Hands-on tutorial on FDMNES and FitIt

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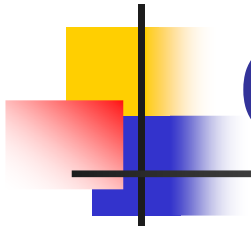
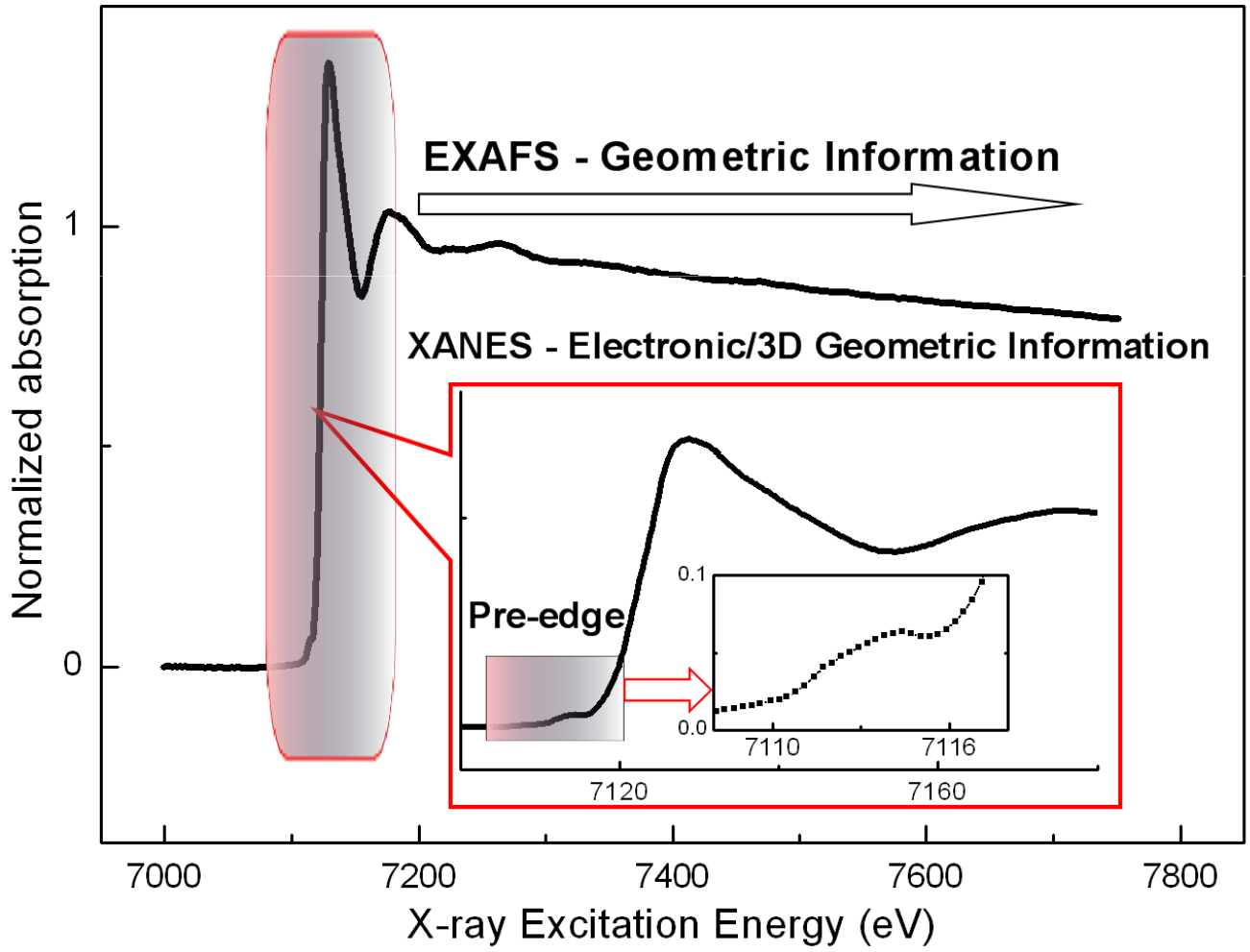


Outline

- **FDMNES** (XANES simulations)
  - program description
  - example FeO_6
- **FitIt** (XANES fitting program)
  - short program description
  - example protein PerR

Basis of XAS


EXAFS - Geometric Information
XANES - Electronic/3D Geometric Information
Pre-edge
Normalized absorption
1
0
7000
7200
7400
7600
7800
X-ray Excitation Energy (eV)
0.1
0.0
7110
7116
7120
7160

FDMNES. Author

Yves Joly
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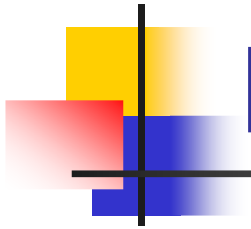
Institut Néel, CNRS, Grenoble, France
http://www.neel.cnrs.fr/fdmnes

Y. Joly "X-ray absorption near edge structure calculations beyond the muffin-tin approximation"

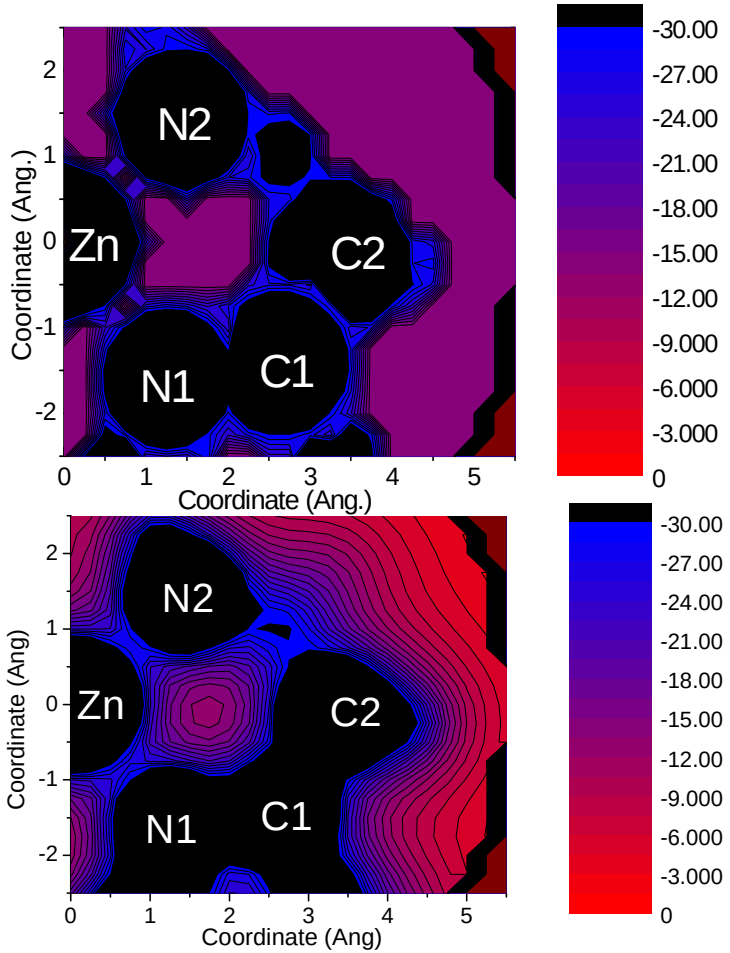
Phys. Rev. B **63, 125120 (2001)**

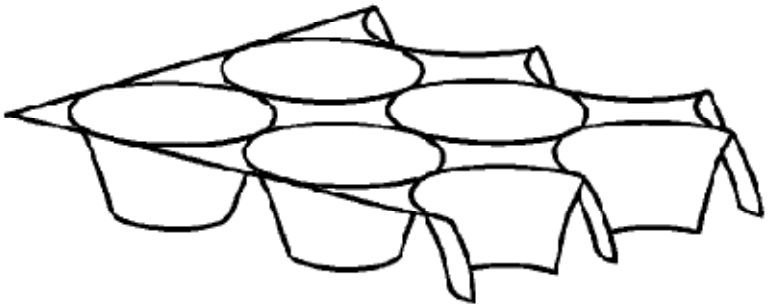


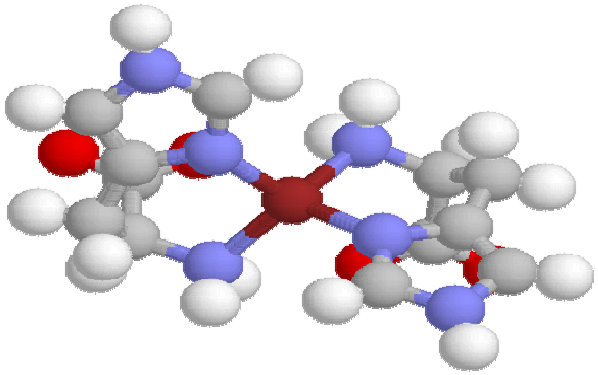
FDMNES. Short description

- XANES (mostly K-, L- edges), DAFS or RXD or RXS
- Full relativistic monoelectronic calculations (DFT-LSDA)
- Finite Difference Method (FDM) to solve the Schrödinger equation. The shape of the potential is free (non muffin-tin approximation)
- Green formalism (multiple scattering) on a muffin-tin potential
- Now. Multi-electronic extension using the "Time-Dependant DFT" and self-consistant potential

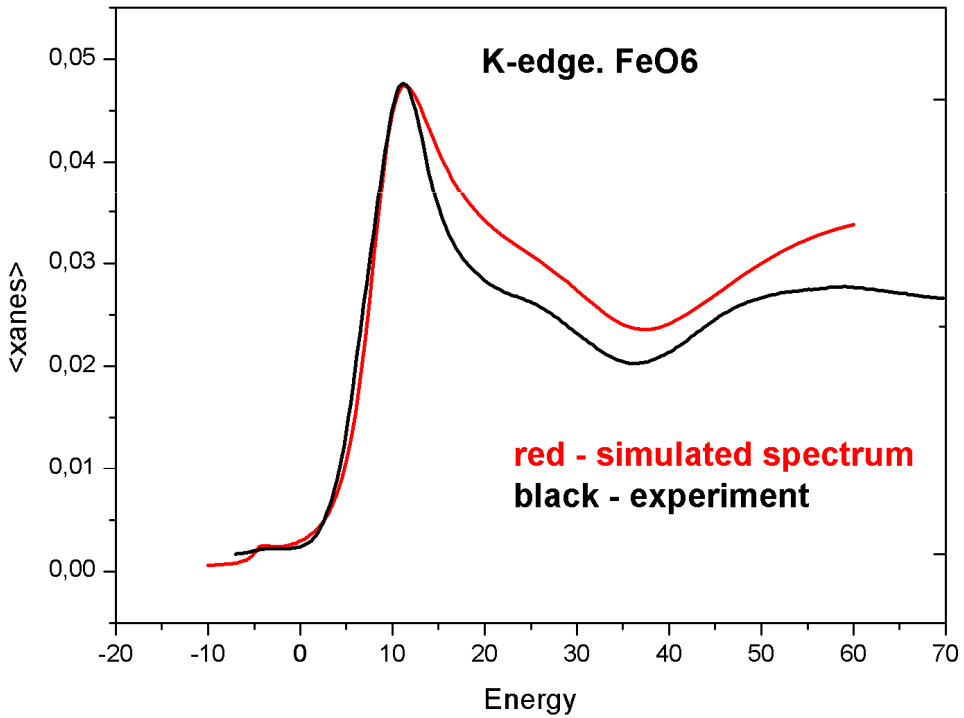
Muffin-tin approximation

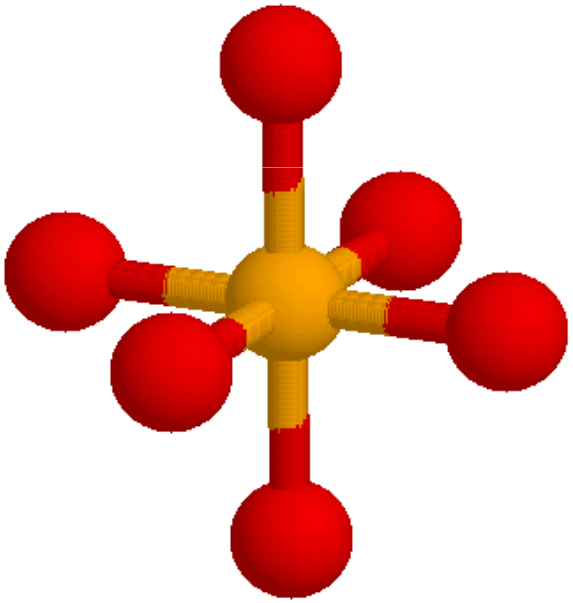






FDMNES. Example: FeO_6





Fe-O distance: 2.16 Å

FDMNES. Input file. The first part

fdmnes/entree/test_stand/feo6_inp.txt ! Main indata file for fdmnes to simulate FeO6 molecule
! Calculation on FeO6 using the multiple scattering approch
! with convolution, comparison with an experimental spectra and fit.

Filout
  xanout/test_stand/feo6 / name of output file and directory

Range
-6. 0.1 -3. 0.2 0. 0.5 20. 1. 40. 2. 60. / energy range

Radius / radius of calculated cluster, Å
 3.0

Green /multiple scattering aproach
/ by defaut: finite difference method

FDMNES. Input file. The second part

```
Molecule                                                    /molecule or crystal
    2.16  2.16  2.16  90. 90. 90.    = a, b, c, alpha, beta, gamma
 26  0.0   0.0   0.0                 = Z, x, y, z        / atomic number and position
  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

! keywords for the convolution          / convolution of the spectrum. Might be
 Convolution                            / done separately. "arctangeant" shape for
                                          /the broadening
 Efermi                                /cutting of the occupated states
  -4.8
 Estart
 -10.
End
```

FDMNES running. Step-by-step

- Prepare or modify the input file. For FeO6 example go to fdmnes/entree/test_stand/feo6_inp.txt
- Go to the mail folder with the fdmnes.exe ->/fdmnes/
- Modify the file fdmfile.txt ->

1

entree/test_stand/feo6_inp.txt

entree/test_stand/cu_inp.txt

- Run fdmnes.exe
- Trace the output files with calculated spectra -> fdmnes/xanout/test_stand/

feo6.txt – without convolution

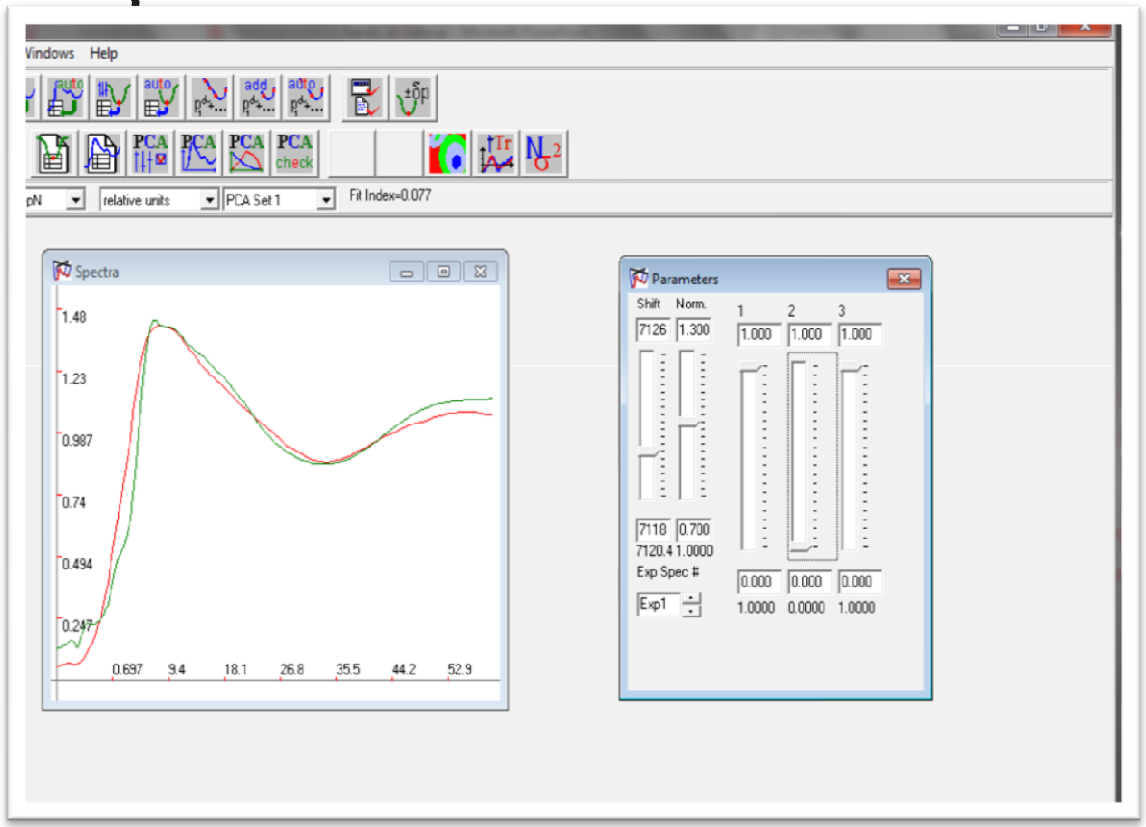
feo6_conv.txt – with convolution

FitIt. Athours

Grigory Smolentsev and Alexandre Soldatov
Southern Federal University &Lund University
http://www.nano.sfedu.ru/fitit.html

G. Smolentsev, A. Soldatov, **Journal of Synchrotron Radiation 2006, 13, 19-29**
G. Smolentsev and A.V. Soldatov, **Comp. Matter. Science 39 (2007) 569.**

FitIt. GUI



- Multidimensional interpolation approximation.
- Quantitative determination of the local atomic structure
- Use external programs as FEFF and FDMNES
- It allows to minimize the number of time-consuming XANES calculations required to find optimal values of the parameters.

New FitIt project. Step-by-step. Part 1

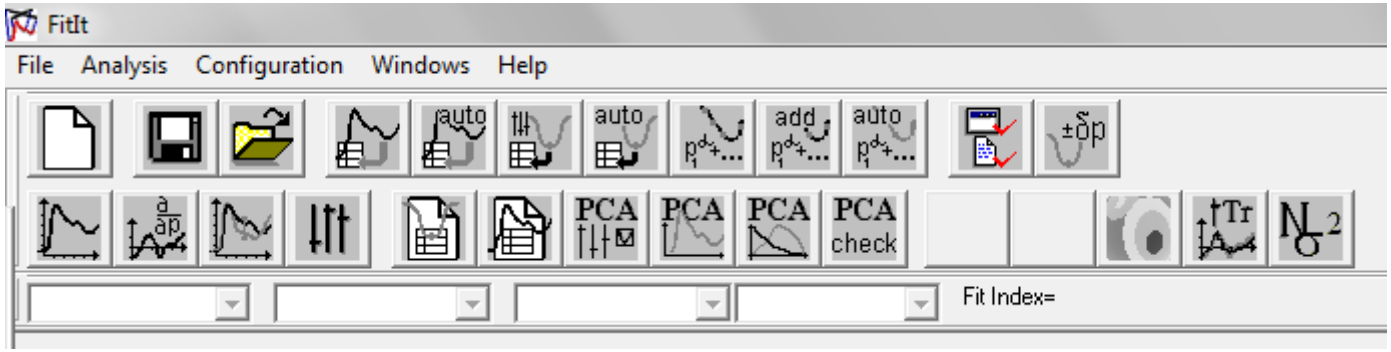
- Install FitIt package. Tick FDMNES during the installation process
- Prepare a work folder with files (see for example PerR_Madrid folder):

in.pdb - PDB file with initial structure

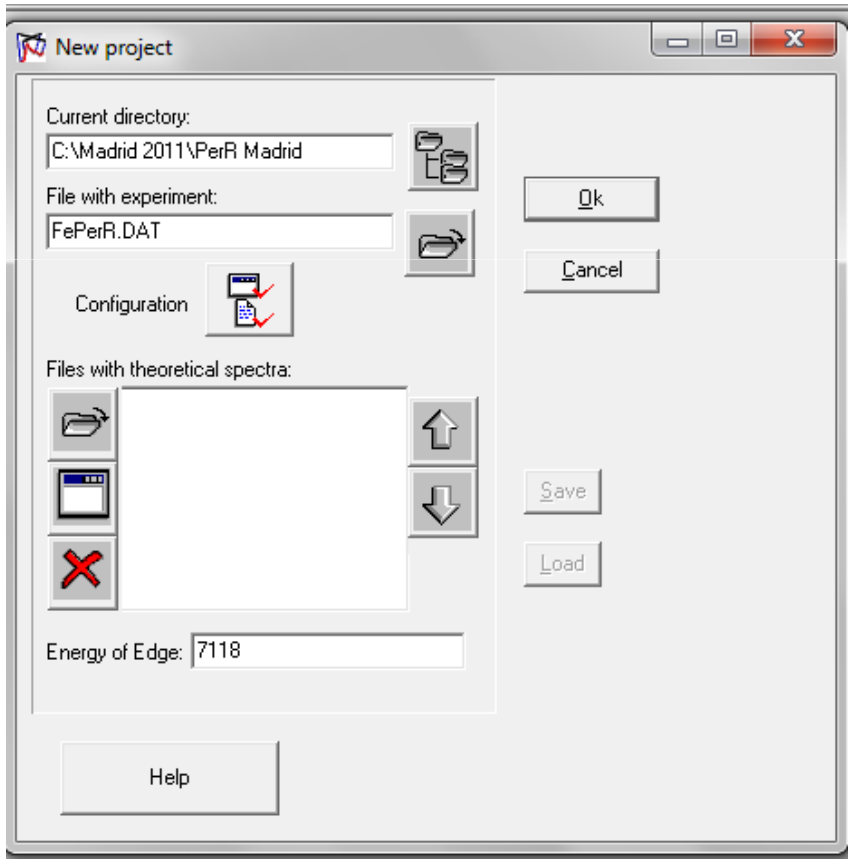
fdmnes.inp – input fdmnes file without atomic coordinates

File with experiment – should consist number of energy points of and two coulumns with energy and absorption signal (see PerR_Madrid/FePerR.dat)

- Run FitIt for example from the ”Start menu”
- Press the first button ”New project”

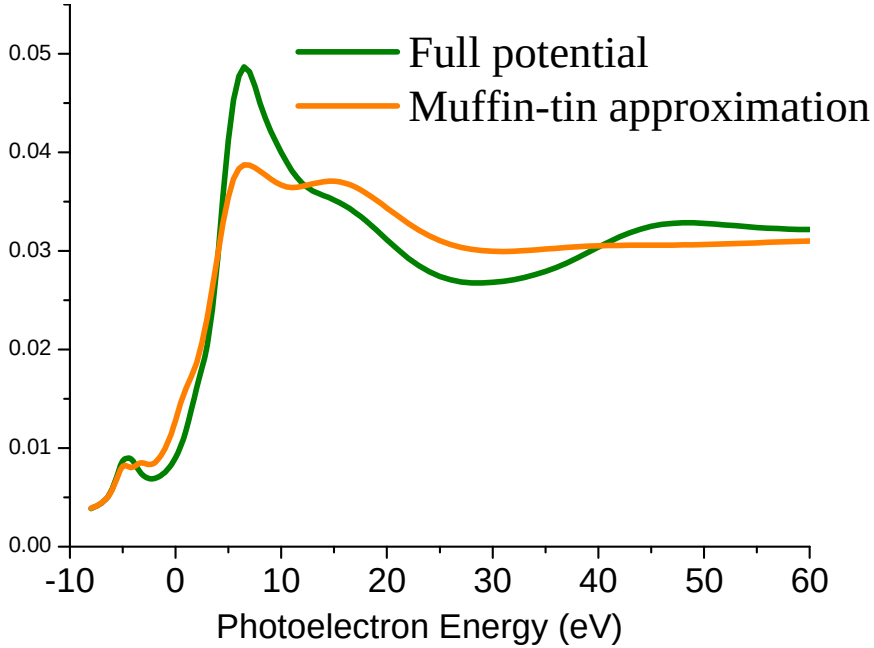


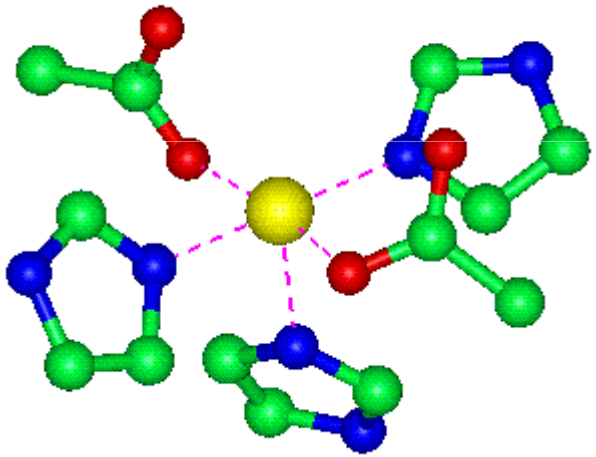
New FitIt project. Step-by-step. Part 2



- Specify your working folder and file with experiment pressing the buttons to open files
- Make a programm configuration. **Tip**: Open in the executable list the fdmnes template /Program files/FitIt/fdmnes.wrk
- Leave empty the field with theoretical spectra if you don't have them
- Specify the Energy range for experiment
- Press "OK"

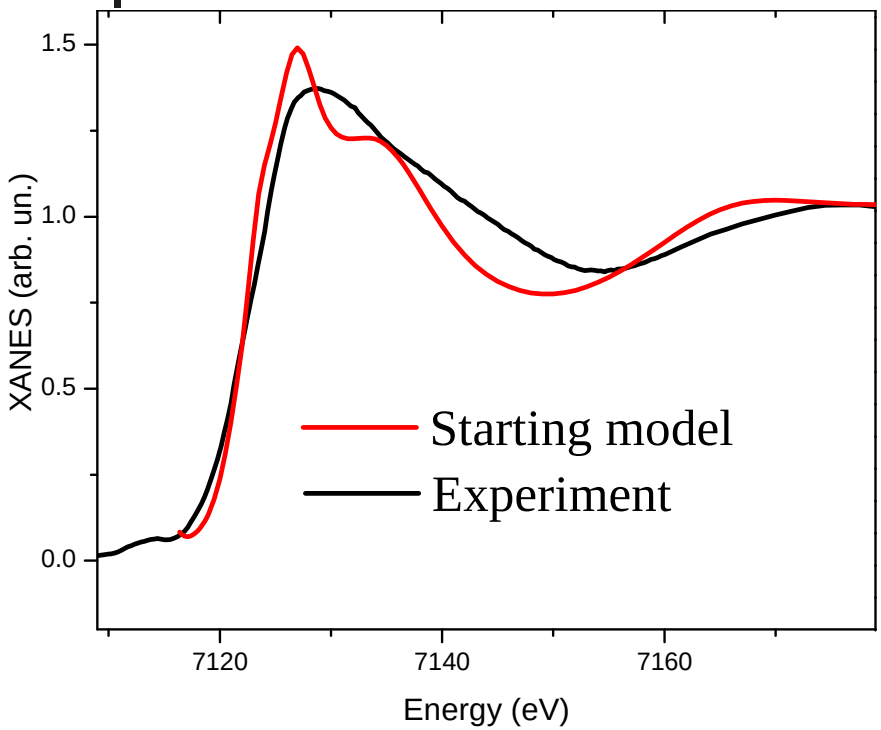
Simulations of Fe-edge PerR protein



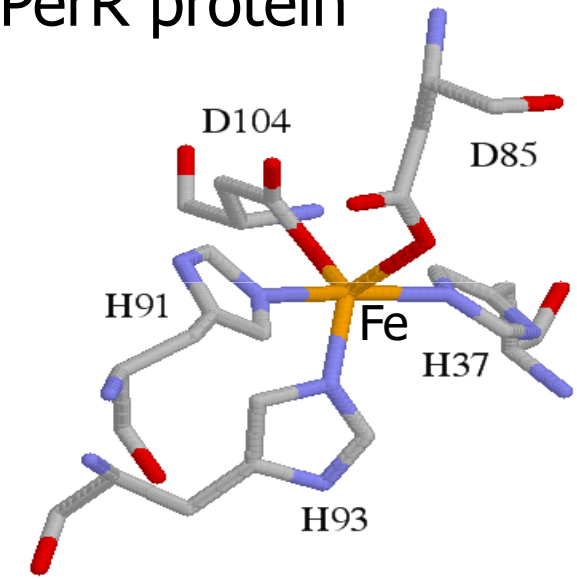


- **Strong non muffin tin effects - Full potential (beyond the *muffin tin approximation*) calculations using FDMNES code.**
- **Cluster 4.5 Ă**
- **Quantitative XANES fitting using FitIt package**

What kind of structural information we can see from XANES?



PerR protein



- Distances Fe-His&Fe-Asp (1.9-2.1A)
- Angle between Asp changes from 120° to 180°
- In plane rotation of aspartates

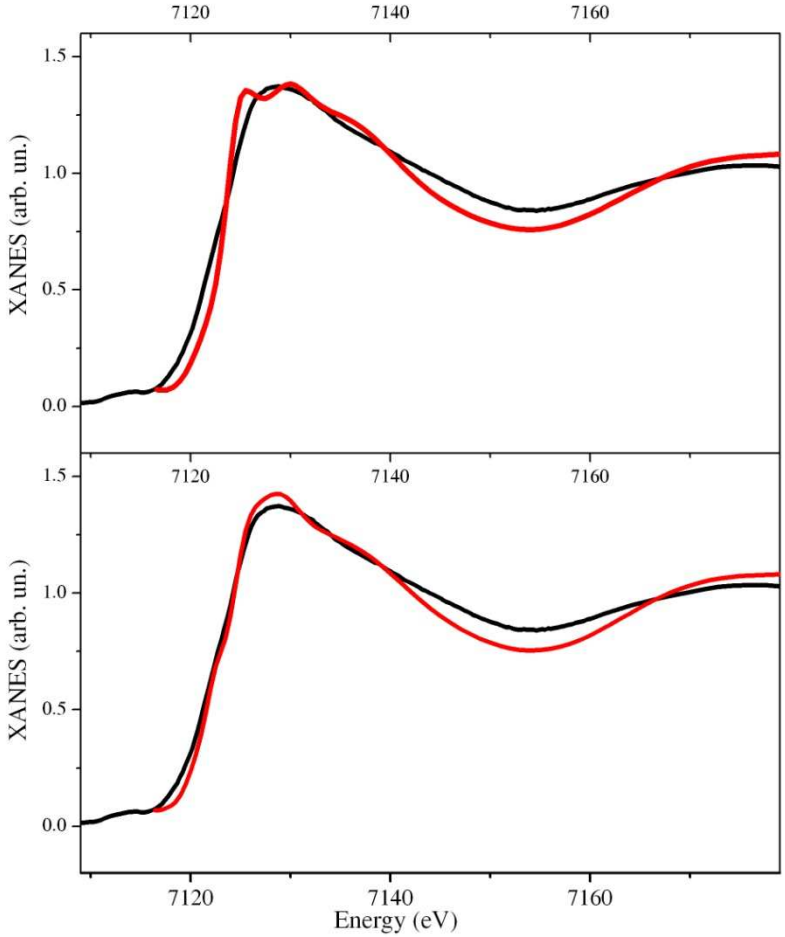
} influence significantly

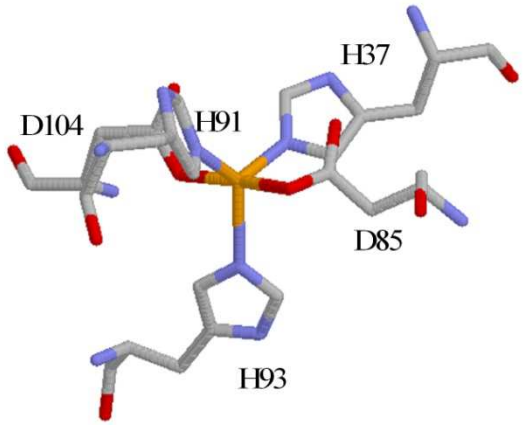
- Axial rotations of aspartates - influence very slightly

FitIt. PerR example. Step-by-step

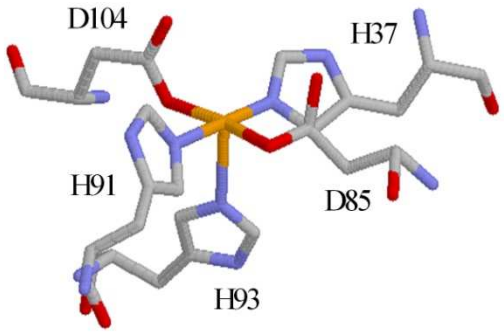
- Go to the folder /PerR Madrid/
- Run fit_PerR.fbf
- Play with the parameters on the slider bar
- Look on the table with calculated spectra. Look how are different the calculated (blue one) and interpolated spectra (green one).
- Remember the spectra with the big difference which you should include in the polinomial.
- Press the button ”auto polynomial” and tick these spectra.
- Play with the parameters on the slider again.
- Try to find the combination of parameters wich gives the best fit results

Structural model of iron binding site





Trigonal dipyramid



Bestfit model:square pyramid

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Thank you for your attention!

Poster MS42.P01(C516). **X-ray absorption spectroscopy studies of copper site in the ubiquinol oxidase**

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