XPS, XES, XAS, EELS, BSE

Peter Blaha

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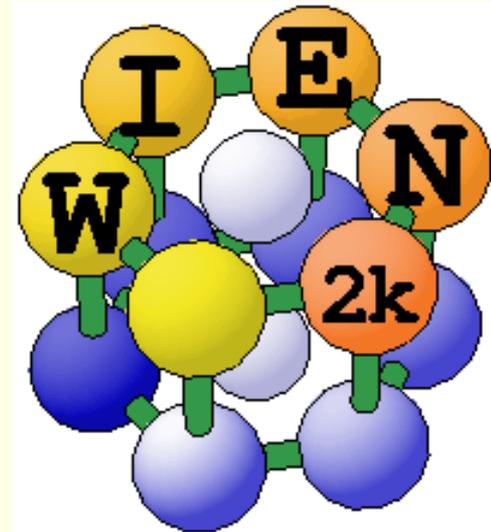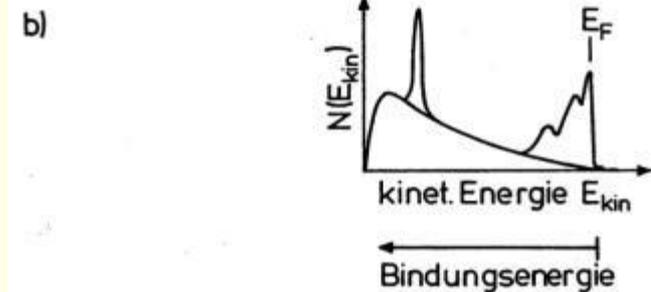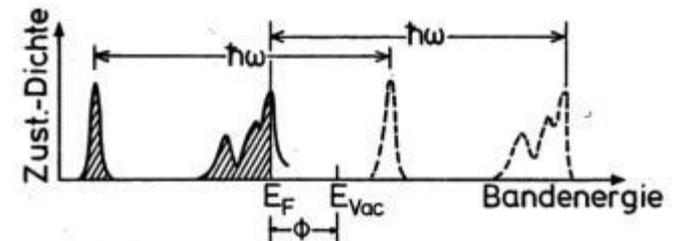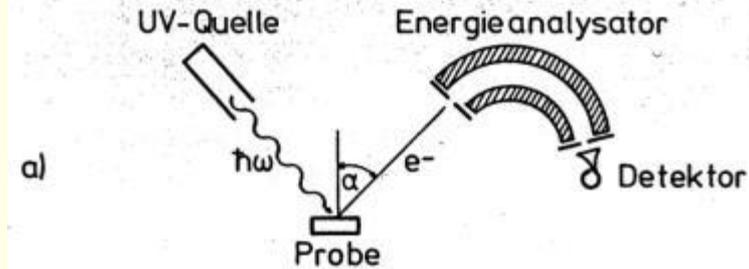
• Illuminate sample with light of known energy, measure kinetic E of emitted electrons e⁻

→ core-e⁻, Valence-DOS

■ Energy conservation:

$$\hbar\omega = \phi + E_{kin} + E_b$$

■ ϕ: work function
■ E_{kin}: kinetic E of e⁻
■ E_b: bindingenergy of e⁻

■ UPS: UV (He-light, 21.1 und 40.4 eV), for valence-electrons
■ XPS, ESCA: X-rays (Al 1486 eV), for core and valence-electrons
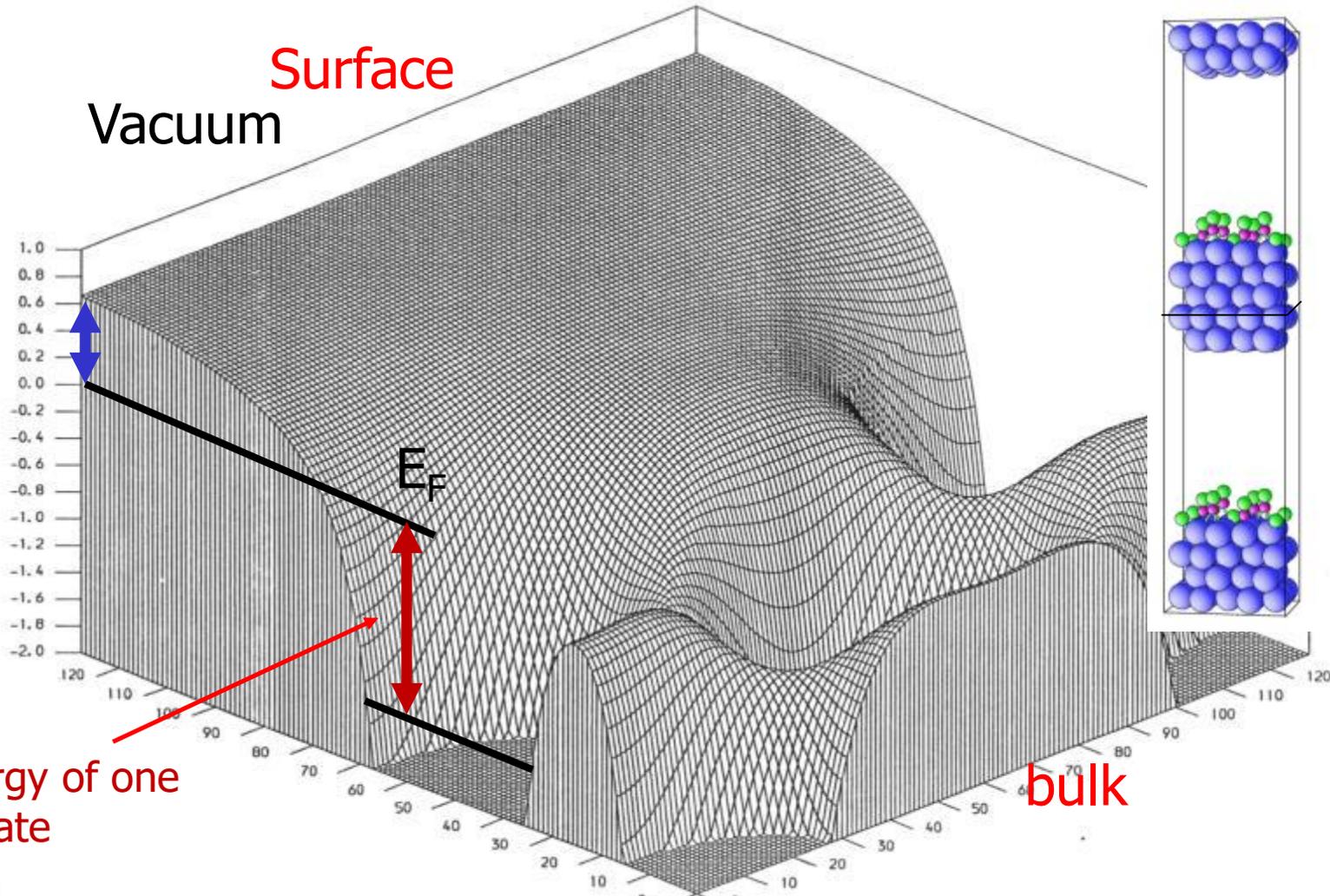■ Synchrotronradiation: UV or X-rays of "any" wavelength

Work function

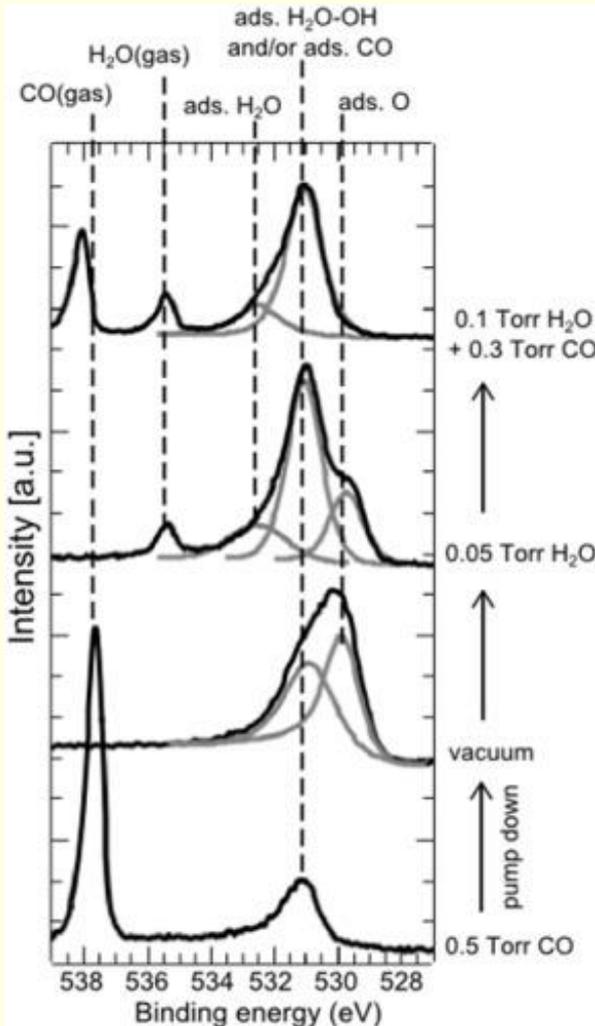potential   supercell

Surface

Vacuum

Work-function

E_F

binding energy of one particular state

bulk

WF= :VZERO - :FER   (check convergence with vacuum)

- Ionizationpotential of core-e⁻, IP= $E^{tot}(N) - E^{tot}(N-1)$
  - *gives information on charge state and bonding of the atom*
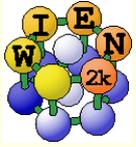

O-1s XPS on Cu(111)

adsorbed O is gone

free and adsorbed H_2O

adsorbed O and OH from H_2O splitting

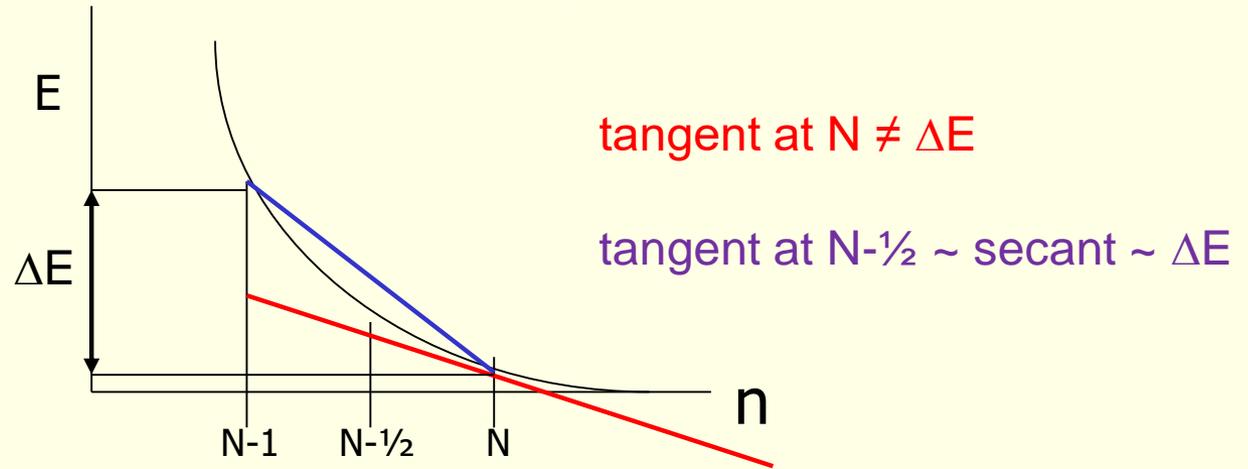free CO gas + adsorbed OH

B.Eren etal., Science 2016, 351, 475–478

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

tangent at N ≠ ΔE

tangent at N-½ ~ secant ~ ΔE

E

ΔE

N-1   N-½   N

n

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

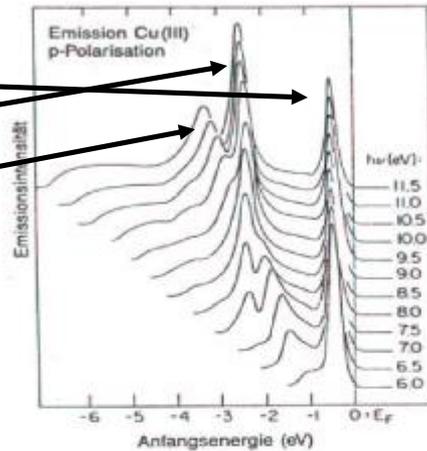| C 1s	exp.(eV)	ε_i	Δ-SCF or Slater
TiC	281.5	264.7	281.9

Normalemission:

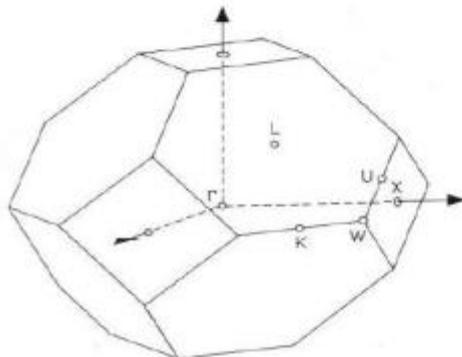Surface state
d-band
sp-band

Abb. 3.11 a. UP-Spektren einer Cu(111)-Oberfläche
bei Detektion normal zur Oberfläche
und Variation der Photonenenergie von 6 bis 11,5 eV.
Als Energieachse dient die Bindungsenergie
bezogen auf die Fermi-Energie, hier als
Anfangsenergie der Elektronen bezeichnet [29].
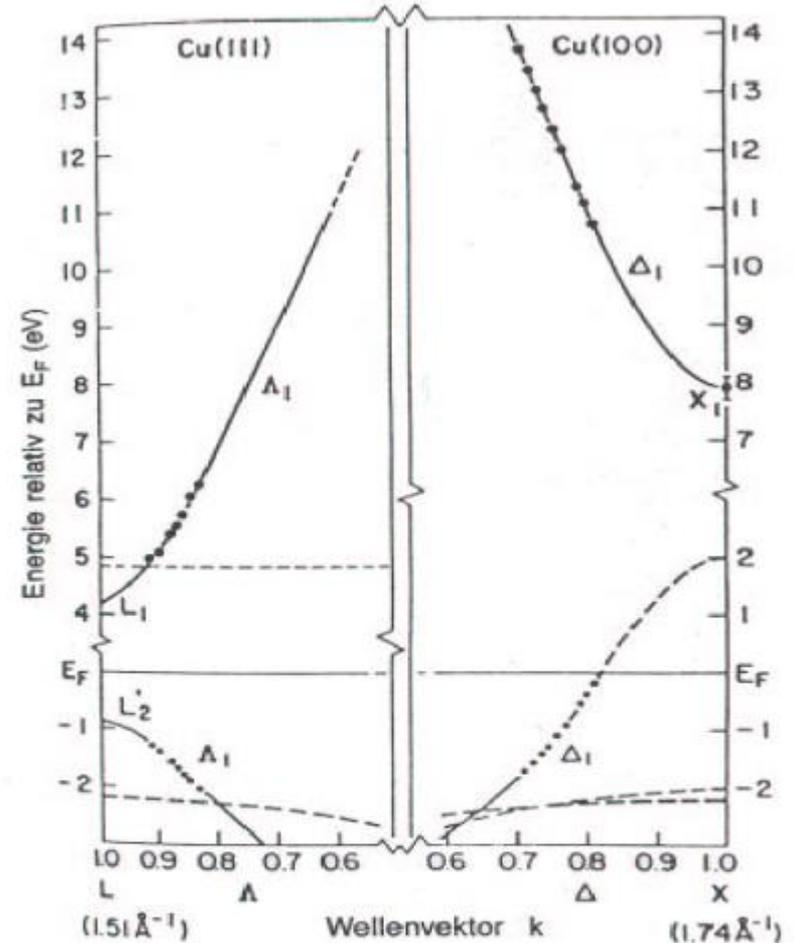
Brillouinzone fcc:

Volumenbandstruktur:

Abb. 3.11 b. Aus den Spektren von Abb. 3.11 a
ermitteltes Bänderschema in den [111]-(Γ−L)- und
[110]-(Γ−X)-Richtungen. Die Punkte geben die
gemessenen Peakpositionen aus 3.11 a wieder, die Linien
sind aus einer theoretischen Bandstruktur. Beim
Vergleich mit der Cu-Bandstruktur in der Abb. 3.10
beachte man den unterbrochenen Energiemaßstab
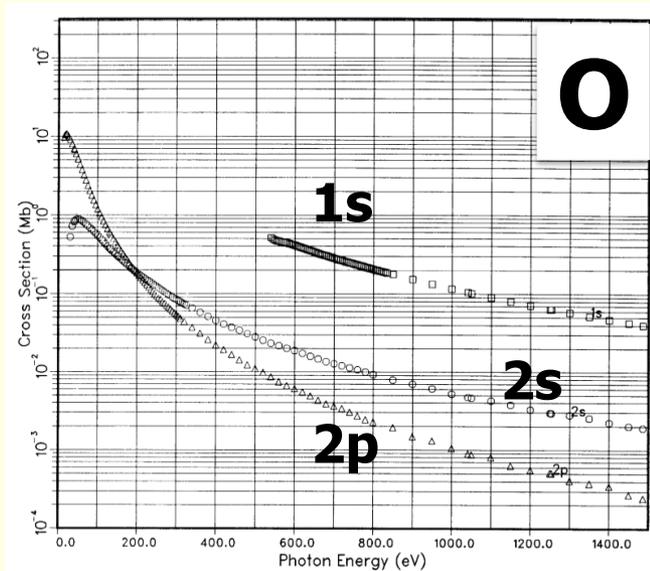und den unterdrückten Γ-Punkt in Abb. 3.11 b [29].

- a single DOS cannot explain the E-dependency of PES
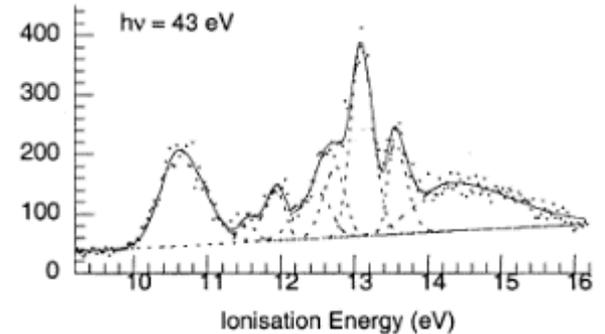
- $$I = \sum_{atoms,l} N_{a,l}\sigma_{a,l}$$
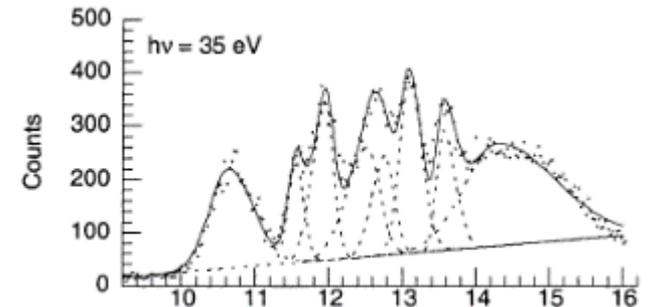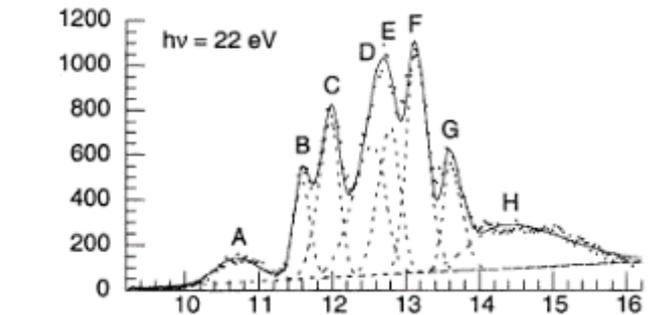
- $N_{a,l}$ = Partial DOS
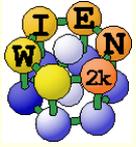- $\sigma_{a,l}$ = atomic cross section

O

1s

2s

2p

Photoionization cross-sections: a guide to electronic structure

Jennifer C. Green [a,*], Piero Decleva [b]

hν = 22 eV

hν = 35 eV

hν = 43 eV

PE spectra of TiMeCl₃ at 22, 35 and 43 eV.

SiO$_2$ valence band XPS

- **Total DOS** gives 5 peaks, but wrong intensities

- **Cross section modulated PDOS** gives better intensities

- **Renormalized PDOS * σ** gives perfect intensities

  - *renormalization according to the **inverse charge fraction** of an orbital within the atomic sphere + removal of interstital DOS:* $N_{tot} = \Sigma_{atoms,l} N_{a,l} + N_{int}$

Legend (plot):
- ⋯•⋯ XPS–1486 eV
- — — Si–3s
- —·—· Si–3p
- —— Tot
- ⋯⋯ O–2s
- —— O–2p

a — Calculated DOS
b — Calculated DOS * Cross section
c — Simulated Spectra at 1486 eV

Intensity (arb. units) vs Energy (eV), from −16 to −6
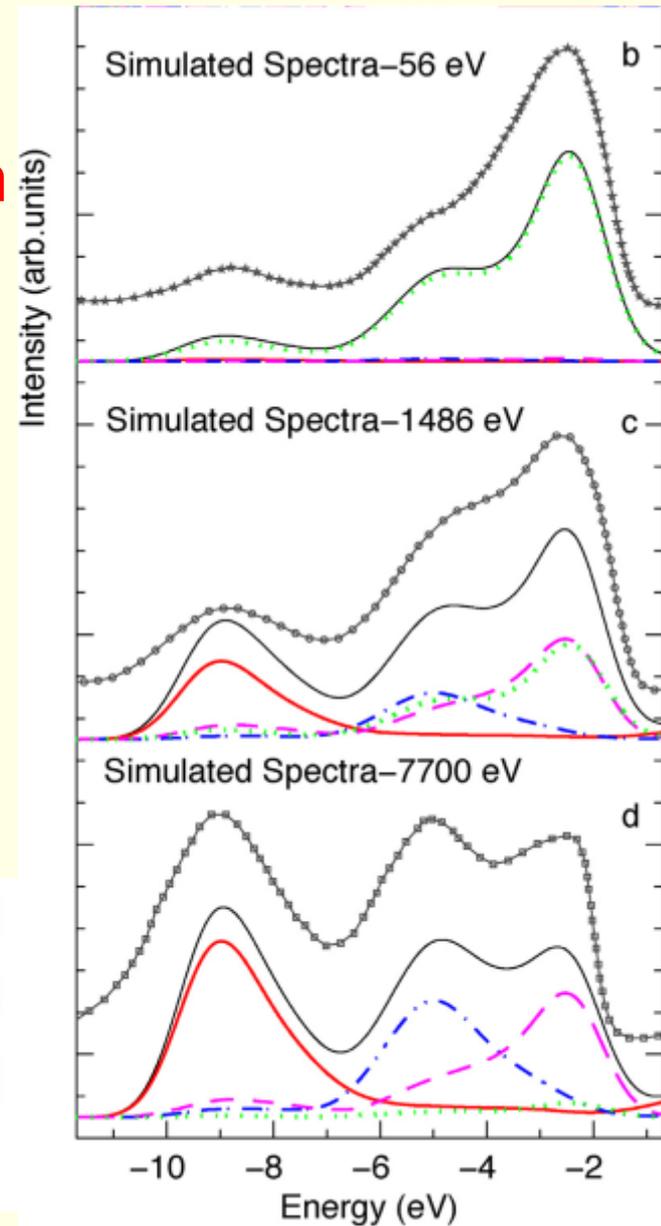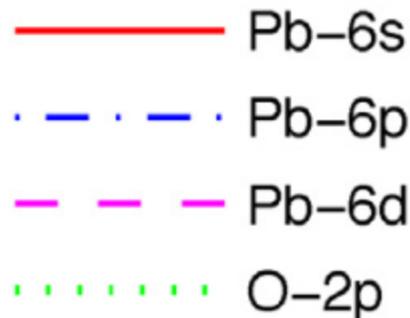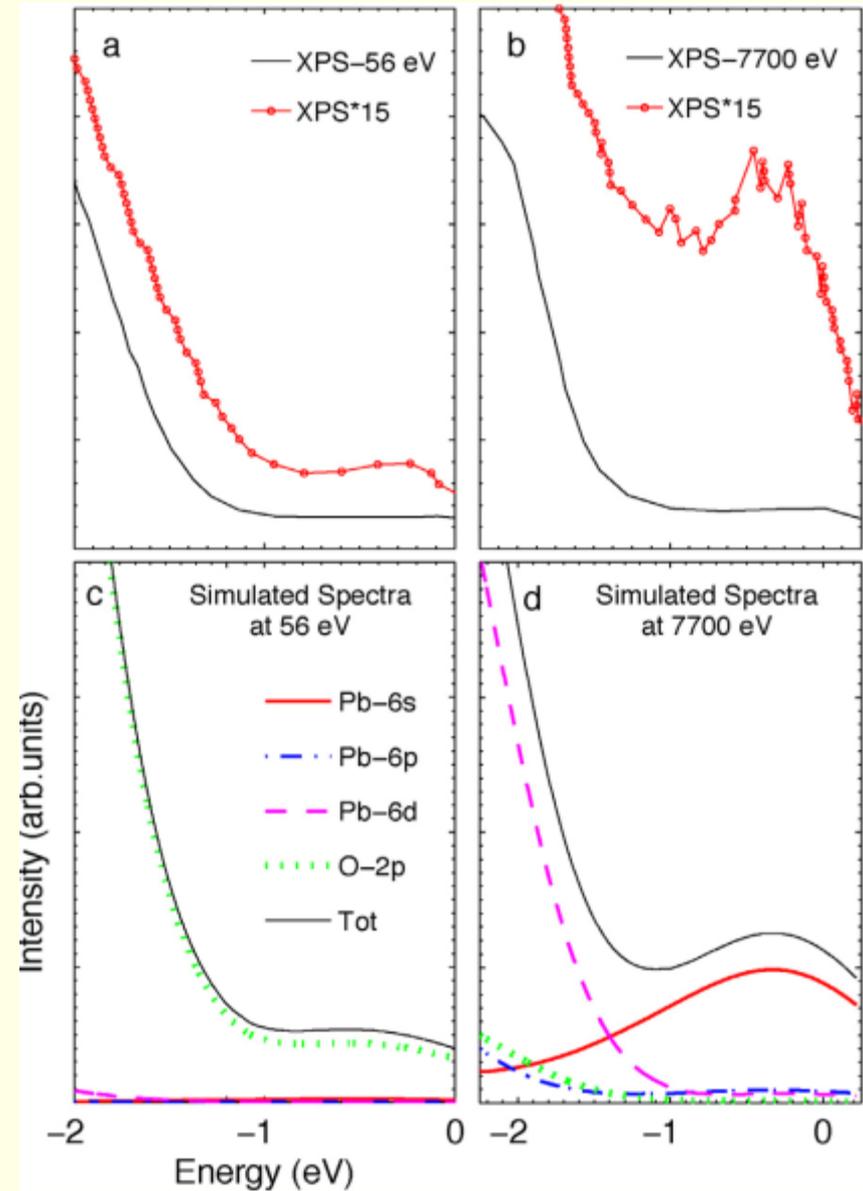
PbO$_2$ at 3 different energies

- 56eV: O-2p PDOS explains the spectrum

- 1486 eV: all orbitals contribute

- 7700 eV: O-2p not important

Simulated Spectra–56 eV

Simulated Spectra–1486 eV

Simulated Spectra–7700 eV

Pb–6s
Pb–6p
Pb–6d
O–2p

Intensity (arb.units)

Energy (eV)

- 56 eV: almost no intensity till -1 eV

- 7700eV: strong contribution from antibonding Pb-6s
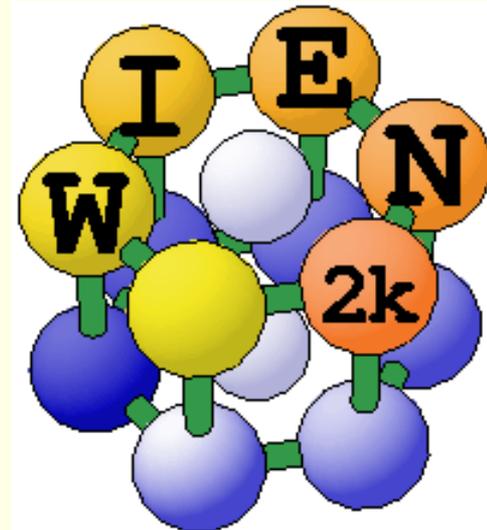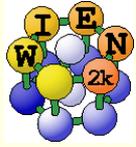
- **Time dependent perturbation theory:** $\hat{H}'(t) = \hat{H}'_0 \left(e^{iE_v t} + e^{-iE_v t} \right)$

- **EM-radiation with energy ω, polarisation α and direction of propagation $\boldsymbol{k}$ acts on the momentum $\boldsymbol{p}$ of the electron**

$$\vec{E} = \sum_{\vec{k},\alpha} \left[\vec{e}_\alpha(\vec{k}) e^{i(\vec{k}.\vec{x} - \omega t)} \right]$$

The transition probability W from state i to f is then given by **Fermi's "golden rule"** :

$$W_{f \leftarrow i} = \left\langle f_f \left| e^{i\vec{k}\cdot\vec{x}} \hat{e}_\alpha(\vec{k}) \cdot \vec{p} \right| f_i \right\rangle^2 \rho_N(E) \quad with \quad E = E_f - E_i - E_v$$

Number of states with energy E

E-conservation

W: proportional to the square of the transition matrix element

momentum of photons << momentum of e⁻;

momentum conservation ⟶ e⁻ cannot change its momentum

$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{x} + \ldots$$
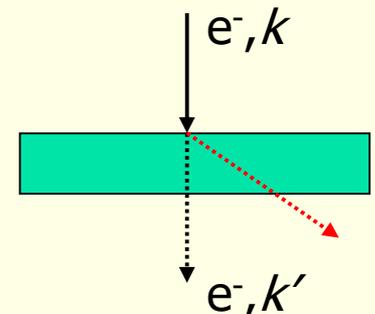
dipole quadrupole … approximation

$$e^{i\vec{k}\cdot\vec{r}} \approx 1$$

1-3% error (even for keV X-rays), but:
EELS (electron energy loss spectr.) may violate
dipole approximation (selection rules!!)

$$\left\langle f_f \left| \hat{H}' \right| f_i \right\rangle = \hat{e}_\alpha \left\langle f_f \left| \vec{p} \right| f_i \right\rangle = \hat{e}_\alpha \left\langle f_f \left| \vec{r} \right| f_i \right\rangle$$
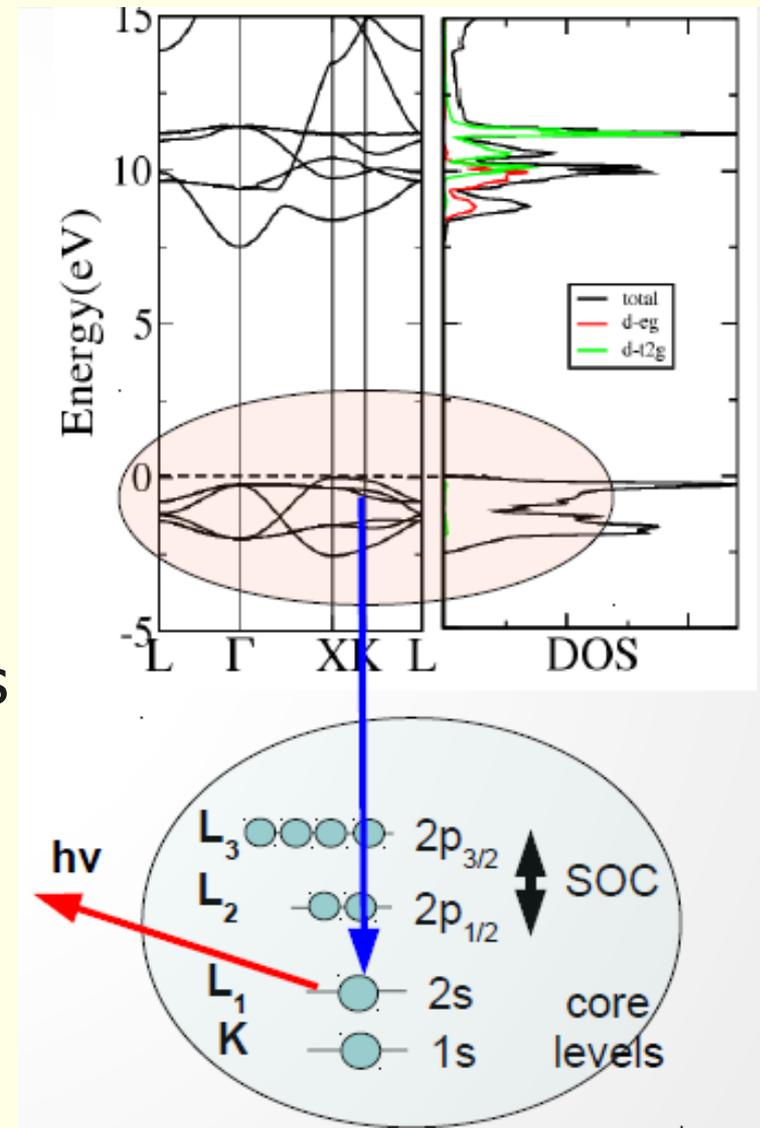
e⁻,k

e⁻,k'

⟹ selection rules: $\ell \pm 1$

XES (X-ray emission spectroscopy)

- knock out a core e⁻

- valence e⁻ fills core hole

- measure the emitted X-ray

- XES intensity given by the $\ell \pm 1$ **partial DOS** of the **valence** bands of the **specific atom** (with core state $n\ell$) times the **squared transition matrix element**.
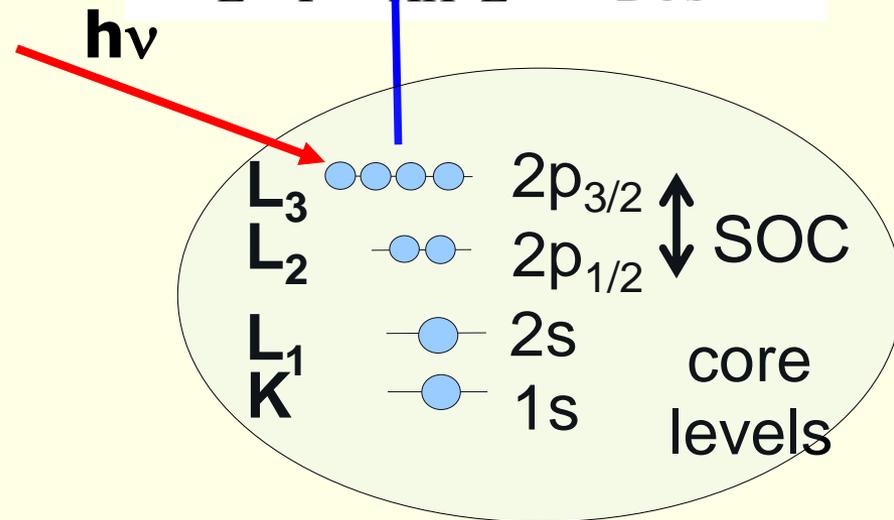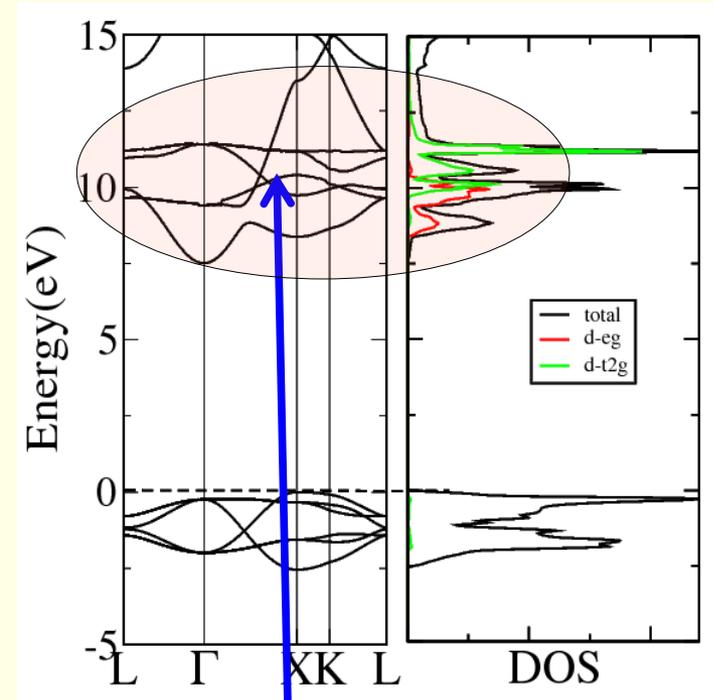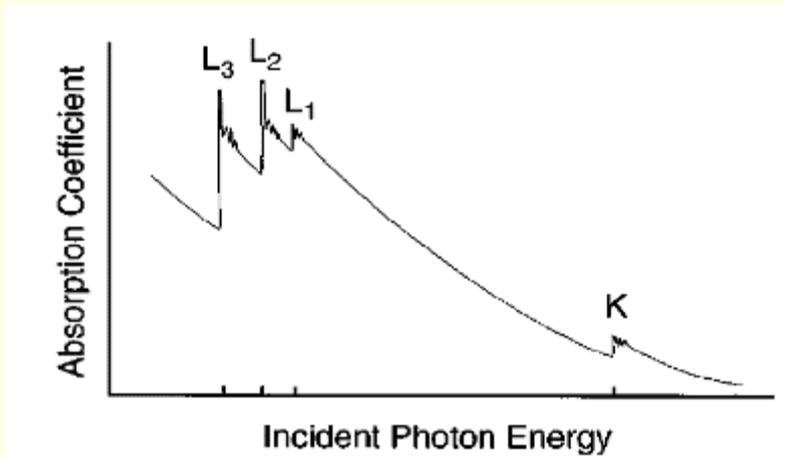
XAS (XANES), **EELS** (ELNES)

- **core electrons are excited into the 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-$p_{3/2}$

- **XAS:** given by the $\ell \pm 1$ **partial DOS** of the **conduction** bands of the **specific atom** (with core state ℓ) times the **TME²**
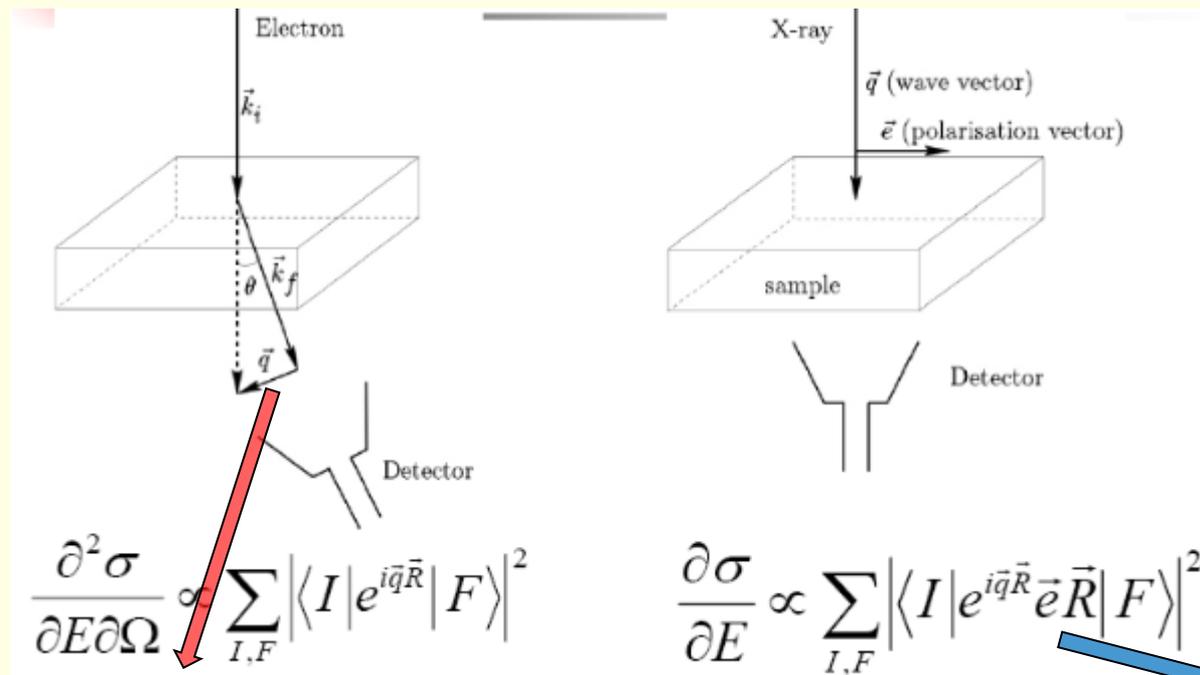
XAS: synchrotron   EELS: microscope

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

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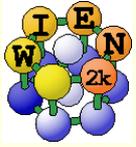
E - conservation

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

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

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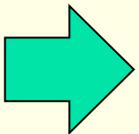
core-valence spectroscopies give information on the local DOS (because of $\langle \Psi_{core} | r | \Psi_{val} \rangle$) of angular momentum character $\ell \pm 1$

"Final state" determines the spectrum:

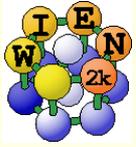•Emission spectroscopy:
Final state has filled core, but valence hole.
This is usually well screened, thus one "sees" the groundstate.

•Absorption spectroscopy:
Final state has a "hole" in core state, but additional e⁻ in conduction band.
Core-hole may have a large effect on the spectrum
   • **electron – hole interaction, "excitonic effects"**
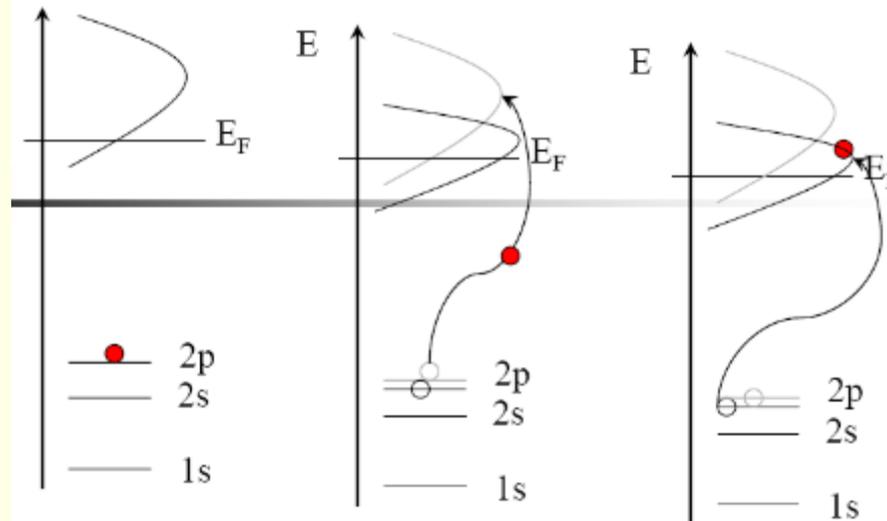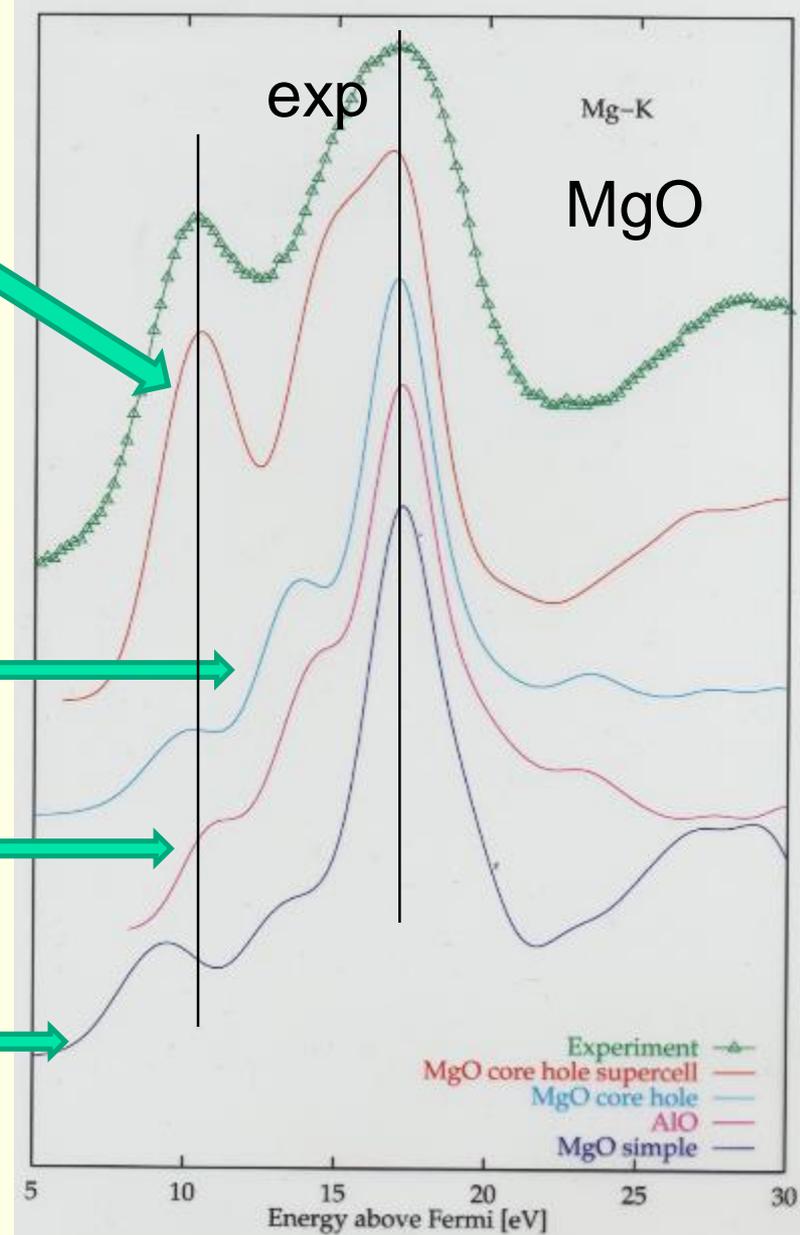
"Final state rule" + core hole:

2x2x2 **supercell** calculation with core hole in **one** of the Mg atoms (add e⁻ to valence or "background").

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

exp

MgO

Mg–K

Experiment
MgO core hole supercell
MgO core hole
AlO
MgO simple

Energy above Fermi [eV]

generate super-cell (x supercell)

label core-hole atom „Mg1"

initialize SCF, define core hole/add extra valence electron

edit case.inc and case.in2 (inm)

run SCF

remove extra valence electron

execute **xspec** task in w2web
- calculate eigenstates (x lapw1 -up/dn)
- calculate partial charges (x lapw2 -qtl -up/dn)
- execute **x xspec**

(needs case.inxs)

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

EELS in WIEN2k

- supercell calculations as for XAS
- TELNES3 task in w2web

- when the e⁻ is not ionized, but stays in the solid:

non-interacting case

independent particle approx.

e-h are correlated

$\hbar\nu$

$\hbar\nu$

- excitation is a single particle process
- electron and hole are not correlated

- needs to include e-h interaction in the excitation
- excitation is a two-particle process
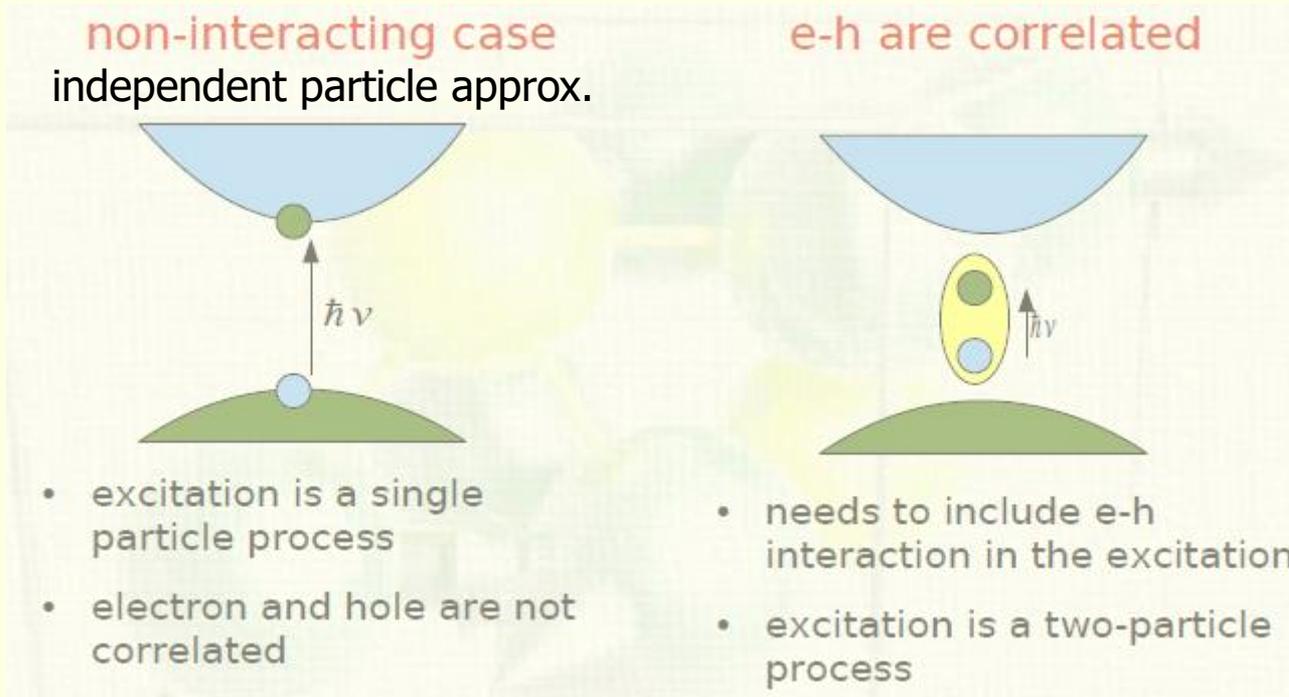
- ⟶ **excitonic effects**

- **Frenkel (localized) and Wannier (delocalized) excitons**
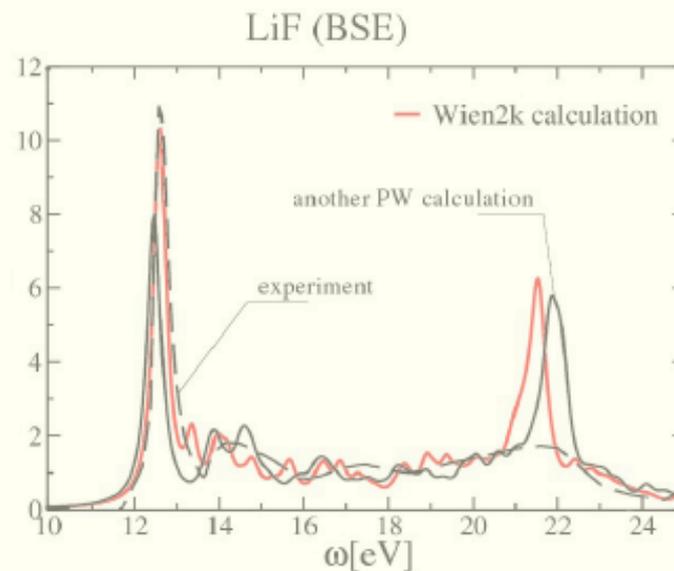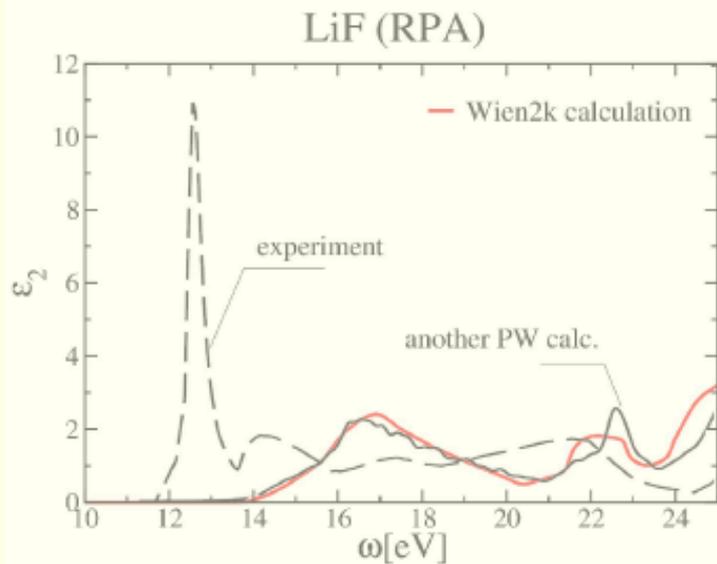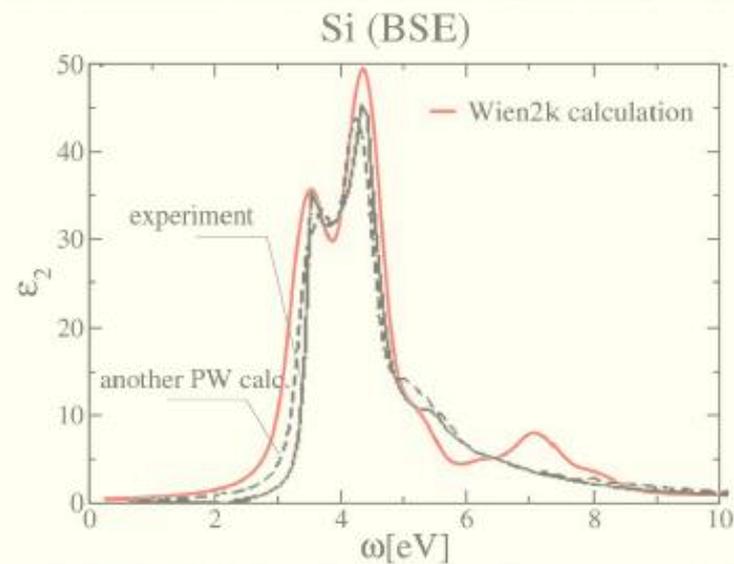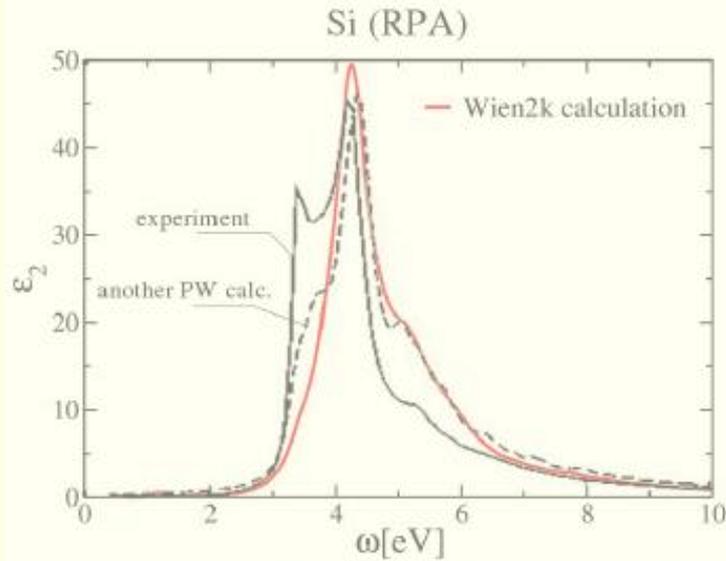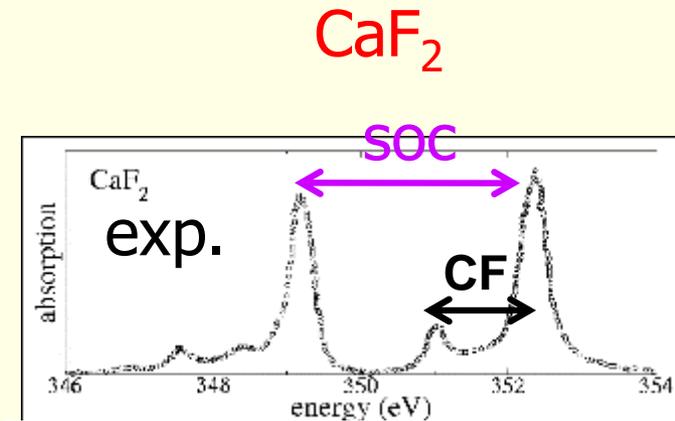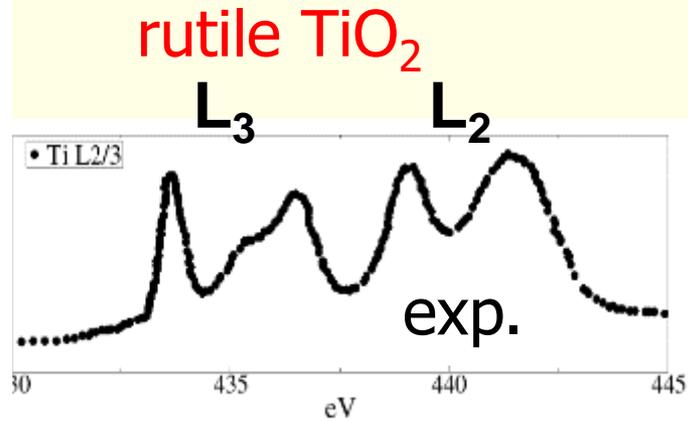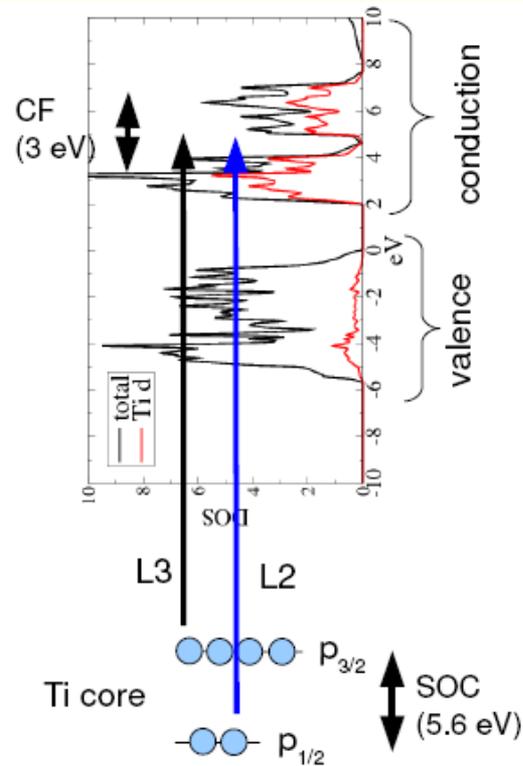
$L_{2,3}$ spectra: failure of the single particle approach

- **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*
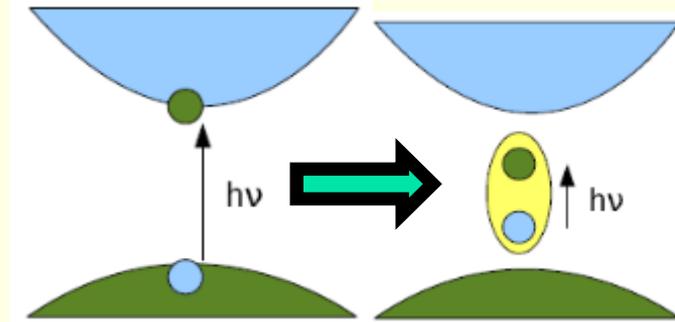
rutile TiO_2

CaF$_2$
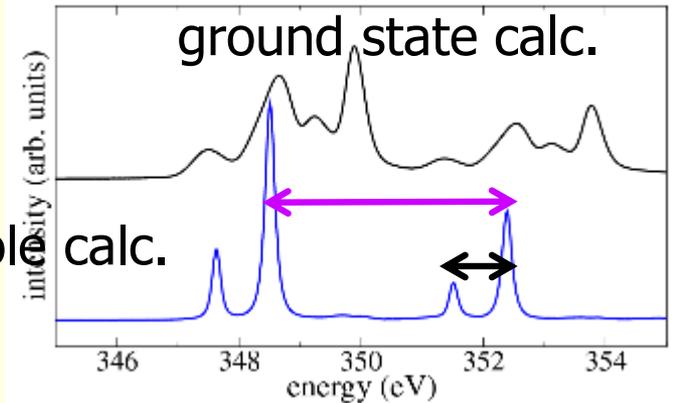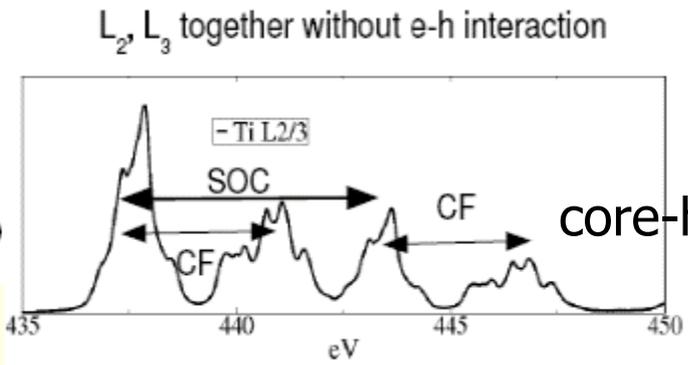
fully relativistic electron-hole interaction (BSE)

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

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

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

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

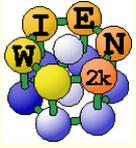eigenvalue difference between hole (v) and electron(c) state

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

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

$$H^{x}_{vckv'c'k'} = \int d^3r \, d^3r' \, \Psi_{vk}(r)\Psi^*_{ck}(r)\bar{v}(r,r')\Psi^*_{v'k'}(r')\Psi_{c'k'}(r')$$
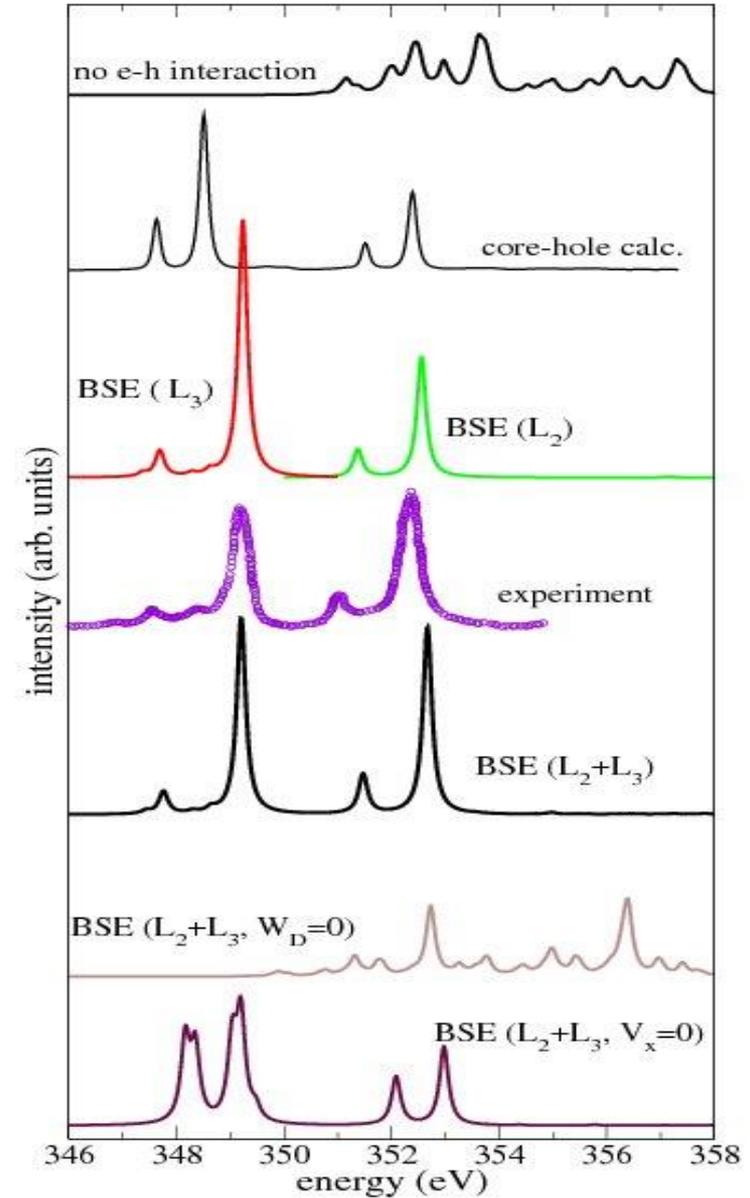
e-h exchange with bare Coulomb potential *v*

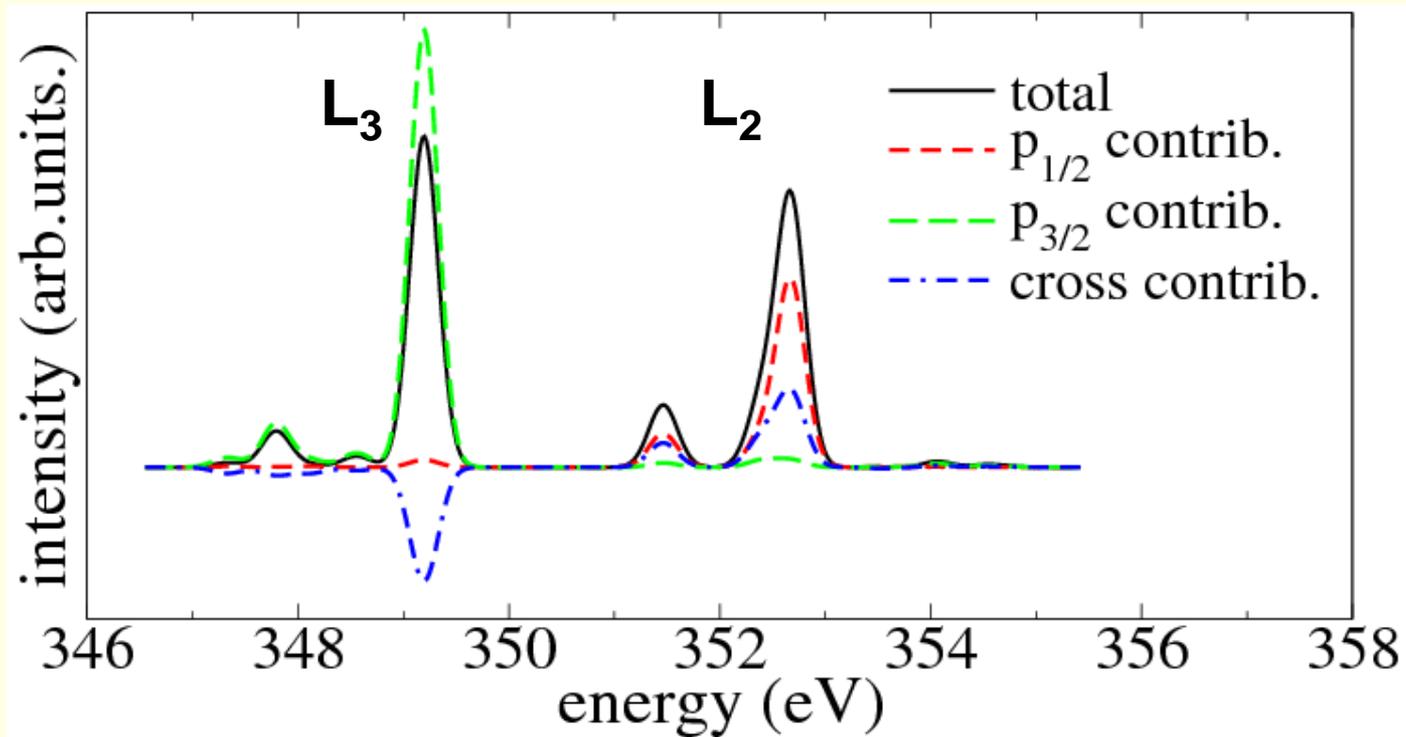**R. Laskowski, P. Blaha, Phys. Rev. B, 81, 075418 (2010)**

- "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$_2$

$$\varepsilon_2^{xx}(\omega) = \frac{8\pi^2}{\Omega}\sum_\lambda \left| \sum_{he\mathbf{k}} A_{he\mathbf{k}}^\lambda \frac{\langle h\mathbf{k}| - i\nabla_x|e\mathbf{k}\rangle}{\varepsilon_{e\mathbf{k}} - \varepsilon_{h\mathbf{k}}} \right|^2 \times \delta(E^\lambda - \omega)$$