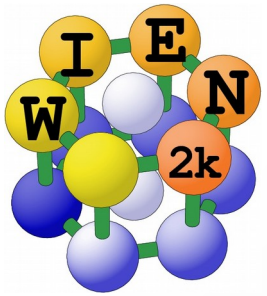
Optical properties by wien2k

Robert Laskowski

rolask@ihpc.a-star.edu.sg

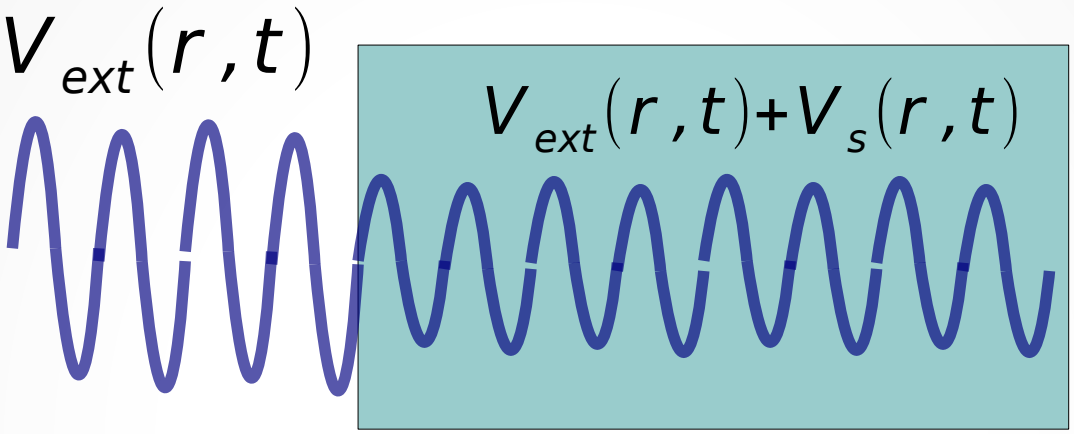
Institute of High Performance Computing
Singapore



outline

- Theory: independent particle approximation
- *optic*, *joint*, *tetra ….*
  - inputs / outputs, examples

Dielectric function



- Electrons respond, screening potential (V_s)

$$V(r,t)=V_{ext}(r,t)+V_s(r,t)$$

Photon electric field

Screening potential

$$V_G^{ext}=\sum_{G'}\epsilon_{GG'}V_{G'}$$

dielectric constant

Independent particles

- single particle eigenstates (**IPA**) $\hat{H}_0 |nk\rangle = \varepsilon |nk\rangle$

- Time dependence in the linear regime: $V_{ext}, V_s, n \sim e^{i\omega t}$

- general form of the potential $V(r) = \frac{1}{\Omega} \sum_{q,G} V_G e^{-i(q+G)r}$

- irreducible of polarizability: $P = \frac{\delta n}{\delta V}$

$$n_G(q,\omega) = \sum_{G'} P^0_{GG'}(q,\omega) V_{G'}(q,\omega)$$

$$P^0_{GG'}(q,\omega) = \frac{1}{\Omega} \sum_{lmk} \frac{f_{m,k+q} - f_{l,k}}{\varepsilon_{m,k+q} - \varepsilon_{l,k} - \omega} [M^G_{lm}(k,q)]^* M^{G'}_{lm}(k,q)$$

$$M^G_{lm}(k,q) = \langle lk | e^{-i(q+G)r} | m, k+q \rangle$$

Random phase approximation

- The screening potential $\boldsymbol{V_s}$ connects to the induced charge density $\boldsymbol{n}$ by Poisson equation

$$V_G^s = \nu(q+B)\, n_G(q)$$

Definition of $\epsilon_{GG'}$:

$$V_G^{ext} = \sum_{G'} \epsilon_{GG'} V_{G'}$$

$$\epsilon_{GG'} = \delta_{GG'} - \nu(q+G)\, P^0_{GG'}(q,\omega)$$

random phase approximation (RPA)

S. L. Adler, Phys. Rev. 126, 413 (1962)
N. Wiser, Phys. Rev. 129, (1963)

Macroscopic dielectric constant

Macroscopic external field has no ***G*** dependence

$$V_G^{ext}(q) = \delta_{G,0} V_{ext}(q)$$

$$V_G^{ext} = \sum_{G'} \epsilon_{GG'} V_{G'} \quad V_0 = \varepsilon_{00}^{-1} V_0^{ext}$$

with local field effects:

$$\epsilon_M(q,\omega) = \frac{1}{\epsilon_{00}^{-1}(q,\omega)}$$

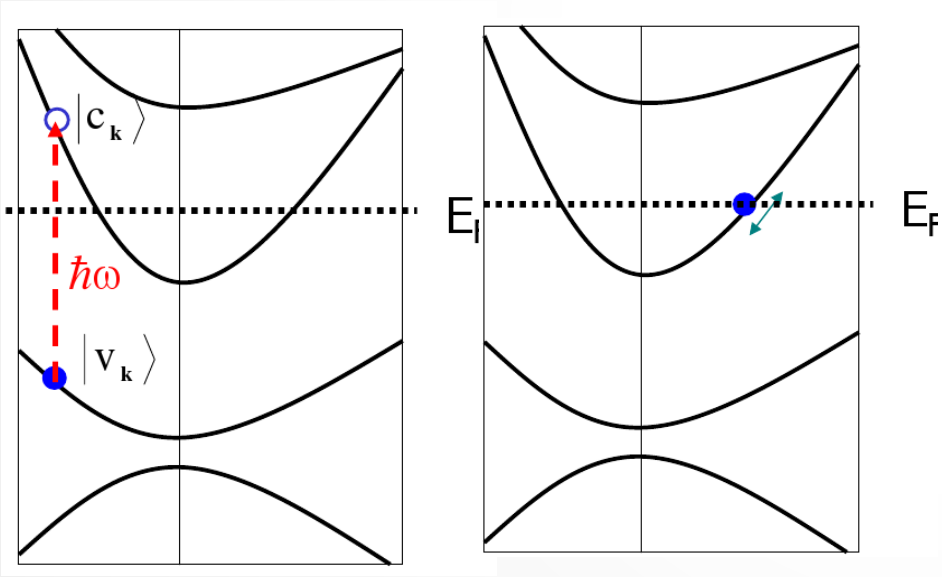
neglecting local field effects:

$$\epsilon_M(q,\omega) = \epsilon_{00}(q,\omega) = 1 - v(q) P_0(q,\omega)$$

$\epsilon_M(q,\omega)$ in periodic systems

$$\epsilon_M(q,\omega)=1-v(q)P_0(q,\omega)$$

$$\varepsilon(q,\omega)=1-\lim_{\eta\to 0}\frac{4\pi e^2}{q^2\Omega}\sum_{k,i,j}A_{k,q}^{i,j'}\frac{f\left(\varepsilon_{k+q}^{i}\right)-f\left(\varepsilon_{k}^{j}\right)}{\varepsilon_{k+q}^{i}-\varepsilon_{k}^{j}-\omega-i\eta}$$



inter-band transitions

intra-band transitions

$$A_{k,q}^{i,j}=\delta_{i,j}+(1-\delta_{i,j})\frac{q^2}{m\omega_{i,j}^2}\langle P_{i,j}\rangle^2$$

intra-band

inter-band

Long wave limit

Find q $\rightarrow$ 0 limit of P, use k·p method

$$P^0(q\rightarrow 0,\omega)=4\pi\sum_{vck}\frac{\langle vk|p_i|ck\rangle\langle ck|p_j|vk\rangle}{(\varepsilon_{ck}-\varepsilon_{vk}-\omega)(\varepsilon_{ck}-\varepsilon_{vk})^2}$$

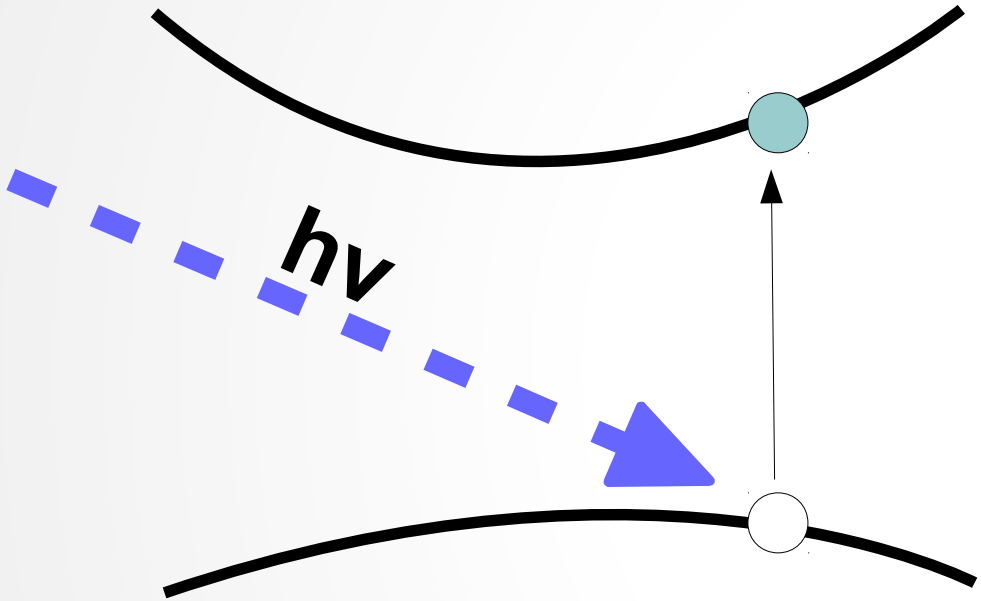
The expression for calculations of single particle excitation spectra

$$\Im(\epsilon_{ij})=\frac{16\pi^2}{\Omega\omega^2}\sum_{vck}\langle vk|p_i|ck\rangle\langle ck|p_j|vk\rangle\delta(\varepsilon_{kc}-\varepsilon_{vk}-\omega)$$

Key quantity is the momentum matrix (optic program):

$$\langle vk|p_i|ck\rangle$$

Interpretation



joint density of states

$$\sum_{vck} \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$

transition probability

$$\Im(\epsilon_{ij}) = \frac{16\pi^2}{\Omega\omega^2} \sum_{vck} \langle vk|p_i|ck\rangle\langle ck|p_j|vk\rangle \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$

Momentum matrix elements

$$\langle vk | p_i | ck \rangle \sim \int \Psi_{vk} \frac{\partial}{\partial x_i} \Psi_{ck}$$

$$\Psi_{n,\mathbf{k}}(\mathbf{r}) = \begin{cases} \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} C_G^{n,\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}, & \mathbf{r} \in I \\ \sum_{lm} W_{lm}^{n,\alpha,\mathbf{k}}(r) Y_{lm}(\hat{r}), & \mathbf{r} \in S_\alpha \end{cases}$$

l,m determines character of the state

$$\begin{aligned} \nabla_0 \left(W(r) Y_{lm}(\hat{\mathbf{r}}) \right) &= F_+^0(lm) W_+(r) Y_{l+1,m} \\ &\quad + F_-^0(lm) W_-(r) Y_{l-1,m} \end{aligned}$$

Derivative of the wave function in ***z*** direction

$$\begin{aligned} W_+(r) &= \frac{\partial}{\partial r} W(r) - \frac{l}{r} W(r) \\ W_-(r) &= \frac{\partial}{\partial r} W(r) + \frac{l+1}{r} W(r) \end{aligned}$$

Interpretation

$$\langle vk | p_i | ck \rangle \sim \sum_L \langle W^L | W_{\pm}^{L\pm 1} \rangle$$

- ***L*** character of the **valence** state couples to ***L-1*** or ***L+1*** character of the ***conduction*** band

$$\Im(\epsilon_{ij}) = \frac{16\pi^2}{\Omega\omega^2} \sum_{vck} \langle vk | p_i | ck \rangle \langle ck | p_j | vk \rangle \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$

Symmetry

- triclinic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{xz} \\ \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{yy} & \mathrm{Im}\,\epsilon_{yz} \\ \mathrm{Im}\,\epsilon_{xz} & \mathrm{Im}\,\epsilon_{yz} & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

- monoclinic (α, $\beta = 90°$)

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & \mathrm{Im}\,\epsilon_{xy} & 0 \\ \mathrm{Im}\,\epsilon_{xy} & \mathrm{Im}\,\epsilon_{yy} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

- orthorhombic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{yy} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

- tetragonal, hexagonal

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix}$$

- cubic

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{xx} \end{pmatrix}$$

Optical functions

- Dielectric tensor

$$\Im \epsilon_{ij} = \frac{16\pi^2}{\Omega \omega^2} \sum_{vck} \langle vk | p_i | ck \rangle \langle ck | p_j | vk \rangle \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$

$$\Re \epsilon_{ij} = \delta_{ij} \frac{2}{\pi} P \int_0^\infty \frac{\omega' \Im \epsilon_{ij}(\omega')}{\omega'^2 - \omega^2} d\omega'$$

- Optical conductivity

$$\Re \sigma_{ij}(\omega) = \frac{\omega}{4\pi} \Im \epsilon_{ij}(\omega)$$

- Refractive index

$$n_{ii} = \sqrt{\frac{|\epsilon_{ii}(\omega)| + \Re \epsilon_{ii}(\omega)}{2}} \qquad k_{ii}(\omega) = \sqrt{\frac{|\epsilon_{ii}(\omega)| - \Re \epsilon_{ii}(\omega)}{2}}$$

- Reflectivity

$$R_{ii}(\omega) = \frac{(m_{ii} - 1)^2 + k_{ii}^2}{(n_{ii} + 1)^2 + k_{ii}^2}$$

- Absorption

$$A_{ii}(\omega) = \frac{2\omega k_{ii}(\omega)}{c}$$

- Loss function

$$L_{ii}(\omega) = -\Im\left(\frac{1}{\epsilon_{ii}(\omega)}\right)$$

Magneto-optics

- Cubic, no SOC

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{xx} \end{pmatrix} \xrightarrow{KK} \begin{pmatrix} \mathrm{Re}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Re}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Re}\,\epsilon_{xx} \end{pmatrix}$$

- Cubic, with SOC and magnetism along ***z***

$$\begin{pmatrix} \mathrm{Im}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Im}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Im}\,\epsilon_{zz} \end{pmatrix} \xrightarrow{KK} \begin{pmatrix} \mathrm{Re}\,\epsilon_{xx} & 0 & 0 \\ 0 & \mathrm{Re}\,\epsilon_{xx} & 0 \\ 0 & 0 & \mathrm{Re}\,\epsilon_{zz} \end{pmatrix}$$

$$\begin{pmatrix} 0 & \mathrm{Re}\,\epsilon_{xy} & 0 \\ -\mathrm{Re}\,\epsilon_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \xrightarrow{KK} \begin{pmatrix} 0 & \mathrm{Im}\,\epsilon_{xy} & 0 \\ -\mathrm{Im}\,\epsilon_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

How to do calculations ?

Run SCF calculations

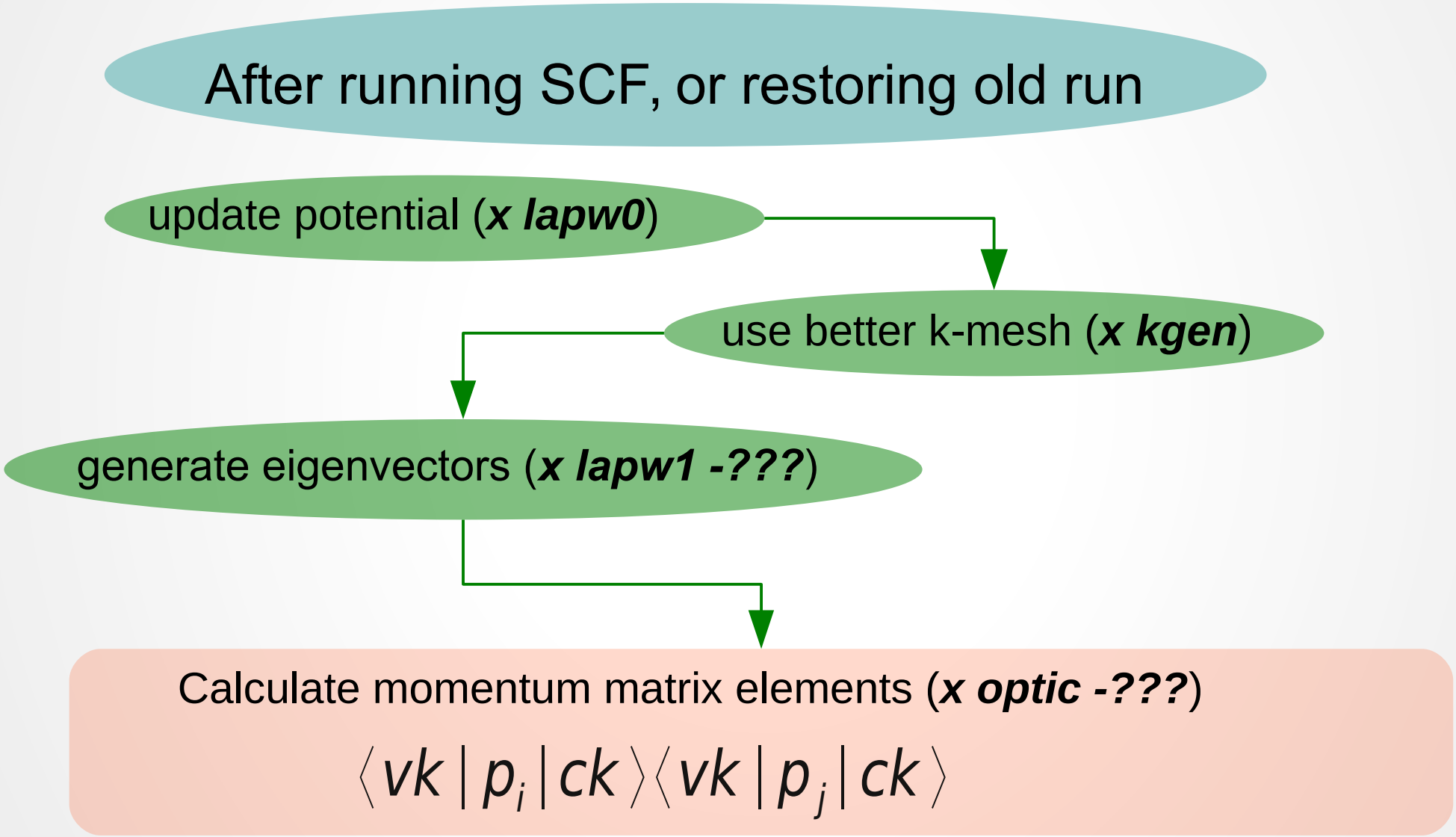
Increase k-mesh !!!

compute momentum matrix elements with ***optic*** program (x optic)

compute imaginary part of the dielectric function with ***joint*** program (x joint)

use ***kram*** program for computing other optical constants (x kram)

Computing momentum matrix elements



optic program – input, output

input

- ***case.inop***

800	1	number of k-points, first k-point
-5.0	5.0	energy window for matrix elements
3		number of cases (see choices)
1		Re <x><x>
3		Re <z><z>
7		Im <x><y>
OFF		write not-squared matrix elements to file?

Choices:
1.....Re<x><x>
2.....Re<y><y>
3.....Re<z><z>
4.....Re<x><y>
5.....Re<x><z>
6.....Re<y><z>
7.....Im<x><y>
8.....Im<x><z>
9.....Im<y><z>

output

- ***case.symmat***
  $\langle vk | p_i | ck \rangle \langle vk | p_j | ck \rangle$
- ***case.mommat*** (ON)
  $\langle vk | p_j | ck \rangle$

Integrate joint DOS, ***joint*** program

x joint, computes imaginary part of the dielectric tensor components, and more

get Fermi level (***x lapw2 -fermi -???***)

do the BZ integration (**x joint -???**)

$$\Im(\epsilon_{ij}) = \frac{16\pi^2}{\Omega\omega^2} \sum_{vck} \langle vk | p_i | ck \rangle \langle ck | p_j | vk \rangle \delta(\varepsilon_{kc} - \varepsilon_{vk} - \omega)$$

joint program – input, output

input

- ***case.injoint***

1 18	lower and upper band index
0.000 0.001 1.000	Emin, dE, Emax [Ry]
ev	output units eV / Ry
4	switch
1	number of columns
0.1 0.2	broadening for Drude terms
	choose gamma for each case!

output

- ***case.joint***

Switch:
0...JOINT DOS for each band combination
1...JOINT DOS sum over all band combinations
2...DOS for each band
3...DOS sum over all bands
4...Im(EPSILON) total
5...Im(EPSILON) for each band combination
6...intraband contributions
7...intraband contributions including band analysis

kram program – input, output

input

- ***case.inkram*** (metal)

0.1	broadening gamma
0.0	energy shift (scissors operator)
1	add intraband contributions 1/0
12.6	plasma frequency
0.2	broadening for intraband part

- ***case.inkram*** (semiconductor)

0.05	broadening gamma
1.000	energy shift (scissors operator)
0	add intraband contributions 1/0

output

- ***case.epsilon***
- ***case.sigmak***
- ***case refraction***
- ***case.absorp***
- ***case.eloss***

Intra-band contribution

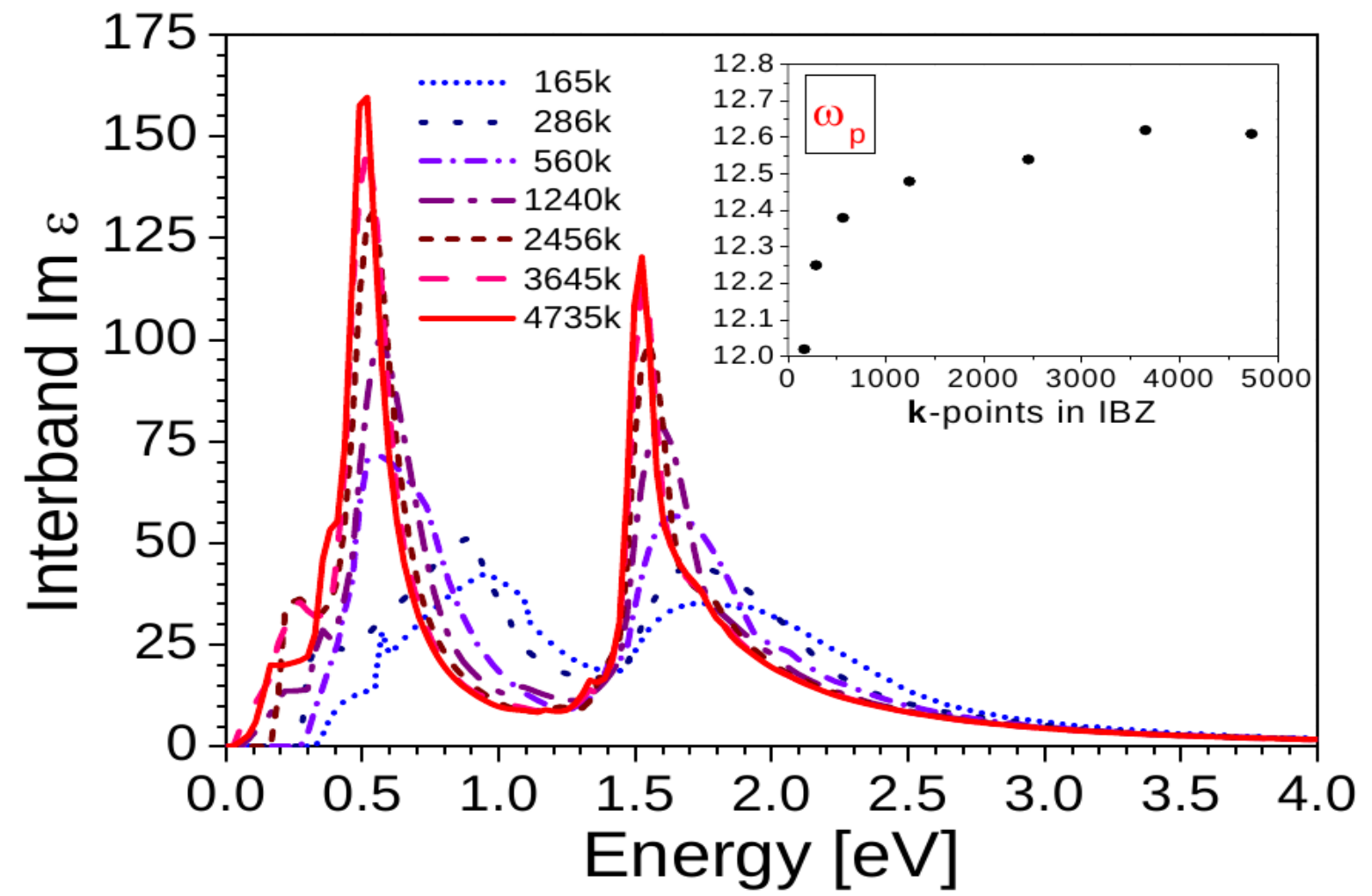
$$\mathrm{Im}\,\epsilon_{\alpha\beta}(\omega) = \frac{4\pi N e^2}{m}\frac{\Gamma}{\omega(\omega^2+\Gamma^2)} = \frac{\Gamma\omega^2_{p,\alpha\beta}}{\omega(\omega^2+\Gamma^2)}$$

$$\mathrm{Re}\,\epsilon_{\alpha\beta}(\omega) = 1 - \frac{\omega^2_{p,\alpha\beta}}{(\omega^2+\Gamma^2)}$$

$$\omega^2_{p,\alpha\beta} = \frac{e^2}{m^2\pi^2}\sum_l \int d\mathbf{k}\ \langle l|p^\alpha|l\rangle_{\mathbf{k}}\langle l|p^\beta|l\rangle_{\mathbf{k}}\ \delta(\varepsilon_l - \varepsilon_F)$$

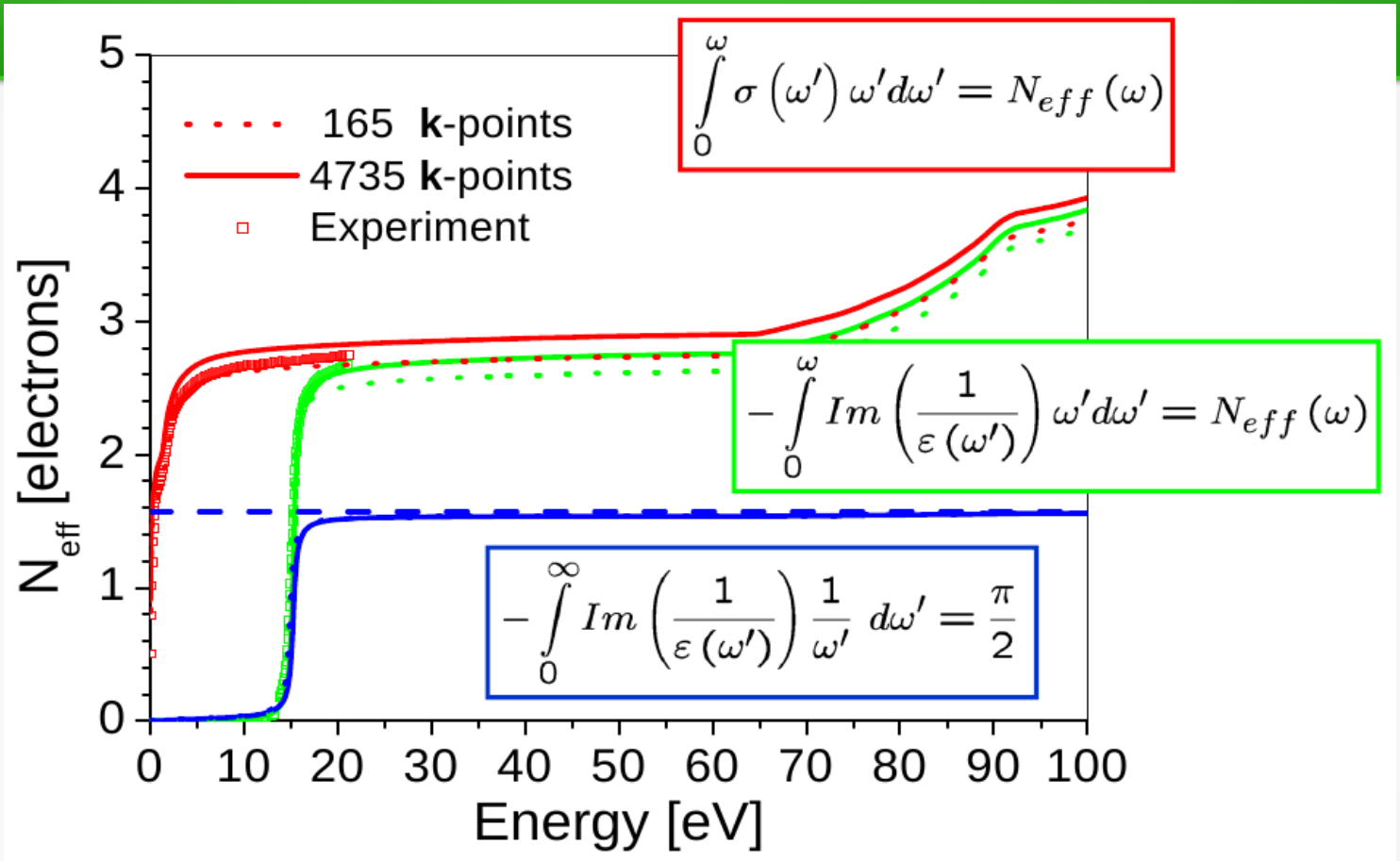
$$\Re\,\epsilon_{ij} = \delta_{ij}\frac{2}{\pi}P\int_0^\infty \frac{\omega'\,\Im\,\epsilon_{ij}(\omega')}{\omega'^2-\omega^2}d\omega'$$

Example: Al, k-point convergence



- always check **k-point convergence** (use dense k-mesh !!!)

Example: Al, sumrules

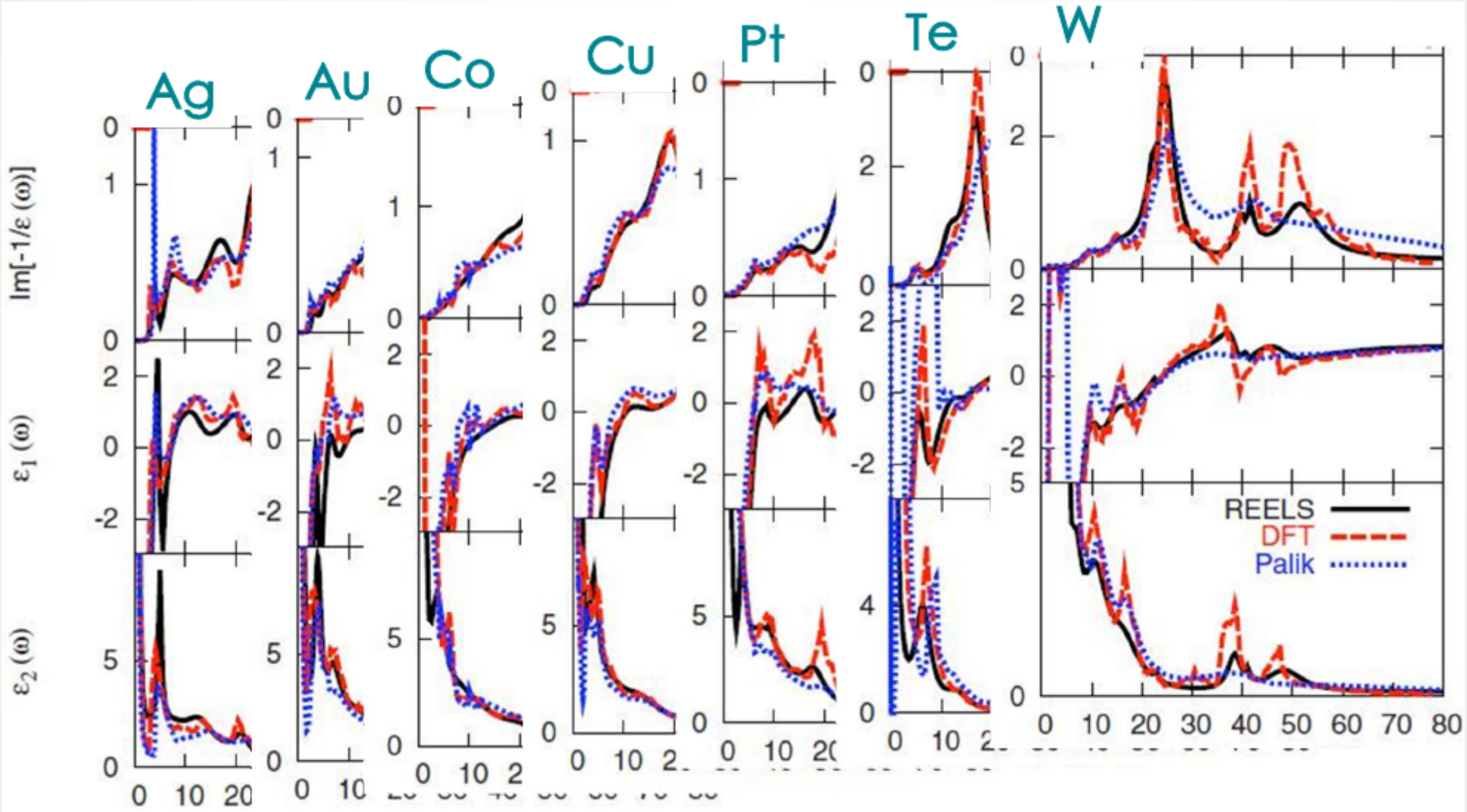


- for KK transformation you need *Im(ε)* in a wide energy range

$$\Re\,\epsilon_{ij} = \delta_{ij}\frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \Im\,\epsilon_{ij}(\omega')}{\omega'^2 - \omega^2} d\omega'$$

- be aware that LAPW linearization breaks down for high conduction states !!!

Theory vs experiment



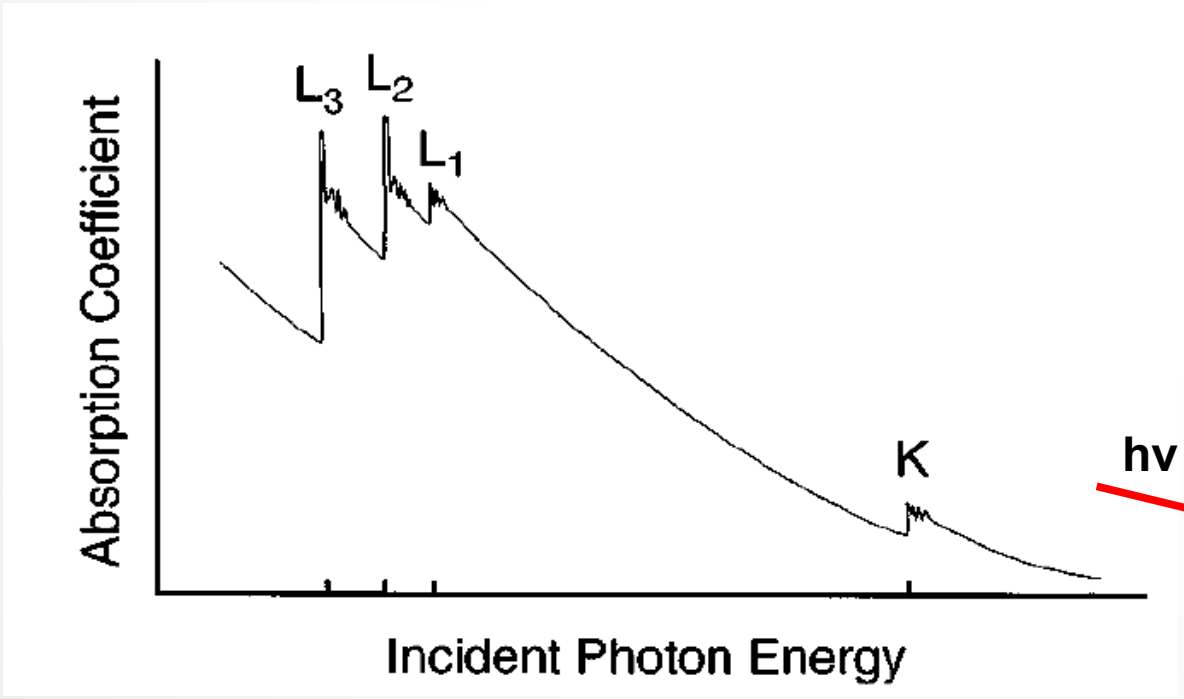
W. Werner, et al J. Phys. Chem. Ref. Data 38, 1013 (2009)

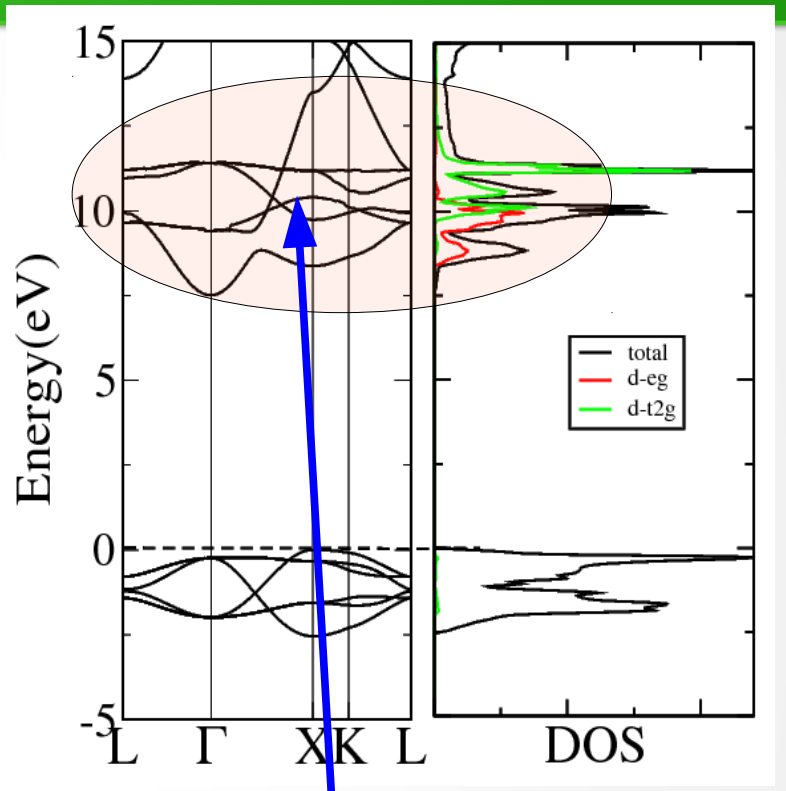
Core level spectroscopy

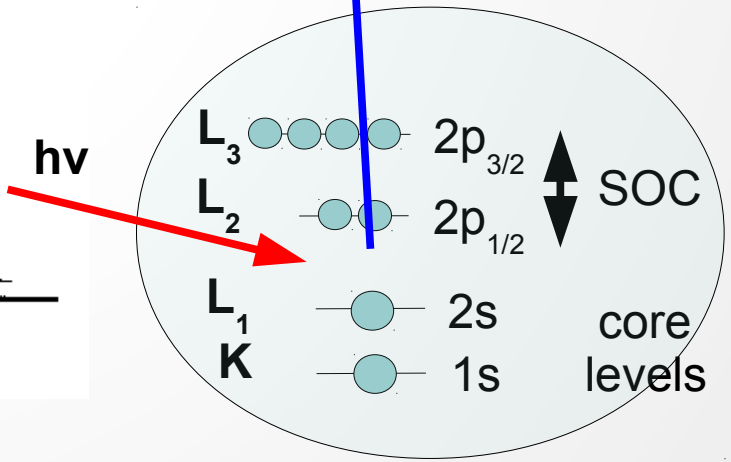
- absorption (XAS)
- emission (XES)
- core-hole

Core level spectroscopy (XAS)

- X-ray absorption (XAS)
  - core electrons are excited in to a conduction band
  - each core shell introduces an absorption edge, (indexed by the principal number of a core level)

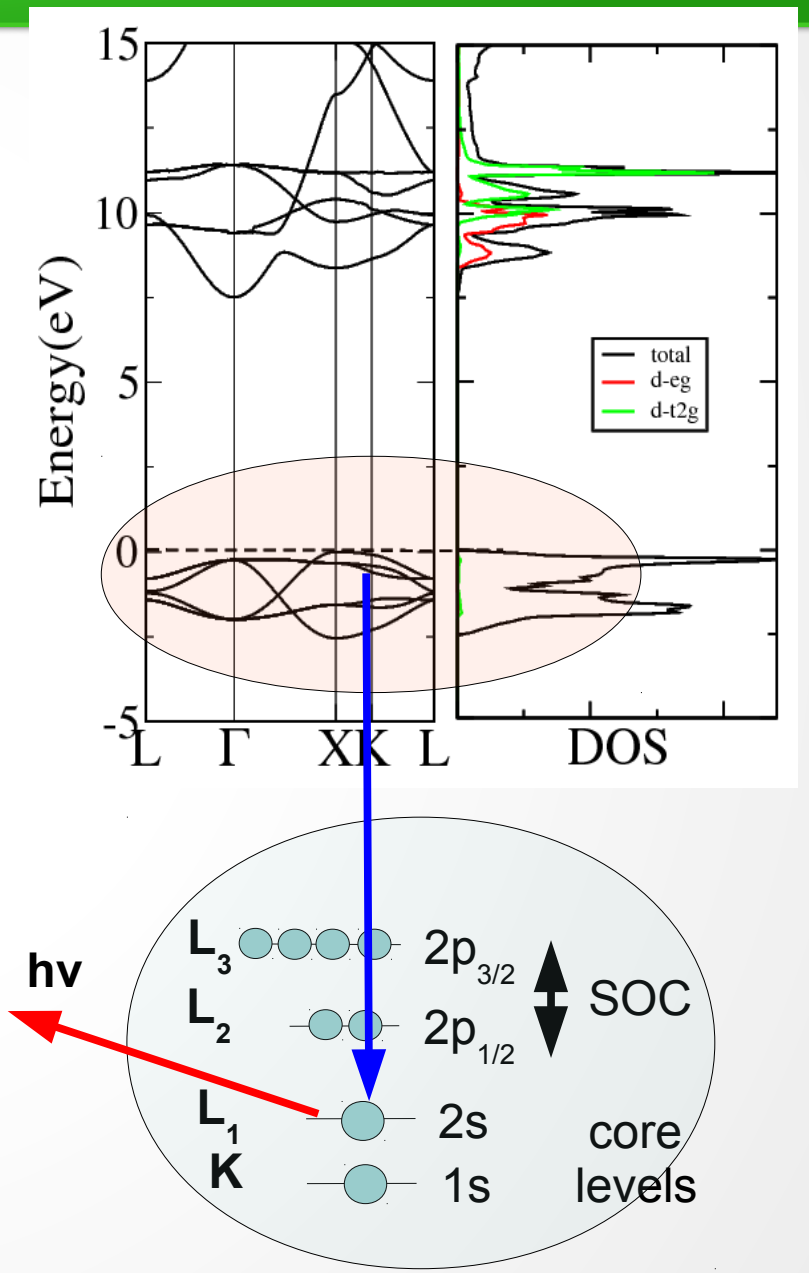






Core level spectroscopy (XES)

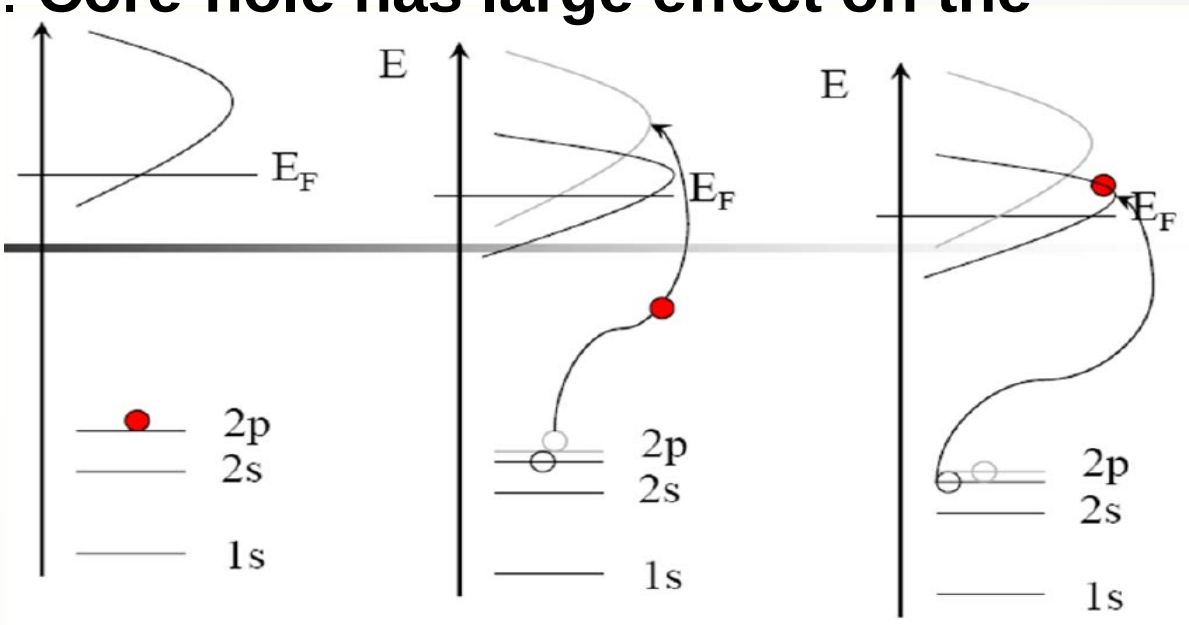
- X-ray emission (XES)
  - Knock out core electron, valence electron fills core level and *hv* is emitted



XAS, XES, final state rule

“Final state” determines the spectrum

- **XAS** - final state has a “hole” in core state, and additional e- in conduction band. **Core-hole has large effect on the spectrum**



- **XES** - final state has filled core, but **valence hole**, this is usually **well screened**, thus one “sees” the groundstate.

Core hole in wien2k

- No core hole (ground state)
  - 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)

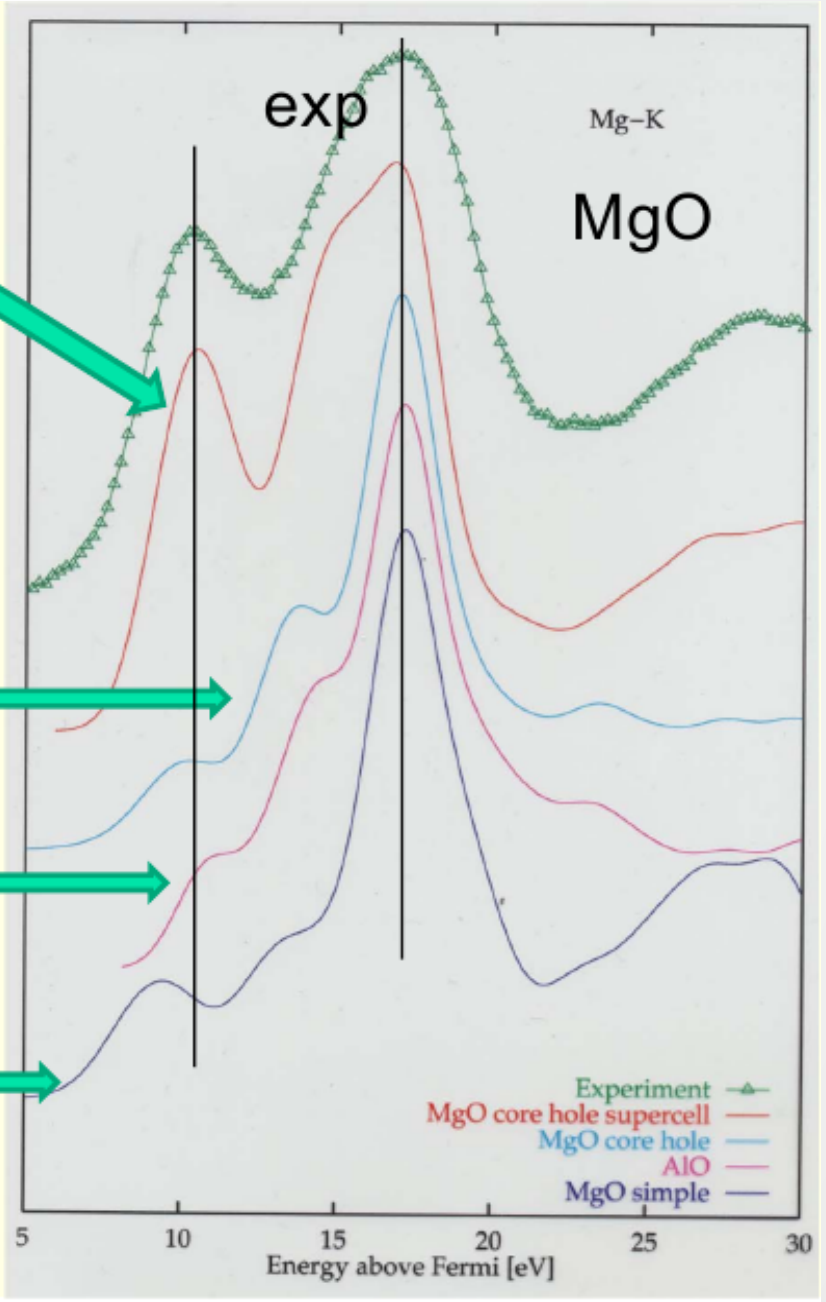
XAS, Mg K-edge in MgO

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

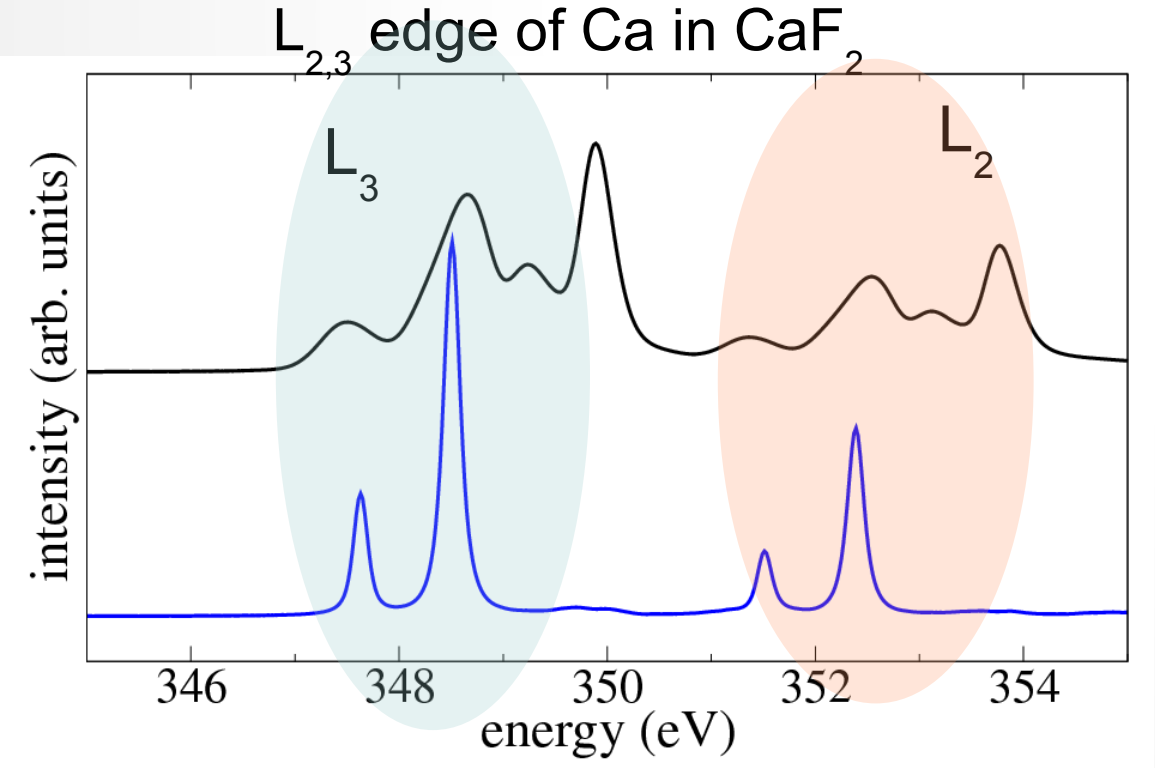


Core-hole approach, limitation

- absorption is proportional to the projected DOS (empty band)

$$\Im \epsilon_M(\omega) = \sum_{\lambda} \left| \frac{\langle vk|p|ck\rangle}{(\varepsilon_{ck} - \varepsilon_{vk})} \right|^2 \delta(E^{\lambda} - \hbar\omega)$$

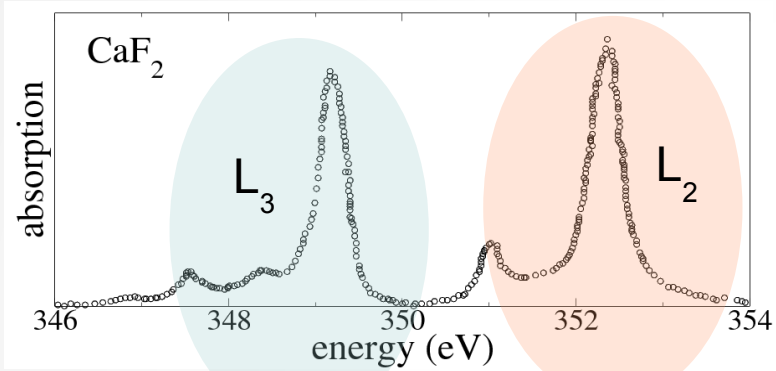
- branching ratio (eg. L_2/L_3) is proportional to multiplicity of involved core states ($2p_{1/2}$, $2p_{3/2}$)

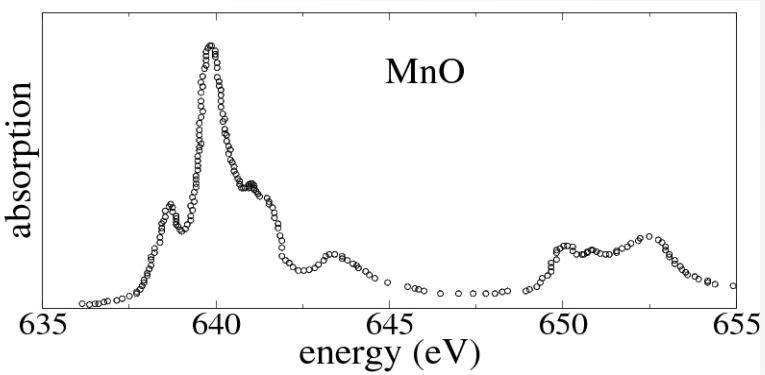


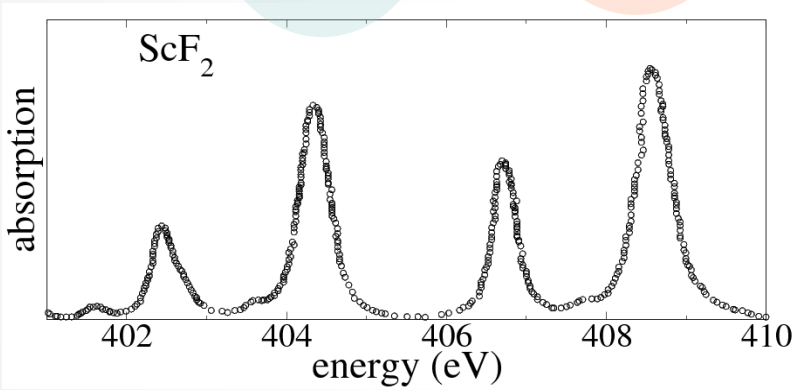
plain DFT

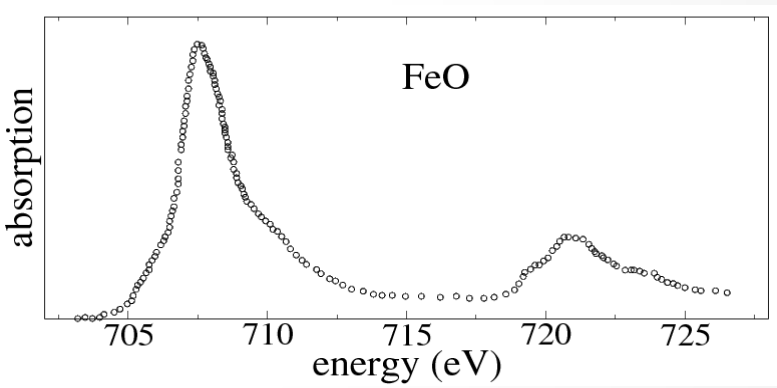
"core hole" DFT
(supercell with core hole on excited atom)

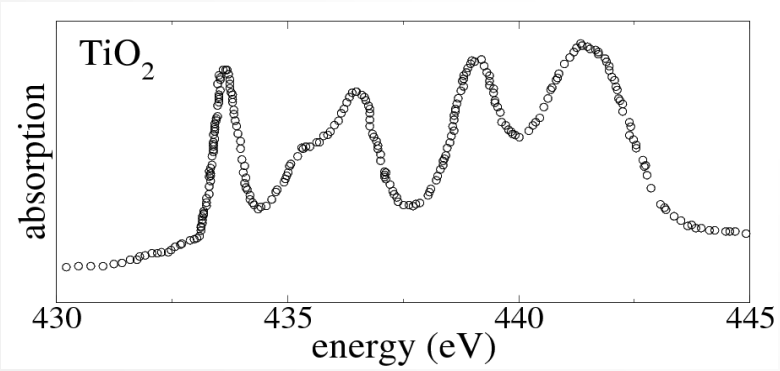
L_2/L_3 edges of 3d metals

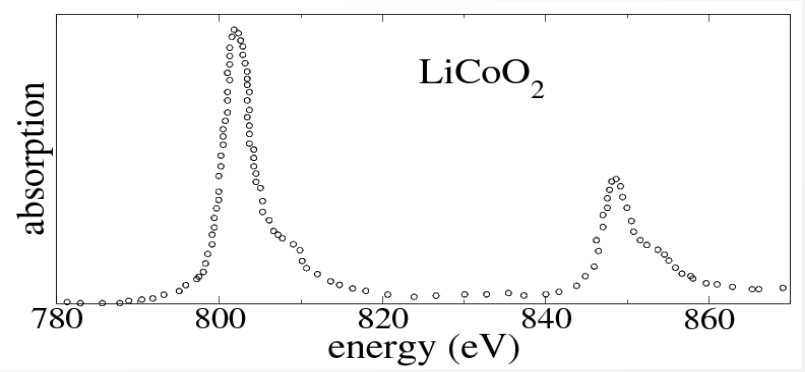












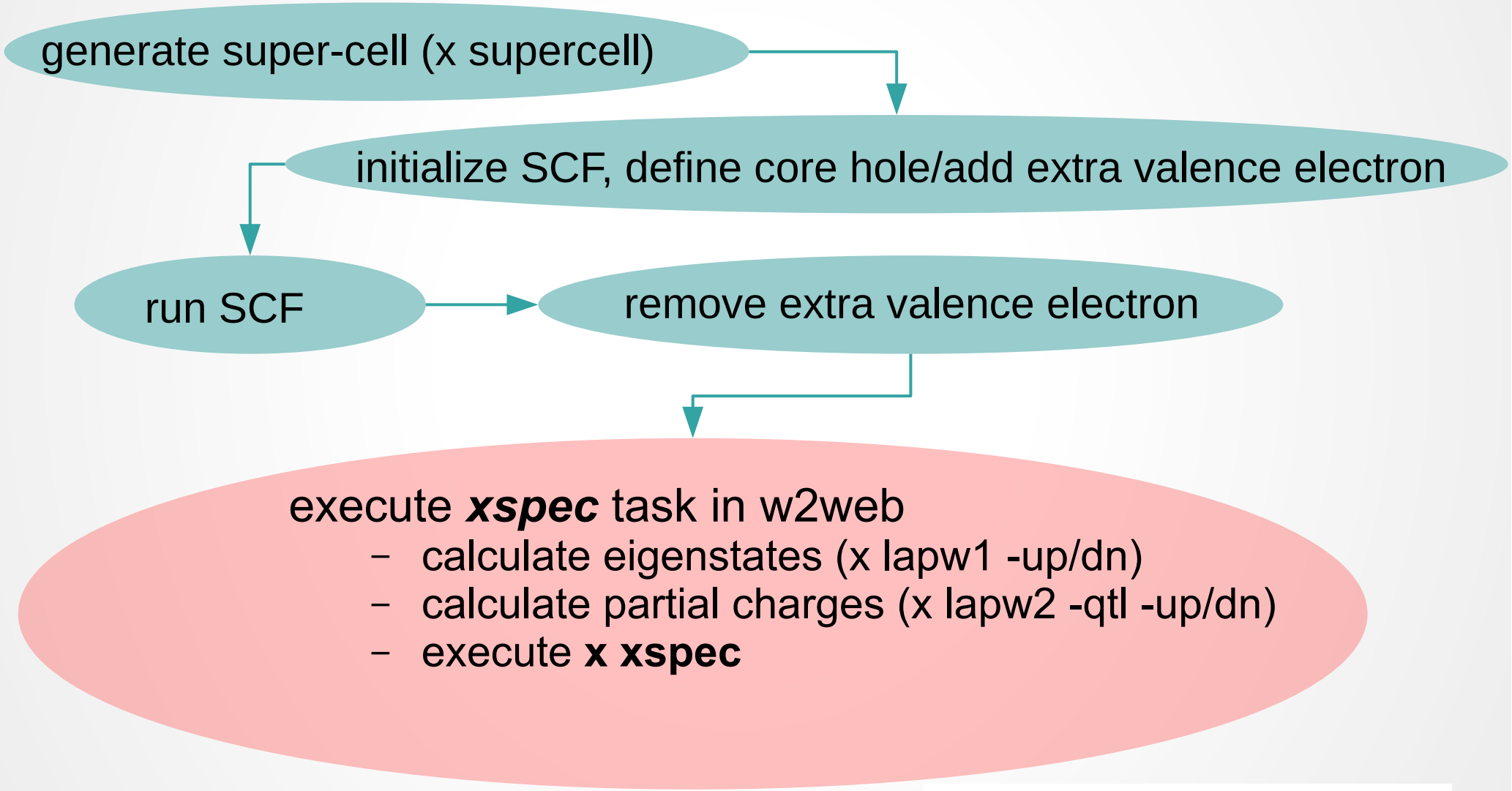
Core-hole calculation in wien2k

- generate super-cell (x supercell)
- initialize SCF, define core hole/add extra valence electron
- 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**

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

Dipole approximation

Core-hole calculation in wien2k



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

xspec input file

XES

```
NbC: C K      (Title)
2             ( atom)
1             (n core)
0             (l core)
0,0.5,0.5     (split, int1, int2)
-20,0.1,3     (EMIN,DE,EMAX in eV)
EMIS          (type of spectrum)
0.35          (S)
0.25          (gamma0)
0.3           (W)
AUTO          (band ranges AUTO or MAN
-7.21         (E0 in eV)
-10.04        (E1 in eV)
-13.37        (E2 in eV)
```

XAS

```
NbC: C K      (Title)
2             (atom)
1             (n core)
0             (l core)
0,0.5,0.5     (split, int1, int2)
-2,0.1,30     (EMIN,DE,EMAX in eV)
 ABS  (type of spectrum)
0.5           (S)
0.25          (gamma0)
```

Details in user guide

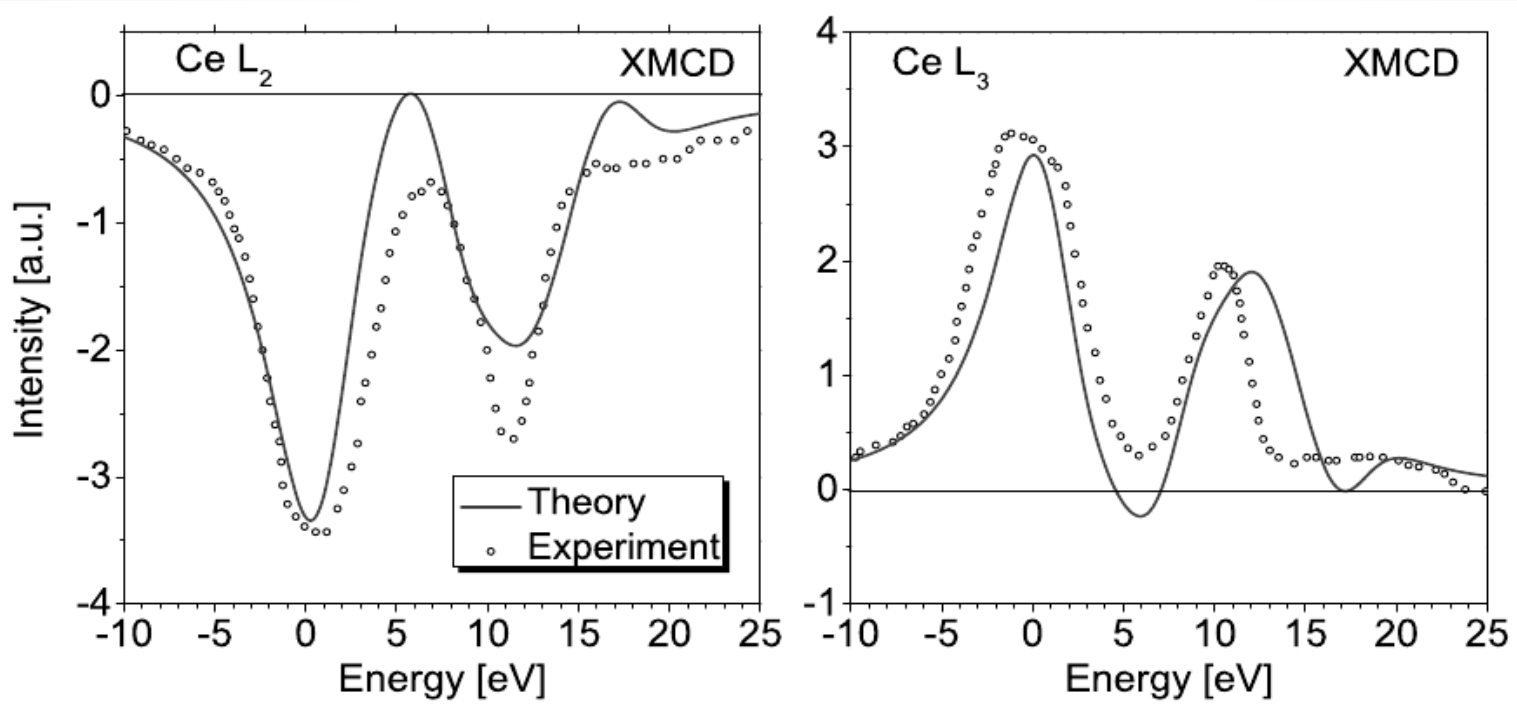
Core level spectroscopy (XMCD)

- X-ray magnetic circular dichroism (optic program)

$$\mu^{\pm}(\omega) \propto \sum_{f} \left| D_{fi}^{\pm 1} \right|^2 \delta(E_f - E_i - \hbar\omega)$$

$$D_{fi}^{\pm 1} = \epsilon^{\pm} \cdot \langle \Psi_i | \mathbf{p} | \Psi_f \rangle \qquad \epsilon_{\pm 1} = \epsilon_x \pm \imath \epsilon_y$$

Independent particles approximation



L Pardini, et al Computer Physics Communications 183 (2012) 628–636

Core level spectroscopy (XMCD)

- X-ray magnetic circular dichroism (***x optic***)
  - ***case.inop***

```
99999 1          : NKMAX, NKFIRST
-5.0 2.0 18      : EMIN, EMAX, NBvalMAX
XMCD 1 L23   : optional line: for XMCD of 1st atom and L23 spectrum
6                : number of choices (columns in *symmat)
1                Re<x><x>
2                Re<y><y>
3                Re<z><z>
4                Re<x><y>
5                Re<x><z>
6                Re<y><z>
OFF              : ON/OFF   writes MME to unit 4
```

- conduction states are calculated with SOC
- Core states are calculated with ***lcore*** program (atomic Dirac solver)

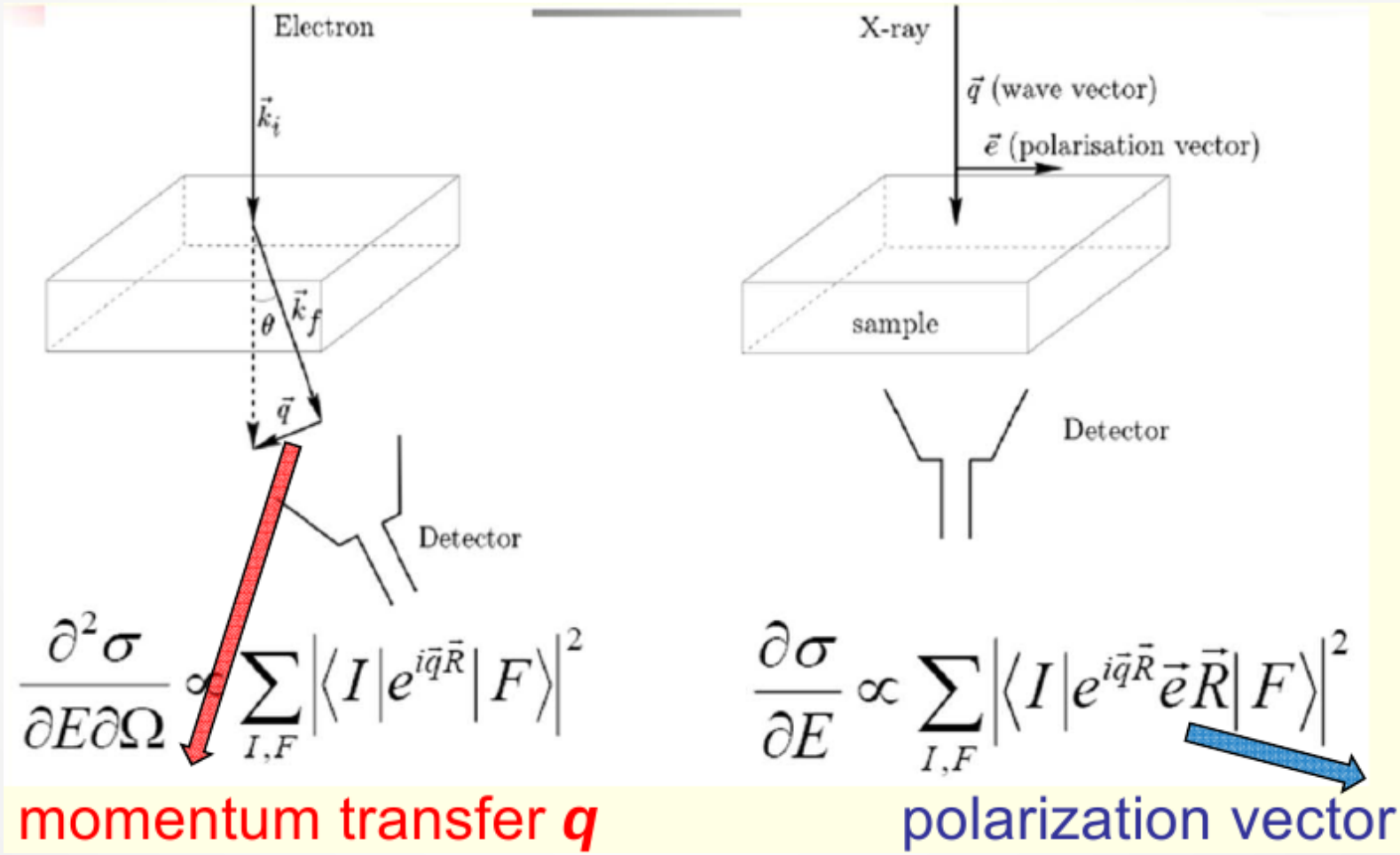
Core level spectroscopy (XMCD)

- X-ray magnetic circular dichroism (***x joint***)

```
1 9999 8                        : LOWER,UPPER,upper-valence BANDINDEX
-0.0000   0.00100 2.0000   : EMIN DE EMAX FOR ENERGYGRID IN ryd
eV                              : output units eV / ryd
XMCD                            : omitt these 4 lines for non-XMCD
-49.88 -50.80                   : core energies in Ry (grep :2P case.scfc)
1.6  0.6                        : core-hole broadening (eV) for both core states
0.1                             : spectrometer broadening (eV)
4                               : SWITCH
2                               : NUMBER OF COLUMNS
0.1 0.1 0.3                     : BROADENING (FOR DRUDE MODEL - switch 6,7)
```

Core level spectroscopy (EELS)

- ELNES vs XAS



EELS in wien2k (**telnes2** program)

- Within the dipole approximation the momentum transfer vector in non-relativistic EELS plays the same role as polarization vector in XAS
- ***telnes3*** program also handles non-dipole transitions and relativistic corrections

See details in users guide

Theory vs experiment

- details of the band structure matter
  - band gap problem
- independent particles approximation, RPA