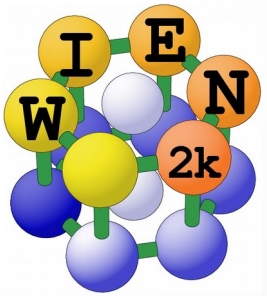
Optical properties by wien2k

Robert Laskowski

rolask@ihpc.a-star.edu.sg

Institute of High Performance Computing
Singapore



outline

- Basics, formalism
- What, how?
  - *optic*, *joint*, *tetra ….*
  - inputs / outputs, examples
- Beyond independent particle approximation
  - The Bethe-Salpeter equation
- Core excitons
  - XAS, XES (*xspec*), XMCD (*optic,joint*), EELS (*telnes*)

Introduction

- independent particles approximation (IPA)
- local field effects
- *matrix elements of momentum operator*
- dielectric function, dielectric tensor

Dielectric function

- photon propagates, external potential (V_{ext})
- Electrons respond, induce screening potential (V_s)

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

External potential

Screening potential

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

dielectric constant ϵ_{GG}

- Dielectric constant (function) contains all information about the response

Light matter interaction

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

- Definition irreducible of polarizability: $P = \frac{\delta n}{\delta V}$ $\qquad V_G^s = \nu(q+B) n_G(q)$

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

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

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

Light matter interaction

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

random phase approximation (RPA)

with local field effects:

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

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

$$V^{ext}_G = \sum_{G'} \epsilon_{GG'} V_{G'} \quad V_0 = \varepsilon^{-1}_{00} V^{ext}_0$$

neglecting local field effects:

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

Light matter interaction

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

Free electrons:
the Lindhard formula

$$\varepsilon(q,\omega)=1-\lim_{\eta\to 0}\frac{4\pi e^2}{q^2\Omega}\sum_k \frac{f(\varepsilon_{k+q})-f(\varepsilon_k)}{\varepsilon_{k+q}-\varepsilon_k-\omega-i\eta}$$

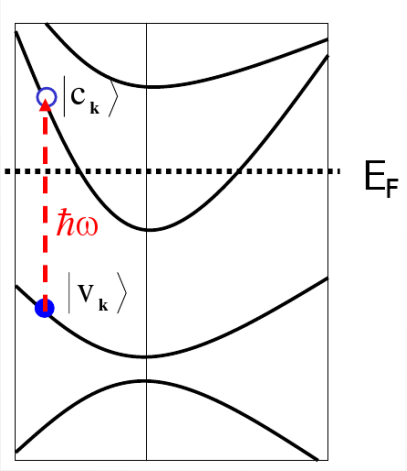
Bloch electrons:

$$\varepsilon(q,\omega)=1-\lim_{\eta\to 0}\frac{4\pi e^2}{q^2\Omega}\sum_k A^{l,l'}_{k,q}\frac{f(\varepsilon_{k+q})-f(\varepsilon_k)}{\varepsilon_{k+q}-\varepsilon_k-\omega-i\eta}$$

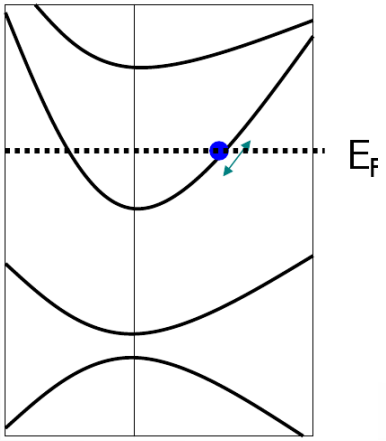
$$A^{l,l'}_{k,q}=\delta_{l,l'}+(1-\delta_{l',l})\frac{q^2}{m\omega^2_{l,l'}}|P_{l,l'}|^2$$

intra-band

inter-band



inter-band



intra-band

Long wave limit

With k·p method we find q $\rightarrow$ 0 limit of P

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

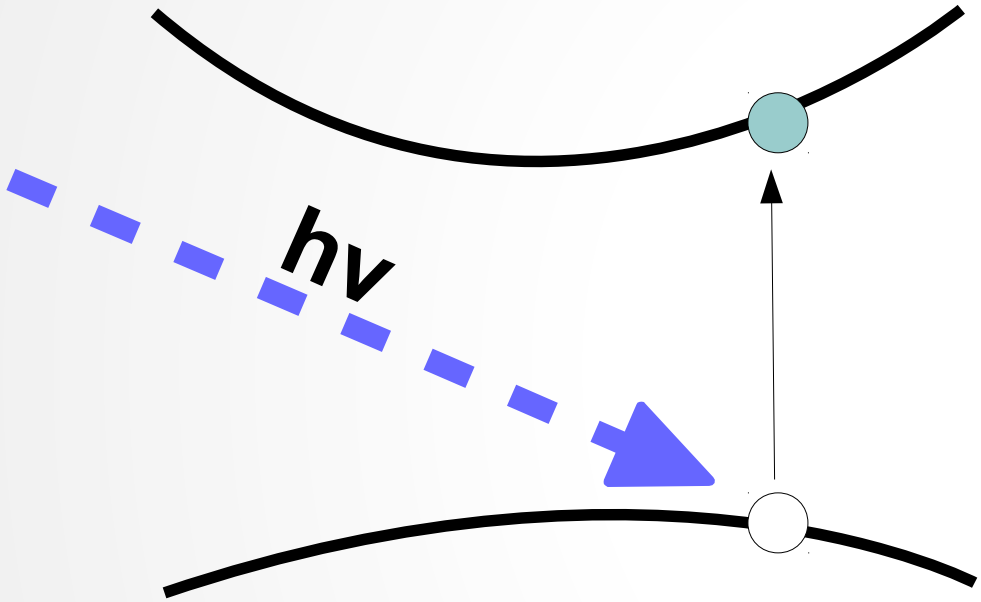
The expression for calculations of single particle excitation spectra

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

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

$$\mathrm{Im}\epsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2} \sum_{c,v} \int d\mathbf{k} \, \langle c_\mathbf{k}|p^\alpha|v_\mathbf{k}\rangle\langle v_\mathbf{k}|p^\beta|c_\mathbf{k}\rangle \, \delta(\varepsilon_{c_\mathbf{k}} - \varepsilon_{v_\mathbf{k}} - \omega)$$

Momentum matrix elements

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

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

The character of the state is hidden here

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

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 ($\alpha, \beta = 90°$)

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

- 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***

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

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

Computing momentum matrix elements

- Run SCF (to get converged density)
- Generate potential (***x lapw0***)
- Generate dense k-mesh (***x kgen***)
- Generate eigenvectors (***x lapw1 -???***)
- Generate Fermi distribution (***x lapw2 -fermi -???***)
- Calculate momentum matrix elements (***x optic -???***)

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

- compute imaginary part of the dielectric function (***x joint***)
- (***x kram***) for computing other optical constants

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 unsquared 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)
  $\langle vk | p_j | ck \rangle$

joint program – input, output

- ***x joint***, computes dielectric tensor components

$$\mathrm{Im}\epsilon_{\alpha\beta}(\omega) = \frac{4\pi e^2}{m^2\omega^2}\sum_{c,v}\int d\mathbf{k}\,\langle c_\mathbf{k}|p^\alpha|v_\mathbf{k}\rangle\langle v_\mathbf{k}|p^\beta|c_\mathbf{k}\rangle\,\delta(\varepsilon_{c_\mathbf{k}}-\varepsilon_{v_\mathbf{k}}-\omega)$$

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!

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

output

- ***case.joint***

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***

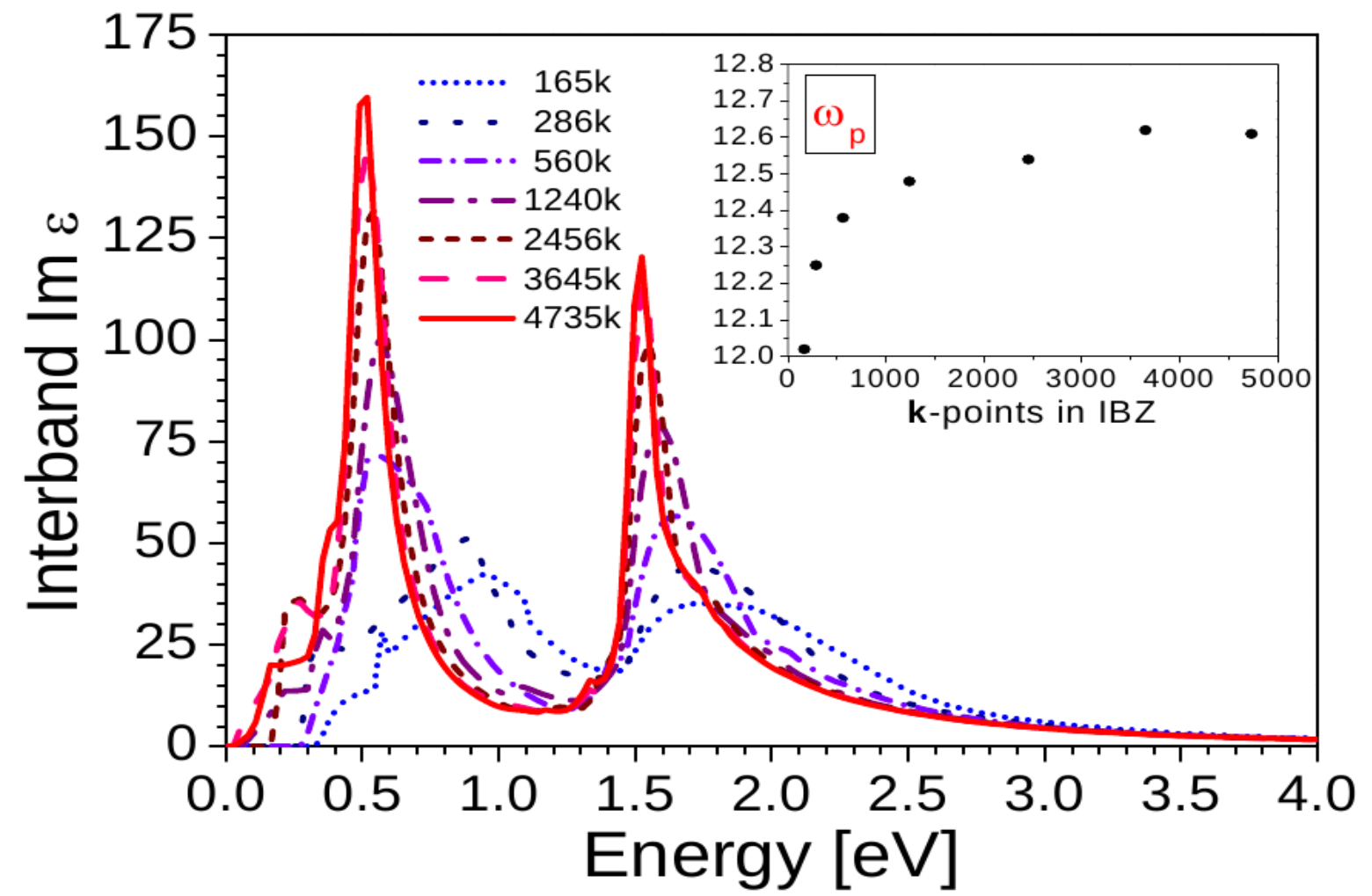
Intra-band contribution

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

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

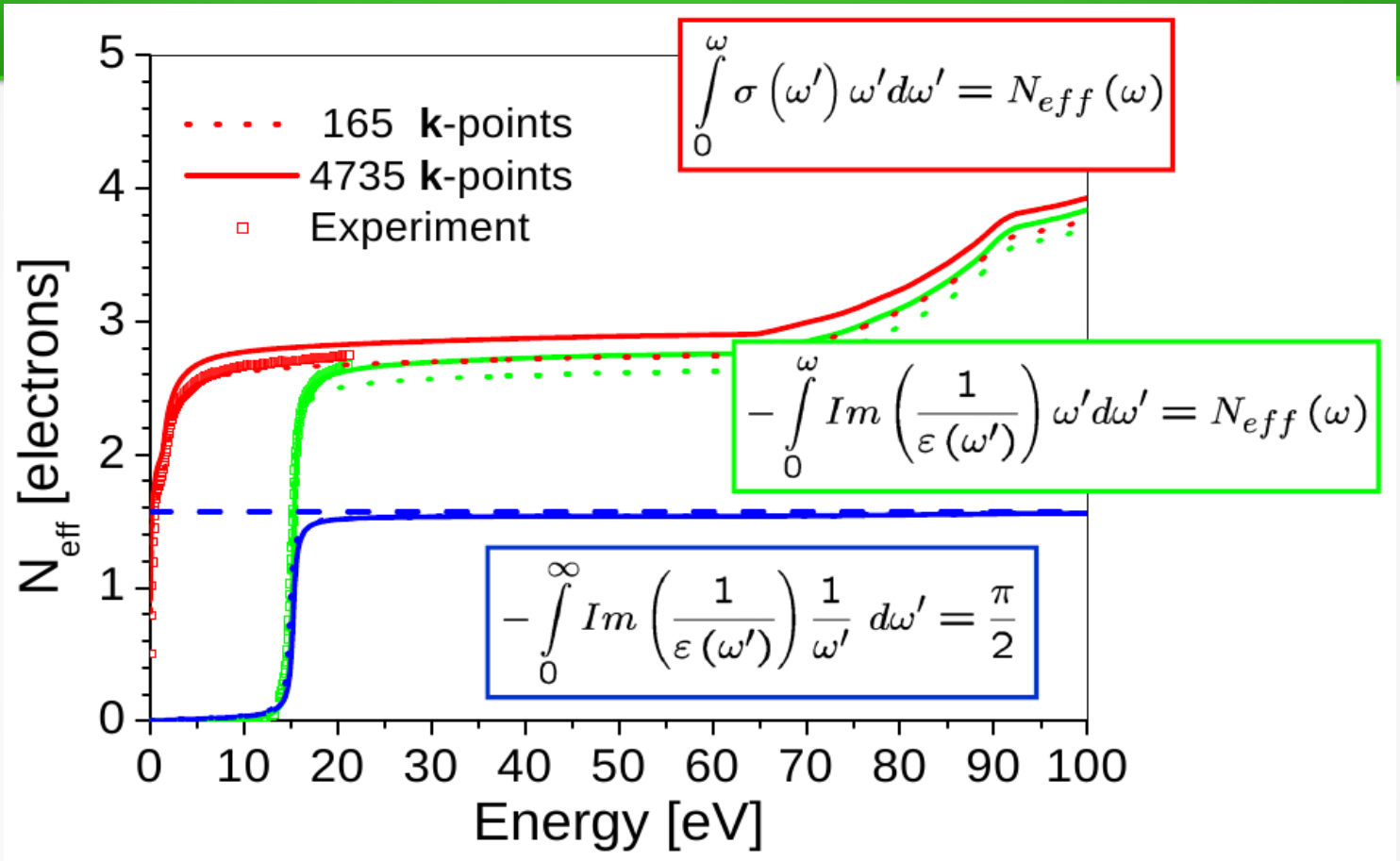
$$\omega^2_{p,\alpha\beta} = \frac{e^2}{m^2\pi^2}\sum_l \int d\mathbf{k}\ \langle l|p^\alpha|l\rangle_{\mathbf{k}}\langle l|p^\beta|l\rangle_{\mathbf{k}}\ \delta(\varepsilon_l - \varepsilon_F)$$

Example: Al, k-point convergence



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

Example: Al, sumrules

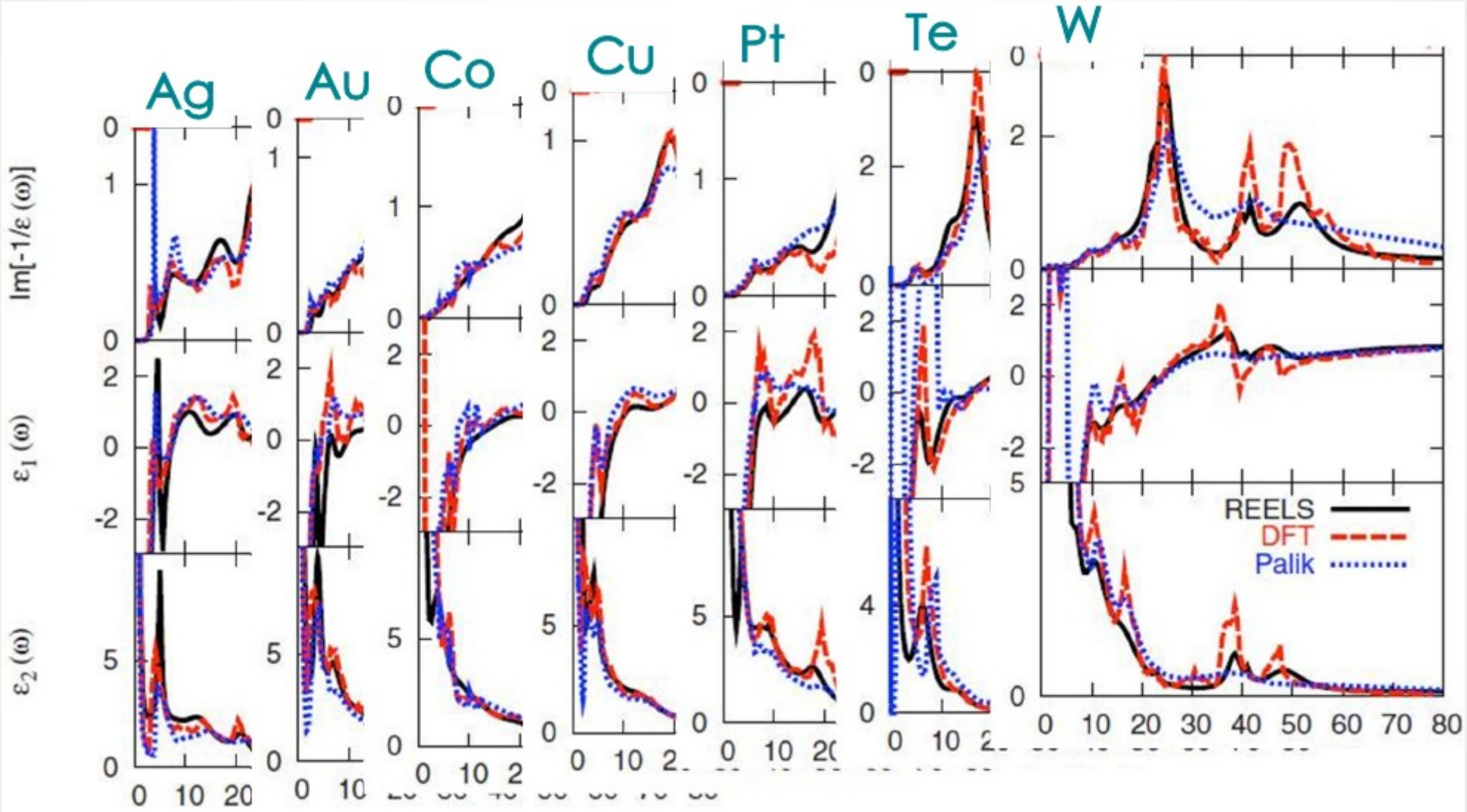


- for KK transformation you need *Im(ε)* in a wide energy range

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

- 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)

Beyond standard DFT

- Hybrid DFT (thanks to F. Tran in wien2k)

  H-F Exchange energy included into KS theory

$$E_{x,\mathrm{vv}}^{\mathrm{HF}} = -\frac{1}{2}\sum_{\sigma}\sum_{n,\mathbf{k},n',\mathbf{k}'} w_{n\mathbf{k}}^{\sigma} w_{n'\mathbf{k}'}^{\sigma} \int_{\Omega}\int_{\mathrm{crystal}} \psi_{n\mathbf{k}}^{\sigma *}(\mathbf{r})\psi_{n'\mathbf{k}'}^{\sigma}(\mathbf{r}) \times v(|\mathbf{r}-\mathbf{r}'|)\psi_{n'\mathbf{k}'}^{\sigma *}(\mathbf{r}')\psi_{n\mathbf{k}}^{\sigma}(\mathbf{r}')d^3r'd^3r,$$

F. Tran, P. Blaha PHYSICAL REVIEW B 83, 235118 (2011)

- GW method (available for wien2k)

Self-energy $$\Sigma(r,r',\omega)=\frac{i}{2\pi}\int d\omega' G(r,r,\omega-\omega')W(r,r',\omega)$$

$$\varepsilon_{nk}^{QP}=\varepsilon_{nk}^{LDA}-\langle nk|\Sigma(\varepsilon_{nk}^{QP})-V_{xc}^{LDA}|nk\rangle$$

M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. 55, 1418 (1985)
M. S. Hybertsen and S. G. Louie, Phys. Rev. B 34, 5390 (1986)
R. Gómez-Abal, et al, PRL 101, 036402 (2008).

Beyond standard DFT

- Effective functionals (mBJ, F. Tran)

F. Tran, P. Blaha PRL 102, 226401 (2009)

$$v_{x,\sigma}^{\mathrm{MBJ}}(\mathbf{r}) = c\,v_{x,\sigma}^{\mathrm{BR}}(\mathbf{r}) + (3c-2)\frac{1}{\pi}\sqrt{\frac{5}{12}}\sqrt{\frac{2t_\sigma(\mathbf{r})}{\rho_\sigma(\mathbf{r})}},$$

$$v_{x,\sigma}^{\mathrm{BR}}(\mathbf{r}) = -\frac{1}{b_\sigma(\mathbf{r})}\left(1 - e^{-x_\sigma(\mathbf{r})} - \frac{1}{2}x_\sigma(\mathbf{r})e^{-x_\sigma(\mathbf{r})}\right)$$

- scissor shift

$$\varepsilon_{ck}^{QP} = \varepsilon_{ck}^{LDA} - \Delta_{scissor}$$

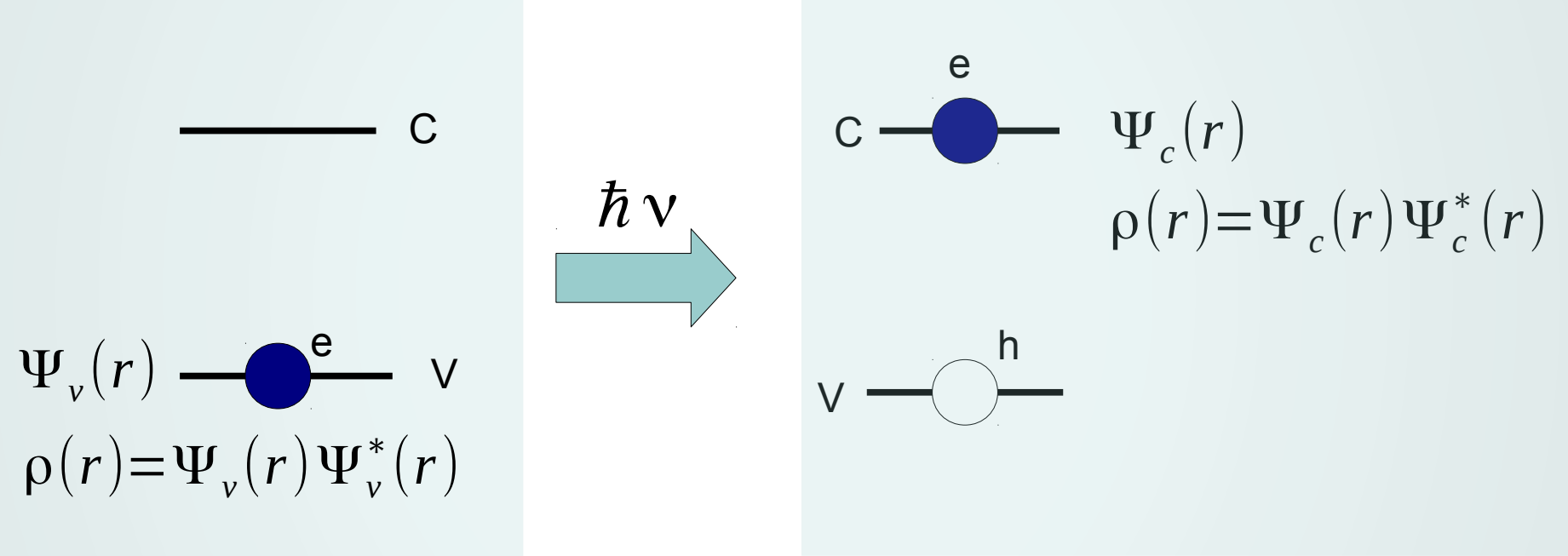
$$\varepsilon_{vk}^{QP} = \varepsilon_{vk}^{LDA}$$

$$\langle vk|p|ck\rangle^{QP} = \frac{E_{ck}-E_{vk}}{\varepsilon_{ck}-\varepsilon_{vk}}\langle vk|p|ck\rangle$$

$$\Im\,\varepsilon(\omega) = \Im\,\varepsilon(\omega-\Delta)$$

non-locality of the self energy operator or scissor shift

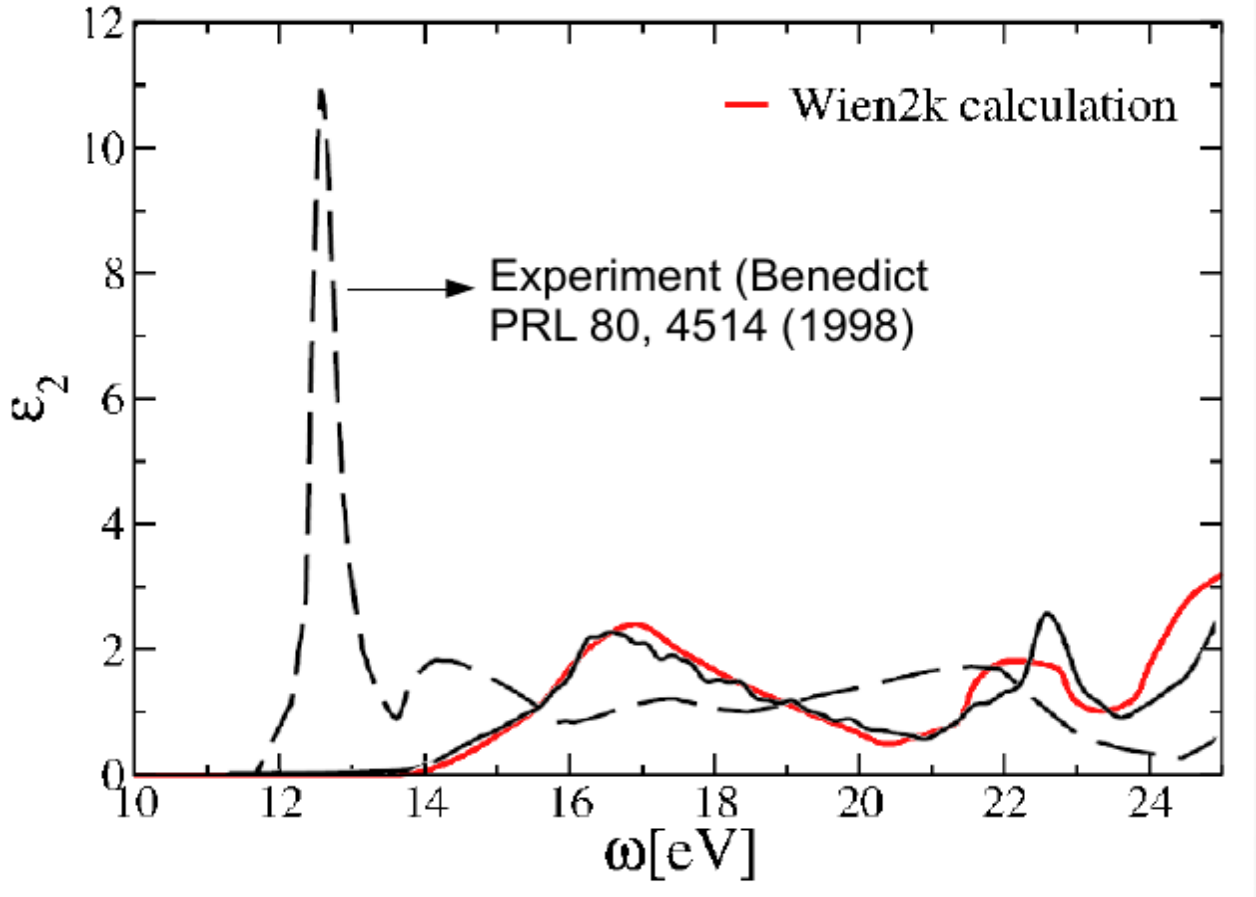
Beyond IPA

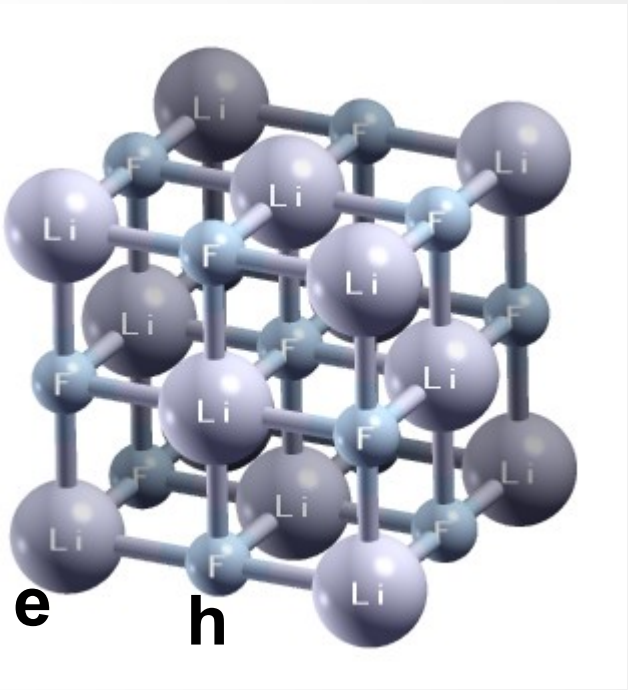


$$\rho_c(r) \neq \rho_v(r)$$

$$H_{initial} \neq H_{final}$$

LiF absorption spectra



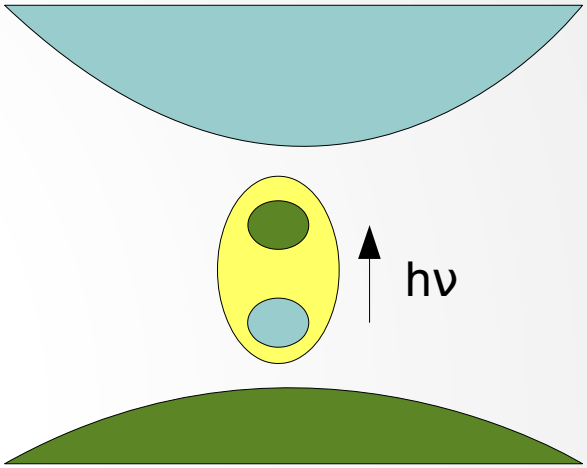


Bethe-Salpeter Equation

- excitation is a two-particle process (electron-hole pair is created)

$$L(12;1'2') = L_0(12;1'2') + \int d(3456) \times L_0(14;1'3') K(35;46) L(62;52')$$

equation of motion of two particle Green's function



- BSE is simplified into a two particles eigenvalue equation (in a basis of valence (*vk*) and conduction (*ck*) states)

$$(E_c - E_v) A^{\lambda}_{vc} + \sum_{v'c'} K_{vc,\,v'c'} (E_\lambda) A^{S}_{v'c'} = E_\lambda A^{S}_{vc}$$

band energies

$K = V^x + W^d$
interaction kernel

excitation energies

e-h coupling coef.

BSE, kernel and dielectric function

Exchange:

$$\langle vc|V^x(E_\lambda)|v'c'\rangle = \int dr\,dr'\,\psi_c^*(r)\psi_{c'}(r')\upsilon(r,r')\psi_v(r')\psi_{v'}^*(r)$$

Direct term:

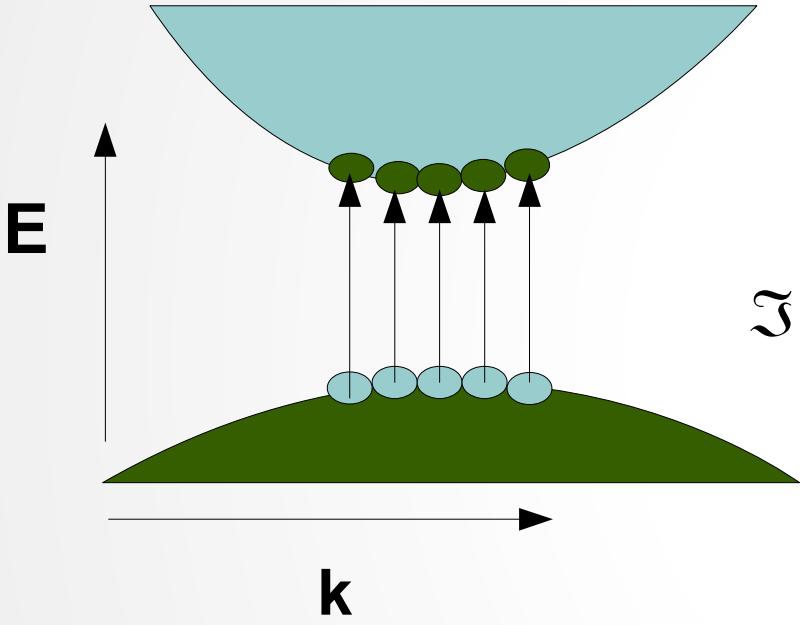
$$\langle vc|W^d(E_\lambda)|v'c'\rangle = \int dr\,dr'\,\psi_c^*(r)\psi_{c'}(r)\psi_v(r')\psi_{v'}^*(r')\frac{i}{2\pi}\int d\omega\, e^{i\omega 0^+} W(r,r',\omega)$$
$$\times\left[\frac{1}{E_\lambda-\omega-(E_{c'}-E_{v'})+iO^+}+\frac{1}{E_\lambda+\omega-(E_c-E_v)+iO^+}\right]$$

screened e-h interaction

Usual approximation valid for: $(E_c-E_v)\approx E_\lambda$

$$\langle vc|W^d(E_\lambda)|v'c'\rangle = \int dr\,dr'\,\psi_c^*(r)\psi_{c'}(r)\psi_v(r')\psi_{v'}^*(r')W(r,r',\omega=0)$$

BSE, kernel and dielectric function

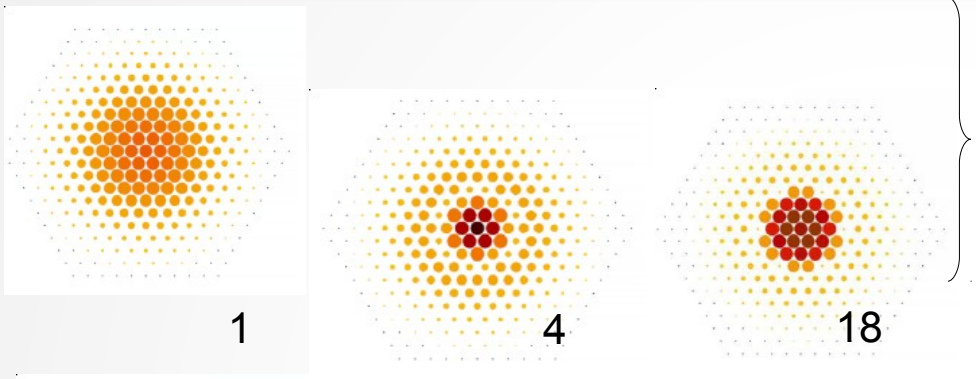


macroscopic dielectric function

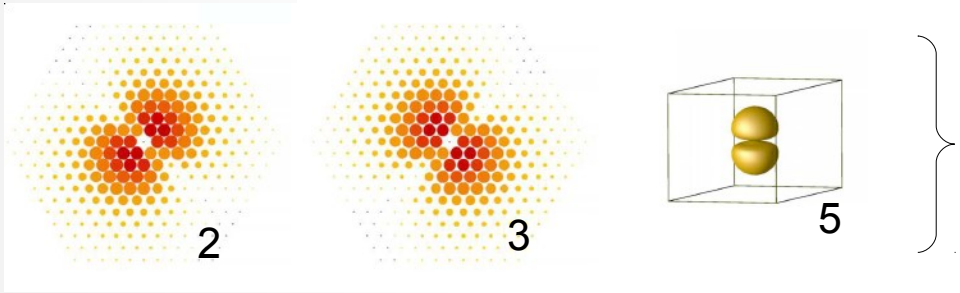
$$\Im\,\epsilon_M(\omega) = \sum_{\lambda} \left| \sum_{vck} A^{\lambda}_{vck} \frac{\langle vk|p|ck\rangle}{(\varepsilon_{ck} - \varepsilon_{vk})} \right|^2 \delta(E_\lambda - \hbar\omega)$$

oscillator strength are proportional to coherent sum of the momentum matrix elements

Exciton envelope function in AlN



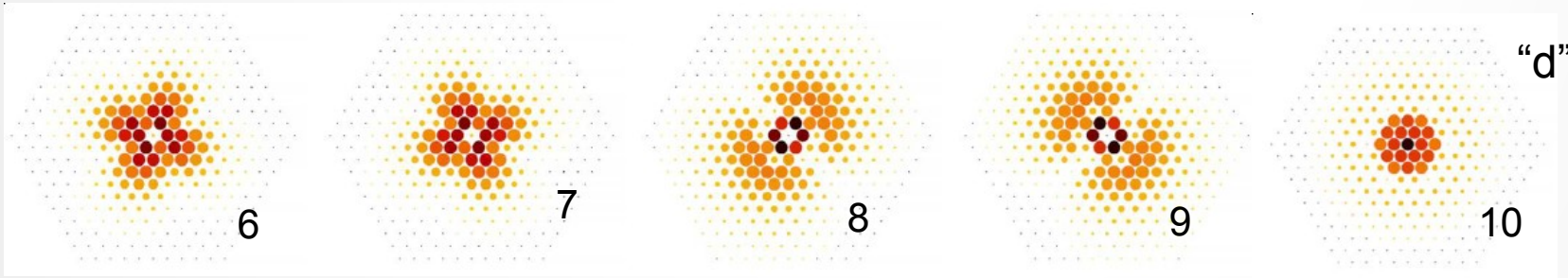
"s"- dipole active



"p"- dipole inactive

$$E_n = E_g - E_B \frac{1}{n^2}$$

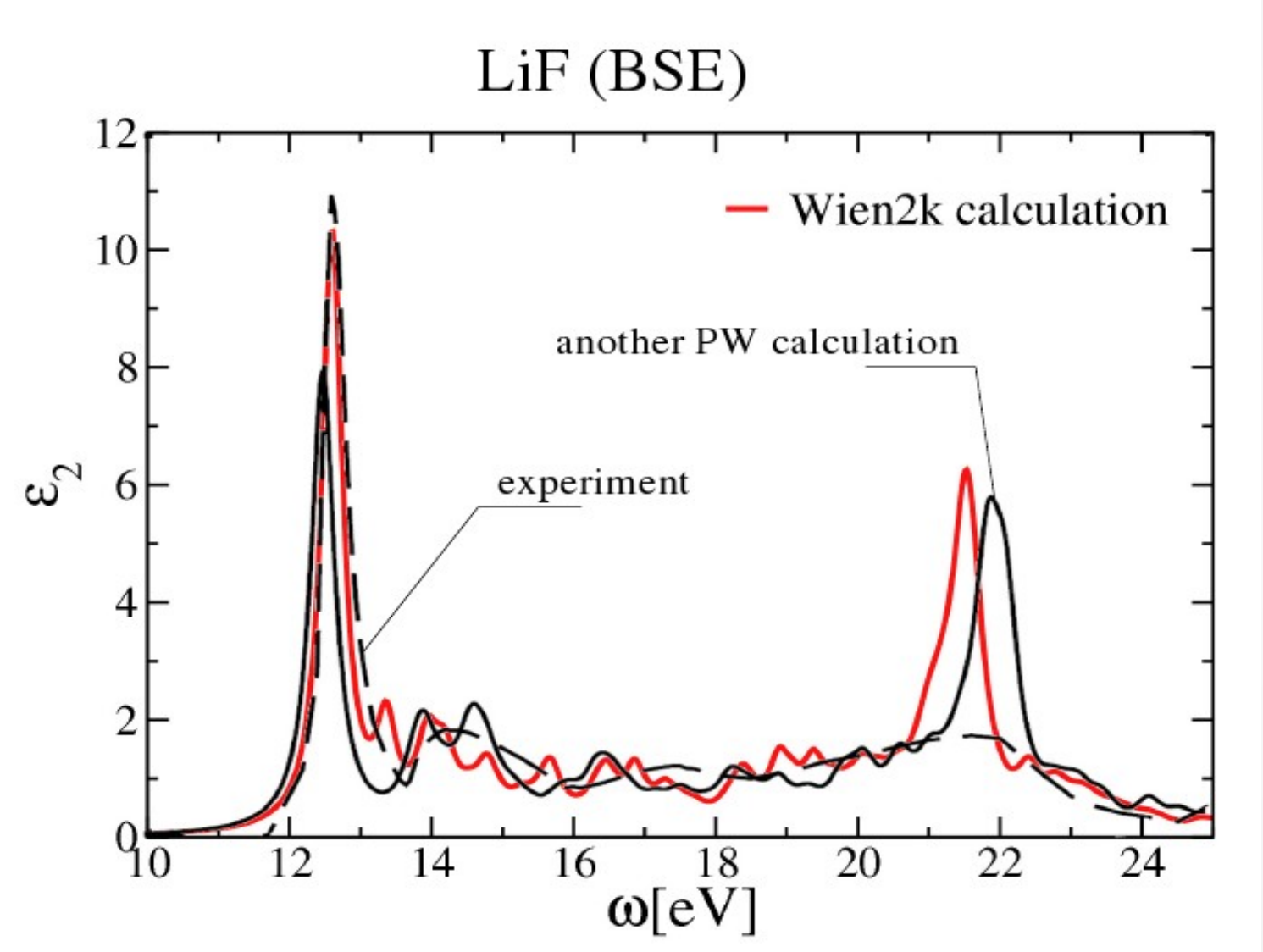
$$oscil.\,strength \sim \frac{1}{n^3}$$



"d" - dipole inactive

$\left| A^{\lambda}_{vck} \right|$ in BZ plotted for "s", "p" and "d" excitons

LiF absorption spectra

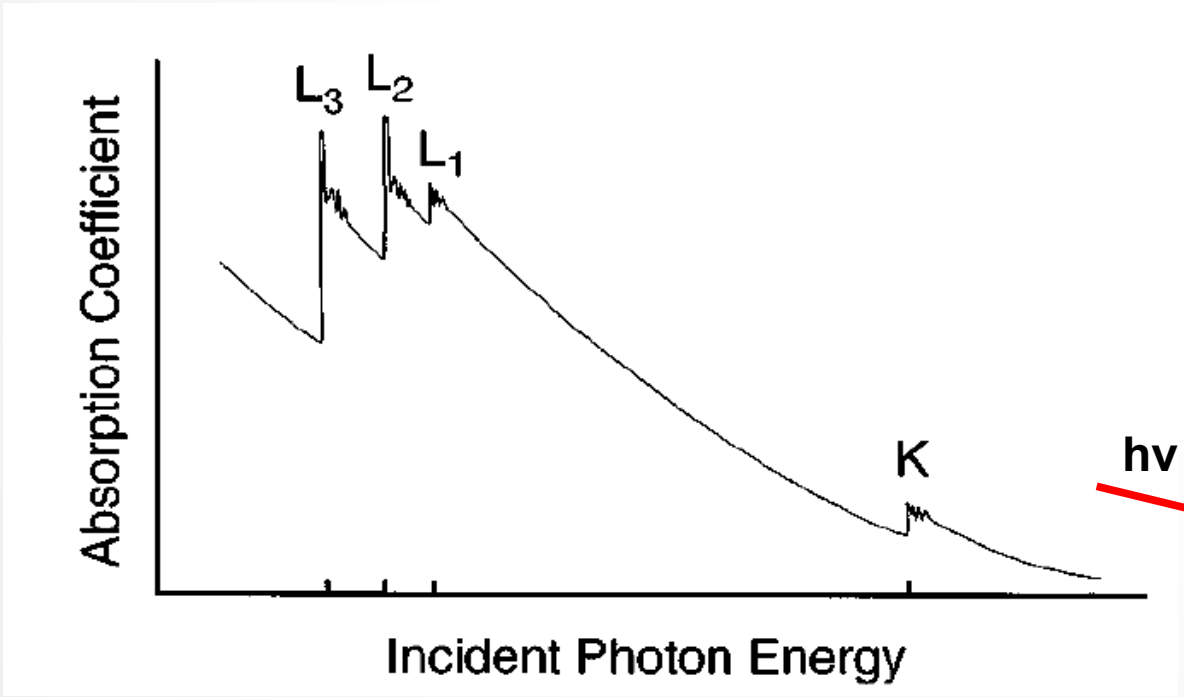


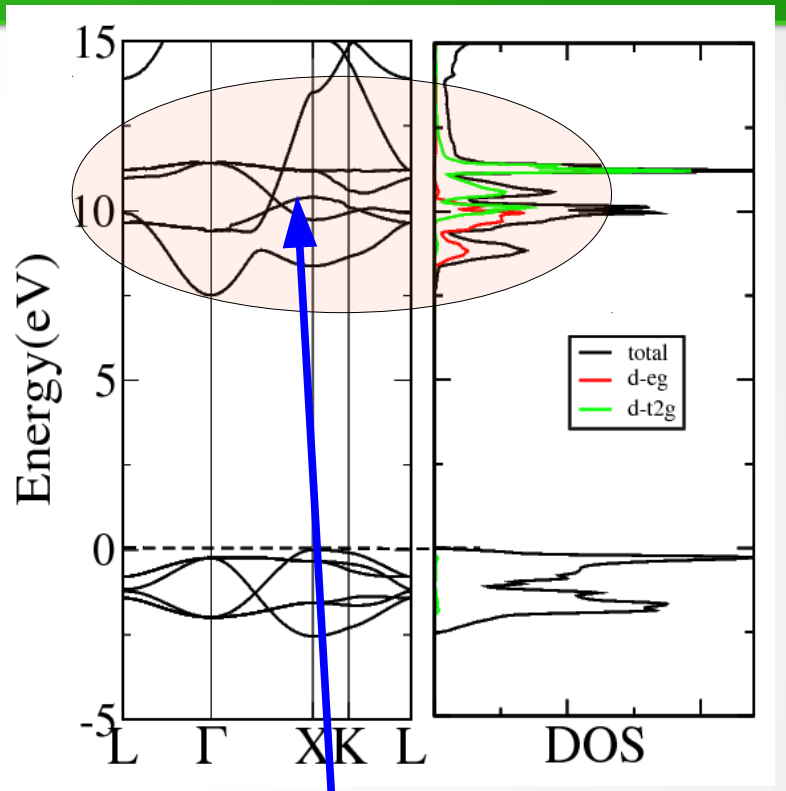
Core level spectroscopy

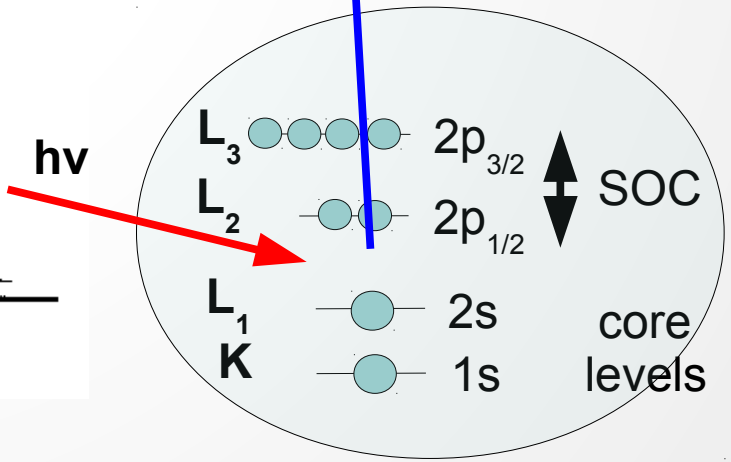
- absorption (XAS)
- emission (XES)
- core-hole

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)

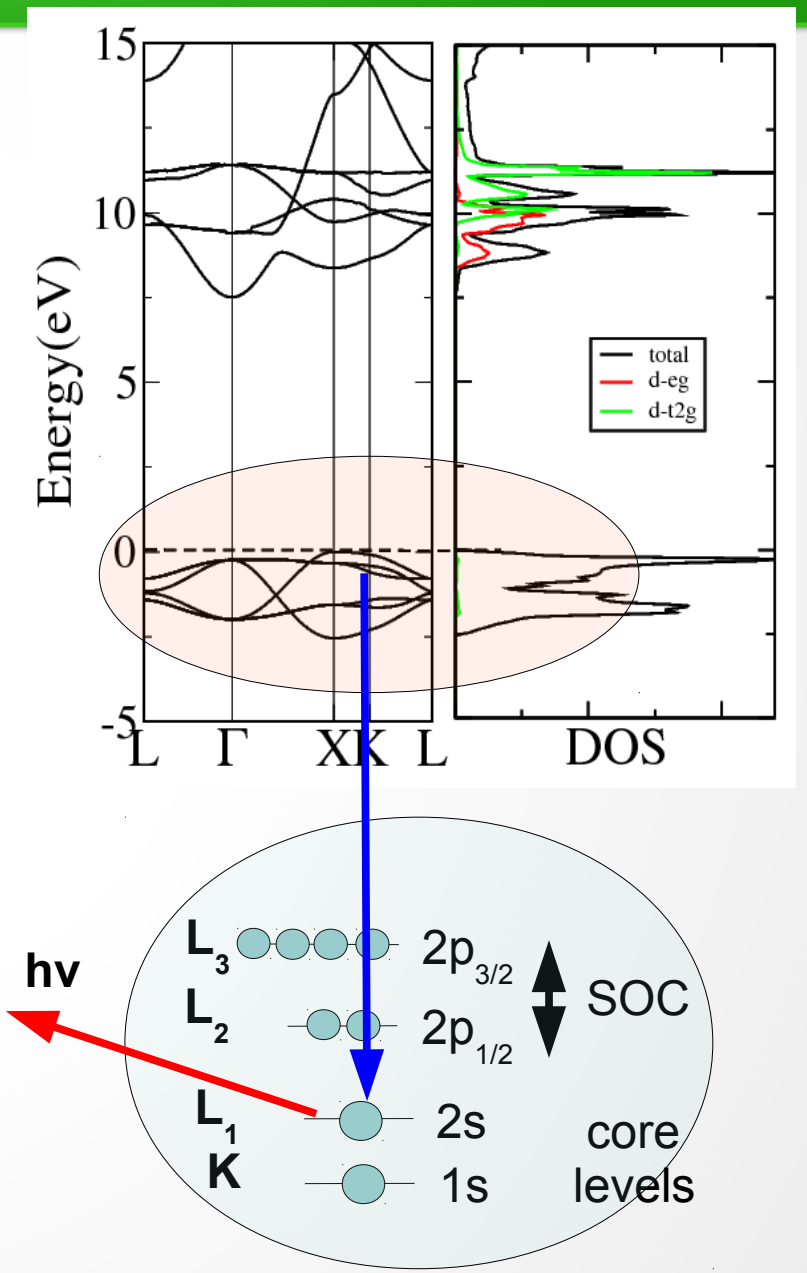






Core level spectroscopy (XES)

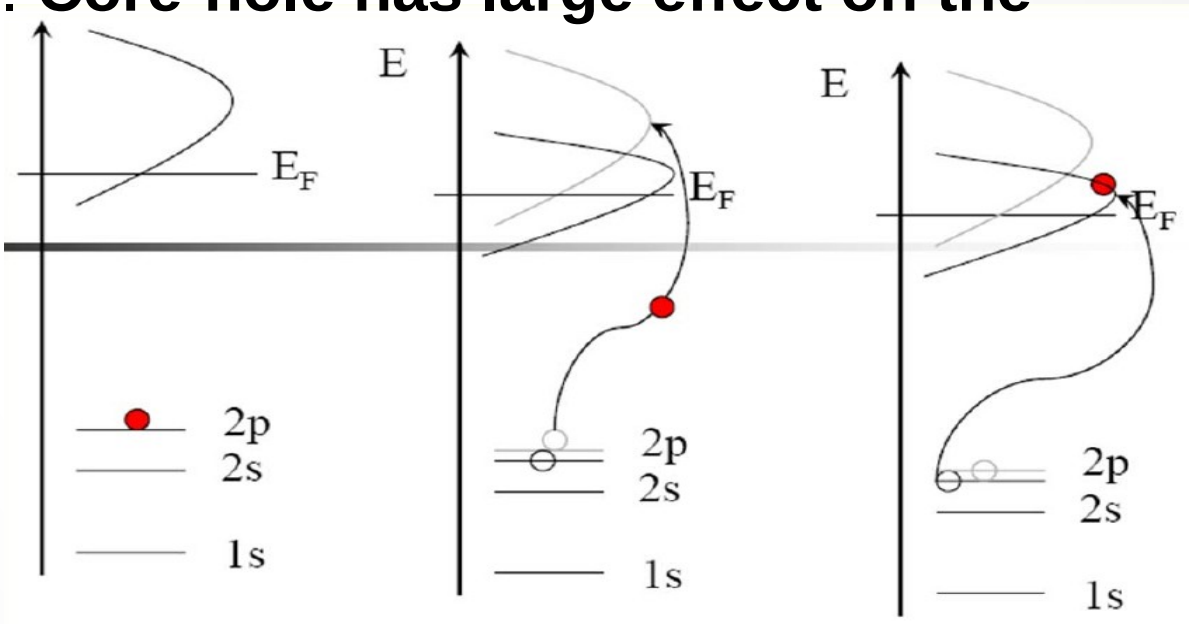
- X-ray emission (XES)
  - Knock out core electron, valence electron fills core level and *hv* is emitted



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 ?)
- **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)

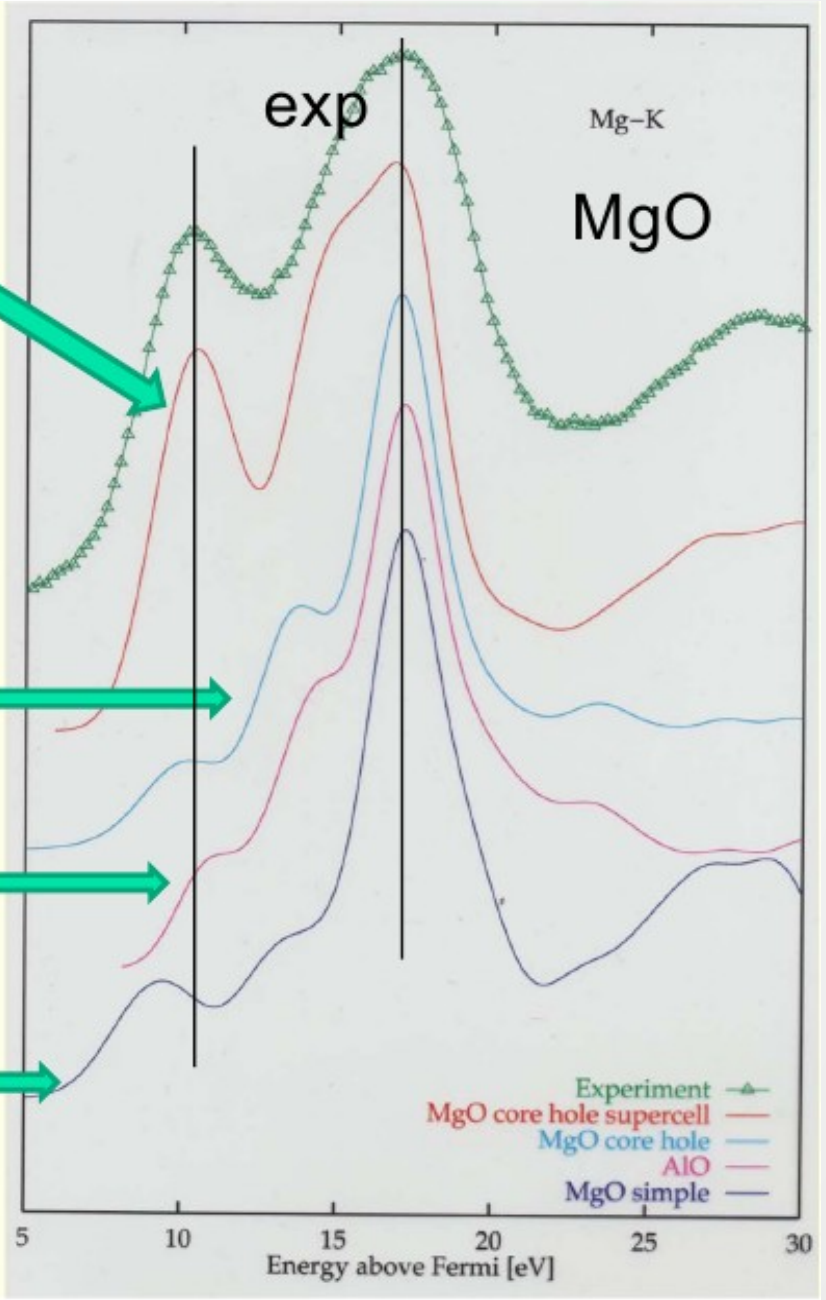
XAS, Mg K-edge in MgO

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



XAS, XES in wien2k (xspec)

- 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

XAS, XES in wien2k (xspec)

- 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

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

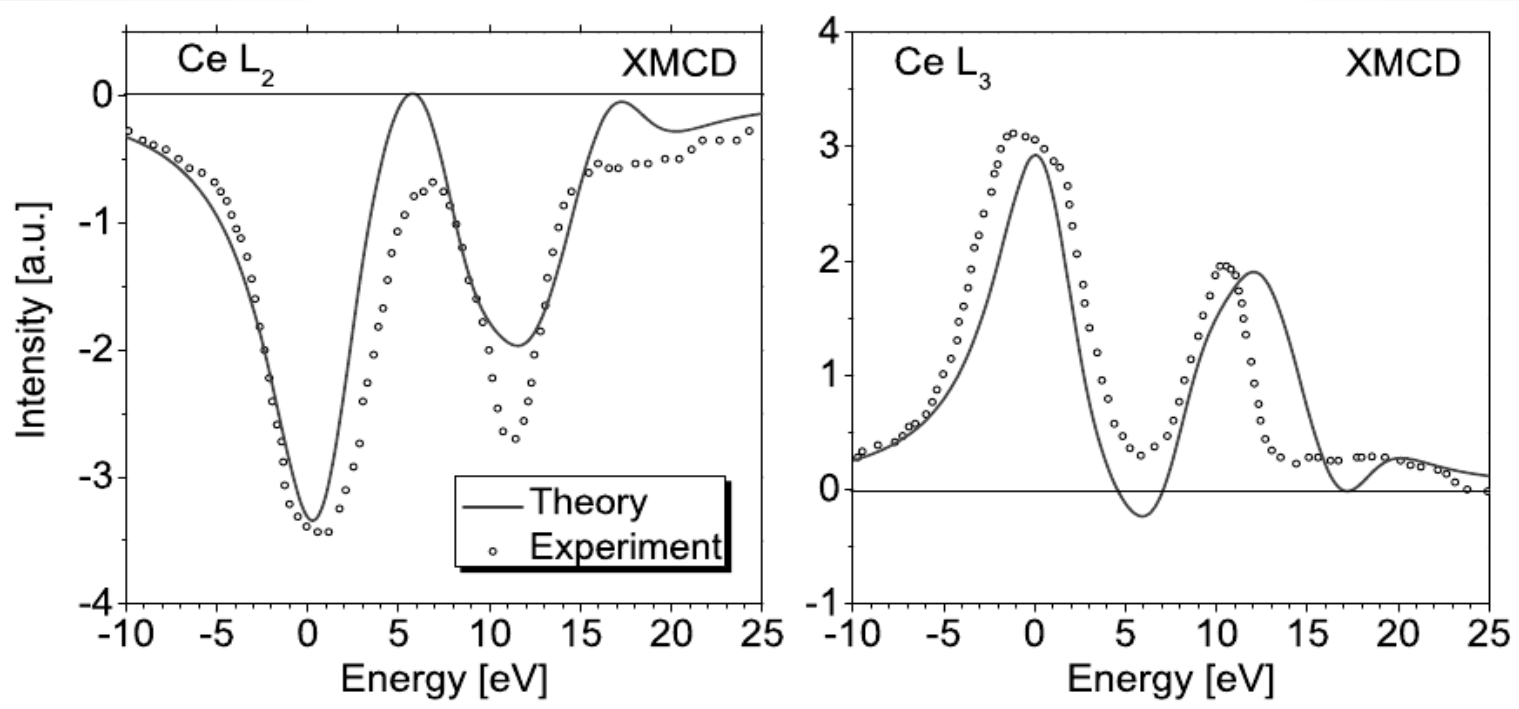
Core level spectroscopy (XMCD)

- 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)

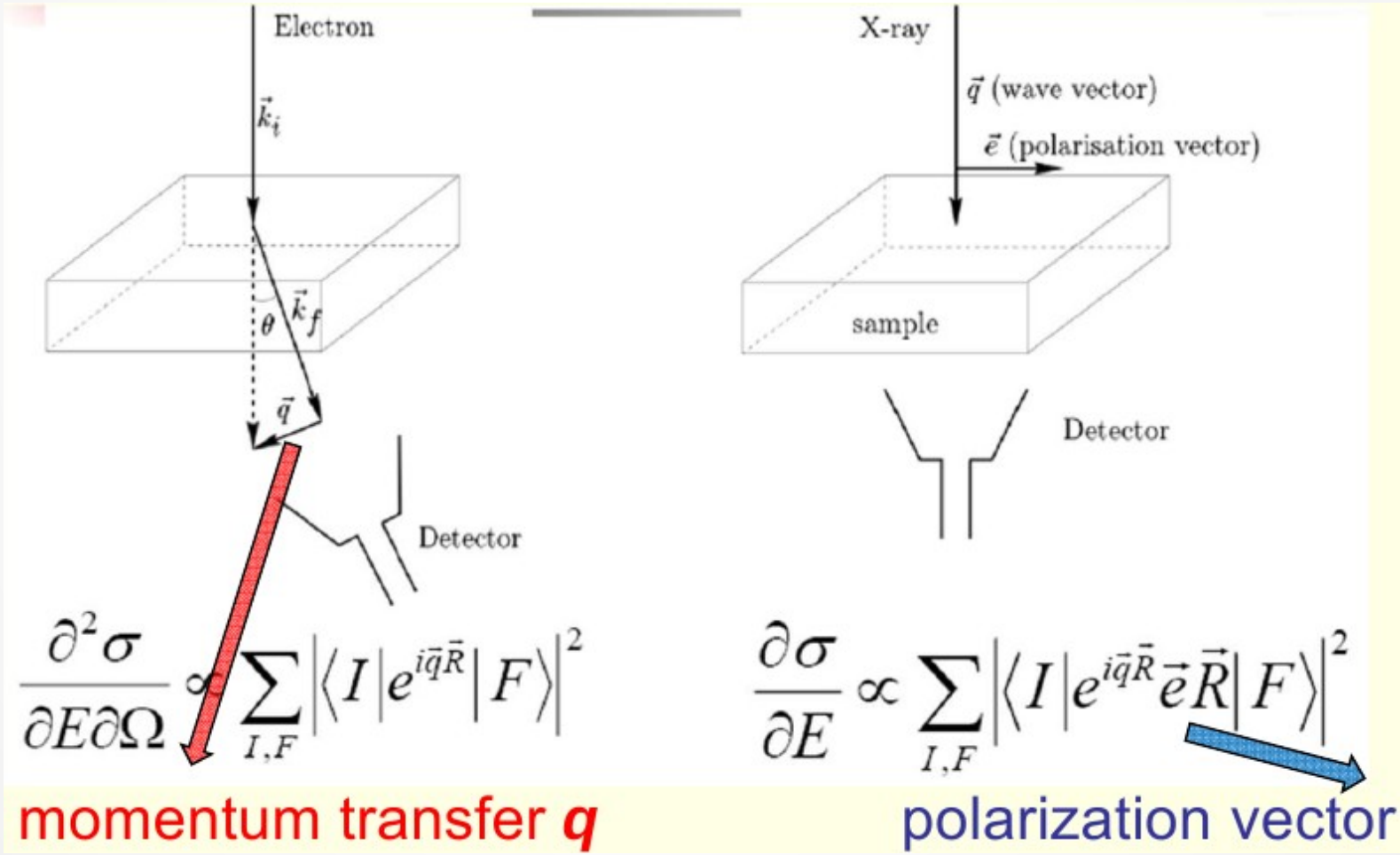
Core level spectroscopy (XMCD)

- 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 playes the same role as polarization vector in XAS
- ***telnes2*** program also handles non-dipole transitions and relativistic corrections

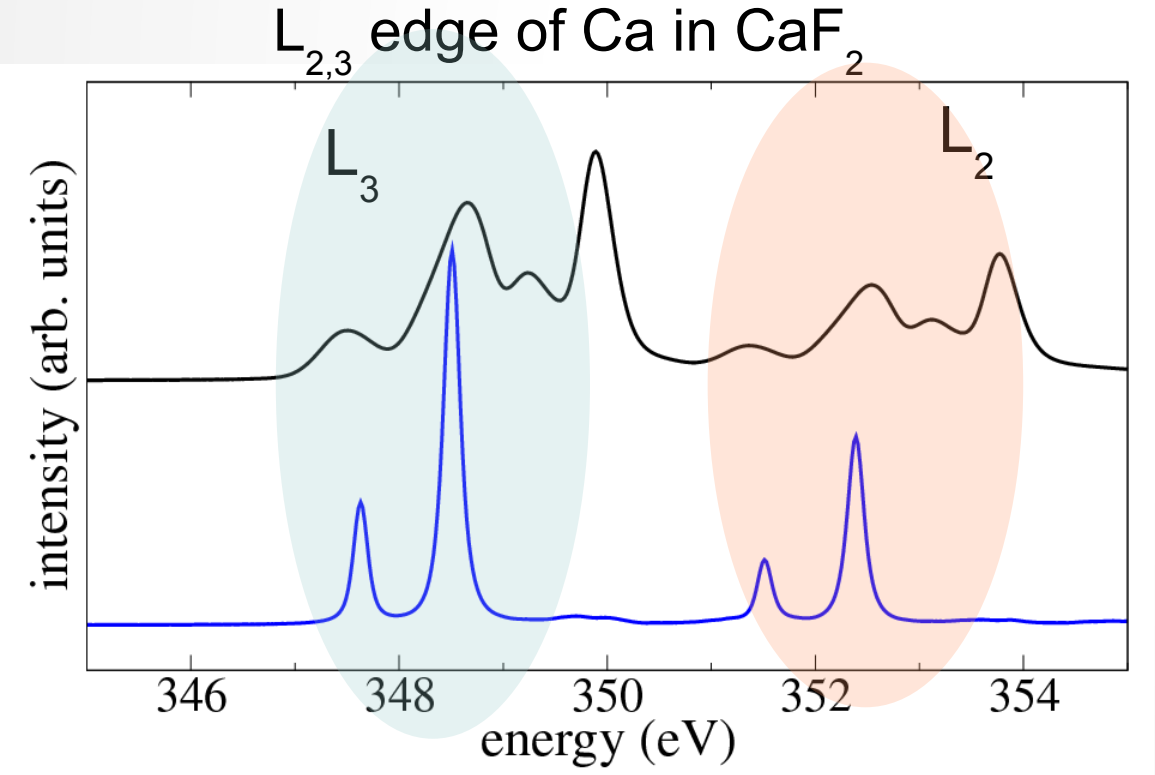
See details in users guide

When IPA fails

- in IPA X-ray absorption is proportional to the projected DOS of the conduction band

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

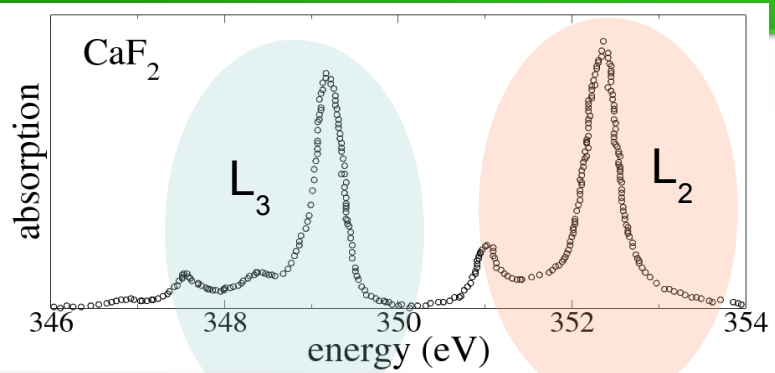
- branching ratio (L_2/L_3) is 1:2 (proportional to occupation of $2p_{1/2}$, $2p_{3/2}$)

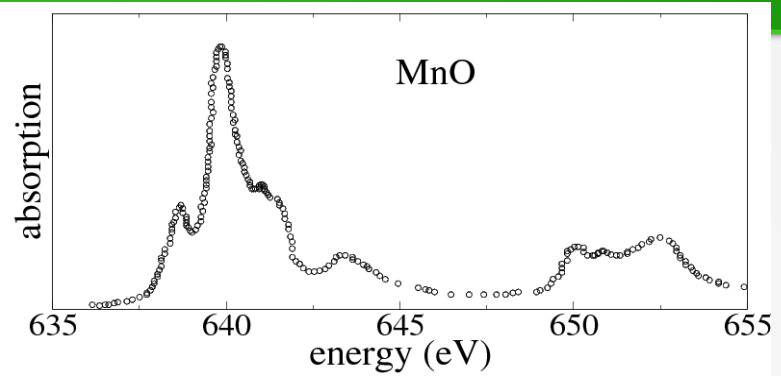


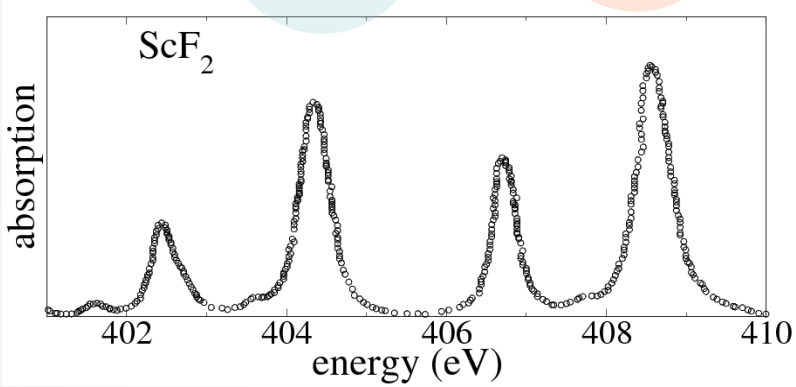
plain DFT

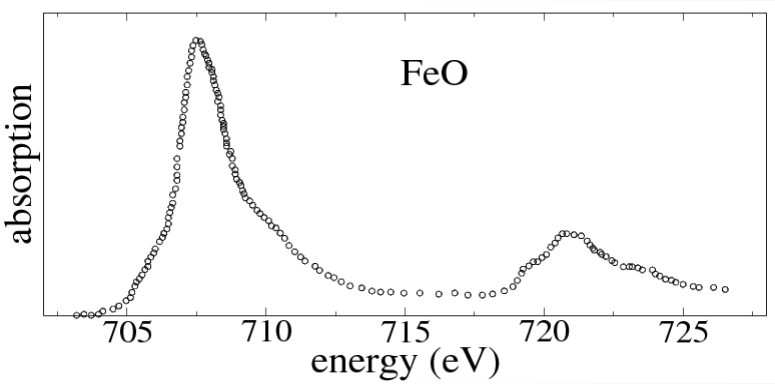
"core hole" DFT
(supercell with core hole on excited atom)

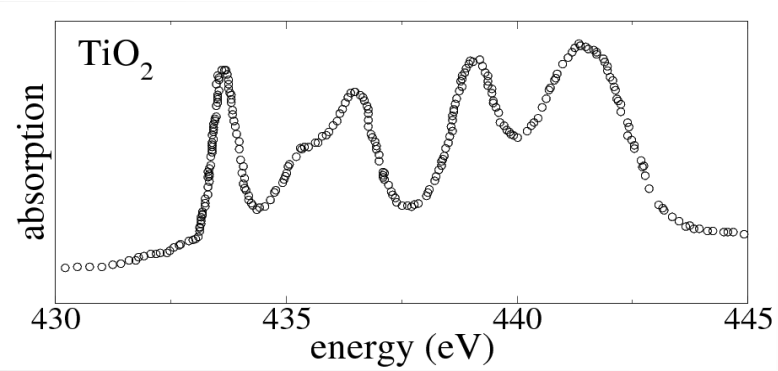
Measured L edges of 3d metals

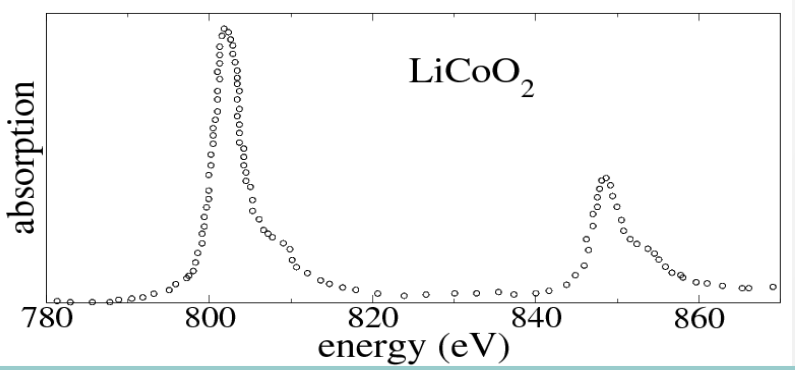






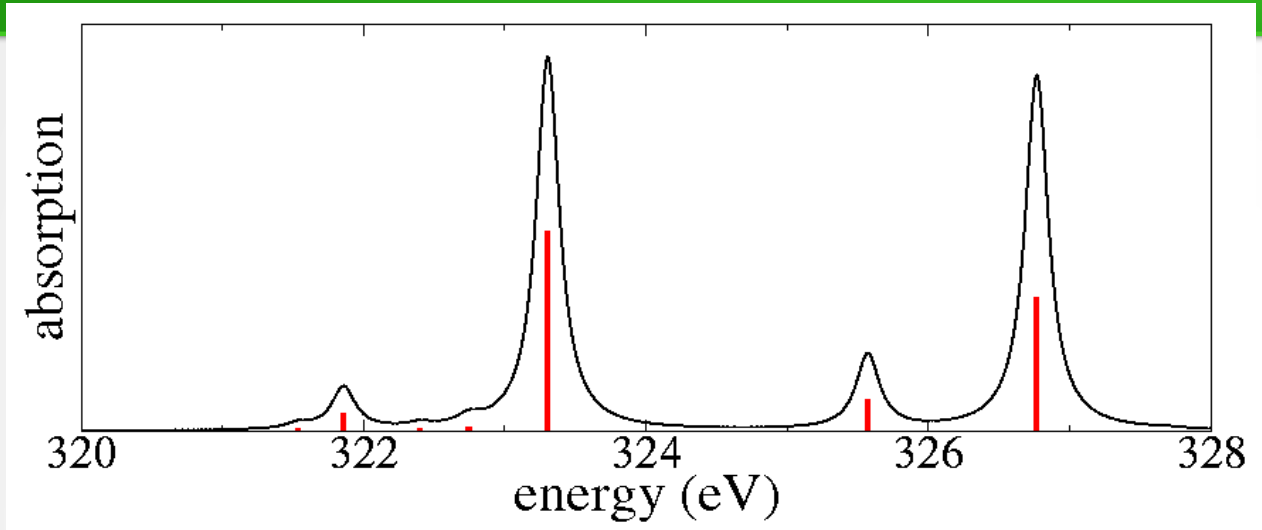




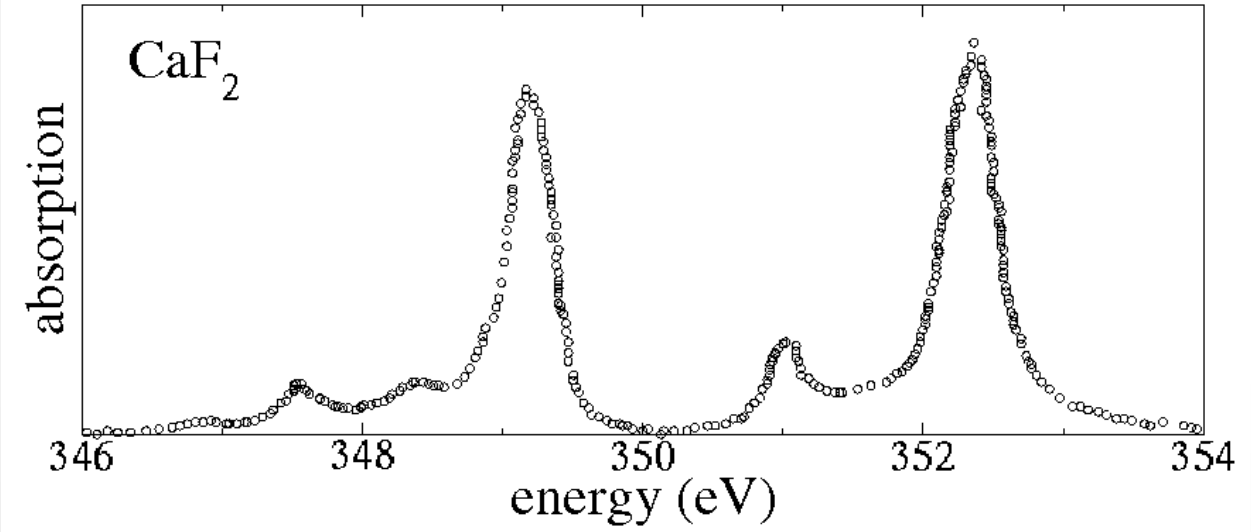


IPA can not give correct L_2/L_3 branching rations

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



transitions from $2p_{1/2}$ and $2p_{3/2}$ are included at the same time into the BSE Hamiltonian



experiment

- **Only coherent mixing of transitions from $2p_{1/2}$ and $2p_{3/2}$ results in proper branching ratio**