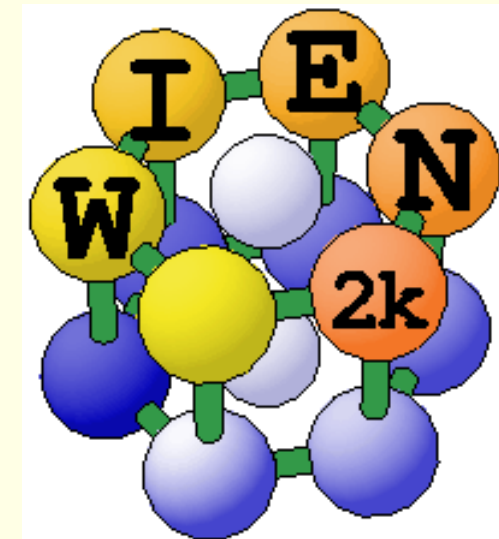


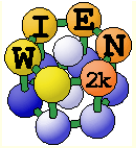
Core-level spectroscopy (XES, XAS, EELS)

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 \mathbf{k} acts on the momentum \mathbf{p} of the electron

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

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

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

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 \ll momentum of e^- ;

momentum conservation \longrightarrow e^- cannot change its momentum

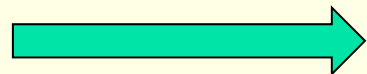
$$e^{i\vec{k}\cdot\vec{r}} = 1 + i\vec{k}\cdot\vec{x} + \dots$$

dipole quadrupole ... approximation

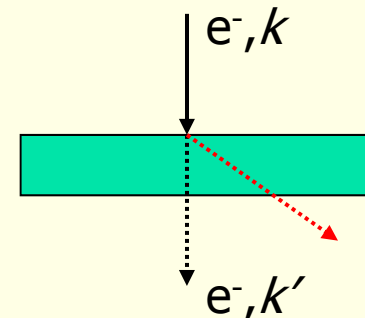
$$e^{i\vec{k}\cdot\vec{r}} \approx 1$$

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

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



selection rules: $\ell \pm 1$

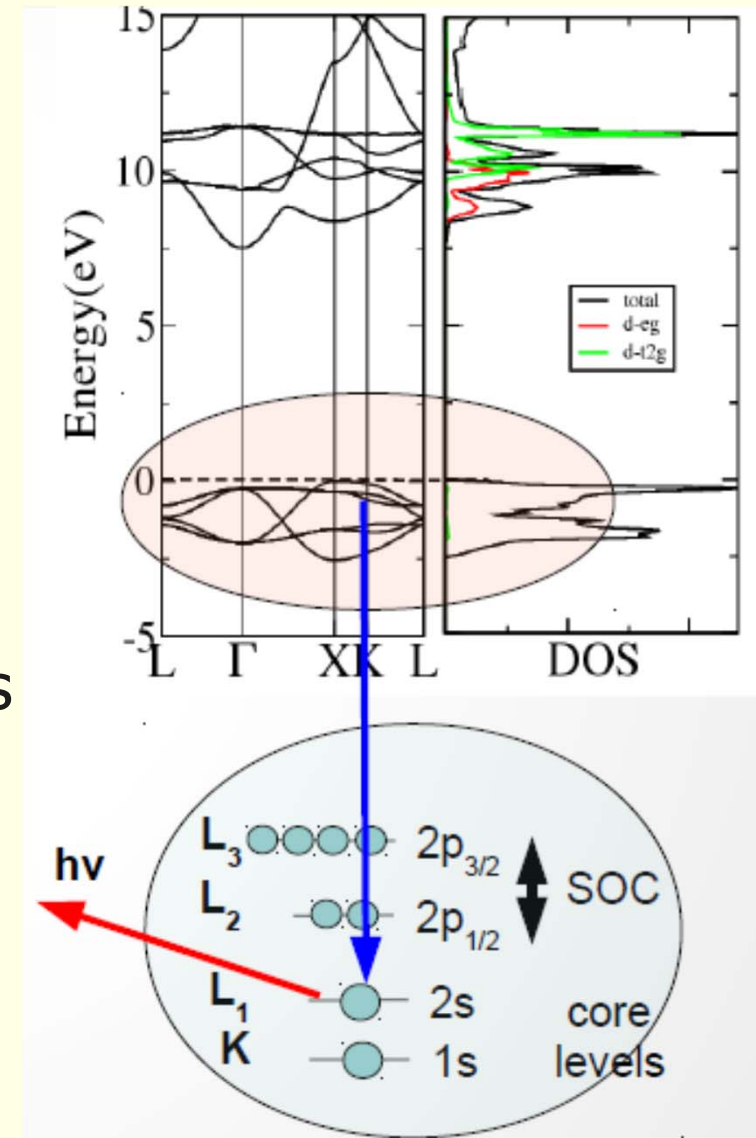


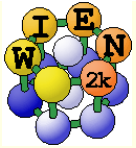


XES (X-ray emission spectroscopy)



- 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**.



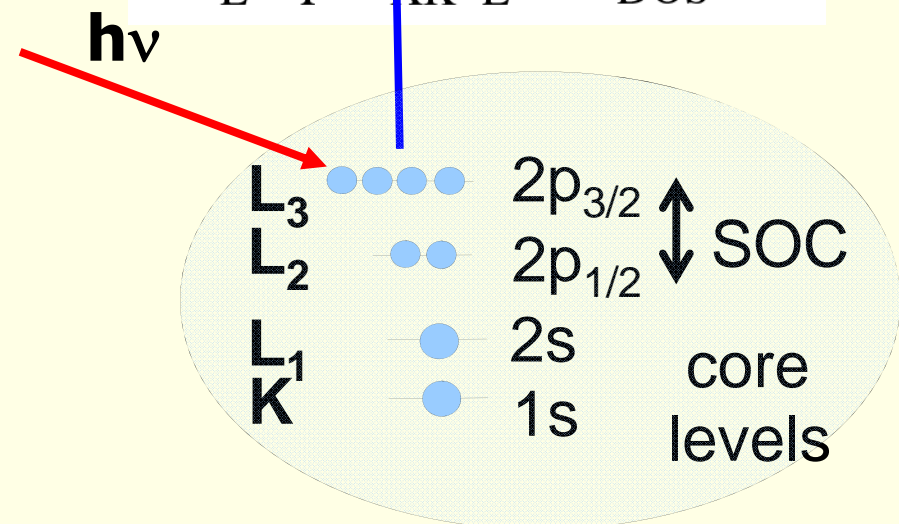
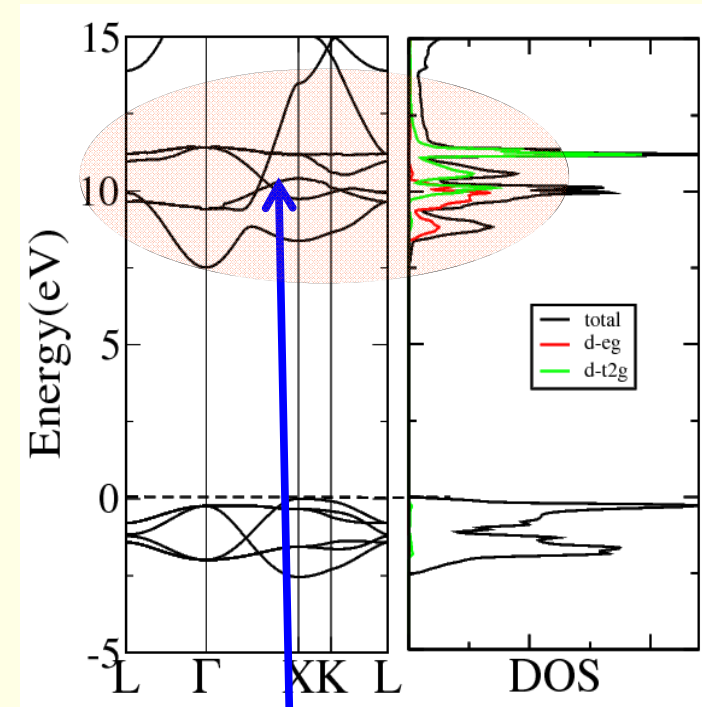
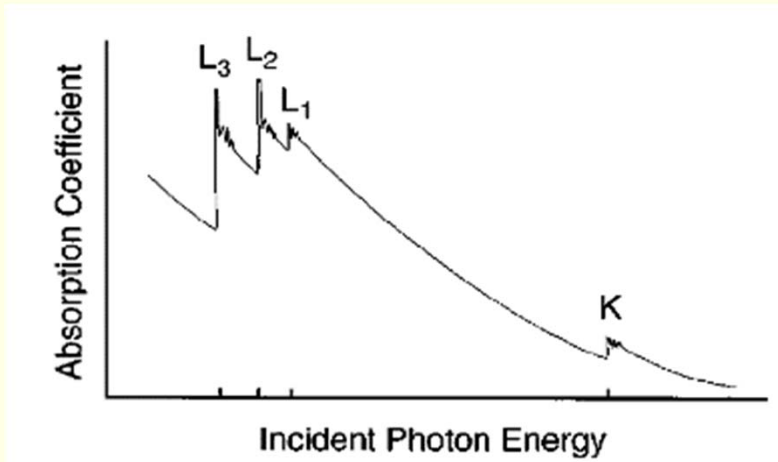


XAS (XANES), EELS (ELNES)



- 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**



Difference between EELS and XAS

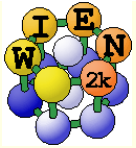


XAS: synchrotron



EELS: microscope



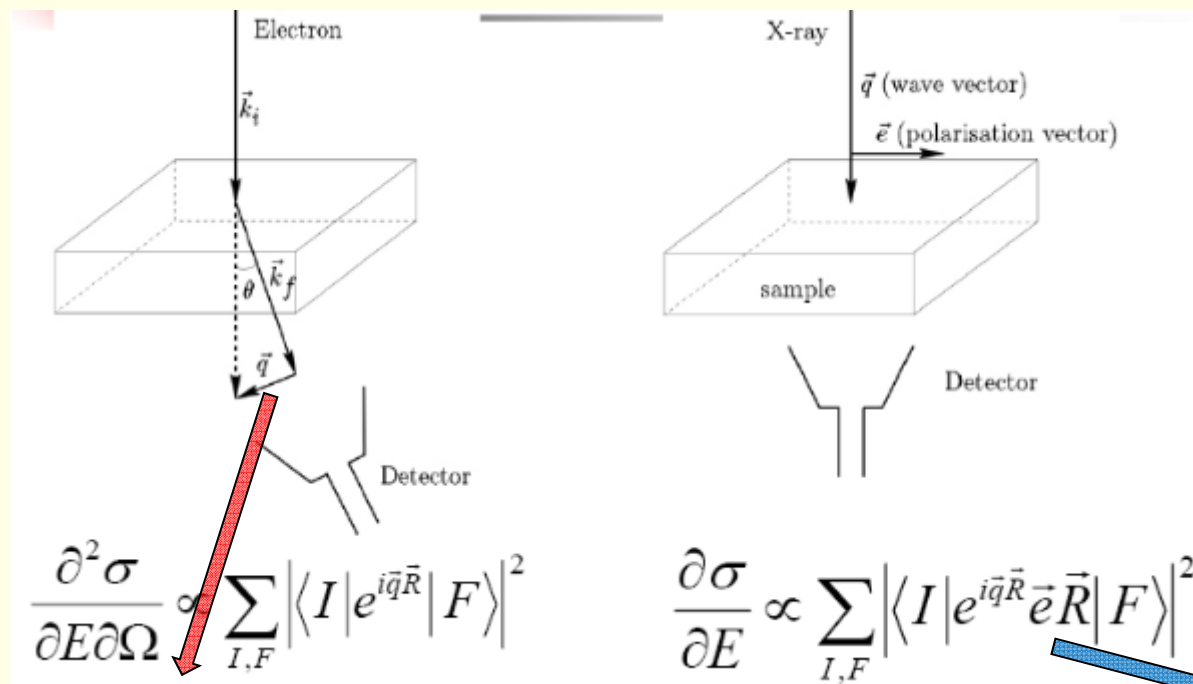


XAS vs. EELS: theory



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

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



momentum transfer \mathbf{q}

polarization vector \mathbf{e}

single diff. cross section



dipole approximation



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

EELS

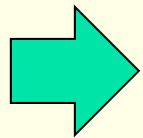
$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} \propto \sum_{I,F} \left| \langle I | \vec{q}\vec{R} | F \rangle \right|^2$$

XAS

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

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 $\langle \Psi_{\text{core}} | r | \Psi_{\text{val}} \rangle$) of angular momentum character $l \pm 1$



“Final state rule”:

“Final state” determines the spectrum:

- **Emission spectroscopy:**

Final state has filled core, but valence hole.

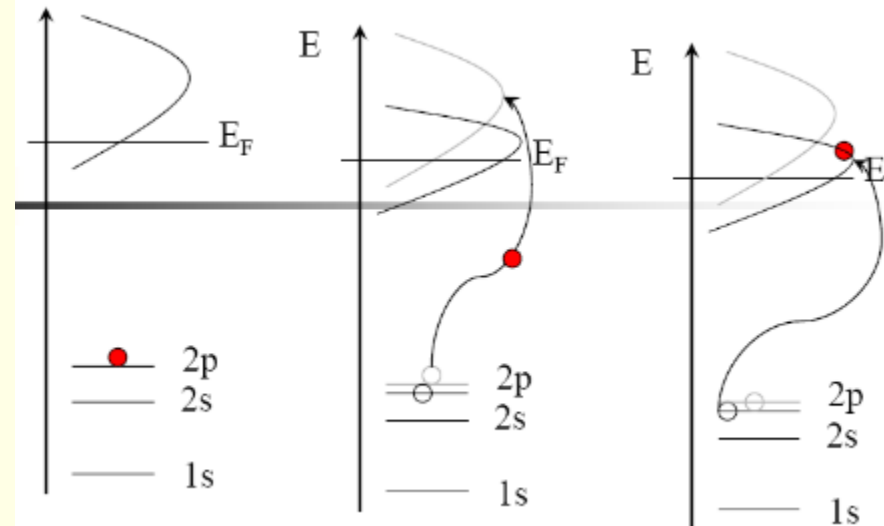
This is usually well screened, thus one “sees” the **groundstate**.

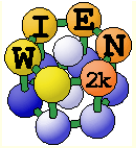
- **Absorption spectroscopy:**

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:

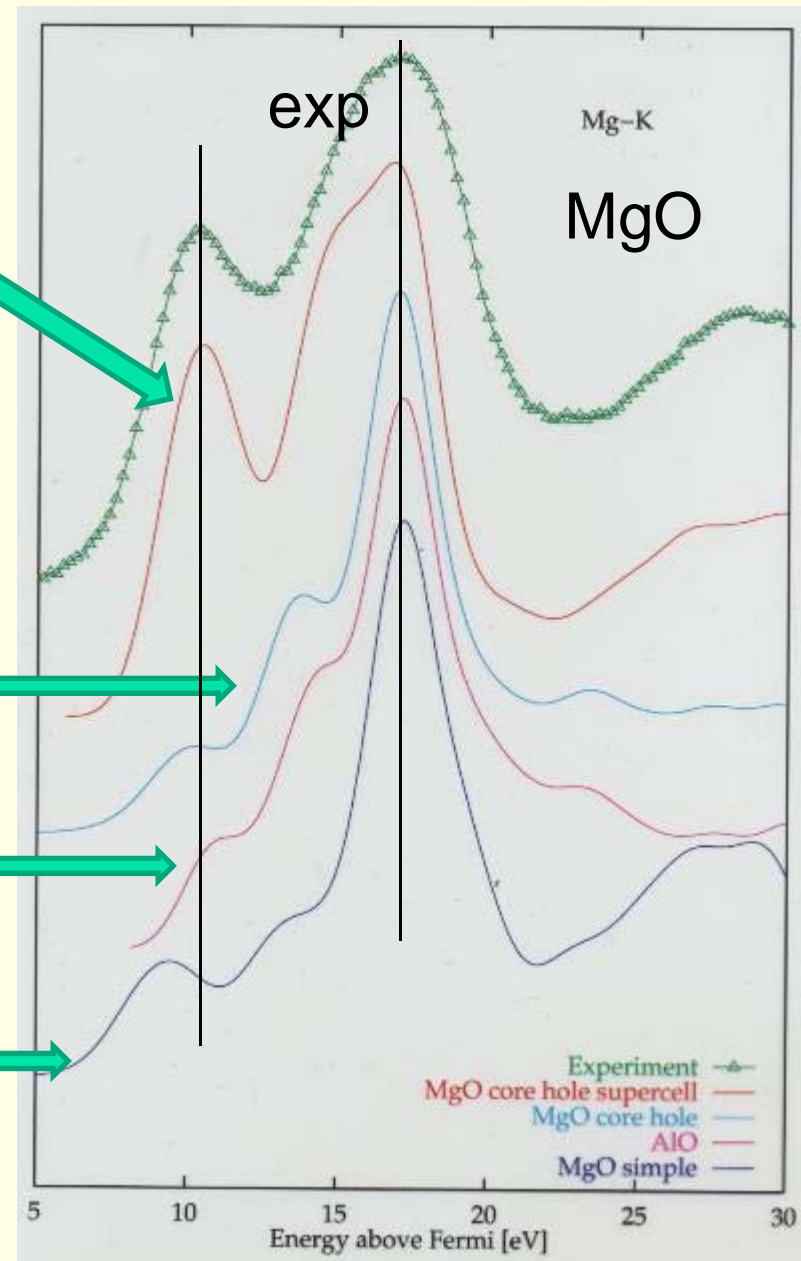
2x2x2 **supercell** calculation with core hole in **one** of the Mg atoms (add e^- to valence or “background”).

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:

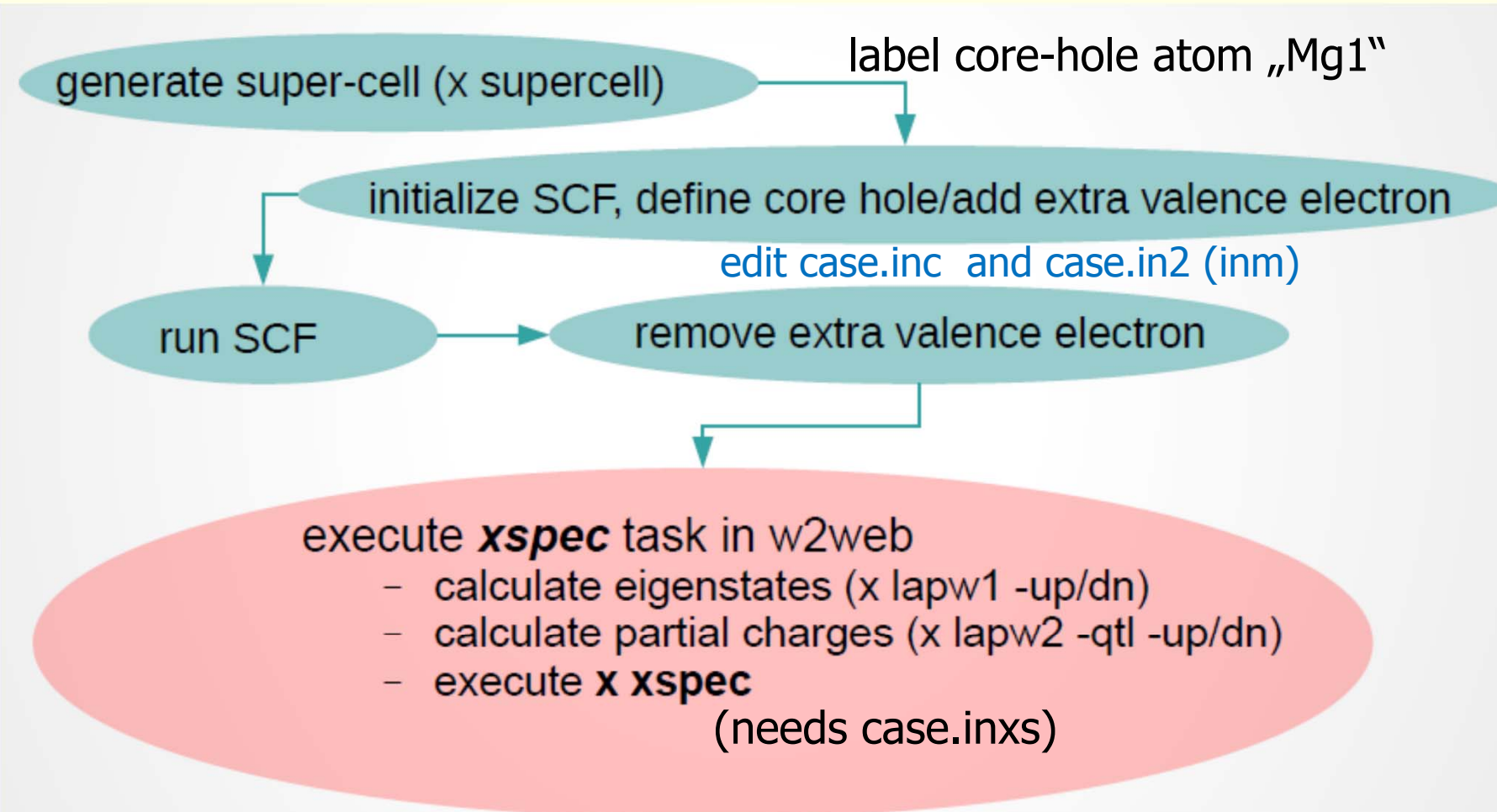
Z+1 (AlO)

groundstate

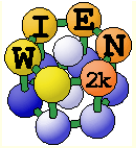




Core hole calculations in WIEN2k



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



EELS in WIEN2k



- supercell calculations as for XAS
- TELNES3 task in w2web

Title: Cr L1 edge of first atom

Atom: 1: Cr0+ **Edge:** L1 (n=1 |l=0)

Edge onset: 696 eV **Beam energy:** 200 keV

Energy grid: 0.0000 eV to 15.0000 eV in steps of 0.0500 eV

Collection s.a.: 5.00 mrad **Convergence s.a.:** 1.87 mrad

Spectrometer broadening: 0.50 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: $\alpha=0^\circ$, $\beta=90^\circ$, $\gamma=0^\circ$

Integrate over equivalent atoms: (all eq. atoms if empty)

Detector position: θ_x 0.000 mrad, θ_y 0.000 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 $\theta_0=$ (not used for uniform grid)

Interaction order: all & lambda (default) **Final state selection rule:** 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

Cr3C2@raphael.phys.washington.edu - Windows Internet Explorer

http://raphael.phys.washington.edu/7890/index.pl?SID=954086

Session: **Cr3C2**
/phys/users/jorissen/Cr3C2

TELNES3

Edit input-file for ELNES (InnesGen™)

Only if you want to include states with higher energy

Edit in1

Calculate eigenvalues interactively

Calculate partial charges interactively

Calculate ELNES spectra interactively

display Cr3C2.outputelnes (optional)

Edit input-file for BROADENING

Broaden the spectrum interactively

Plot ELNES

Save an elnes calculation into a directory

Execution >>
[StructGen™](#)
[initialize calc.](#)
[run SCF](#)
[single prog.](#)
[optimize\(V,c/a\)](#)
[mini_positions](#)

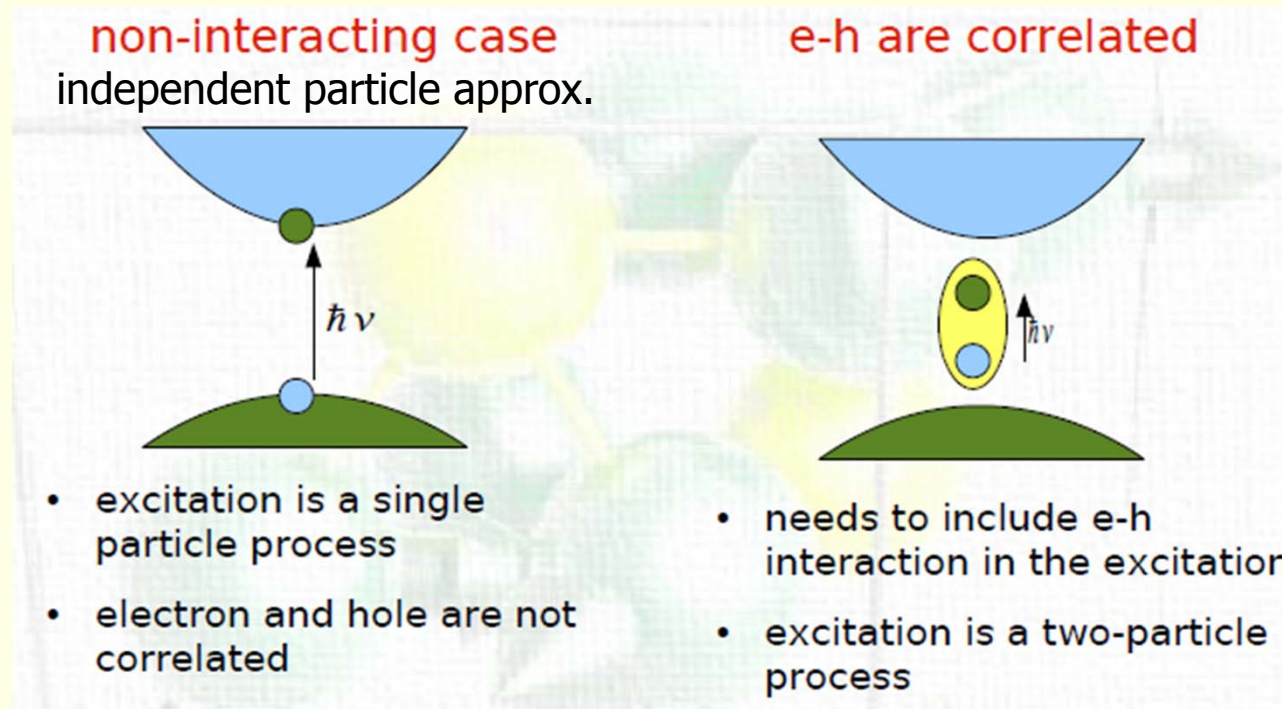
Utils. >>
<< Tasks
[El_Dens.](#)
[DOS](#)
[XSPEC](#)
[TELNES3](#)
[OPTIC](#)
[Bandstructure](#)

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

Session Mgmt. >>
[change session](#)
[change dir](#)
[change info](#)

Configuration

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



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