Core level spectroscopy: XPS, XAS, EELS, XES (XSPEC, TELNES)

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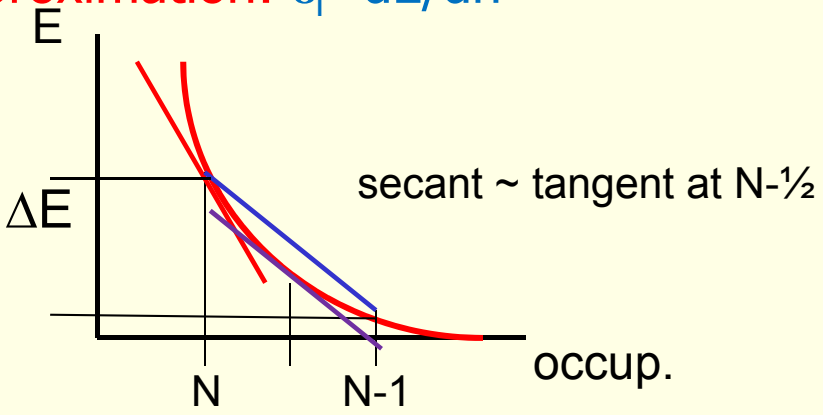
XPS, core-level shifts

- Ionizationpotential of core-e^-, IP= $E^{tot}(N) - E^{tot}(N-1)$
  - *gives information on charge state of the atom*
- core-eigenvalues ε_i are NOT a good approximation: $\varepsilon_i = dE/dn$
- Slater's "transition state":
  - *core-eigenvalues ε_i for half occupancy*



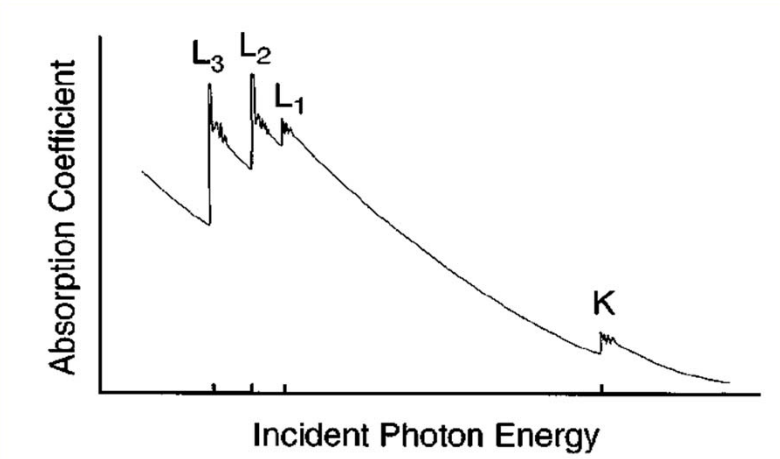
- Δ-SCF-calculation with and without core-hole: $E^{tot}(N) - E^{tot}(N-1)$
  - *supercells to reduce hole-hole interaction*

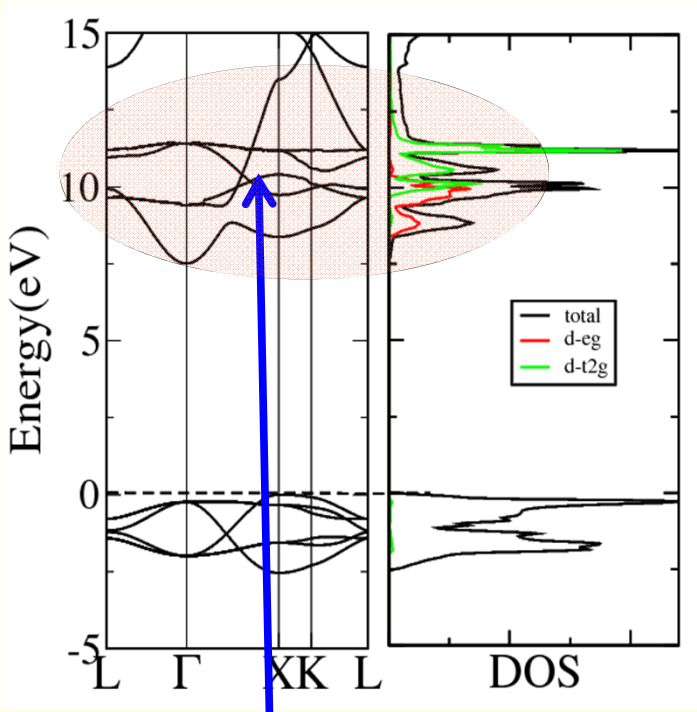
C,N 1s	exp.(eV)	ε_i	Δ-SCF
TiC	281.5	264.7	281.9
Ti_4C_4	281.5	263.3	281.1
TiN	397.0	377.5	397.1

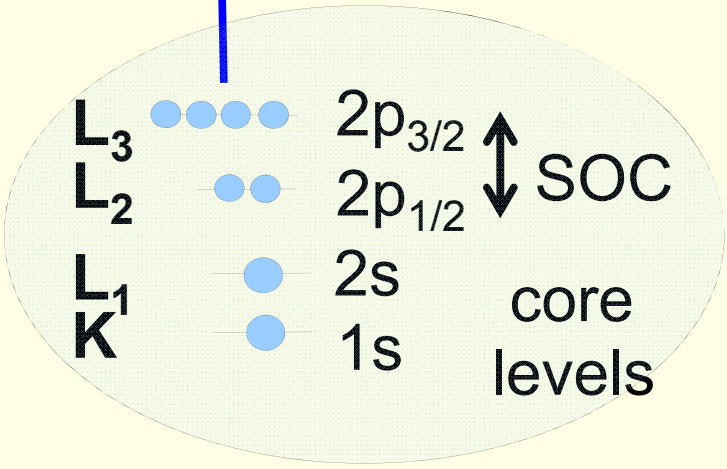
XAS (XANES), **EELS** (ELNES), **XES**:

- **core electrons are excited into a conduction band**
- Each core shell introduces an absorption edge, (they are indexed by the principal number of a core level)

  K-1s, L_1-2s, L_2-$2p_{1/2}$, L_3-$p_{3/2}$



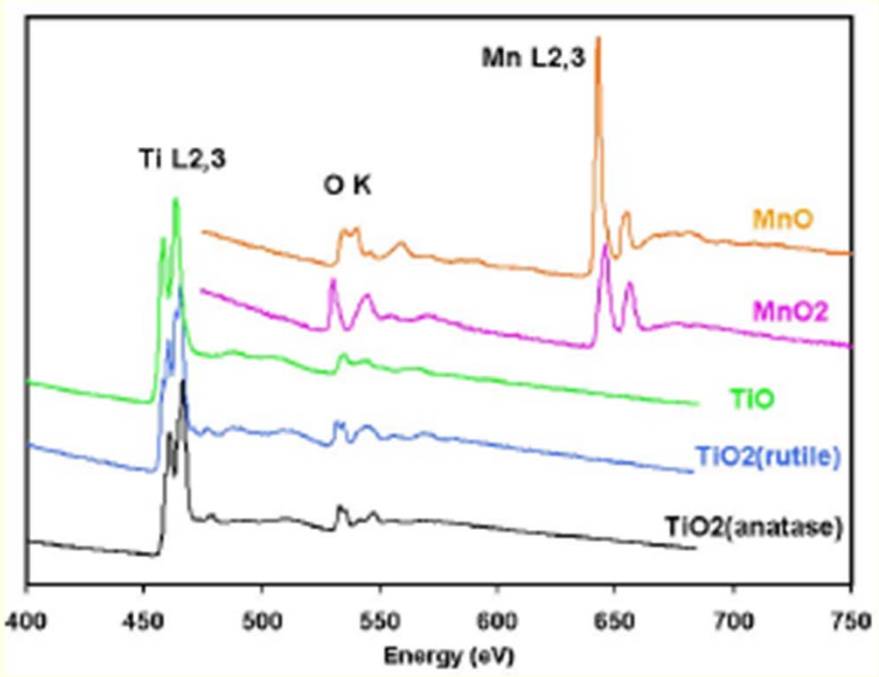




- **XES:**

knock out a core electron, **valence electron** fills core hole and ***hv*** is emitted

X-ray absorption spectroscopy - XAS
Electron energy loss spectroscopy - EELS



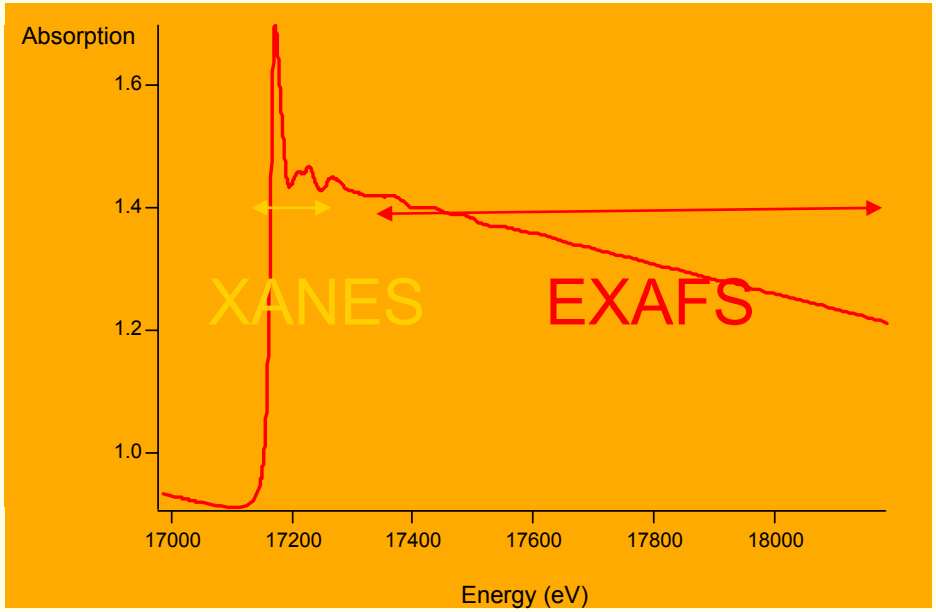
EELS spectrum of various TM oxides

X-ray Absorption

Near-Edge Structure

Extended X-ray

Absorption Fine Structure



Difference between EELS and XAS

XAS: synchrotron

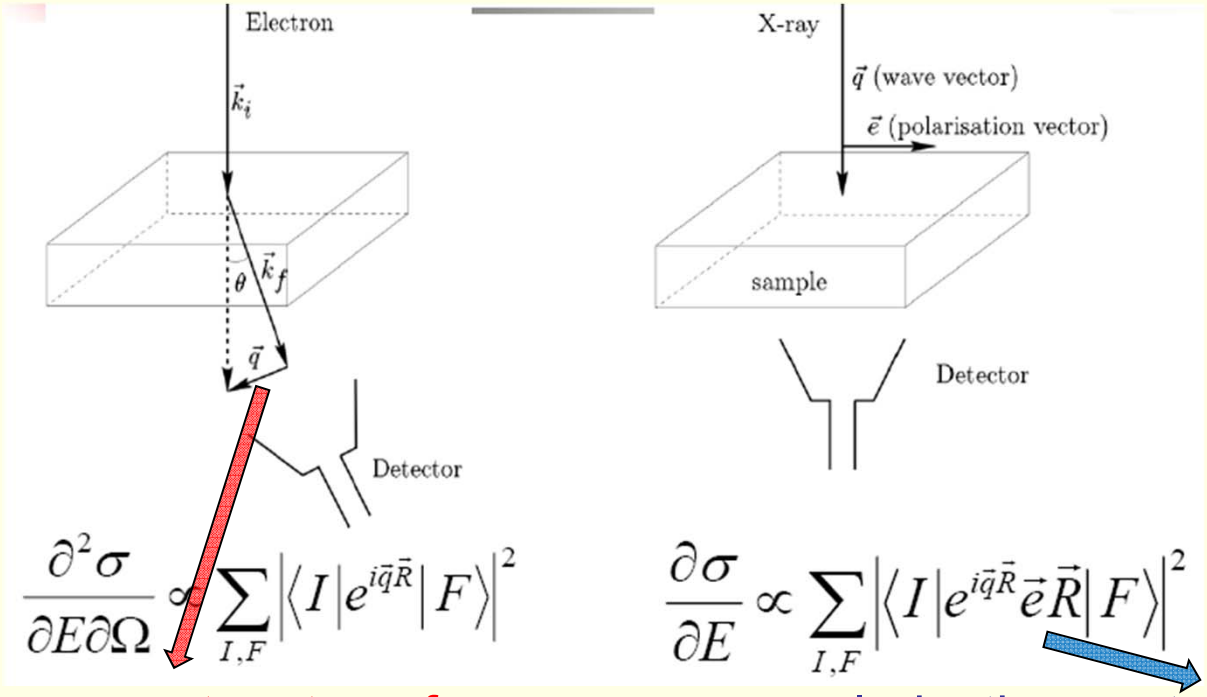
EELS: microscope

XAS vs. EELS: theory

- transition described by Fermis "golden rule" between initial (core) and final (conduction-band) state and the e^- or photon
- double differential cross section:

$$\frac{\partial^2\sigma}{\partial E\partial\Omega}(E,\boldsymbol{Q}) = \zeta\sum_{I,F}\frac{k_F}{k_I}\left|\left\langle I\,k_I\left|V\right|k_F\,F\right\rangle\right|^2\delta(E_I - E_F)$$

E - conservation



$$\frac{\partial^2\sigma}{\partial E\partial\Omega} \propto \sum_{I,F}\left|\left\langle I\left|e^{i\vec{q}\vec{R}}\right|F\right\rangle\right|^2$$

$$\frac{\partial\sigma}{\partial E} \propto \sum_{I,F}\left|\left\langle I\left|e^{i\vec{q}\vec{R}}\vec{e}\vec{R}\right|F\right\rangle\right|^2$$

single diff. cross section

momentum transfer ***q***

polarization vector ***e***

dipole approximation

$$\vec{q}\vec{R} << 1 \rightarrow e^{i\vec{q}\vec{R}} = 1 + i\vec{q}\vec{R} + \frac{(\vec{q}\vec{R})^2}{2!} + \ldots$$

EELS

$$\frac{\partial^2\sigma}{\partial E \partial \Omega} \propto \sum_{I,F} \left| \langle I | \vec{q}\vec{R} | F \rangle \right|^2$$

XAS

$$\frac{\partial^2\sigma}{\partial E \partial \Omega} \propto \sum_{I,F} \left| \langle I | \vec{\varepsilon}\vec{R} | F \rangle \right|^2$$

The polarization vector in XAS plays the same role as momentum transfer in (nonrelativistic) ELNES within the dipole approximation.

(TELNES3 can also handle non-dipole transitions + relativistic corrections)

core-valence spectroscopies give information on the local DOS (because of $\langle \Psi_{core} | r | \Psi_{val} \rangle$) of angular momentum character $\ell \pm 1$

"Final state rule":

"Final state" determines the spectrum:

- Emission spectroscopy:
  Final state has filled core, but valence hole.
  This is usually well screened, thus one "sees" the groundstate.
- Absorption spectroscopy:
  Final state has a "hole" in core state, but additional e^- in conduction band.
  Core-hole has large effect on the spectrum
  - **electron – hole interaction, "excitonic effects"**

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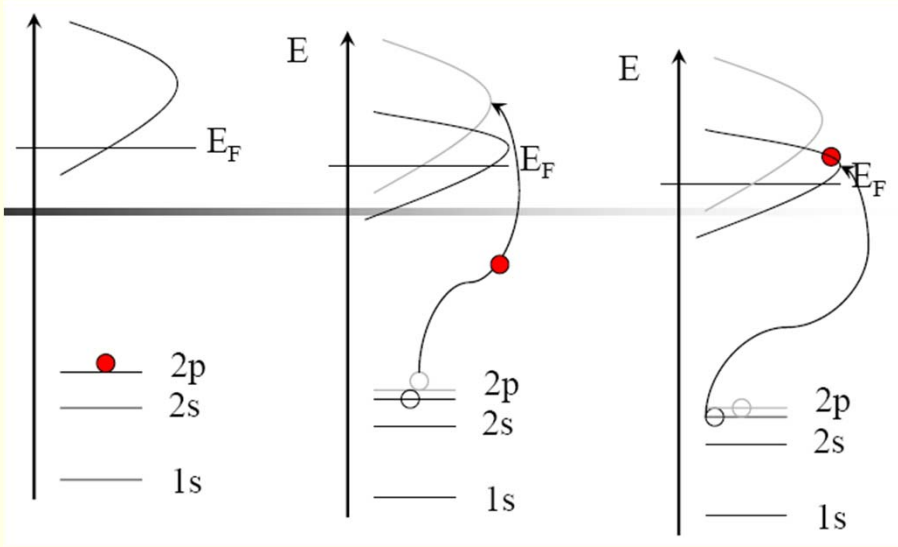


Treating the core hole within WIEN2k

- No core hole (= ground state, sudden approximation)
  - *usually not a good approximation (maybe in metals ?)*
- Z+1 approximation (eg., replace C by N)
  - *also not very good*
- Core-hole (supercell) calculations:
  - *Remove 1 core electron on ONE atom in the supercell, add 1 electron to conduction band*
  - *Remove 1 core electron, add 1 electron as uniform background charge*
    - considers statically screened e^- - h coulomb correlation
    - Fractional core hole (consider different screening)
- Explicit treatment of electron-hole interaction (excitonic effects) using Bethe-Salpeter equation (BSE)

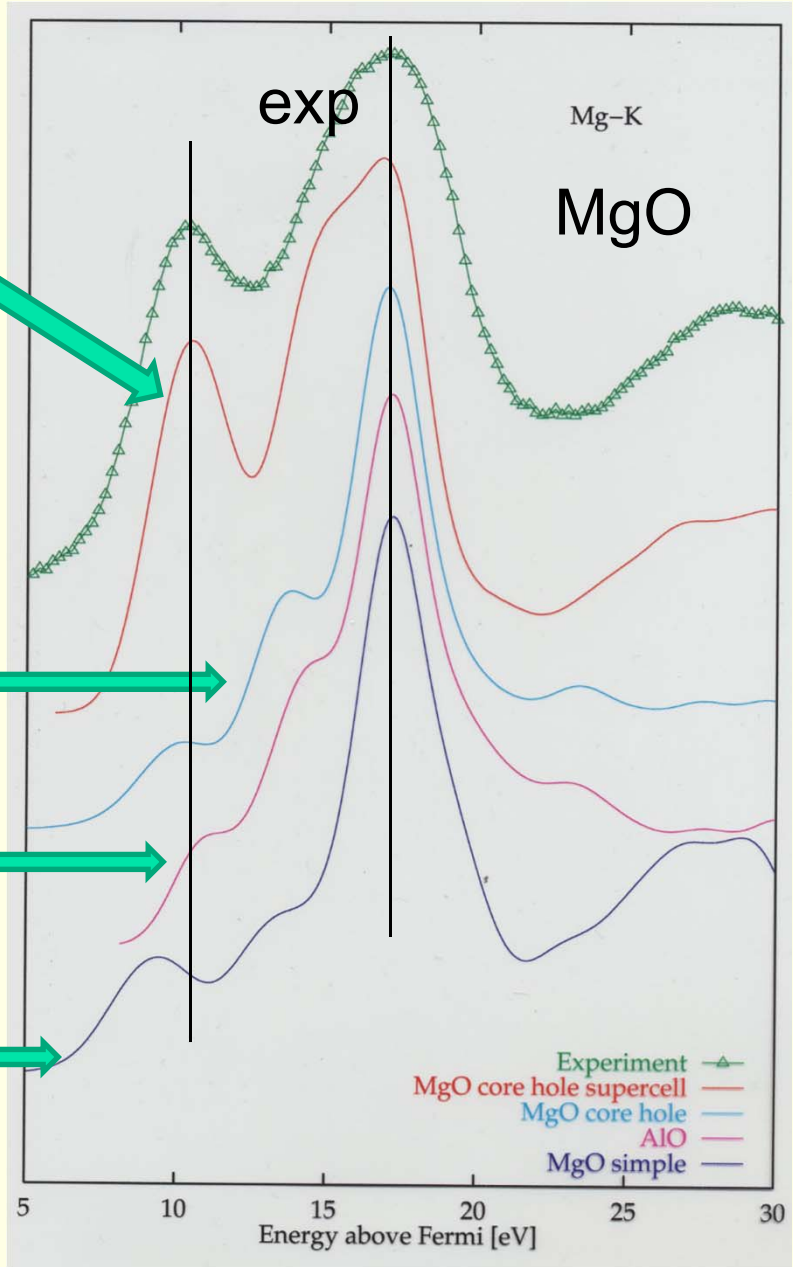
"Final state rule" + core hole:

➔ 2x2x2 supercell calculation, with core hole in one of the Mg atoms. This allows the conduction state to relax (adjust to the larger effective nuclear charge), but also to have static screening from the environment.

core hole, no supercell:

Z+1 (AlO)

groundstate



XAS / TELNES in WIEN2k

define your structure (structgen)

initialize calculation (init_lapw)

run scf-cycle (run_lapw)

geometry optimization of your structure (min_lapw)

generate supercell (x supercell)

initialize supercell structure, define core hole/add valence e^-

run scf-cycle

remove extra valence e^-

run XSPEC / TELNES3 task

XSPEC-task

Session: [magnetite]
/area51/pblaha/lapw/correlated/magnetite

16:42:50 ide
[refresh] | [no refresh]

[Execution >>]
[StructGen™]
[view structure]
[initialize calc.]
[run SCF]
[single prog.]
[optimize(V,c/a)]
[mini. positions]

[Utils. >>]

[<< Tasks]
[El. Dens.]
[DOS]
[XSPEC]
[TELNES.2]
[OPTIC]
[Bandstructure]

[Files >>]
[struct file(s)]
[input files]
[output files]
[SCF files]

[Session Mgmt. >>]
[change session]
[change dir]
[change info]

[Configuration]

Usersguide
[html-Version]
[pdf-Version]

XSPEC

[Spin UP] [Spin DOWN]

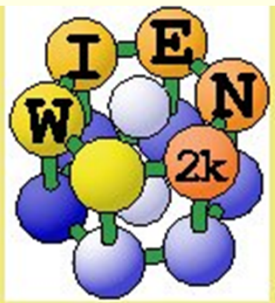
Spin UP selected.

If you want to include states with higher energy

edit magnetite.in1	Edit in1
x lapw1 -up	Calculate eigenvalues ☑ interactively
x lapw1 -dn	Calculate eigenvalues ☑ interactively
x lapw2 -qtl -up	Calculate partial charges ☑ interactively
edit magnetite.inxs	Edit input-file for XSPEC
x xspec -up	Calculate X-ray spectra ☑ interactively
plot	Plot XSPEC

```
Title: Atom 1 L3 absorption spectrum
1               (atom)
2               (n core)
1               (l core)
0,0.5,0.5       (split, Int1, Int2)
-2,0.02,15      (EMIN,DE,EMAX)
ABS             (type of spectrum)
1.00            (S)
2.0             (gamma0)
1.50            (W only for EMIS)
AUTO            (AUTO or MANually select Energy
-6.93
-10.16
-13.9
```

TELNES3 task



[Execution >>]
[StructGen™]
[view structure]
[initialize calc.]
[run SCF]
[single prog.]
[optimize(V,c/a)]
[mini. positions]

[Utils. >>]

[<< Tasks]
[El. Dens.]
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[XSPEC]
[TELNES3]
[OPTIC]
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Session: [rutile]
/psi11/pblaha/lapw/bulk/Rutil_exp

TELNES3

edit Rutil_exp.innes — Edit inpu

Only if you want to include

edit Rutil_exp.in1 — Edit in1

x lapw1 — Calculate eigenva

x qtl -telnes — Calculate parti

x telnes3 — Calculate ELNES

view Rutil_exp.outputelnes — dis

edit Rutil_exp.inb — Edit input-f

x broadening — Broaden the s

plot — Plot ELNES

save_eels — Save an elnes ca

InnesGen™ for TELNES3

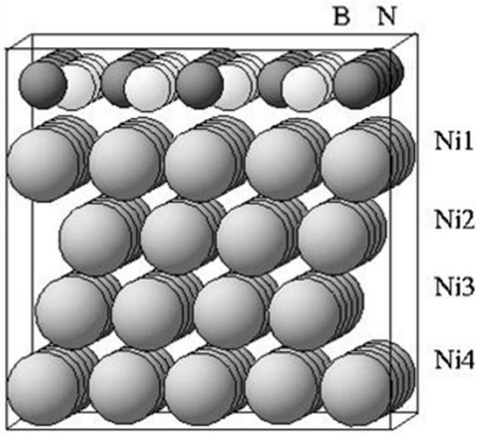
Title: Rutile O- K edge
Atom: 2: O | **Edge:** use n and l | (n= 1, l= 0)
Edge onset: 285 eV **Beam energy:** 300 keV
Energy grid: 0.0 eV to 15.0 eV in steps of 0.05 eV
Collection s.a.: 5.0 mrad **Convergence s.a.:** 1.87 mrad
Spectrometer broadening 0.5 eV **Q-mesh:** NR= 5 NT= 2

Advanced settings:

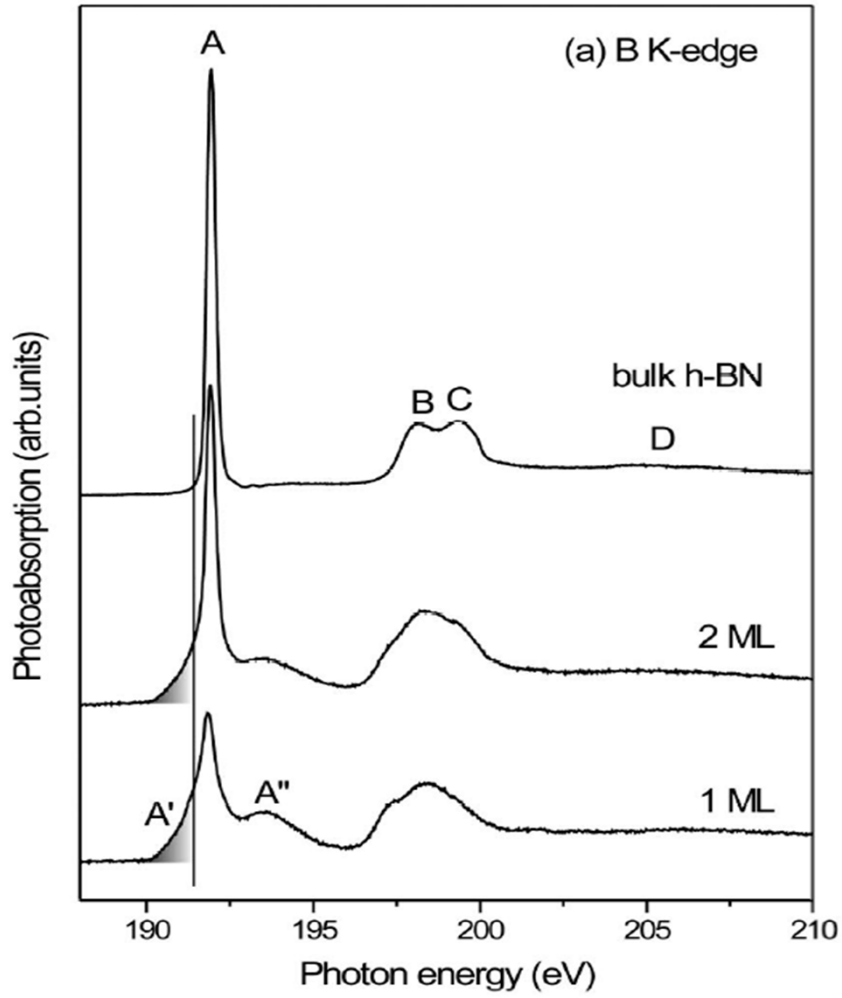
Branching ratio: (statistical if empty)
Spinorbit splitting of core state (eV): (calculated if empty)
Orientation sensitive: α= °, β= °, γ= °
Integrate over equivalent atoms: to (all eq. atoms if empty)
Detector position: θ_x 0.0 mrad, θ_y 0.0 mrad
Modus: energy
Initialization: Calculate DOS write DOS
Calculate rotation matrices write rotation matrices
Verbosity: basic **File headers:** Write headers (default)
Interaction potential: relativistic (recommended)
Q-grid: U uniform θ_0= (not used for uniform grid)
Interaction order: all λ (default) **Final state selection rule:** L=l +/- 1 (default)
Extend potential beyond Rmt: rmax= bohr
Set Fermi energy manually: EF= Ry
Read core state wavefunction: filename= case.cwf
Read final state wavefunctions: filename= case.finalwf
Calculate DOS only
NBTOT: 200

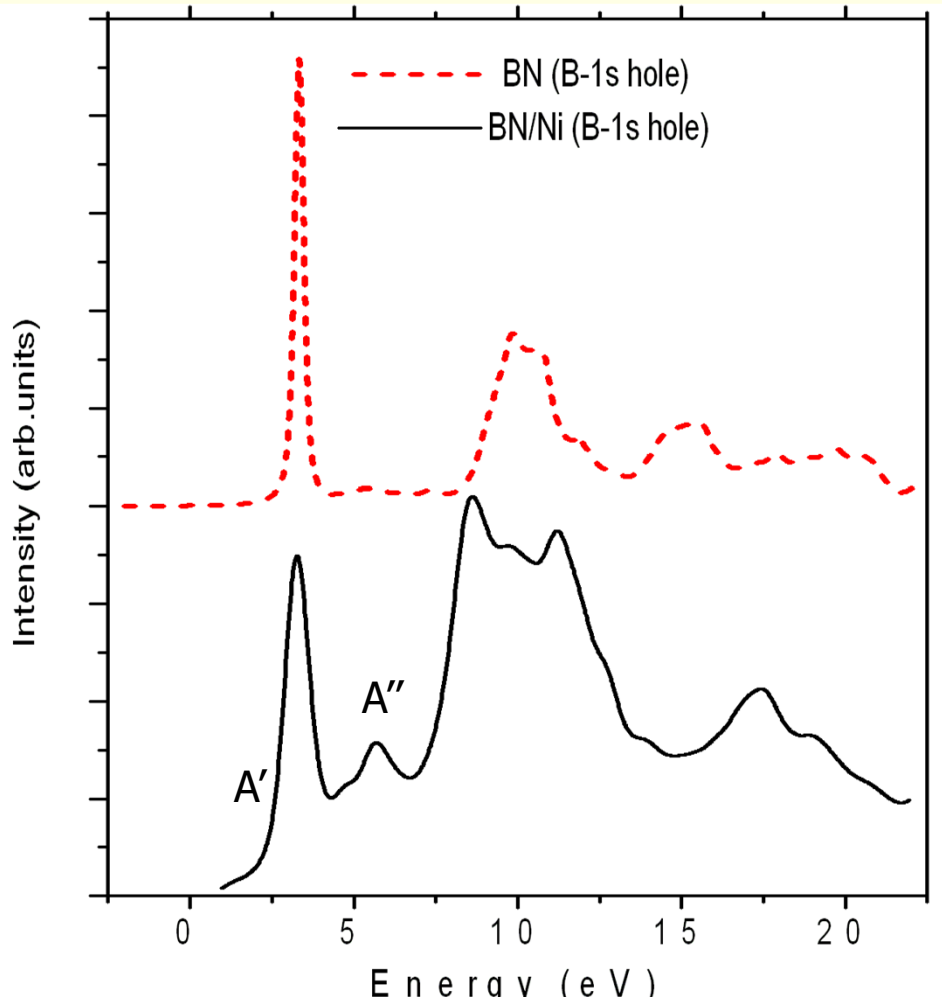
save

B-K XANES in h-BN/Ni(111)

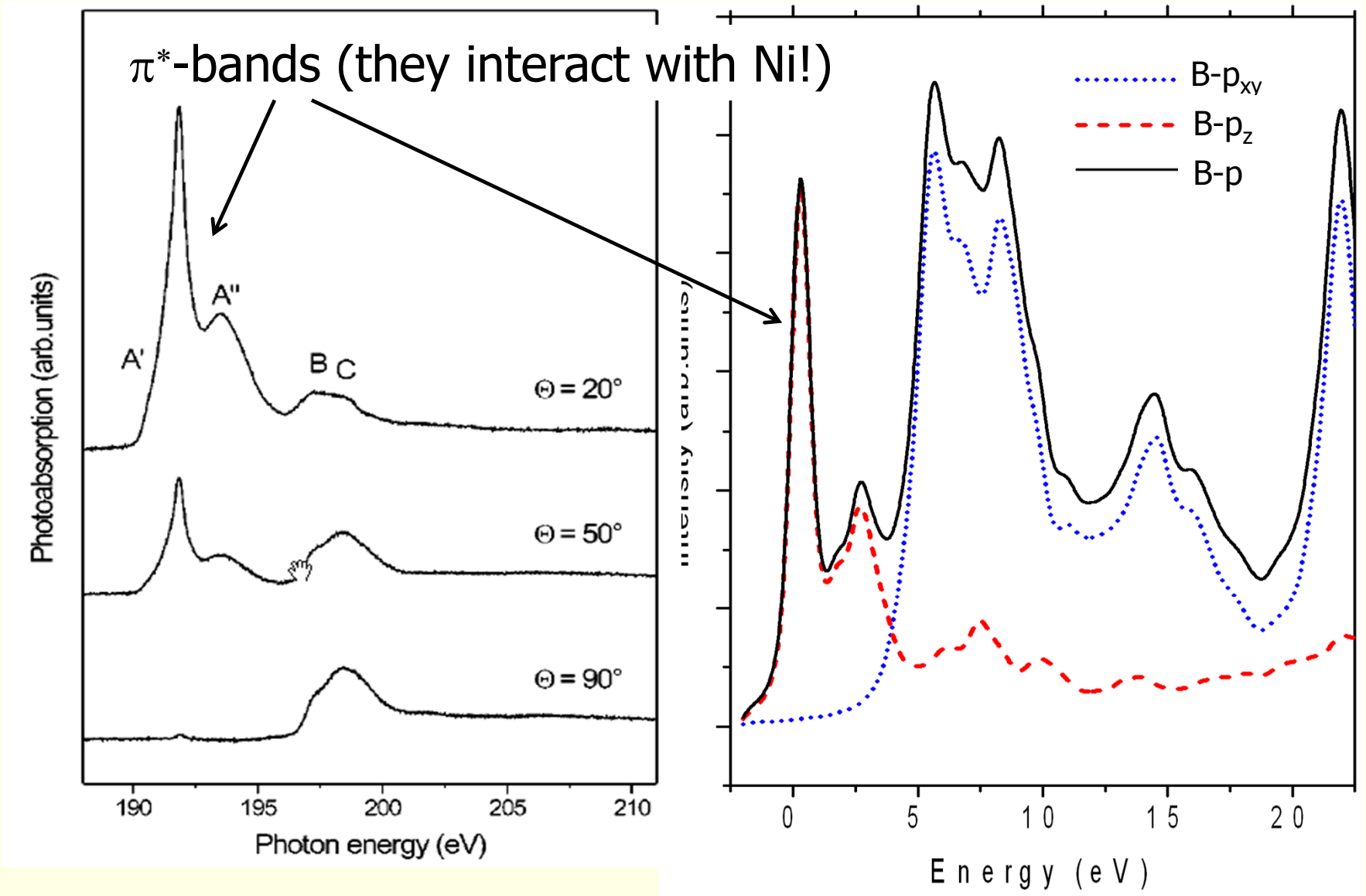


- B-K edge in BN and BN/Ni(111)
- Preobrajenski etal, PRB70, 165404 (2004): "The experiments contradict recent DFT calculations by Grad etal."



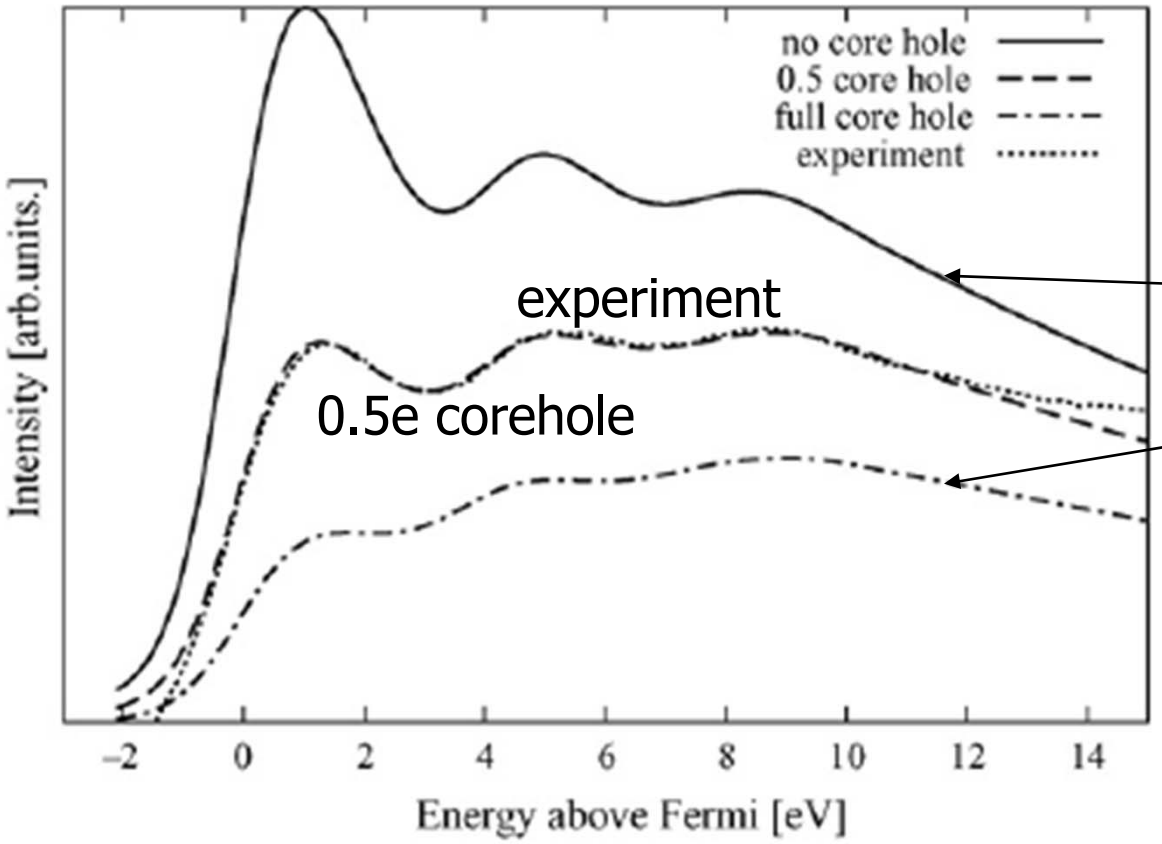


Angle dependency of B-K edge in h-BN/Ni(111)



Partial core hole screening in the Cu L_3 edge

- J.Luitz et al., Eur. Phys. J. B **21**, 363{367 (2001)

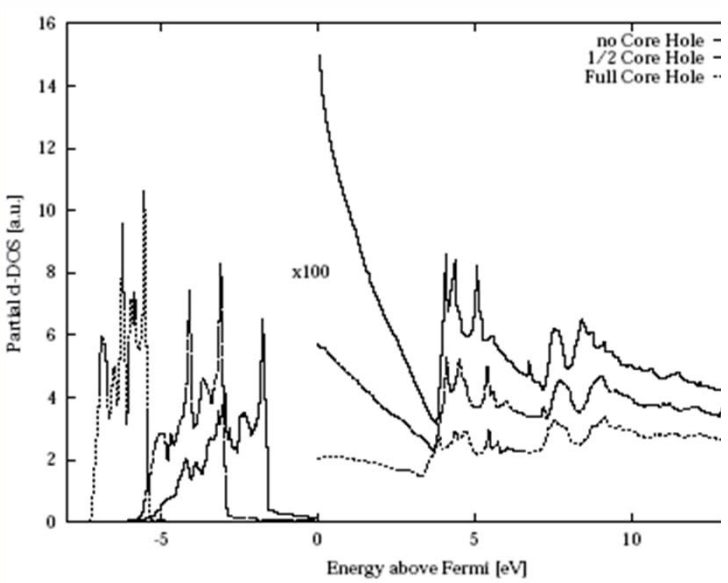


experiment

0.5e corehole

without corehole

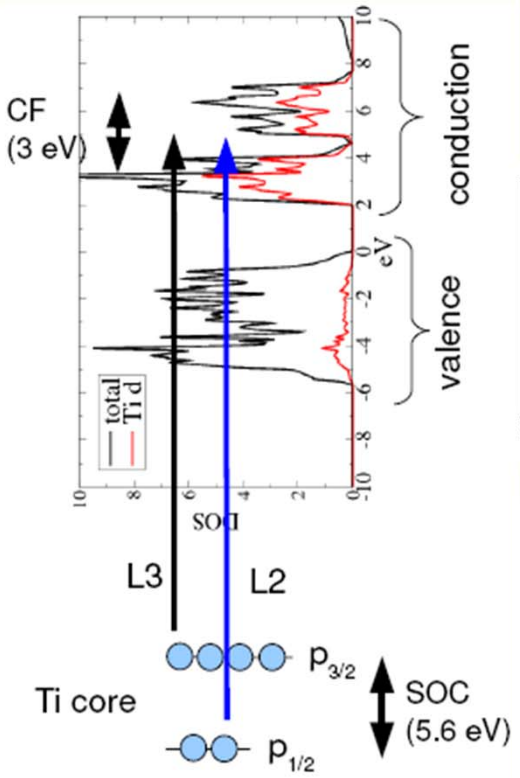
with corehole



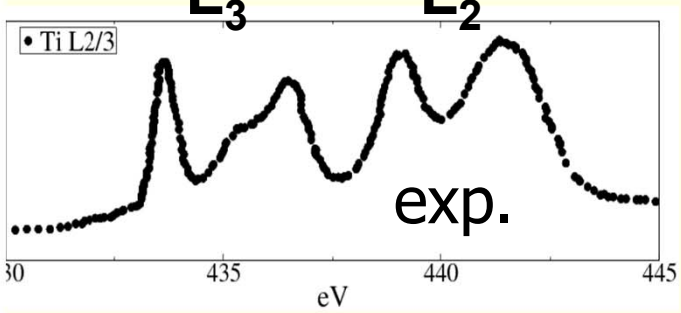
Unexpected effect of core-hole !

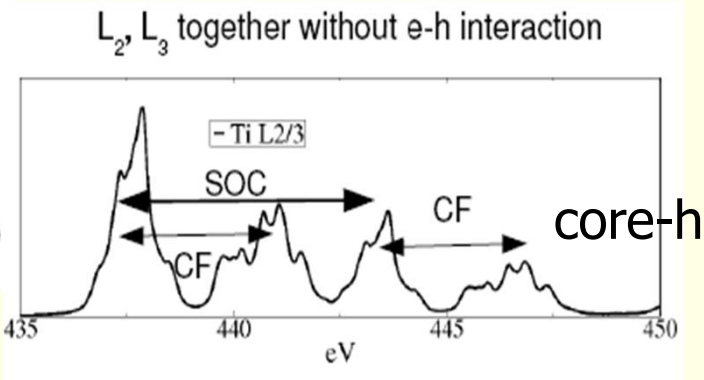
$L_{2,3}$ spectra: failure of the single particle approach

- In particular early 3d TM-compounds show a
  - *non-standard L_2/L_3 branching ratio (1:2)*
  - *sometimes a completely different lineshape (TiO_2)*
  - *„wrong" **SOC** or **CF** splittings*

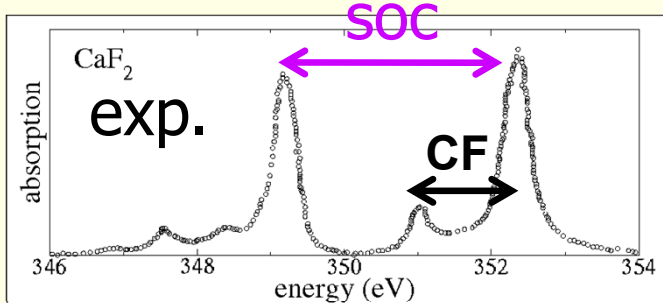


rutile TiO_2

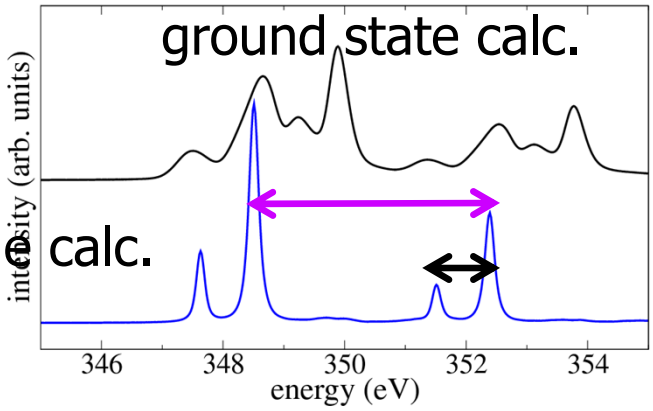




CaF_2



core-hole calc.



Beyond IPA

- *ab-initio* configuration interaction (solid is approximated by finite cluster)

  Y. Kumagai, H. Ikeno, and I. Tanaka, J. Phys.: Condens. Matter 21, 104209 (2009).
  H. Ikeno, F. M. F. de Groot, S. E., and I. Tanaka, J.Phys.: Condens. Matter 21, 104208 (2009).
  H. Ikeno and I. Tanaka, Phys. Rev. B 77, 075127 (2008).

- linear response in time dependent DFT (TDDFT)

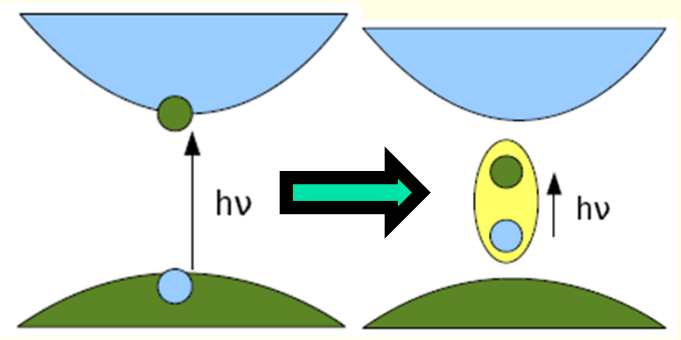
  J. Schwitalla and H. Ebert, Phys. Rev. Lett. 80, 4586 (1998).
  A. L. Ankudinov, A. I. Nesvizhskii, and J. J. Rehr, Phys.Rev. B 67, 115120 (2003).

- Bethe- Salpeter equation (BSE)

  E. L. Shirley, J. Electron Spectrosc. Relat. Phenom. 144-147, 1187 (2005).
  E. L. Shirley, Phys. Rev. Lett. 80, 794 (1998).
  J. A. Soininen and E. L. Shirley, Phys. Rev. B 64, 165112 (2001).
  W. Olovsson, I. Tanaka, T. Mizoguchi, P. Puschnig, and C. Ambrosch-Draxl, Phys. Rev. B 79, 041102 (2009).
  R. Laskowski, P. Blaha, Phys. Rev. B, 81, 075418 (2010)

fully relativistic electron-hole interaction (BSE)

- *Bethe-Salpeter-equation: L(12;1′2′)*
- *solving a 2-particle (e^- - h) equation of large dimension ($N_v N_c N_k \sim 100000$)*



$$\sum_{v'c'k'} (H^{eh}_{v'c'k',vck}) A^{\lambda}_{v'c'k'} = E^{\lambda} A^{\lambda}_{vck}$$

$$H^{eh} = H^{diag} + H^{dir} + 2H^{x}$$

$$H^{diag} = (E_{v,k} - E_{c,k})\delta_{cc'}\delta_{vv'}\delta_{kk'}$$

eigenvalue difference between hole (v) and electron(c) state

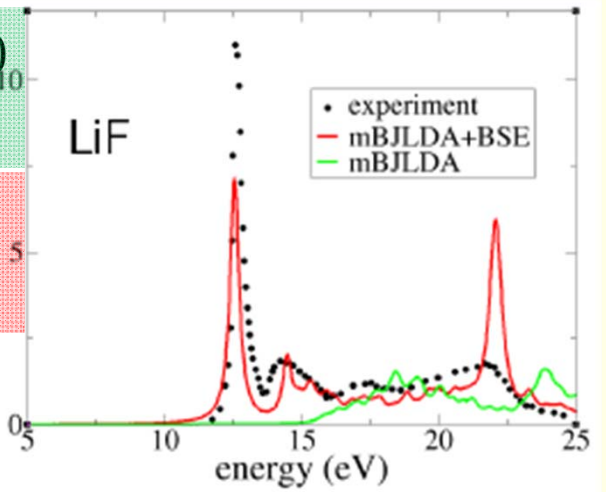
$$H^{dir}_{vckv'c'k'} = -\int d^3r\, d^3r'\, \Psi_{vk}(r)\Psi^{*}_{ck}(r')W(r,r')\Psi^{*}_{v'k'}(r)\Psi_{c'k'}(r')$$

attractive screened static Coulomb interaction *W; $W \sim \varepsilon^{-1}$*

$$H^{x}_{vckv'c'k'} = \int d^3r\, d^3r'\, \Psi_{vk}(r)\Psi^{*}_{ck}(r)\bar{v}(r,r')\Psi^{*}_{v'k'}(r')\Psi_{c'k'}(r')$$

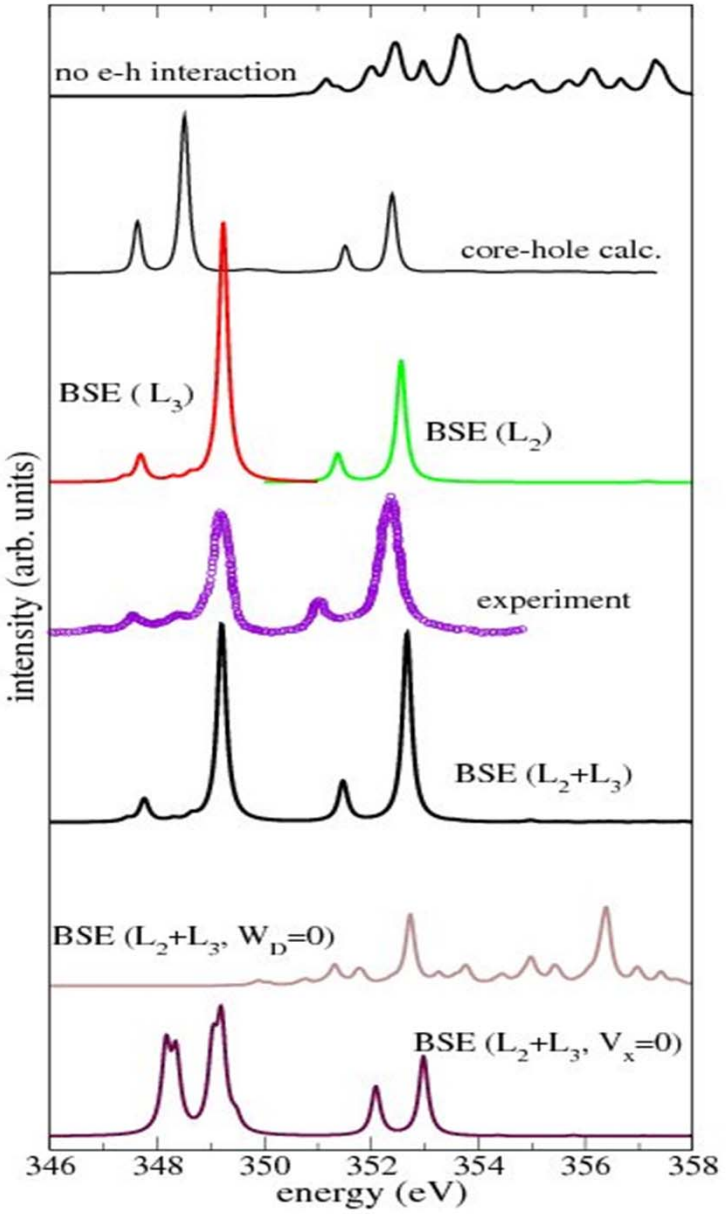
e-h exchange with bare Coulomb potential *v*

Excitons in LiF

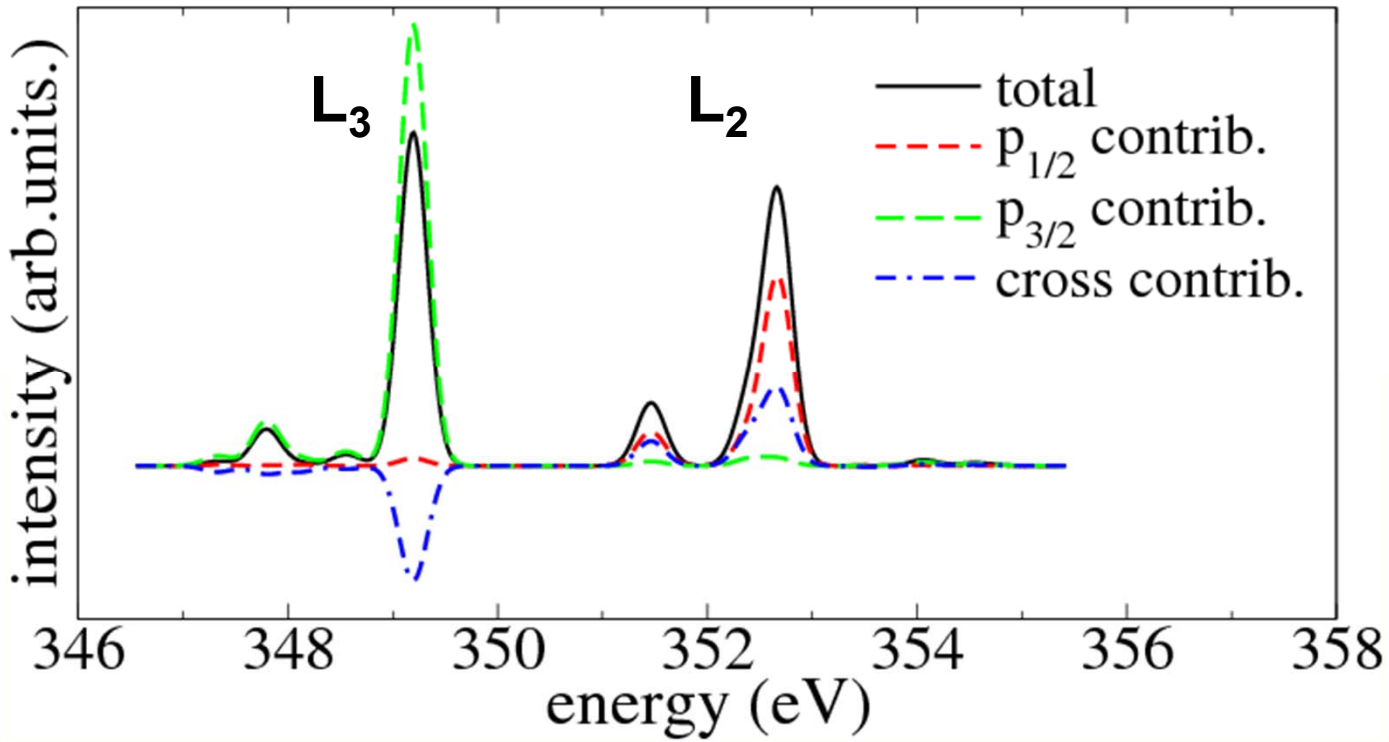


Ca-L_{23} edge in CaF_2

- "ground-state" DOS
-
-
- **experiment**
-
-
-



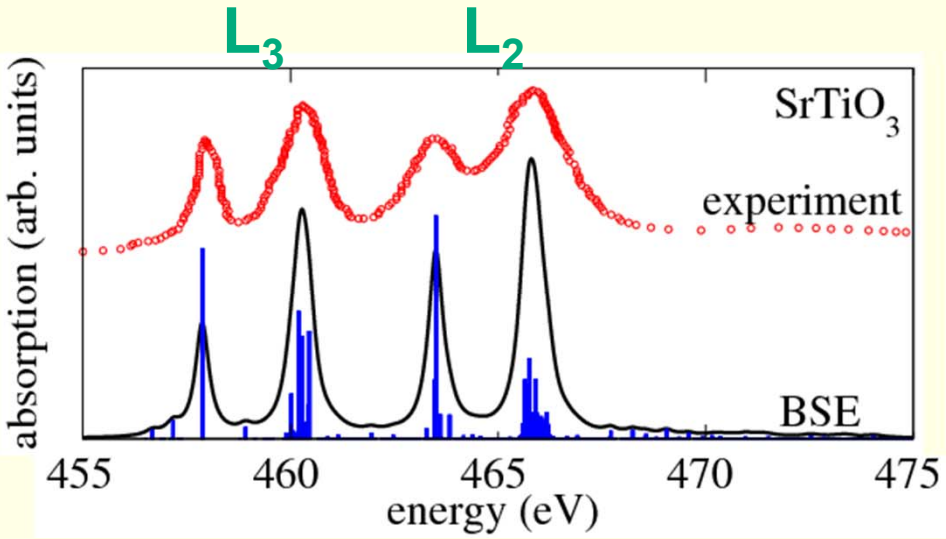
$L_{2,3}$ edge for Ca in CaF_2

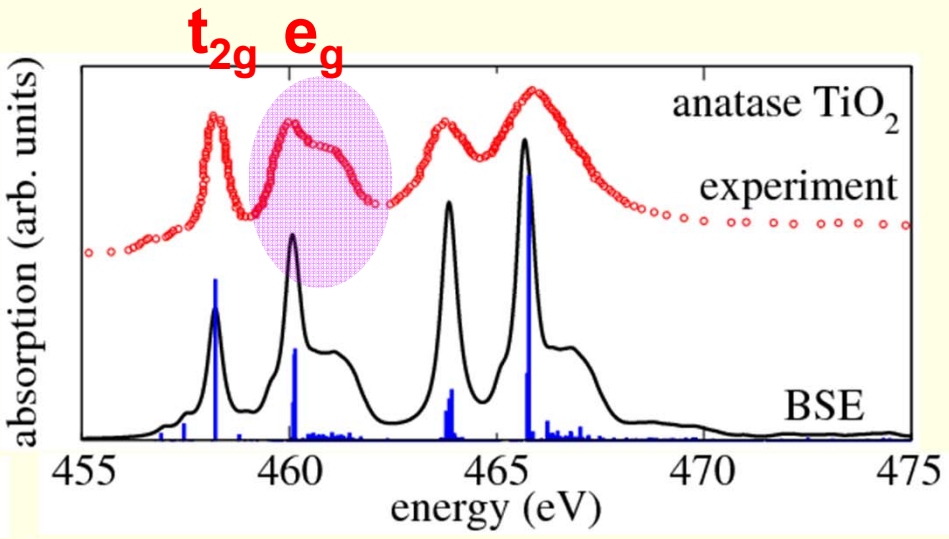


Decomposition of ϵ_2 into the excitation from $p_{1/2}$ and $p_{3/2}$ states
cross terms suppress the L_3 branch and enhance L_2

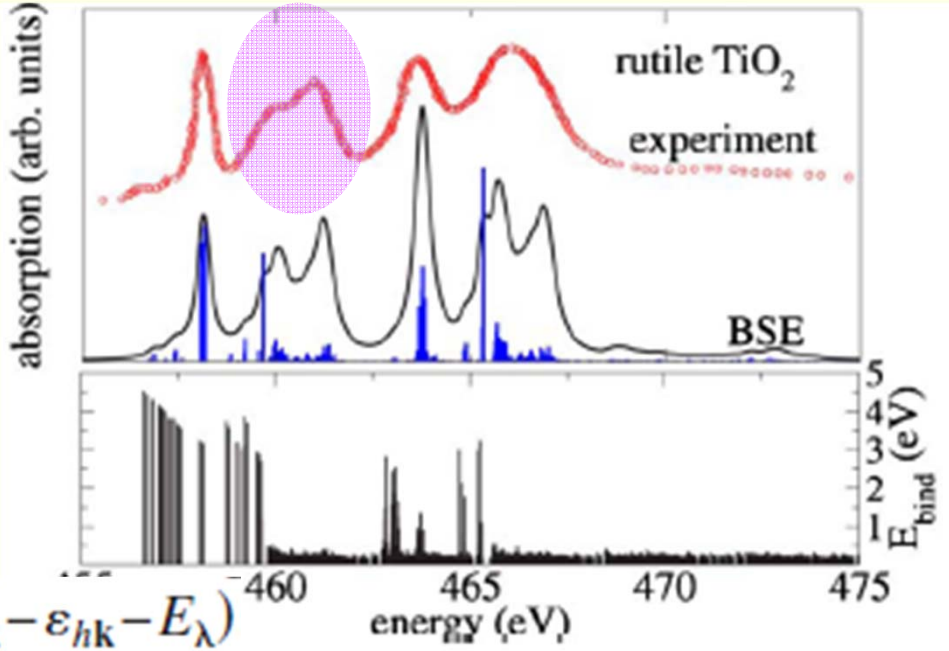
$$\varepsilon_2^{xx}(\omega) = \frac{8\pi^2}{\Omega}\sum_{\lambda}\left|\sum_{hek} A^{\lambda}_{hek}\frac{\langle hk|-i\nabla_x|ek\rangle}{\varepsilon_{ek}-\varepsilon_{hk}}\right|^2 \times \delta(E^{\lambda}-\omega)$$

Ti $L_{2,3}$ in rutile-TiO_2, anatase-TiO_2, $SrTiO_3$





- The experimental Ti $L_{2,3}$ edges are rather well reproduced.
- intensity ratio L_3/L_2 (not 2:1)
- „t_{2g}/e_g“ ratio (not 3:2)
- left/right shoulder in L_3-„e_g“ peak of rutile/anatase



$$E^{\lambda}_{bind} = \Sigma_{k,e,h} A^{2}_{k,h,e} (\varepsilon_{e\mathbf{k}} - \varepsilon_{h\mathbf{k}} - E_{\lambda})$$

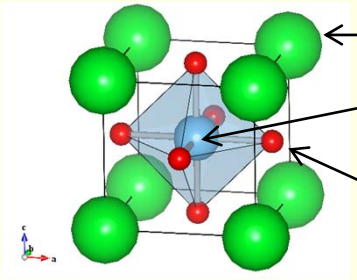
Ti $L_{2,3}$ in $SrTiO_3$, decomposition of ϵ_2

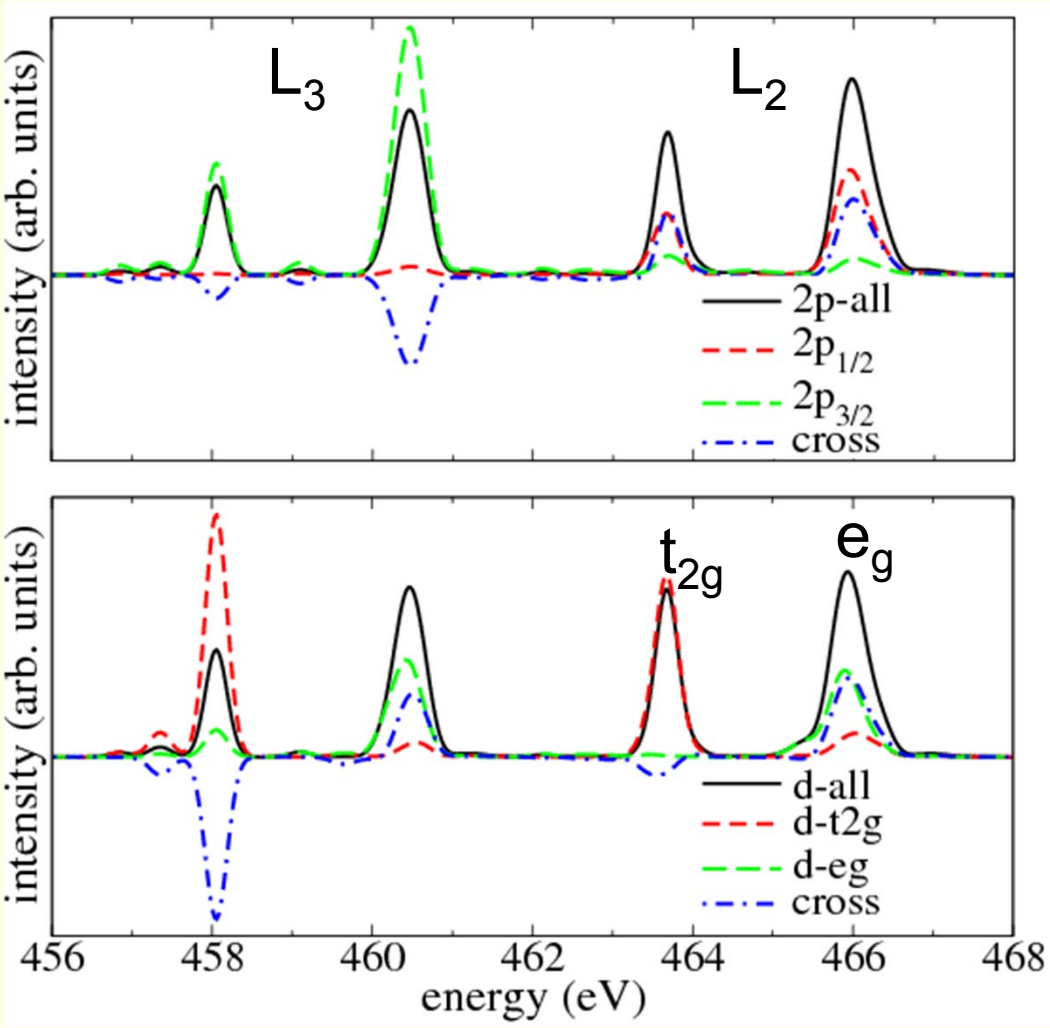
Decomposition into excitations from $p_{1/2}$ and $p_{3/2}$

cross term suppresses the L_3 branch and enhances the L_2

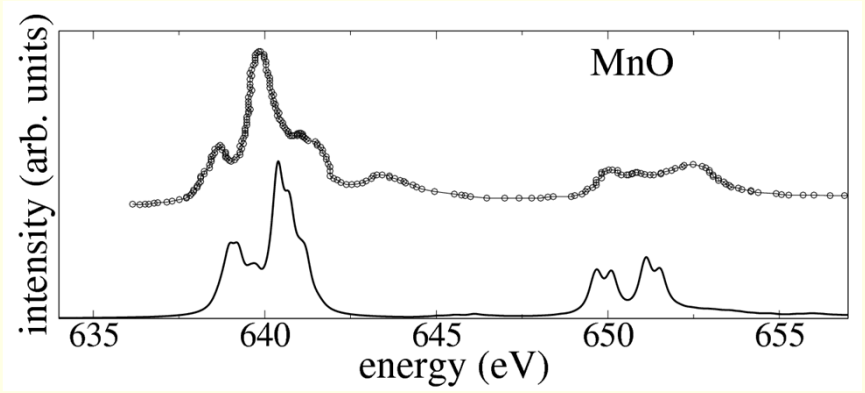
Decomposition into excitation into the e_g and t_{2g} bands

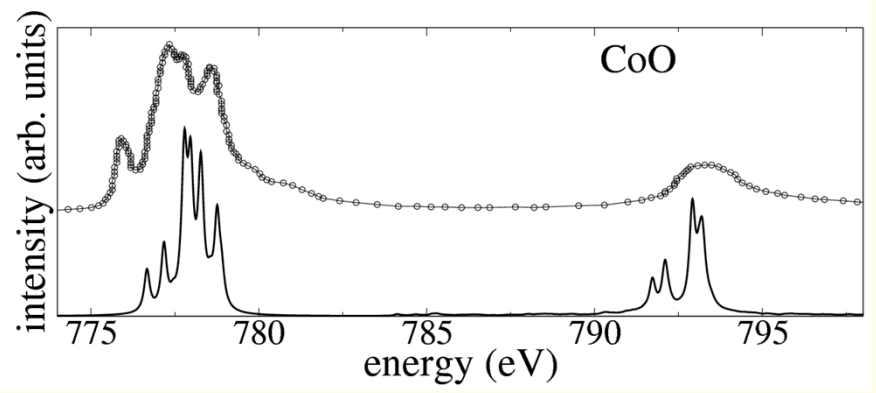
the first peak of L_2 or L_3 is related to excitations into t_{2g}, the second peak is associated with e_g
the cross term strongly modifies the ratio between these peaks

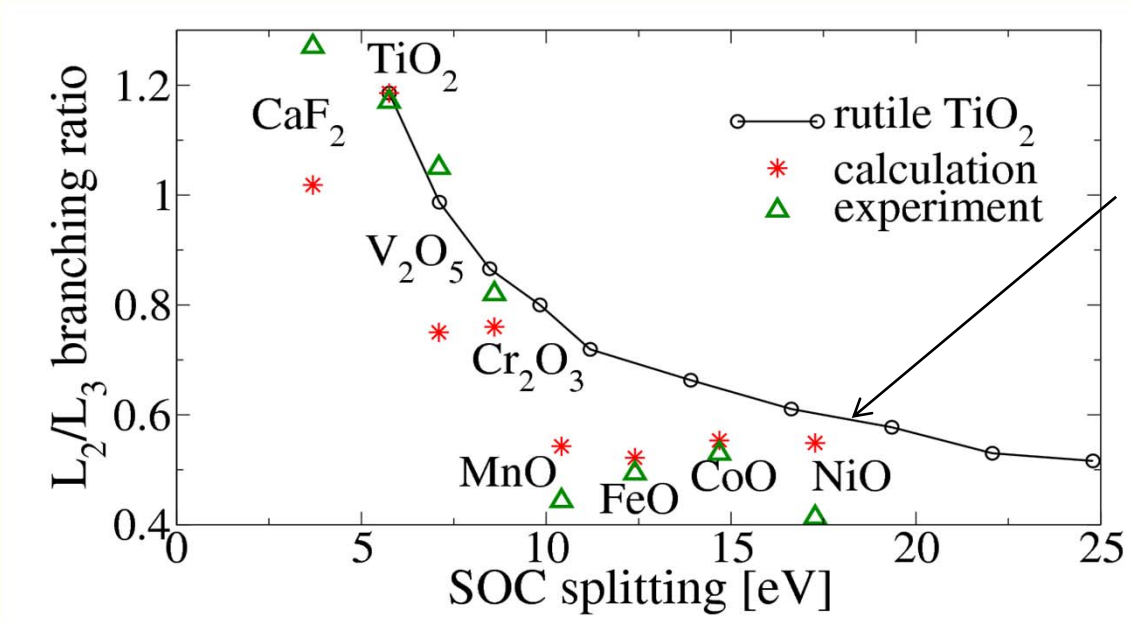




3d metal $L_{2,3}$ branching ratio



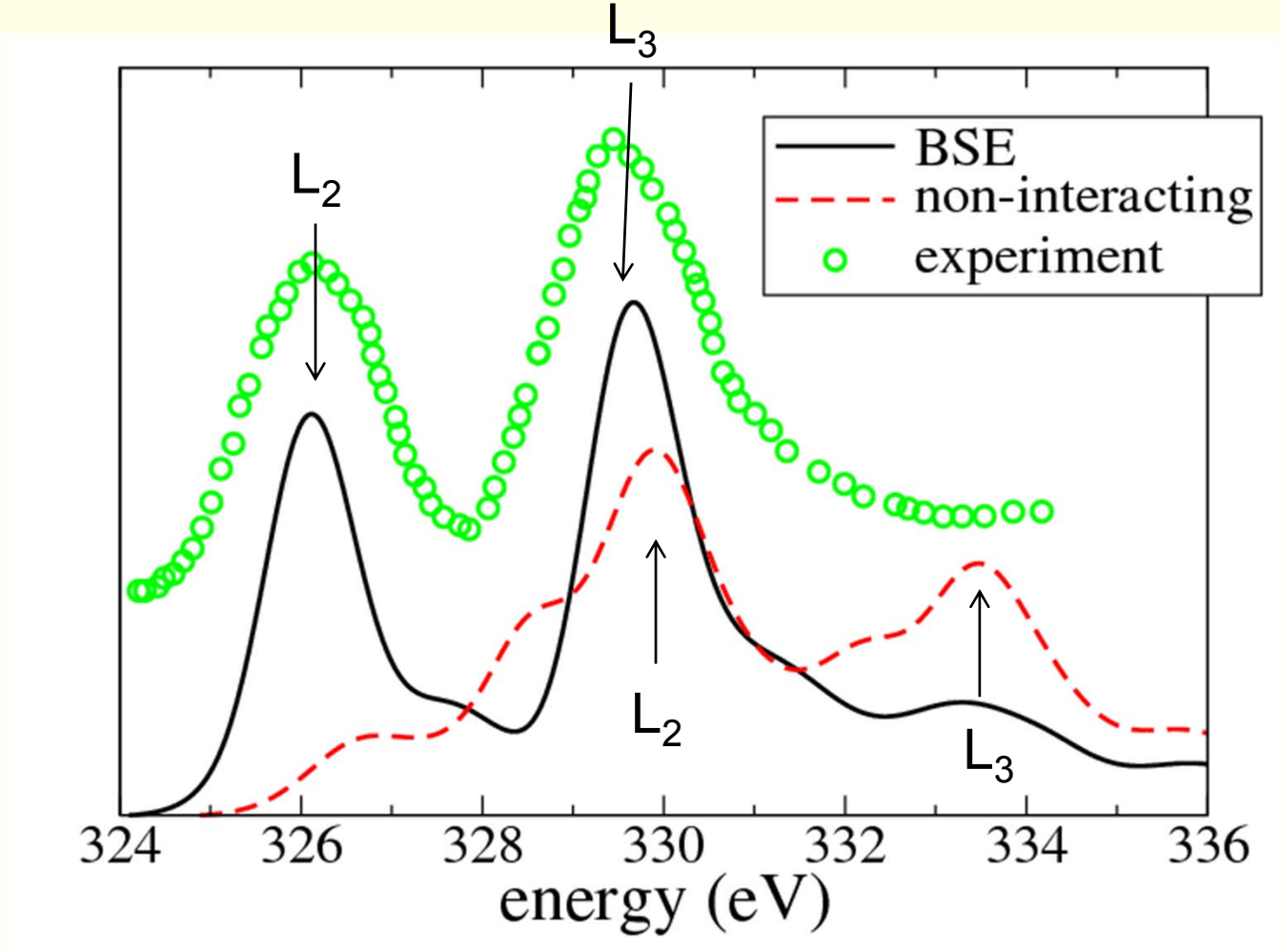




Ti $L_{2,3}$ branching ratio in rutile-TiO_2 (SOC splitting is set to values from 5eV to 25eV)

The size of spin orbit splitting is a main factor determining the branching ratio (deviating from 0.5)

fcc Ca, $L_{2,3}$ edge



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Thank you for your attention !