

# *Ab initio X-ray absorption simulation*

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ESRF Users Meeting, 8<sup>th</sup> February 2021

Own references related to this introduction on computational methods:

*X-Ray Absorption and X-ray Emission Spectroscopy : Theory and Applications*  
Edited by J. A. van Bokhoven and C. Lamberti,  
Wiley and sons (2016).  
ISBN : 978-1-118-84423-6.

and more specifically, chapter 4 :

*"Theory of X-ray Absorption Near Edge Structure"*  
Yves Joly and Stéphane Grenier.

About resonant diffraction:

*"Basics of Resonant Elastic X-ray Scattering theory"*  
S. Grenier and Y. Joly,  
*J. Phys. : Conference Series* **519**, 012001 (2014).

About X-ray Raman spectroscopy:

*"Full potential simulation of x-ray Raman scattering spectroscopy"*  
Y. Joly, C. Cavallari, S. A. Guda, C. J. Sahle  
*J. Chem. Theory Comput.* **13**, 2172-2177 (2017).

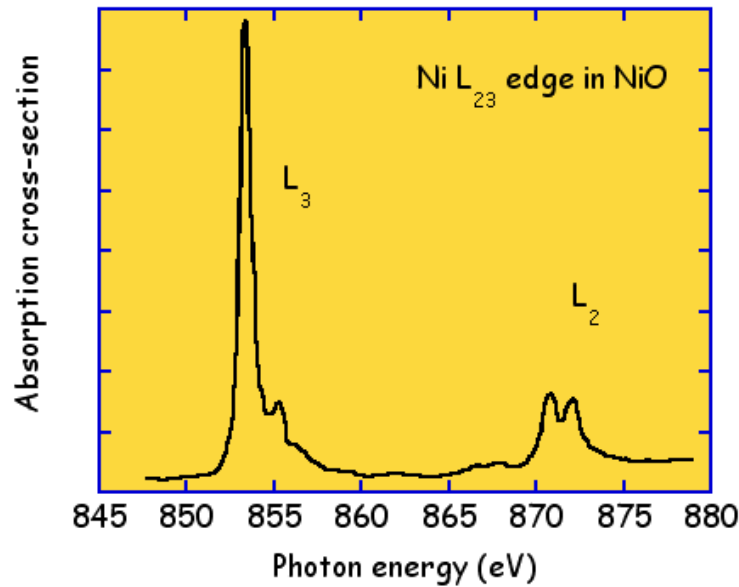
About Surface Resonant X-ray Diffraction:

*"Simulation of Surface Resonant X-ray Diffraction"*  
Y. Joly, et al.  
*J. Chem. Theory Comput.* DOI: 10.1021/acs.jctc.7b01032 (2017).

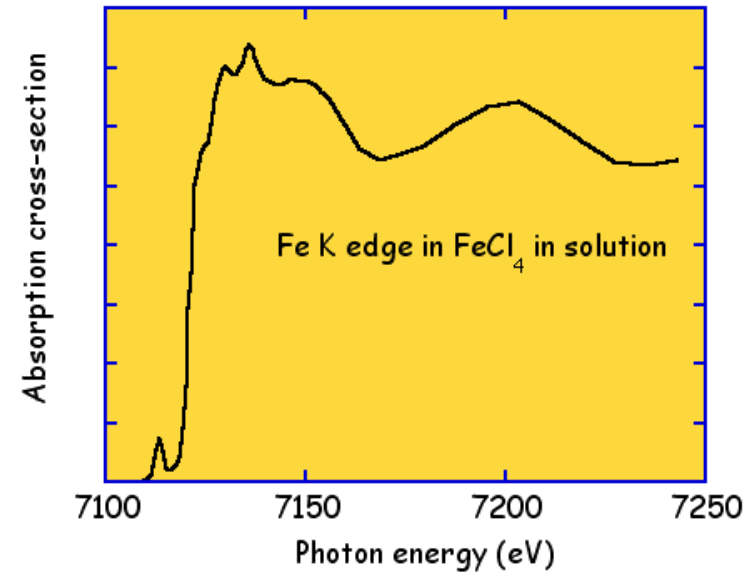
In 2021 (?) → *International Tables for Crystallography, Volume I on XAS*

# I- Mono and multi-electronic approaches

Localized final states



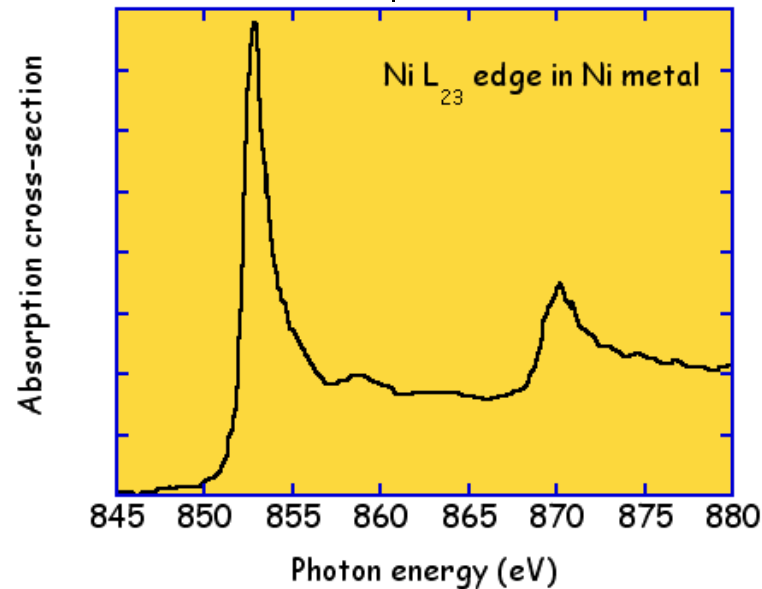
Non localized final states



Excited state theory

→ multiplet

A. Scherz, PhD  
Thesis, Berlin



Ground state theory

→ DFT

O. Proux *et al.*  
FAME, ESRF

Intermediate  
situation ...

In principal:

Multiplet ligand field theory:

multi-electronic but mono-atomic

→  $L_{23}$  edges of 3d elements

→  $M_{45}$  edges of rare earth

DFT:

Multi-atomic but ground state theory (mono-electronic)

→ K,  $L_1$  edges

→  $L_{23}$  edges of heavy elements

Improvements in progress:

Bethe Salpeter Equation (Shirley...)

Time-Dependent DFT (Schwitalla...)

Multiplet ligand field theory using Wannier orbitals (Haverkort...)

Multichannel multiple scattering theory (Krüger and Natoli)

Dynamic mean field theory (Sipr...)

Quantum chemistry techniques, Configuration interaction...

## II- Mono-electronic XANES formula

Multi-electronic system  $\rightarrow$  Transition from  $I$  to  $F$

$F$  and  $I$ : multi-electronic final and initial states

Absorption cross section:

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \sum_F |\langle F | o | I \rangle|^2 \delta(\hbar\omega - E_F + E_I)$$

$$o = \underbrace{\boldsymbol{\varepsilon} \cdot \mathbf{r}}_{\text{Dipole}} + \frac{i}{2} \underbrace{\boldsymbol{\varepsilon} \cdot \mathbf{r} \mathbf{k} \cdot \mathbf{r}}_{\text{Quadrupole}}$$

$\Delta\ell = \pm 1$        $\Delta\ell = (0), \pm 2$

Ground state ( $\approx$  mono-electronic) approximation:

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega S_0^2 \sum_{fg} |\langle f | o | g \rangle|^2 \delta(\hbar\omega - E_f + E_g + \Delta E_{scr})$$

Relaxation effect of the "other" electrons

$f$  is by default calculated in an excited state:

- with a core-hole
- an extra electron on the first non occupied level

## Core-hole and photoelectron time life effects

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \sum_{fg} |\langle f|o|g\rangle|^2 \delta(\hbar\omega - E_f + E_g) \times \text{Lorentzian convolution}$$
$$\frac{1}{2\pi} \frac{\Gamma}{(E - E_f)^2 + (\frac{\Gamma}{2})^2}$$
$$\Gamma = \Gamma_H + \Gamma_e(E)$$

$\Gamma_H$ : core-hole width

Classical experiment: known tabulated values

Experiment using High resolution fluorescence mode:  
Reduced value

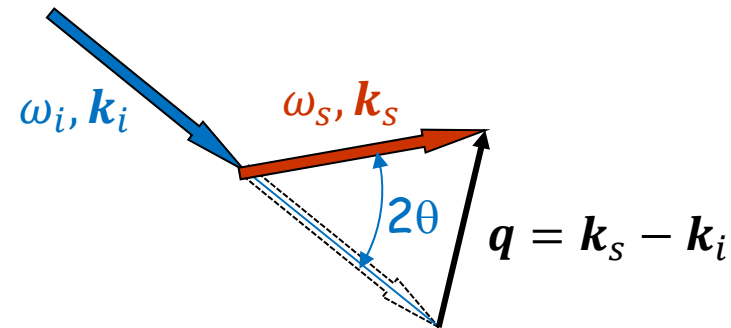
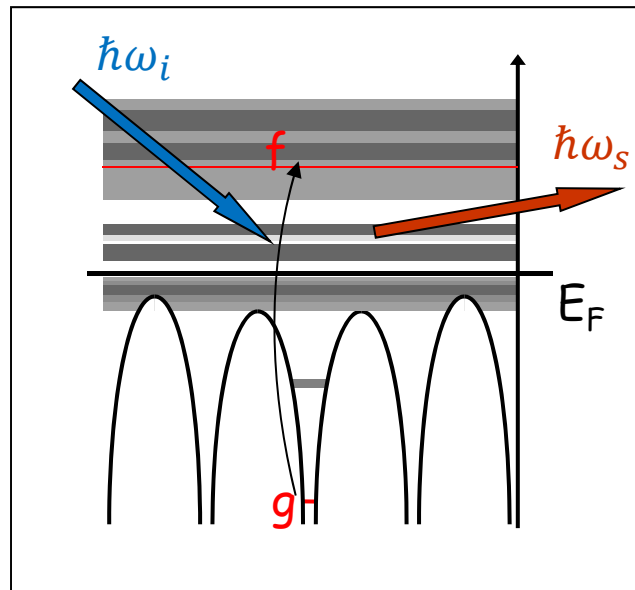
$\Gamma_e$ : photoelectron state width

Due to all possible inelastic process,  
Increase with energy

# III- Related spectroscopies

## X-ray Raman Scattering (XRS)

or Non Resonant X-ray Inelastic Scattering (or EELS on Trans. Elec. Micr.)



Inelastic scattering technique  
→ energy loss  $\approx$  absorption edge energy

$$\hbar\omega = \hbar\omega_s - \hbar\omega_i = E_f - E_g$$

First experiments by Suzuki *et al.* (end of 60<sup>th</sup>)

Main interest → access to low energy edges using hard X-ray  
*in situ, operando, extreme conditions...*

Drawback → low signal

But new synchrotron generation, new spectrometers

→ new XRS beamlines as ID20 at ESRF, EMA at SIRIUS...

Cross section:

$$\frac{d^2\sigma}{d\Omega_s d\hbar\omega_s} = r_0^2 \frac{\omega_s}{\omega_i} |\varepsilon_s \cdot \varepsilon_i|^2 S(\mathbf{q}, \omega)$$

Dynamic structure factor:

$$S(\mathbf{q}, \omega) = \sum_{f,g} |\langle f | e^{-i\mathbf{q}\cdot\mathbf{r}} | g \rangle|^2 \delta(\hbar\omega - (E_f - E_g))$$

First approximation :  $|\langle f | e^{-i\mathbf{q}\cdot\mathbf{r}} | g \rangle|^2 \cong |\langle f | 1 - i\mathbf{q}\cdot\mathbf{r} | g \rangle|^2 \cong |\langle f | \mathbf{q}\cdot\mathbf{r} | g \rangle|^2$

Same than (dipole) XANES, with  $\varepsilon \rightarrow \mathbf{q}$

Exact expansion:  $e^{-i\mathbf{q}\cdot\mathbf{r}} = 4\pi \sum_{\ell m} (-i)^\ell j_\ell(qr) Y_\ell^{m*}(\hat{r}) Y_\ell^m(\hat{q})$   
Bessel function



$$S(\mathbf{q}, \omega) = \sum_{f,g} |\langle f | j_0(qr) - 4\pi i j_1(qr) \sum_m Y_1^{m*}(\hat{r}) Y_1^m(\hat{q}) + \dots | g \rangle|^2 \delta(\hbar\omega - (E_f - E_g))$$

$$\frac{\sin qr}{qr} \quad -\frac{\cos qr}{qr} + \frac{\sin qr}{(qr)^2}$$

$$\approx 1 - \frac{1}{6}(qr)^2 \quad \approx \frac{1}{3}qr$$

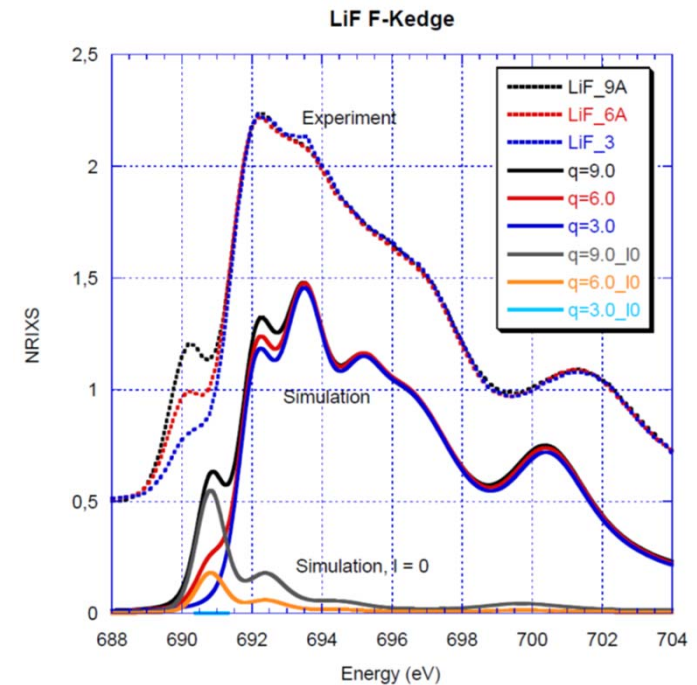
Monopole  
 $\Delta\ell = 0$

Dipole  
 $\Delta\ell = \pm 1$

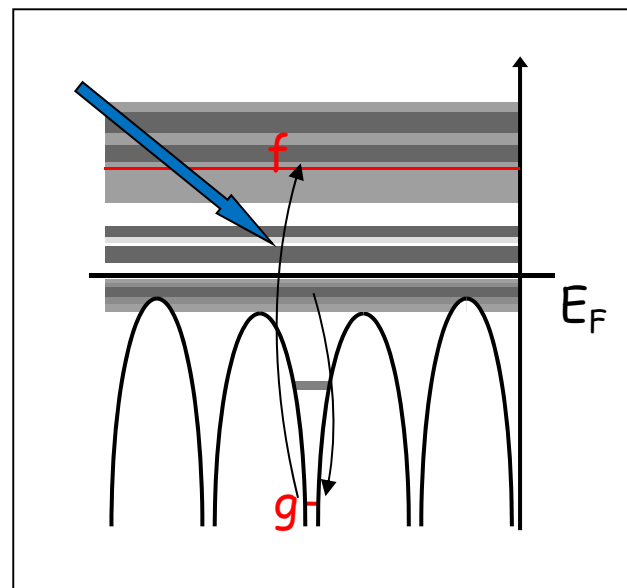
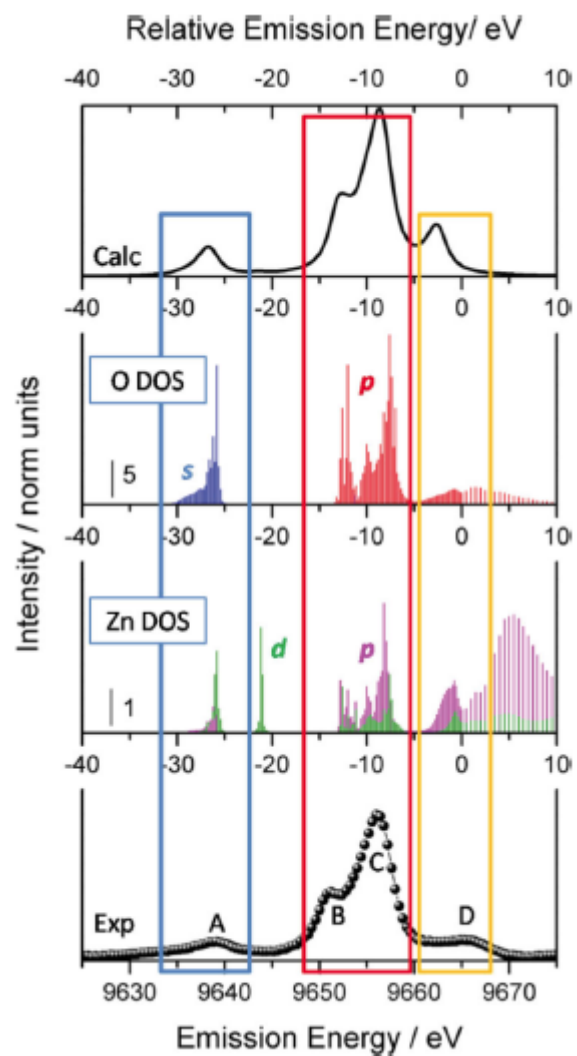
Exp Ch. Sahle  
 ID20, ESRF

→ Dependence on  $q$  (scat. angle)

→ Probe of the different  $\ell$

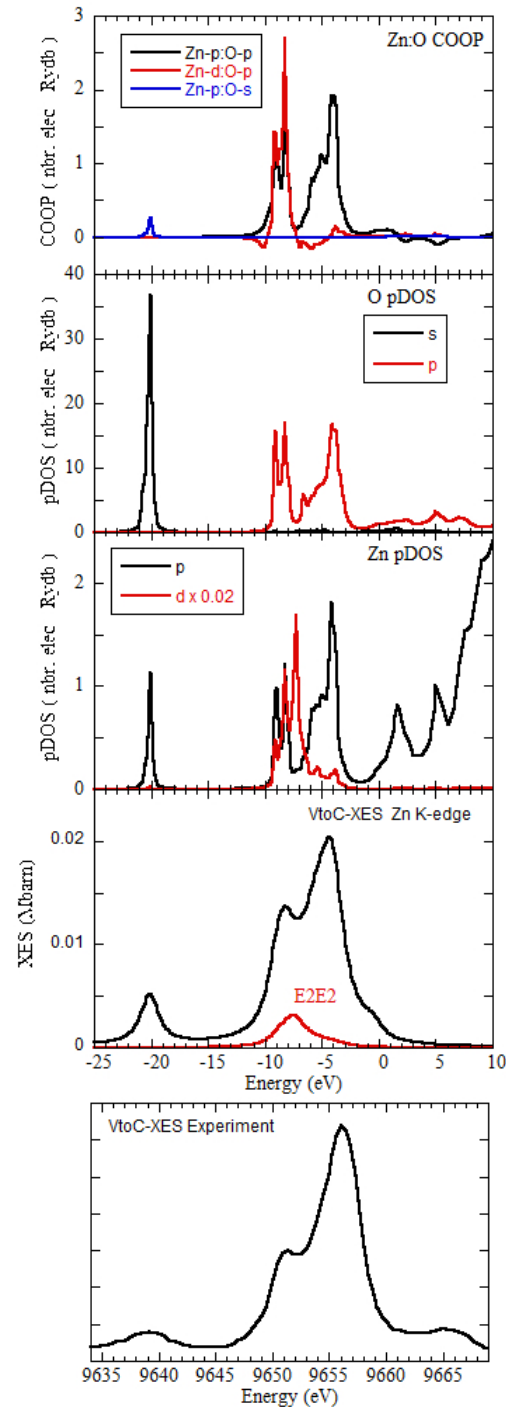


# VtoC-XES

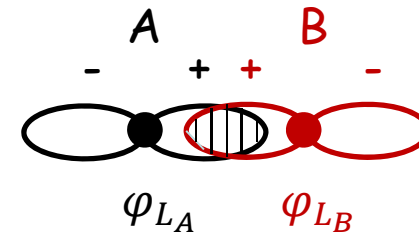


E. Gallo & P. Glazel  
Adv. Mater 2014  
DOI: 10.1002/adma.201304994

Simulation:  
 R = 7 Å  
 SCF  
 Ground state



## COOP Crystal Orbital Overlap Population



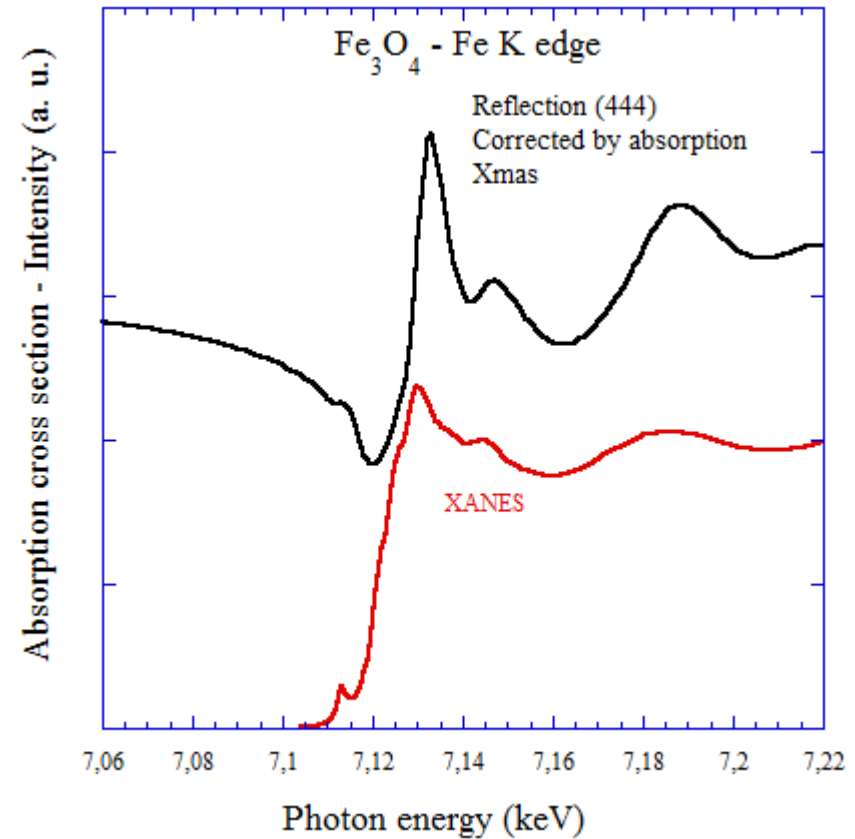
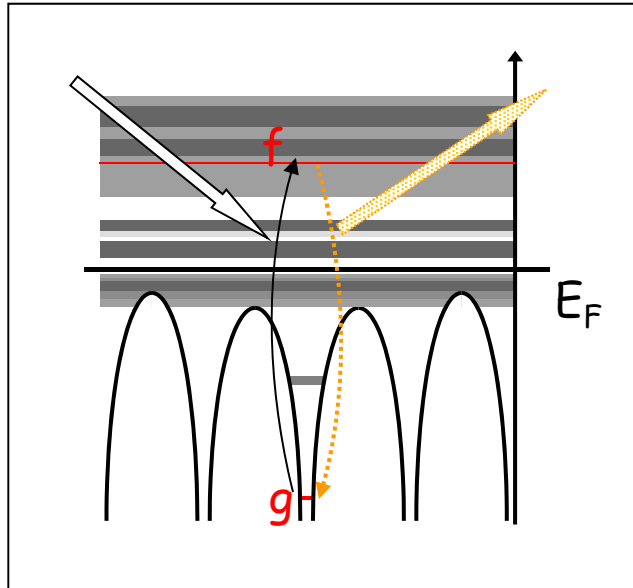
$$C_{L_A L_B}(E) = \sum_f a_{L_A}^f(E) a_{L_B}^f(E) \times \int \varphi_{L_A}(\mathbf{r}, E) \varphi_{L_B}(\mathbf{r}, E) d\mathbf{r}$$

Give the covalency  
 bonding > 0  
 anti-bonding < 0

Dronskowski *et al.* J. Phys Chem 97, 6272 (1993)  
 Canadell *et al.* Orbital approach of the electronic structure of solids, Oxford University Press (2012)

# Resonant X-ray Diffraction (RXD)

or REXS or RXS or DAFS or DANES



$$f'(\omega) - if''(\omega) = m\omega^2 \sum_{fg} \frac{\langle g|o_s^*|f\rangle\langle f|o_i|g\rangle}{\hbar\omega - (E_f - E_g) + i\frac{\Gamma}{2}}$$

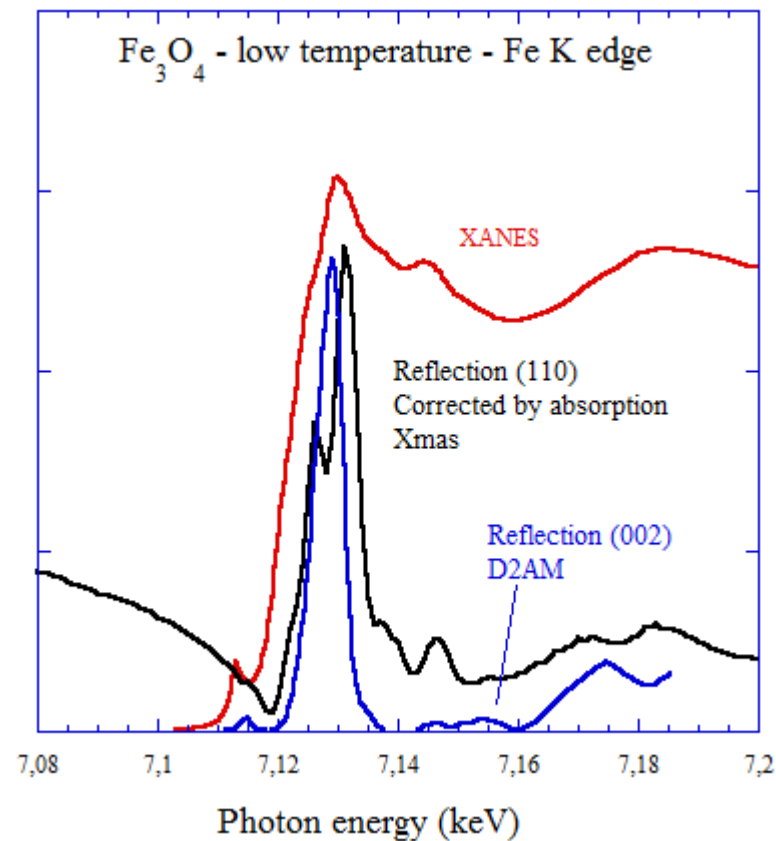
## Summation over the atoms

Bragg factor + Thomson (non resonant) term :

$$I_Q(\omega) = \frac{K}{V^2} \sum_{atoms} e^{-iQ \cdot R_a} (f_{0a} + if_{ma} + f'_a(\omega) - if''_a(\omega))$$

Magnetic non resonant term

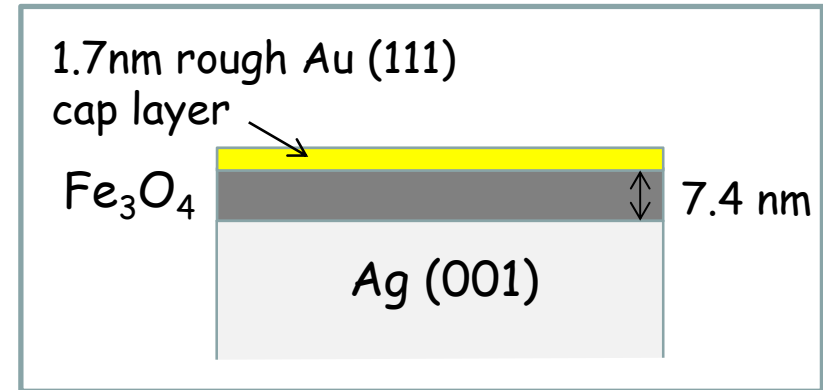
Resonant term



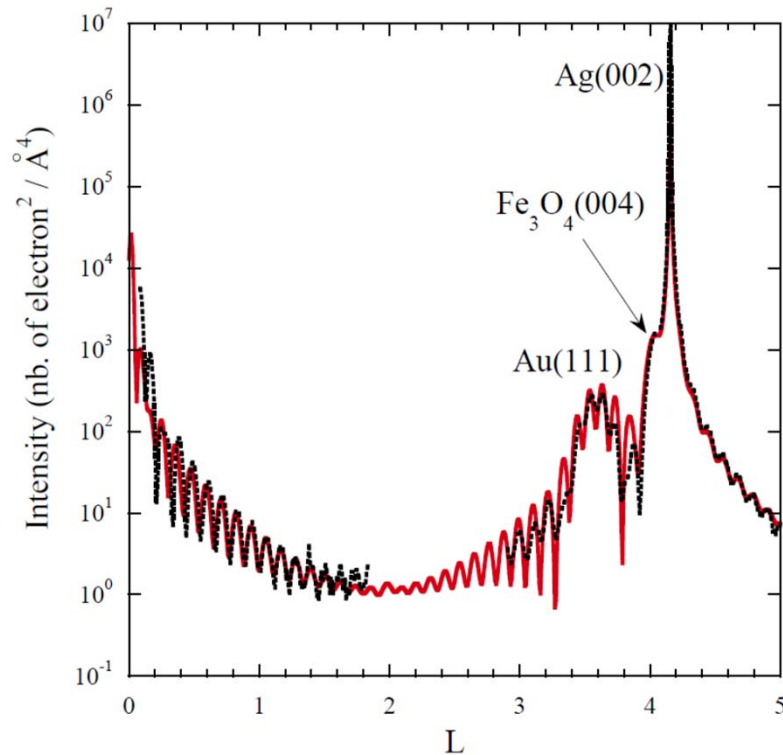
# Surface Resonant X-ray Diffraction (SRXD)

## Au/Fe<sub>3</sub>O<sub>4</sub>/Ag(001)

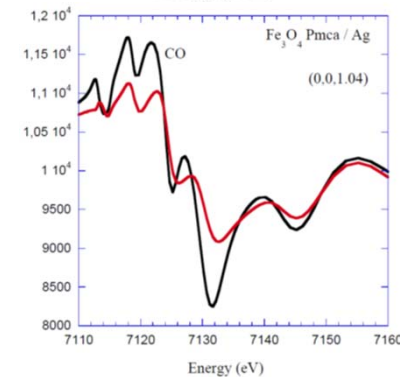
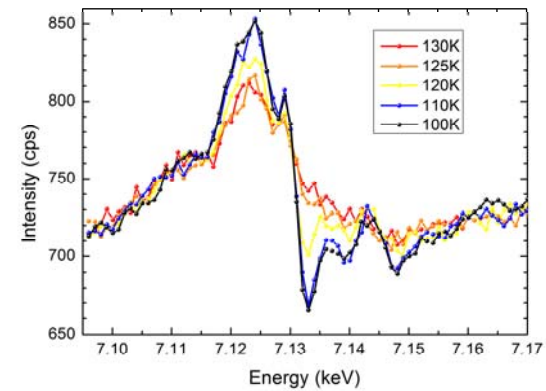
Entangled contributions of layer/substrate/cap layer  
Sensitivity to the nature of the first atomic layers



$$|F_{\text{Fe}_3\text{O}_4 \text{ film}}(Q,E) + F_{\text{Ag substrate}}(Q) + F_{\text{Au cap layer}}(Q)|^2$$



## Spectra at L = 1



## IV- Final states calculation (DFT)

---

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \sum_{fg} |\langle f | \mathbf{o} | g \rangle|^2 \delta(\hbar\omega - E_f + E_g)$$

$$\mathbf{o} = \boldsymbol{\varepsilon} \cdot \mathbf{r} + \frac{i}{2} \boldsymbol{\varepsilon} \cdot \mathbf{r} \mathbf{k} \cdot \mathbf{r}$$

First theories :

Dan Dill and J. L. Dehmer (1974)

P. A. Lee and J. Pendry (1975)

First calculations :

C. R. Natoli (1980)

L. F. Mattheiss and R. E. Dietz (1980)

The final states are calculated using different techniques :

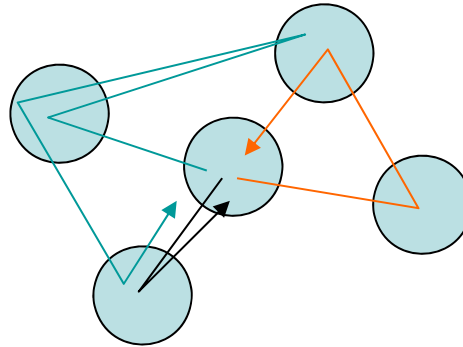
- the multiple scattering theory
- the finite difference method
- other methods

In a cluster approach

Using the 3D periodicity

With or without self consistency

# The multiple scattering theory (MST)



The problem is not spherical

We have to fill a big matrix with the scattering atomic amplitudes of each atom and the propagation function from one atom to another

Multiple scattering amplitude

$$\tau_{LL'}^{aa} = \left[ \frac{1}{1 - TH} T \right]_{LL'}^{aa}$$

Matrix containing the atomic scattering amplitudes

Matrix containing the geometrical terms corresponding to the scattering from any site "a" of the harmonic  $L=(\ell,m)$  towards any site "b" with the harmonic  $L'$



When no spin-orbit:

Wave function in the atom:  $\varphi_f(\mathbf{r}) = \sum_{\ell m} a_{\ell m}^f(E_f) b_{\ell}(r, E_f) Y_{\ell}^m(\hat{r}) \chi_{\sigma_f}$

From the optical theorem:  $\sum_f a_{\ell m}^f a_{\ell' m'}^{f*} = -\mathcal{J}(\tau_{\ell m}^{\ell' m'})$

$$\sigma(\omega) = -4\pi^2 \alpha \hbar \omega \sum_g \sum_{\ell m \ell' m'} \mathcal{J}(\langle g | o^* | b_{\ell} Y_{\ell}^m \rangle \tau_{\ell m}^{\ell' m'} \langle b_{\ell'} Y_{\ell'}^{m'} | o | g \rangle)$$

Green's function

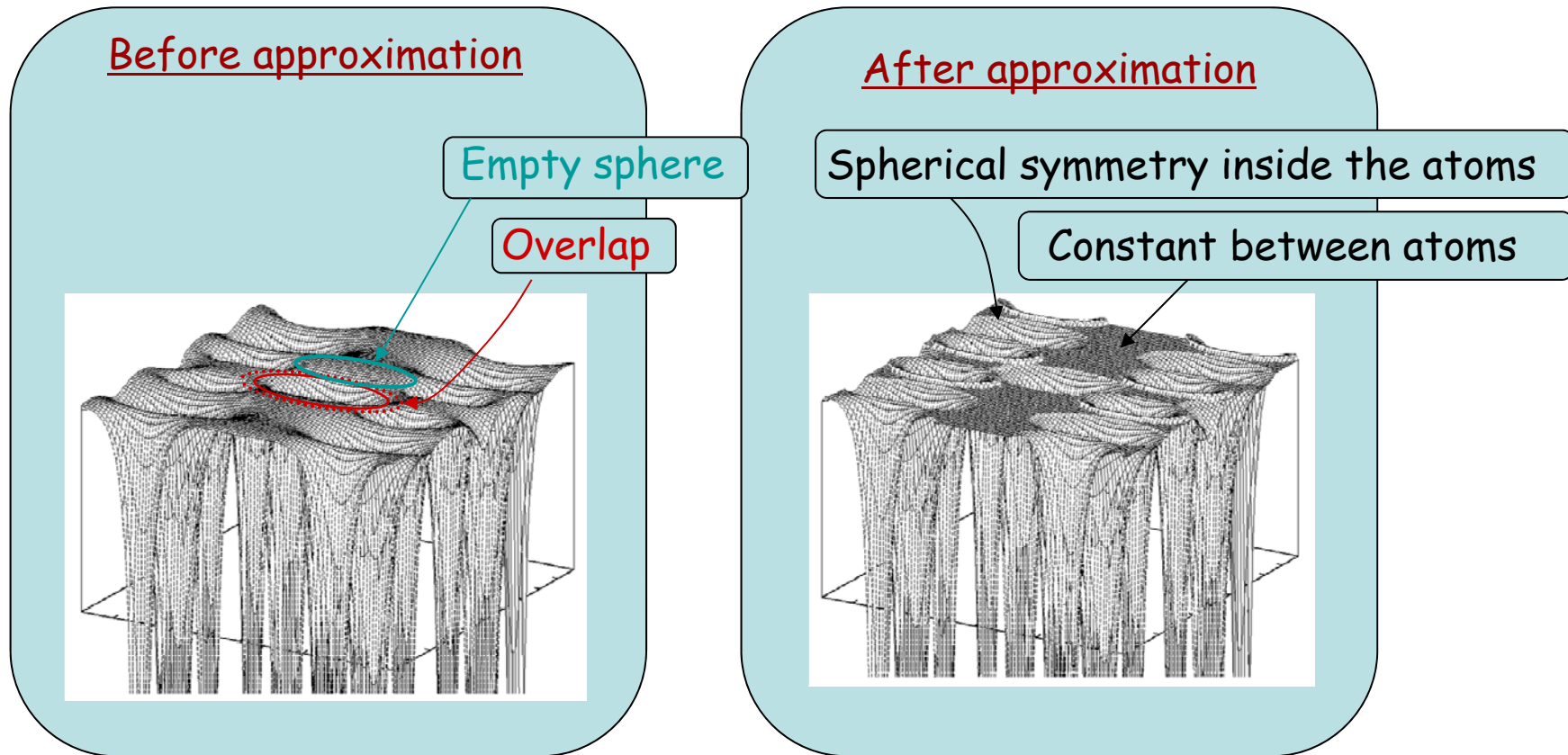


Relatively fast, but (most often) uses MT potential

MST is used by Continuum, Feff, MXAN, FDMNES...

The muffin-tin approximation → the MT of the LMTO program

Most often used in the multiple scattering theory



With the muffin-tin, there are always 2 parameters : overlap and interstitial constant

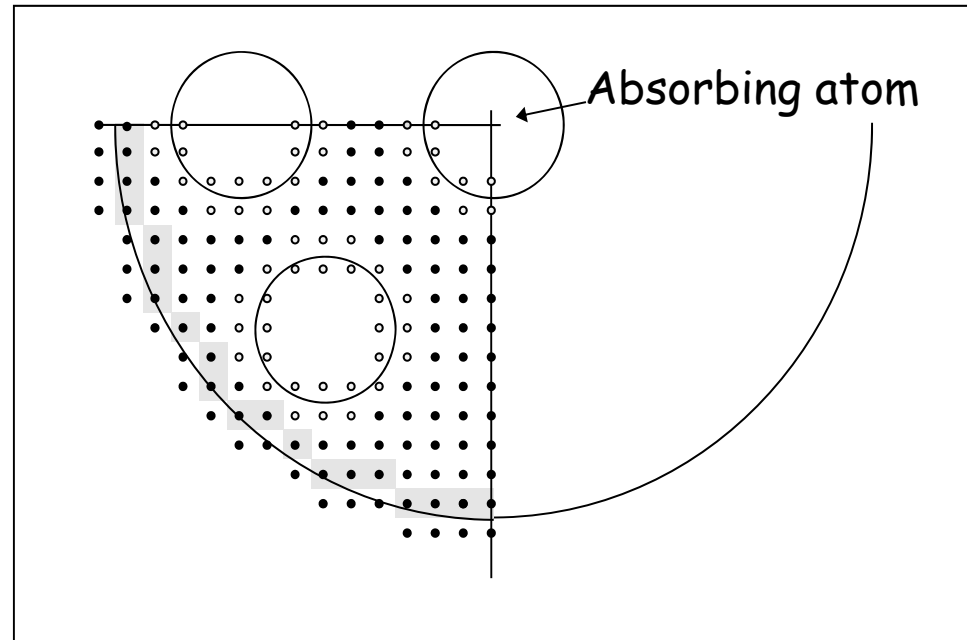
# The Finite Difference Method

Discretization of the Schrödinger equation on a grid of points

$$\frac{\partial^2 \varphi_f(x)}{\partial x^2} = \frac{\varphi_f(x+h) + \varphi_f(x-h) - 2\varphi_f(x)}{h^2}$$

$$\left( \frac{6}{h^2} + V_i - E \right) \varphi_{f,i} - \sum_j \frac{1}{h^2} \varphi_{f,j} = 0$$

+ continuity at area borders



Big matrix, unknowns:  $\varphi_{f,i}$

Interest : free potential shape

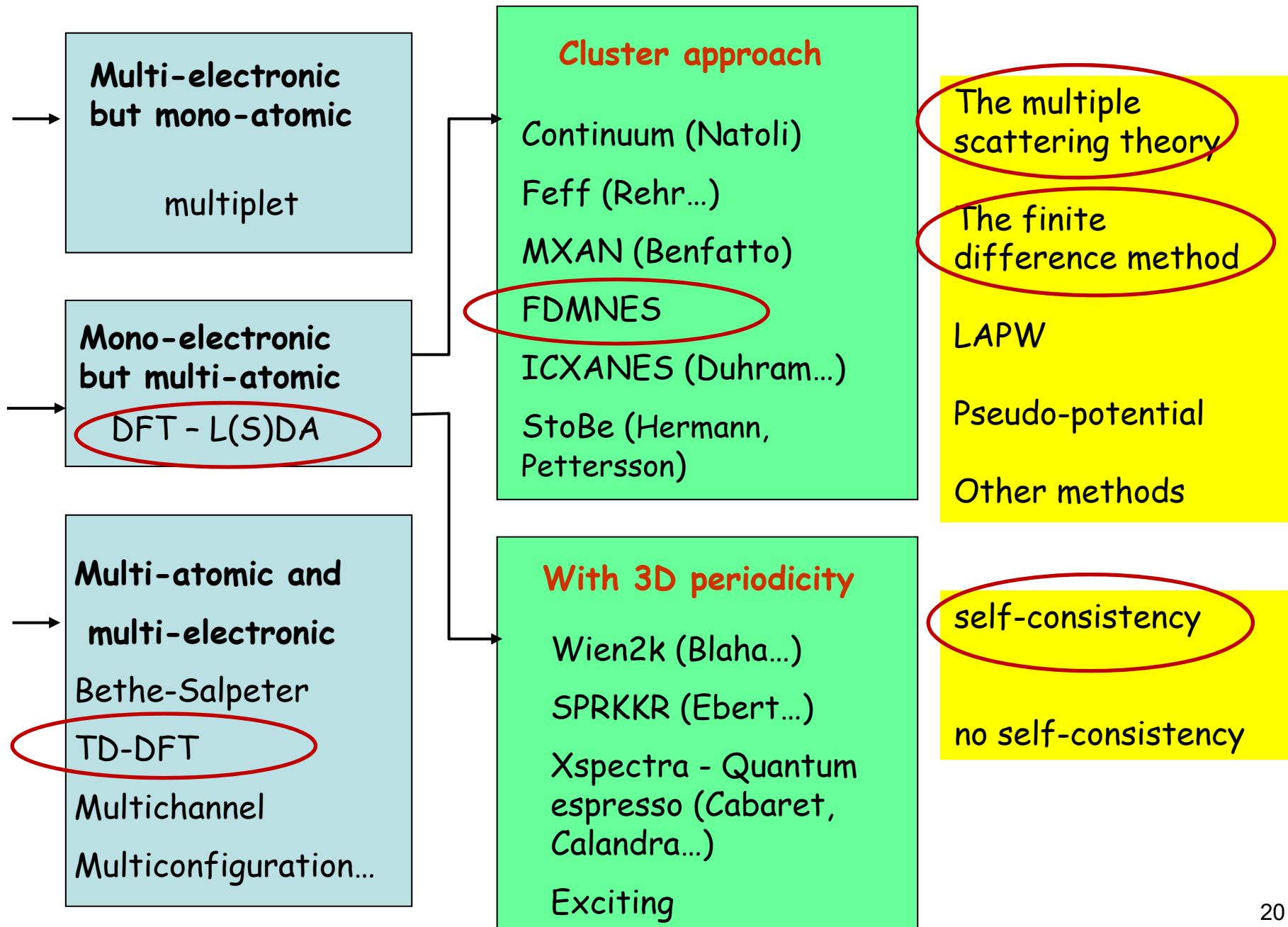
Drawback : time consuming... but:

**Use of MUMPS library (sparse matrix solver)**

by S. Guda, A. Guda, M. Soldatov et al (Rostov, Russia)

**→ 40 times faster → low symmetry possible**

# FDMNES among the other codes



## Main characteristics

*Ab initio* simulation of XANES, XMCD, XES, XRS, RXD, SRXRD

Free open source : [www/neel.cnrs.fr/fdmnes](http://www.neel.cnrs.fr/fdmnes)

Supposed to be user friendly

(Nearly) fully symmetrized

Fully relativistic (with spin-orbit)

Cluster approach

Two techniques to solve Schrödinger (or Dirac) equation :

Multiple Scattering Theory

Finite Difference Method

→ Full potential → more precise but more time consuming

Self-consistent (in MST)

DFT with LSDA+U

→ K edges and  $L_{23}$  edges of heavy elements

TD-DFT →  $L_{23}$  edges of 3d elements or  $M_{45}$  and  $O_{45}$  of heavy elements

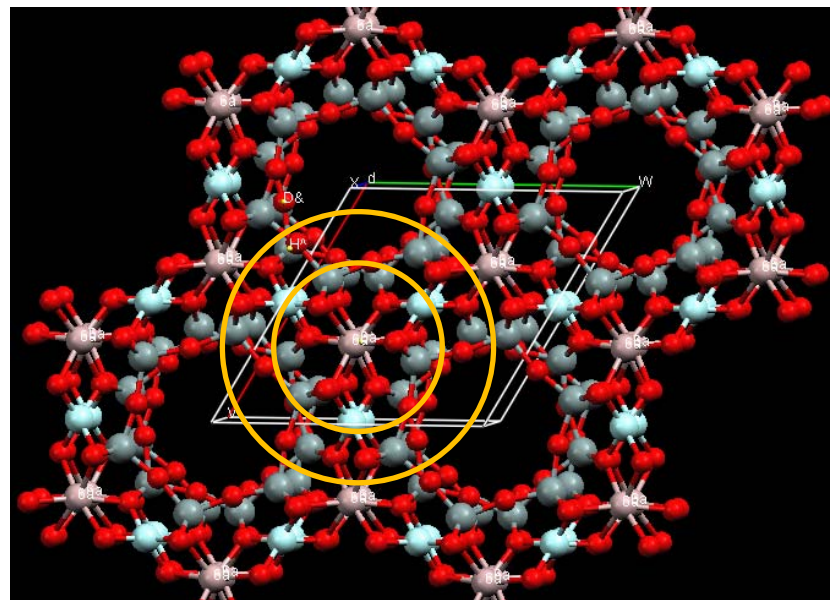
## About the cluster approach

The material can be periodic or not

The absorbing atom is « excited »  
→ 3D periodicity broken

... sometimes negligible effect

But the signal keeps the symmetry of  
« wave + material (+ field...) »



Define a cluster radius around the  
absorbing atom :

... 5, 6, 7... Å

## Running `fdmnes` on parallel Linux computers

Download the executable parrallel version

or

Compile and link the fortran `fdmnes` routines

Need Lapack and MUMPS Library

To use 16 processors in parallel:

```
mpirun -np 16 fdmnes
```

To use the 2 parallelisms:

```
mpirun -np 16 -x HOST_NUM_FOR_MUMPS=2 fdmnes
```

16 processors are used, 8 energies will be calculated in parallel  
For each of them, 2 processors run the MUMPS library

## Manual\_Eng.pdf or Manuel.pdf : User's guide

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At the end:

## List of *fdmnes* keywords

Abs_B_iso	60	Conv_out	52
Abs_U_iso	60	Convolution	55, 57
Abs_before	56	COOP_atom	36
Absorber	17, 41, 43	COOP_dist	36
Adimp	50, 51, 74	COOP_z_axis	36
All_conv	56	Core_resolved	53
All_nrixs	23	Crystal	13, 29, 36
Allsite	44	Crystal_p	15
Ang_spin	31	Dafs	24, 25, 27, 81
Atom	15, 29, 30, 66	DAFS_2D	81
Atom_B_iso	28, 80	Dafs_exp	26
Atom_conf	16, 37	Dafs_exp_type	26
Atom_U_iso	28, 80	Dead_layer	62
Atom_nsph	37	Density	40
Atomic_nu	71	Density_comp	41
Axe_spin	31	Density_all	41
Azimuth	69	Dec	57
Basecomp	48	Delta_E_conv	32
Bulk	77	Dilatorb	38
Bulk_roughness	79	Dip_rel	19
Calculation	55	Dipmag	19
Cap_B_iso	79	Directory	56
Cap_U_iso	79		

# Some advices to make the best possible simulation

The purpose of this little section is to help the user of this code to obtain the best possible simulation, taking into account the limitations of the program.

## 1) DFT

FDMNES is a DFT program with a TDDFT extension. DFT is a ground state theory. It is thus in principal false to calculate the exciting states, the ones probed by x-ray absorption spectroscopies ...

But we do it anyway. Indeed, at least for the K-edges of all elements and the L<sub>2</sub> and L<sub>3</sub> edges of heavy elements (that is from, say, Z = 31), and with some tried and tested options, it is possible to obtain very satisfactory agreement. This leads to the following setting :

→ **The simulation of K (or L<sub>1</sub>) edge of all elements or L<sub>2</sub> or L<sub>3</sub> edges of heavy elements must give a convenient result**

By convenient, one means that most features of the data must be reproduced when the atomic structure is known. They must be reproduced in intensity at typically less than 10% and in position at less than some eV. Often the agreement can be even better.

We can anyway also calculate the other edges. For example L<sub>23</sub> edges of the first half of the 3d elements is improved by the use of the theory (and keyword) "TDDFT", especially for the ratio L<sub>2</sub>/L<sub>3</sub>. One nevertheless must not expect a reproduction of the excitonic states which gives the so-called "multiplet" features often observed for example in oxides.

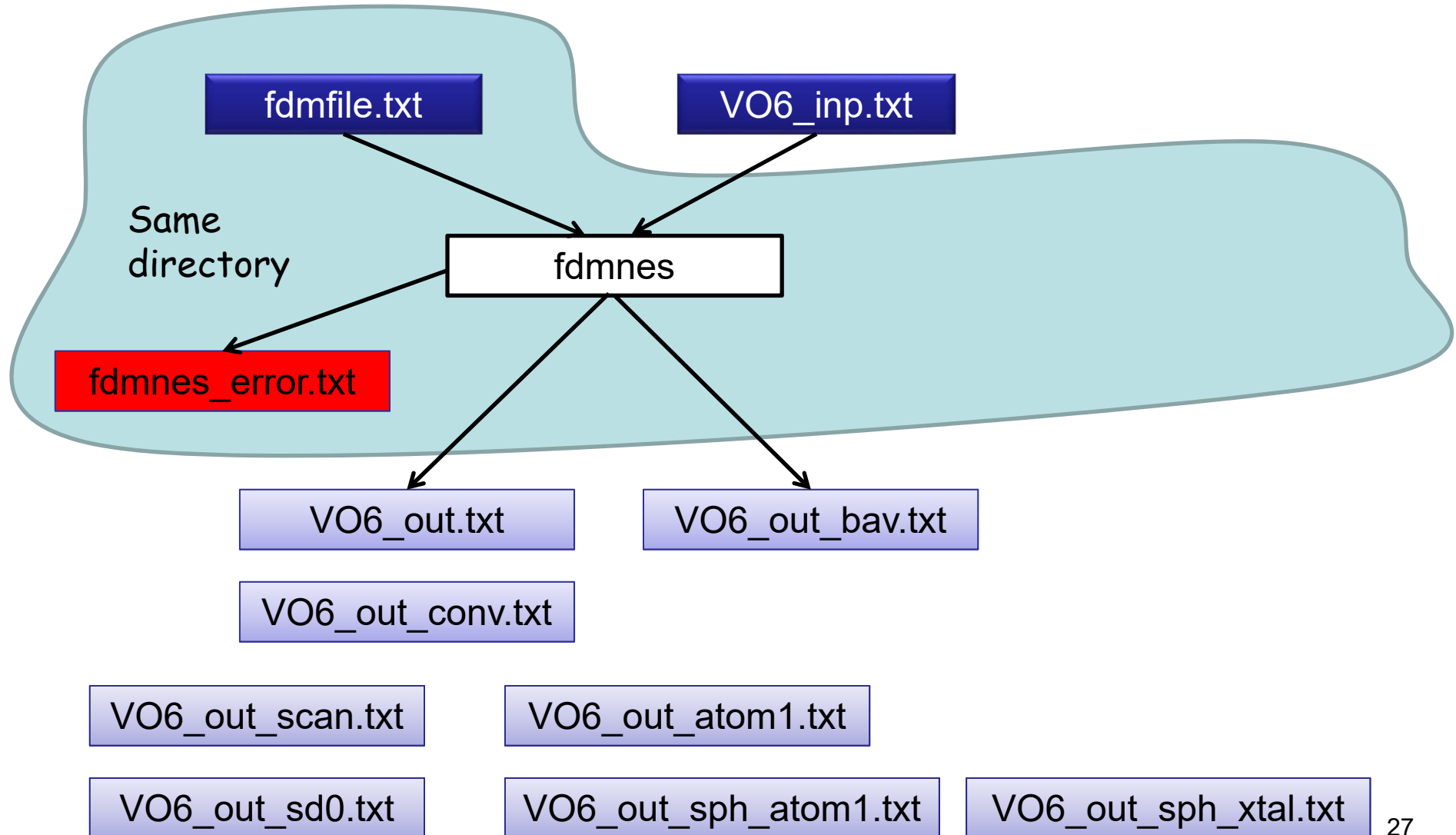
We can also get interesting results playing with screening parameters and option of self-consistency for the heavier elements.

## 2) First calculation

For the first calculation of a new material, one must always start with the most simple indata file, that is:

- 1) Keep all the *fdmnes* default options and so describing only the atomic structure, the energy range and terminating with a "Convolution"
- 2) Make the calculation with a small radius ("Radius" = 3, for example)
- 3) Use the multiple scattering theory (keyword "Green")
- 4) No self-consistent calculation

## Input and output files



## Examples of FDMNES indata file

```
Filout
  Sim/VO6

Range
-2. 0.1 0. 0.5 60.

Radius
2.5

Quadrupole

Polarization

Molecule
2.16 2.16 2.16 90. 90. 90.
23 0.0 0.0 0.0
8 1.0 0.0 0.0
8 -1.0 0.0 0.0
8 0.0 1.0 0.0
8 0.0 -1.0 0.0
8 0.0 0.0 1.0
8 0.0 0.0 -1.0

Convolution

End
```

```
Filout
Sim/Fe3O4

Range
-2. 0.1 -2. 0.5 20. 1. 100.

Radius
5.0

Green
Quadrupole

DAFS
0 0 2 11 45.
0 0 6 11 45.
4 4 4 11 0.

Self_abs

Spgroup
Fd-3m:1

Crystal
      8.3940 8.3940 8.3940 90 90 90
26 0.6250 0.6250 0.6250 !Fe 16d
26 0.0000 0.0000 0.0000 !Fe 8a
8 0.3800 0.3800 0.3800 !O 32e

Convolution

End
```

## Examples of FDMNES indata file

```
Filout
  Sim/VO6

Range
-2. 0.1 0. 0.5 60.

Radius
2.5

Quadrupole

Polarization

Molecule
2.16 2.16 2.16 90. 90. 90.
23 0.0 0.0 0.0
8 1.0 0.0 0.0
8 -1.0 0.0 0.0
8 0.0 1.0 0.0
8 0.0 -1.0 0.0
8 0.0 0.0 1.0
8 0.0 0.0 -1.0

Convolution

End
```

```
Filout
Sim/Fe3O4

Range
-2. 0.1 -2. 0.5 20. 1. 100.

Radius
5.0

Green
Quadrupole

DAFS
0 0 2 11 45.
0 0 6 11 45.
4 4 4 11 0.

Cif_file
Sim/in/Fe3O4.cif

Convolution

End
```