping
- Hund's metal
- Orbital selective Mott interactions
- Thermoelectric properties

$BaFe_2As_2$

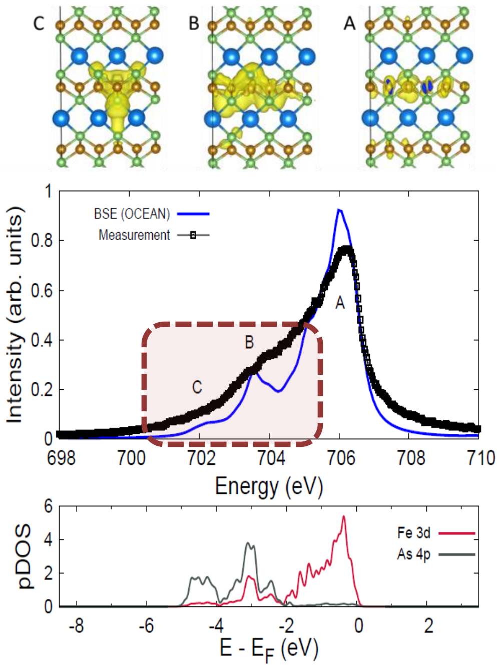


Standard BSE gives reasonable spectra

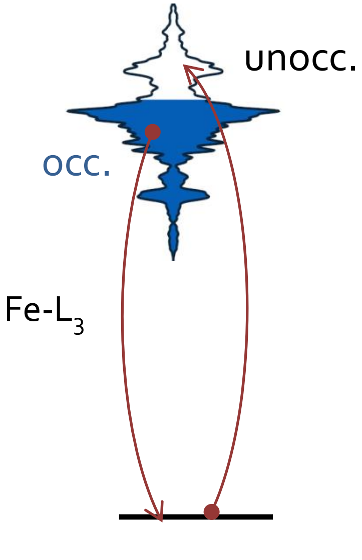
exciting !

Standard Bethe-Salpeter calculations

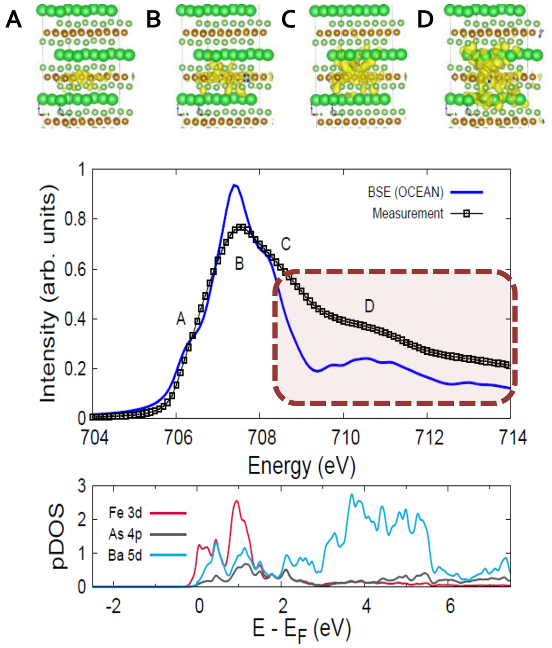
X-ray Emission



Fe 3d pDOS



X-ray Absorption

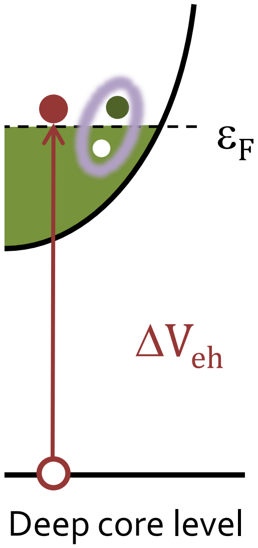


Gilmore *et al.*, Phys Rev X (2021)

Mahan-Nozières-Dominicis (MND) theory

exciting !

$$\mu(\omega) = \int d\omega' \, \mu^{BSE}(\omega - \omega') A(\omega')$$



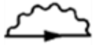
Secondary excitations :

- Electron-hole pairs
- Plasmons
- Magnons
- Phonons
- etc

Mahan, *Phys Rev* **163**, 612-617 (1967)
Nozières and de Dominicis, *Phys Rev* **178**, 1097-1107 (1969)
… many others

Cumulant spectral functions

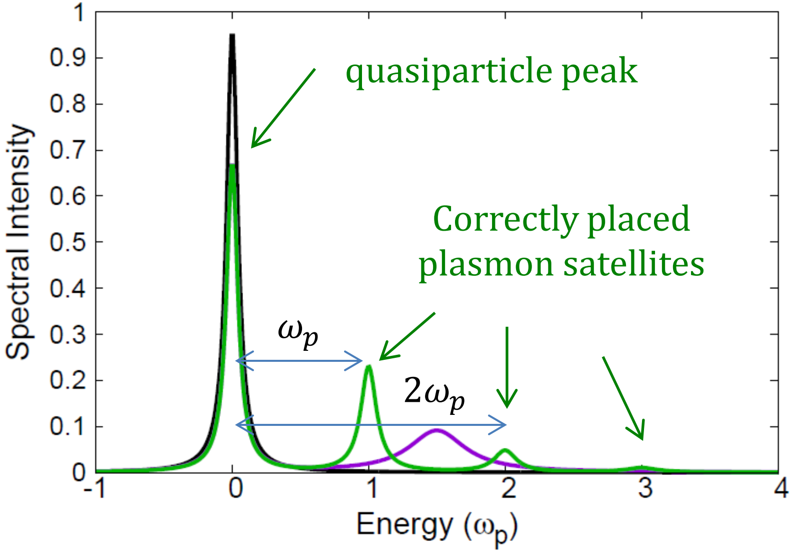
exciting !

Self energy: $\Sigma^{GW} =$ 

Dyson equation: $G(\omega) = G^0(\omega) + G^0(\omega)\Sigma^{GW}G(\omega)$

Cumulant expansion: $G(t) = G^0(t)e^{C(t)}$ $C(t) = C(t)[\Sigma^{GW}]$

Spectral function : $A(\omega) = -\text{Im}\, G(\omega)$



ω_p : plasmon energy

Nozieres & Dominicis, Phys Rev **178**, 1097 (1969)

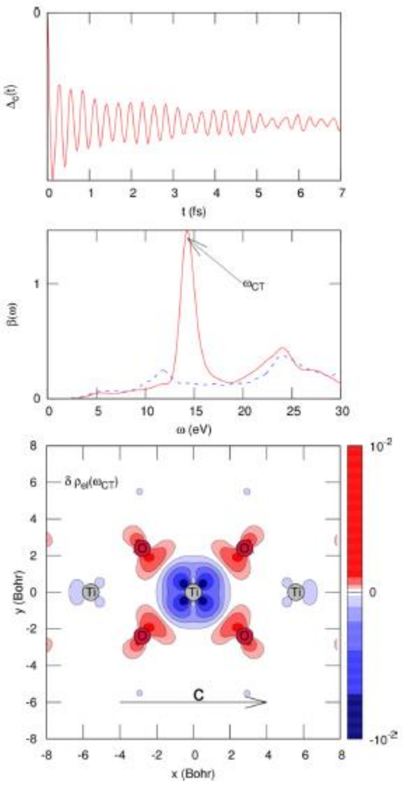
Langreth, Phys Rev B **1**, 471 (1970)

Gunnarsson *et al.*, Phys Rev B **50**, 10462 (1994)

The dynamic response

exciting !

>> Work of Josh Kas *et al.*, Phys Rev B **91**, 121112R (2015)



Charge density response to creation of core-hole

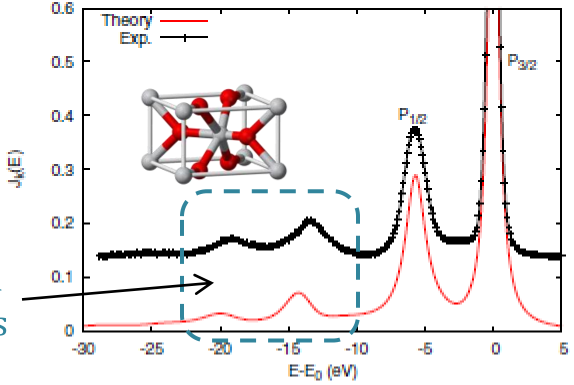
Quasi-boson excitation spectrum β(ω)

Real-space map of charge-density excitation at charge-transfer (CT) frequency

$$g(t) = g^0(t)e^{C(t)}$$

$$C(t) = \int d\omega \frac{\beta(\omega)}{\omega^2}\left(e^{-i\omega t} + i\omega t - 1\right)$$

Ti 2p spectral function



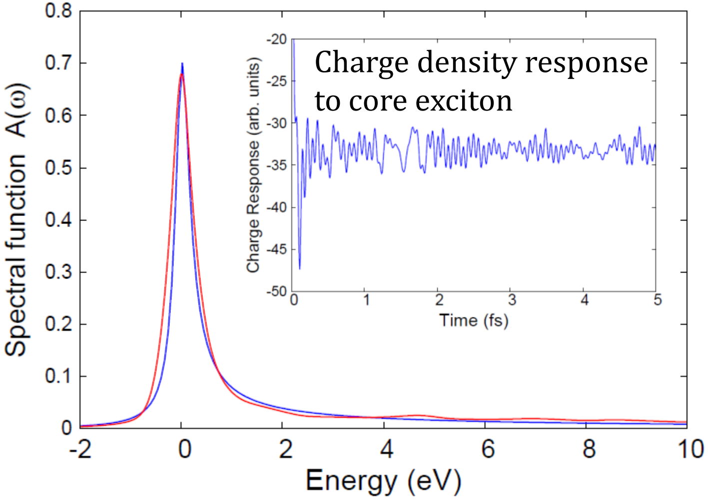
Plasmon satellites

Iron spectral function

exciting !

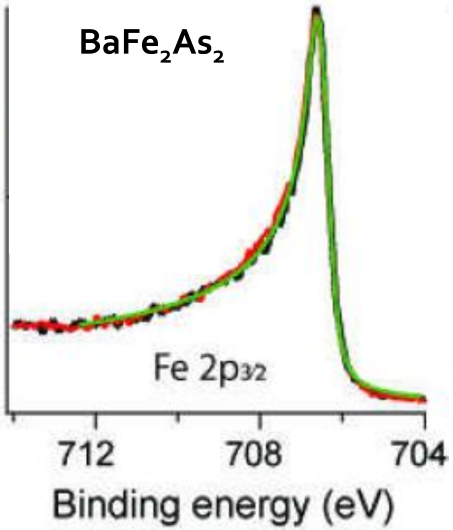
Exciton Green's function $G(t) = G^{BSE}(t)e^{C(t)}$

G^{BSE} is taken as the bare Green's function



Red : cumulant-calculated exciton spectral function
Blue : Doniach-Sunjic lineshape

Doniach-Sunjic lineshape fit to Fe 2p XPS (core spectral function) for $BaFe_2As_2$



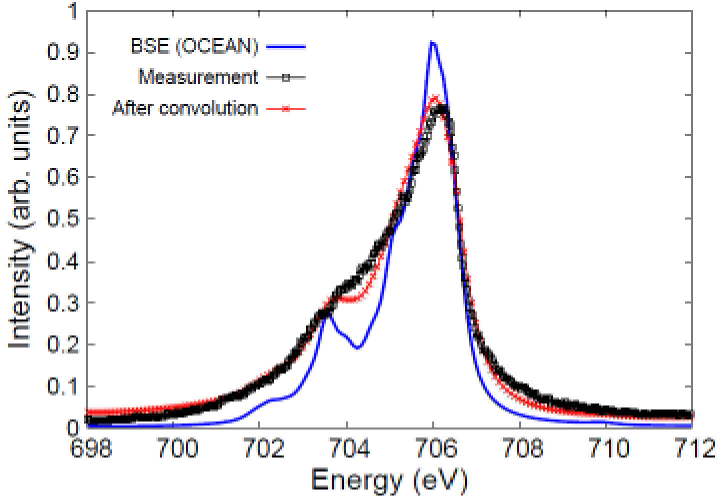
De Jong *et al.*, Phys Rev B **79**, 115125 (2009)

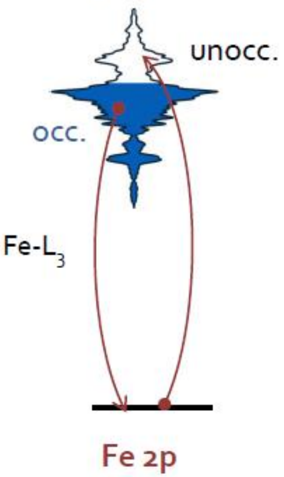
Spectral function accounts for the dynamic response

exciting !

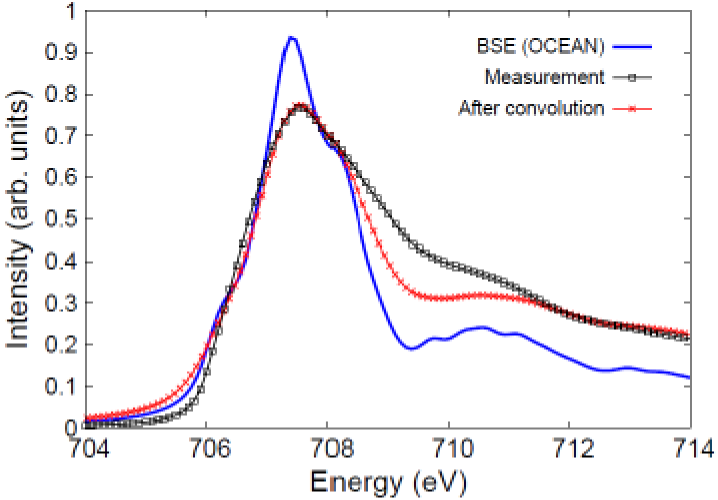
$$\mu(\omega) = \int d\omega' \, \mu^{BSE}(\omega - \omega') A(\omega')$$

X-ray Emission





X-ray Absorption



$BaFe_2As_2$

Gilmore *et al.*, Phys Rev X (2021)

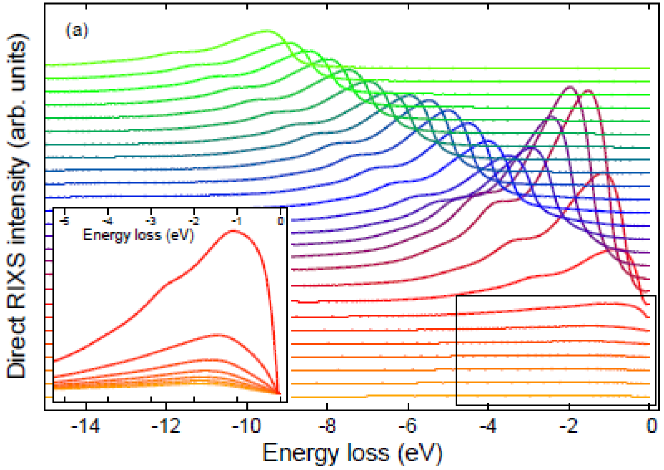
Spectral function accounts for the dynamic response

exciting !

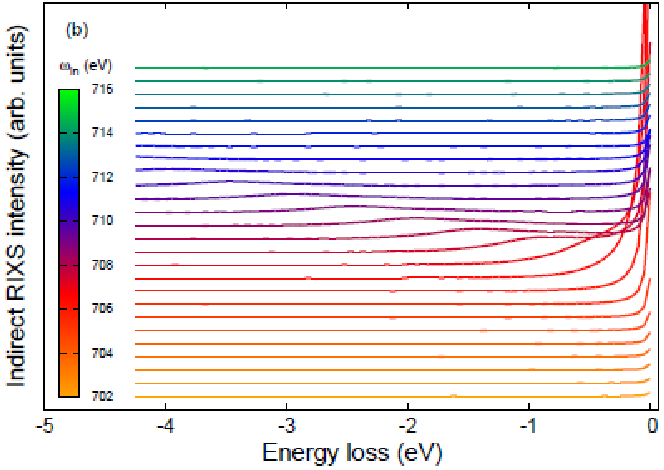
Approximate RIXS as convolution of XAS and XES (reasonable for metals)

$$\sigma(\omega_i, \omega_o) = \int d\tilde{\omega} \, \frac{\mu_a(\tilde{\omega})\mu_e(\tilde{\omega} - \omega_i + \omega_o)}{(\omega_i - \tilde{\omega})^2 + \gamma^2} \quad \longleftarrow \quad \mu(\omega) = \int d\omega' \mu^{BSE}(\omega - \omega') \, A(\omega')$$

Direct channel



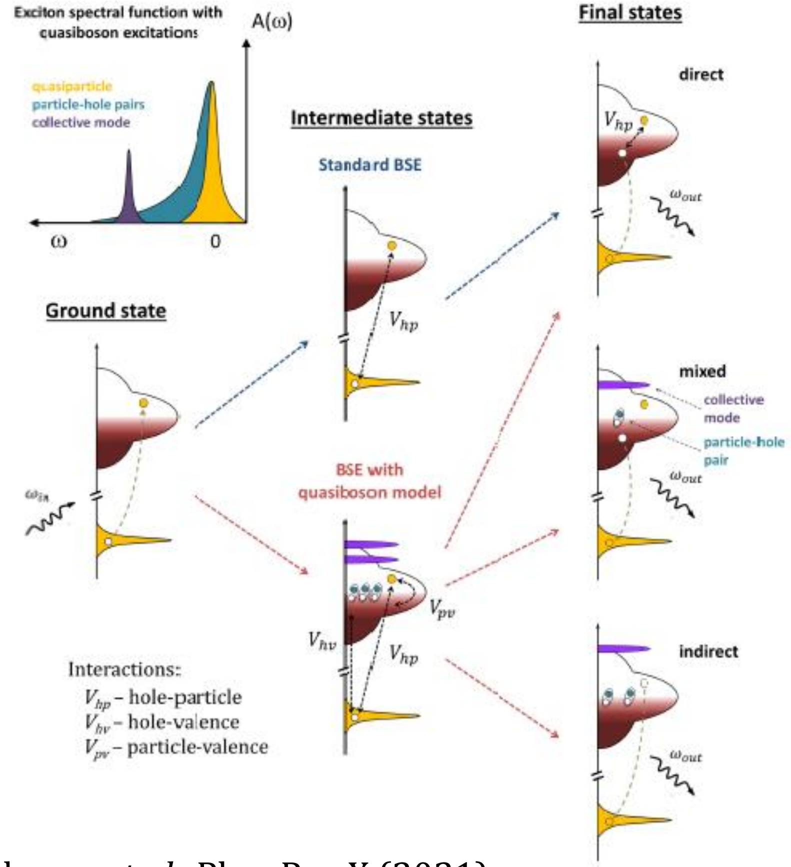
Indirect channel



Gilmore *et al.*, Phys Rev X (2021)

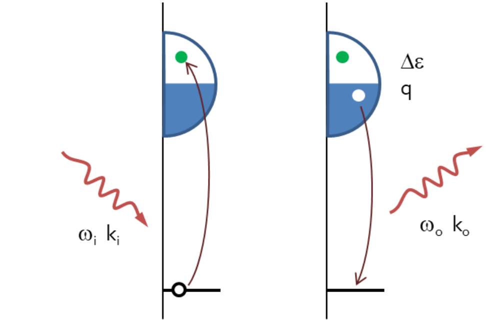
Augmented BSE includes indirect RIXS

exciting !

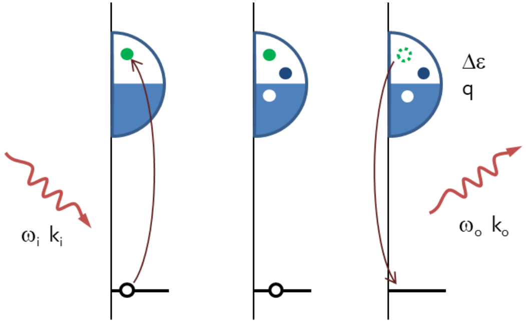


Gilmore *et al.*, Phys Rev X (2021)

Direct RIXS (fluorescence)



Indirect RIXS (Raman)



Summary

Going beyond standard BSE calculations

- Secondary excitations can be effectively incorporated using spectral functions
- Produces much better core-level spectra
- MND spectral function can be calculated from first-principles with rt-TDLDA
- Cumulant expansion gives much better spectral function than GW/Dyson
- Allows for calculation of indirect RIXS and improved direct RIXS

➢ Can generate other secondary excitations: spin, lattice, etc