Core-level spectroscopy (XES, XAS, EELS)

Dipole transitions between core and valence (conduction) band states

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Dipole transitions: Fermi's "golden rule"

- Time dependent perturbation theory: $\hat{H}'(t) = \hat{H}_0' \left(e^{iE_\nu t} + e^{-iE_\nu t}\right)$
- 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"** :

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

Number of states with energy E

E-conservation

W: proportional to the square of the transition matrix element

momentum (= dipole) matrix elements:

momentum of photons << momentum of e^-;

momentum conservation $\Longrightarrow$ e^- cannot change its momentum

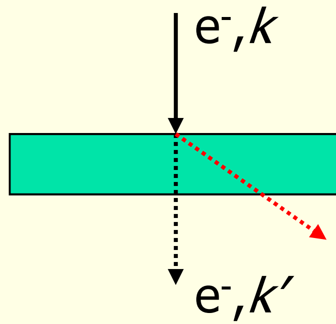
$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{x} + \ldots$$

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!!)

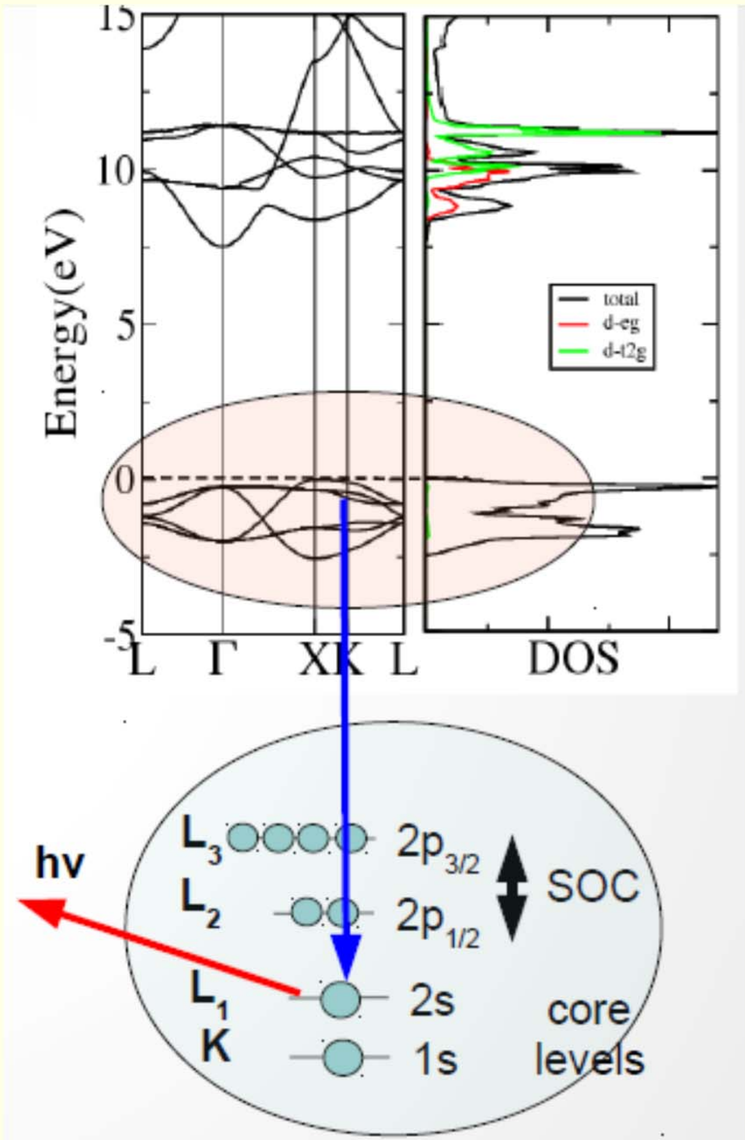
$$\left\langle f_f \left| \hat{H}' \right| f_i \right\rangle = \hat{e}_\alpha \left\langle f_f \left| \vec{p} \right| f_i \right\rangle = \hat{e}_\alpha \left\langle f_f \left| \vec{r} \right| f_i \right\rangle$$



$\Longrightarrow$ selection rules: $\ell \pm 1$

XES (X-ray emission spectroscopy)

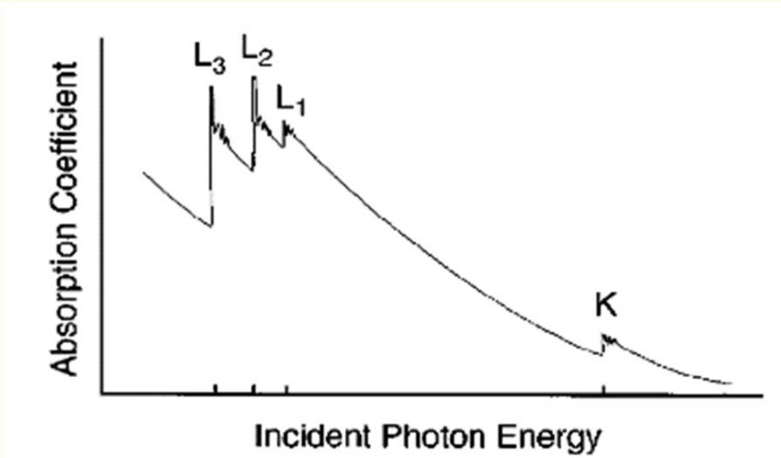
- knock out a core e$^-$
- valence e$^-$ fills core hole
- measure the emitted X-ray
- XES intensity given by the $\ell \pm 1$ **partial DOS** of the **valence** bands of the **specific atom** (with core state $n\ell$) times the **squared transition matrix element**.



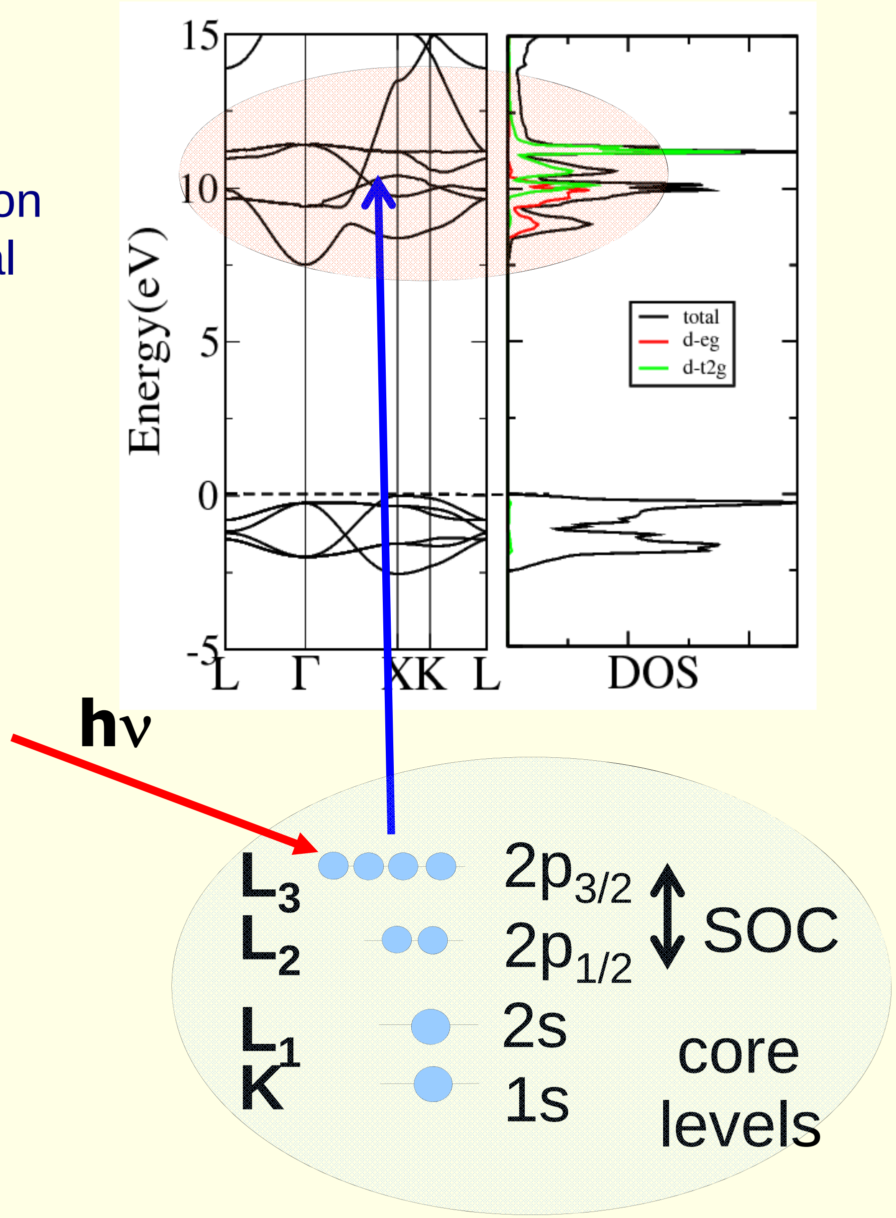
XAS (XANES), EELS (ELNES)

- **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_2-2$p_{1/2}$, L_3-$p_{3/2}$



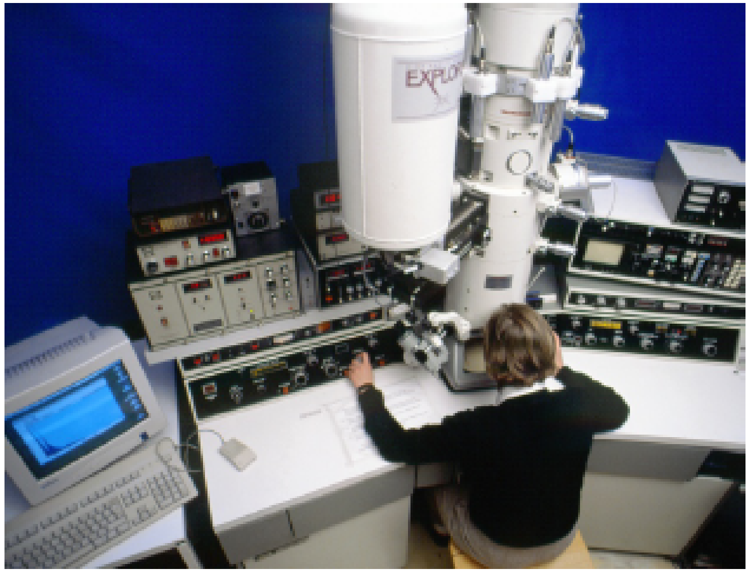
- **XAS:** given by the **ℓ±1 partial DOS** of the **conduction** bands of the **specific atom** (with core state ℓ) times the **TME²**



Difference between EELS and XAS

XAS: synchrotron

EELS: microscope

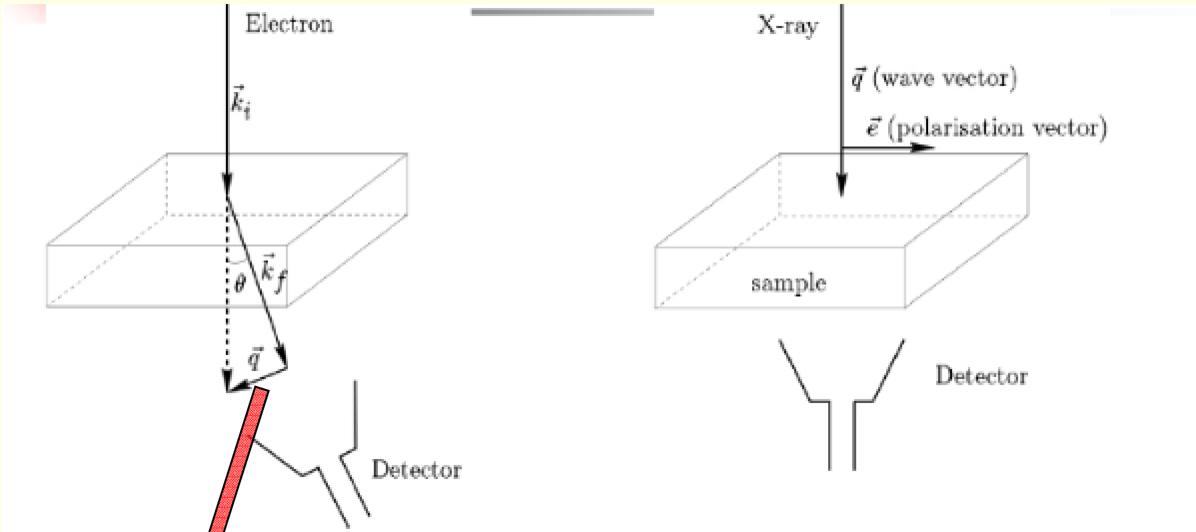


XAS vs. EELS: theory

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

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

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 $<\Psi_{core}|r|\Psi_{val}>$) of angular momentum character $\ell \pm 1$

“Final state rule”:

“Final state” determines the spectrum:

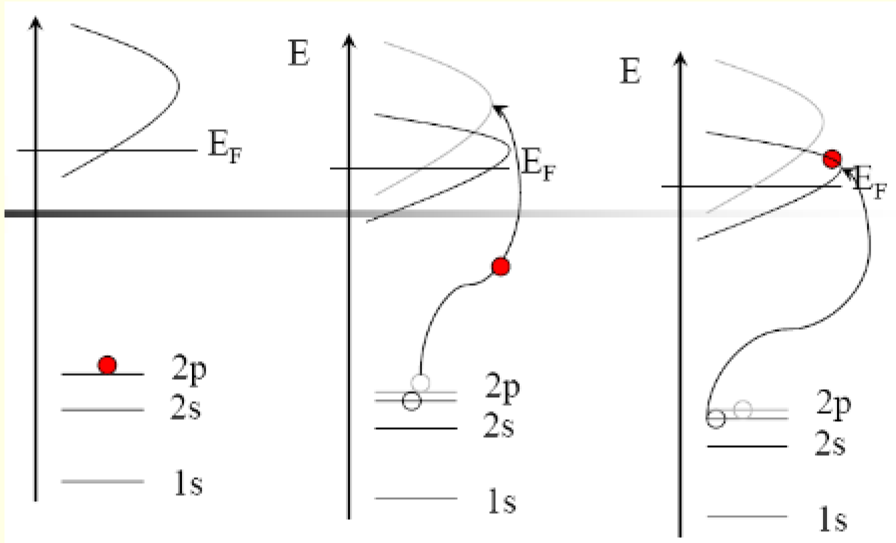
- Emission spectroscopy:

  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 may have a large effect on the spectrum

  - **electron – hole interaction, “excitonic effects”**



“Final state rule” + core hole:

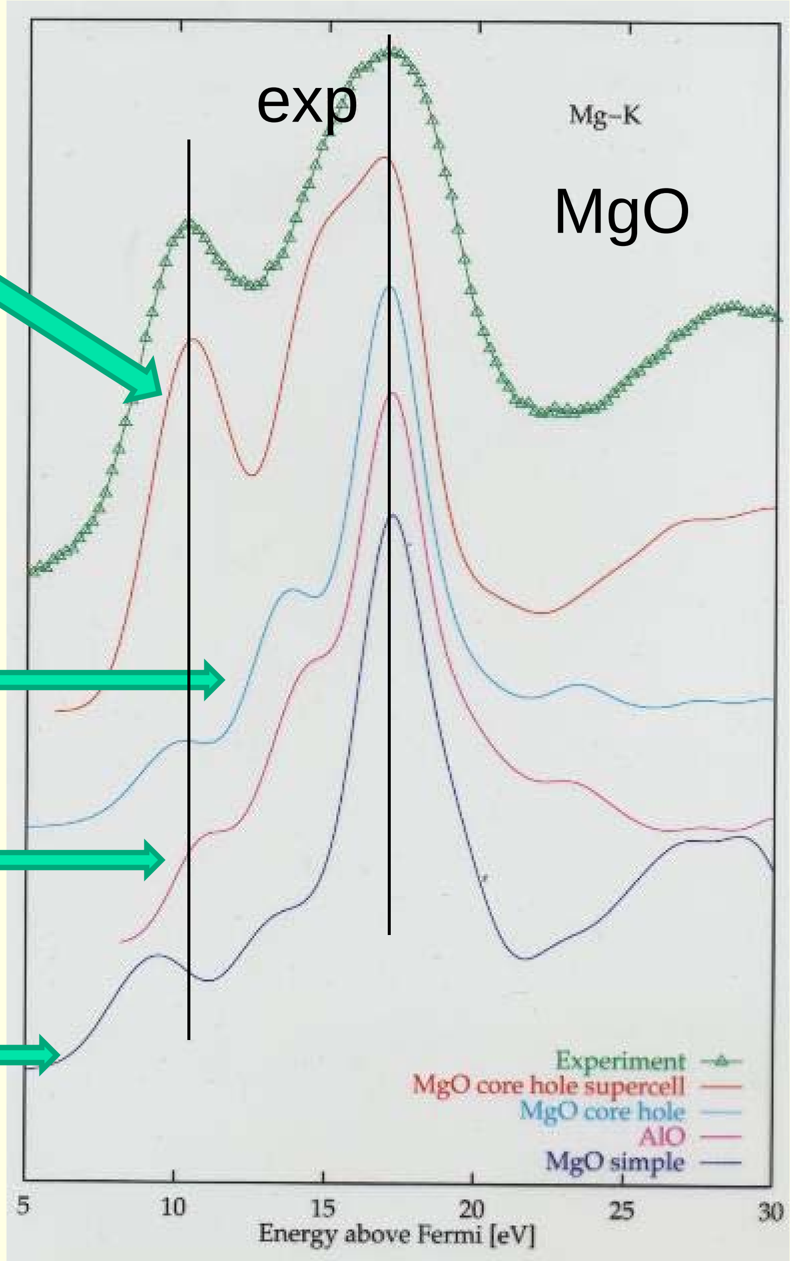
2x2x2 **supercell** calculation with core hole in **one** of the Mg atoms (add e$^-$ to valence or “background”).

This allows the conduction state to relax (adjust to the larger **effective** nuclear charge), but also to have **static screening** from the environment.

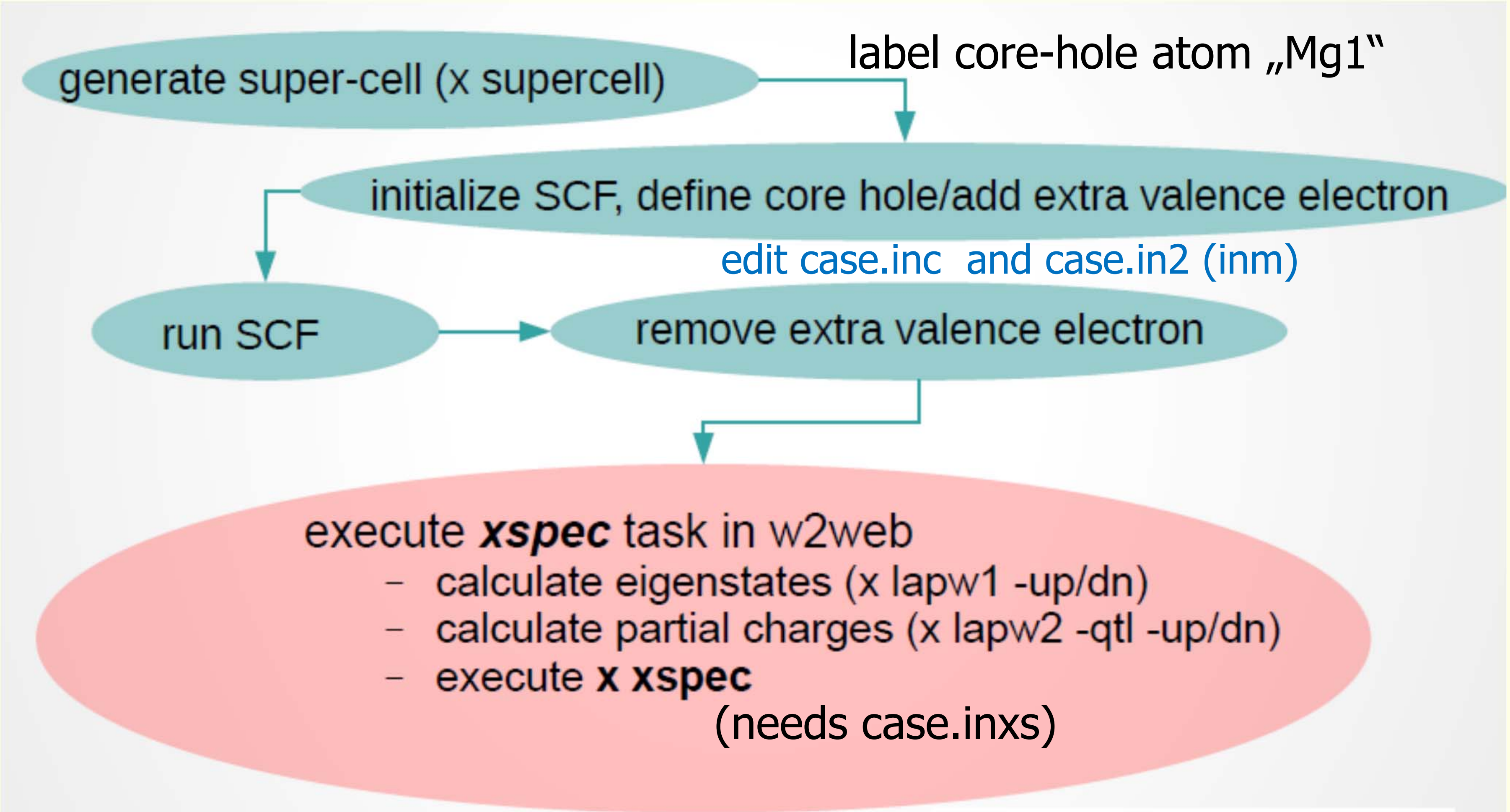
core hole, no supercell:

Z+1 (AlO)

groundstate



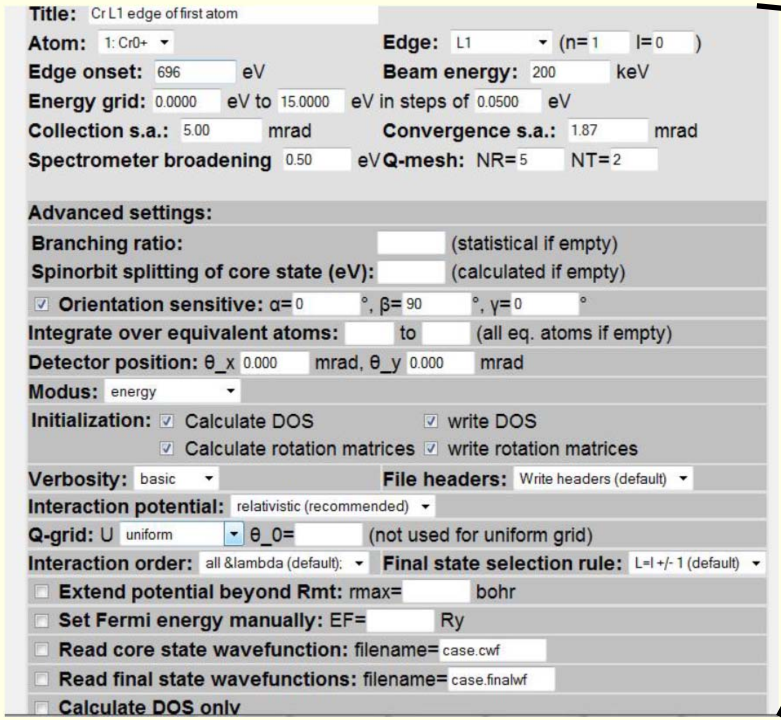
Core hole calculations in WIEN2k

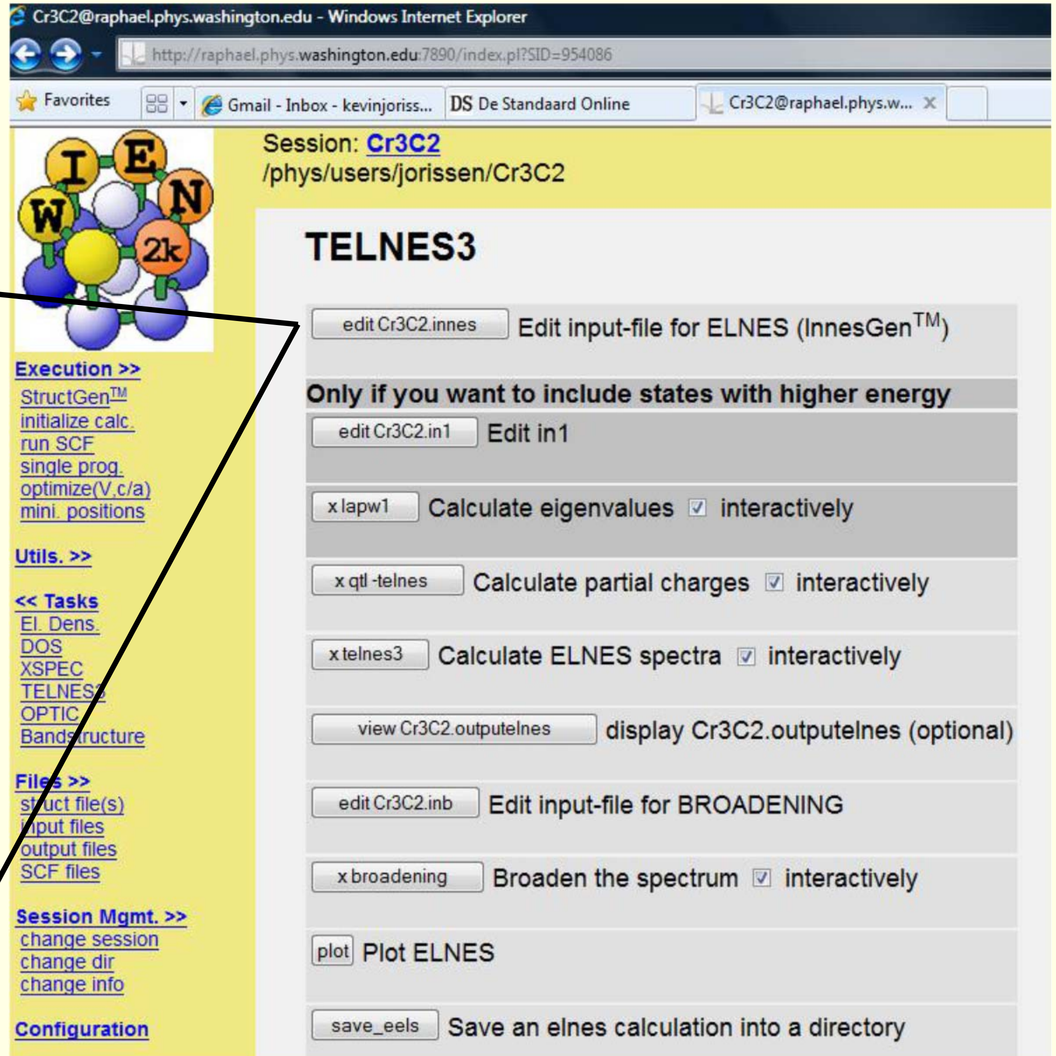


Dipole approximation $$\frac{\partial^2 \sigma}{\partial E \partial \Omega} \propto \sum_{I,F} \left| \left\langle I \left| \vec{\varepsilon} \vec{R} \right| F \right\rangle \right|^2$$

EELS in WIEN2k

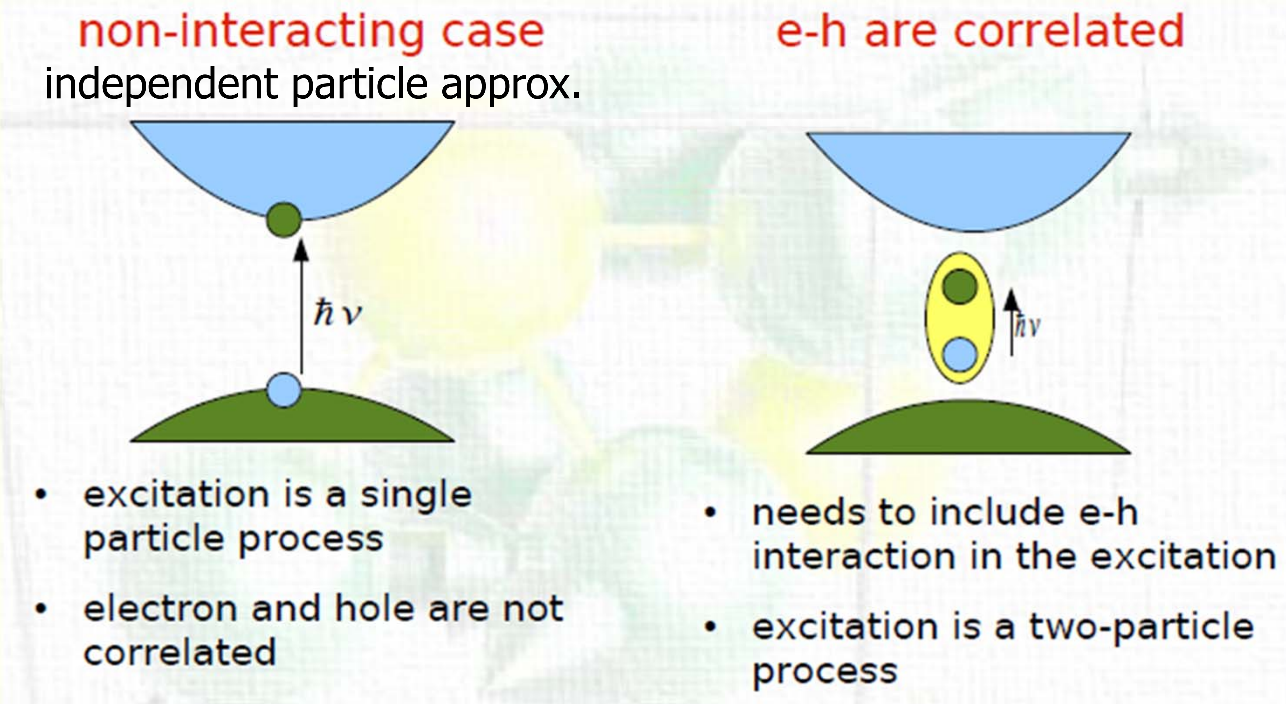
- supercell calculations as for XAS
- TELNES3 task in w2web





When IPA fails: Electron – hole interactions

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



- ⟹ **excitonic effects**
- **Frenkel (localized) and Wannier (delocalized) excitons**