XANES: MXAN and FPMS codes

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  Many thanks!

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Multiple scattering approach

KKR (band): Korringa (1947), Kohn and Rostoker (1954)
SCF-SW (Quantum Chemistry:MO): Slater and Johnson (1966),
Smith and Johnosn (1969)

For spectroscopy,

LEED: Pendry
XPD : Rennert, Natoli & Sebilleau
XAFS: Natoli (1980), Rehr (FEFF code), Benfatto, Brouder, Foulis,
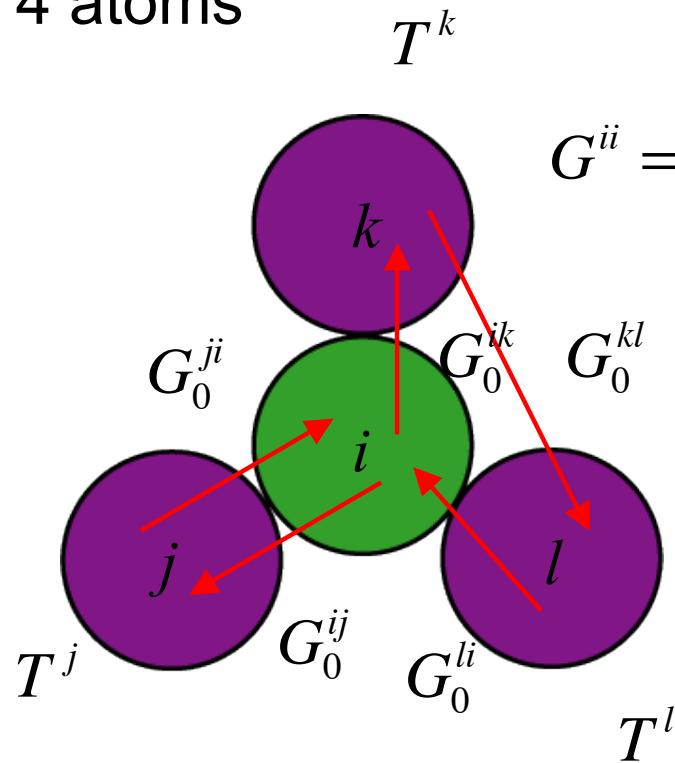   Ebert, Fujikawa, Sipr, …

  Also for ELNES, RXS

wide application of MS theory

K. Hatada, *IXAS Web Magazine*, 2nd issue, July (2010)

Multiple scattering with Muffin-tin approximation : Green's function picture

4 atoms

Obtain G^{ii}:

$$G^{ii} = \underline{G_0^{ii}} + \sum_n G_0^{in} T^n G_0^{ni} + \sum_{nm} G_0^{in} T^n G_0^{nm} T^m G_0^{mi} + \cdots$$

G_0^{ii} :isolated

$\sum_n G_0^{in} T^n G_0^{ni}$:single scattering

$\sum_{nm} G_0^{in} T^n G_0^{nm} T^m G_0^{mi}$
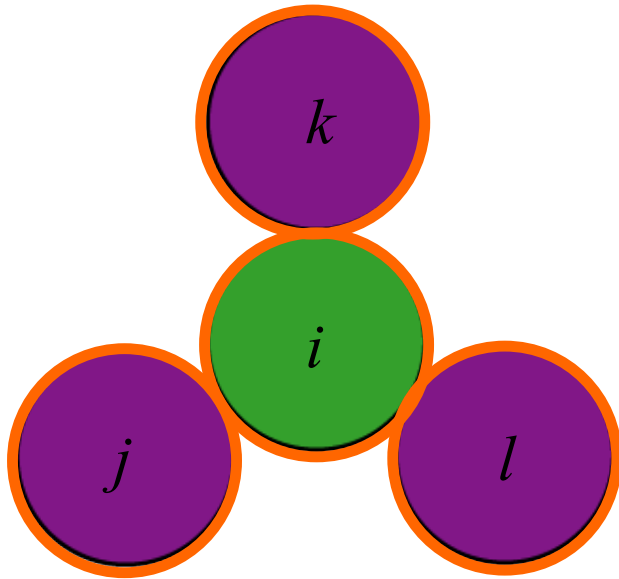
:double scattering

$$G^{ii} = G_0^{ii} + \sum_{n \neq i} G_0^{in} T^n G_0^{ni} + \sum_{n \neq m \neq i} G_0^{in} T^n G_0^{nm} T^m G_0^{mi} + \cdots$$

$$= [G_0 (I - G_0 T)^{-1}]^{ii}$$

Full Multiple Scattering

Multiple scattering : wave function (WF) picture

WF is expanded by local solutions

Site i: $\Psi(\mathbf{r}_i;\mathbf{k}) = \sum_L B_L^i(\mathbf{k})\Phi_L^i(\mathbf{r}_i)$

Site j: $\Psi(\mathbf{r}_j;\mathbf{k}) = \sum_L B_L^j(\mathbf{k})\Phi_L^j(\mathbf{r}_j)$

Site k: $\Psi(\mathbf{r}_k;\mathbf{k}) = \sum_L B_L^k(\mathbf{k})\Phi_L^k(\mathbf{r}_k)$

Site l: $\Psi(\mathbf{r}_l;\mathbf{k}) = \sum_L B_L^l(\mathbf{k})\Phi_L^l(\mathbf{r}_l)$

Matches WF and its derivative on the surface of cells!

$B_L^i(\mathbf{k})$: amplitude

$\Phi_L(\mathbf{r}_i)$: local solution of SE

$\Psi(\mathbf{r}_i;\mathbf{k})$: global solution of SE

$$\sum_{jL'} [T^{-1}(I - TG_0)]_{LL'}^{ij} B_{L'}^{j} = I_L^i(\mathbf{k})$$

This gives amplitudes on each sites. In other words matching will be done implicitly by solving this equation.

$I_L^i(\mathbf{k})$:Boundary condition of the cluster for the cite i centered.

MXAN code: fitting structural and electronic properties by XANES spectra for molecule, protein and amorphous. (disordered system)

M. Benfatto and S. Della Longa, *J. Synchrotron Rad.*, **8**, 1087 (2001)

- XANES (X-ray Absorption Near Edge Structure) from edge to ~100 eV

- 3 dimensional information, sensitive to atomic species

Many applications have been done.

- S. Della Longa et al. Biophy. Jour. 85, 549 (2003)
- P. Frank et al. Inorganic Chemistry 44, 1922 (2005)
- C Monesi et al. PRB 72, 174104 (2005)
- R. Sarangi et al. Inorganic Chemistry 44, 9652 (2005)
- P. D'Angelo et al. JACS 128, 1853 (2006)
- S. Marino et al. Biophy. Jour. 93, 2781 (2007)
- ....
- M. Bortolus et al. JACS 132, 18057 (2010)

Two ways to calculate the scattering path operator

by series:

Exactly: all MS contributions are included

We have developed a new fitting method, called MXAN, that use the exact calculation of the scattering path operator

i)   We work in the energy space
ii) We can start from the edge
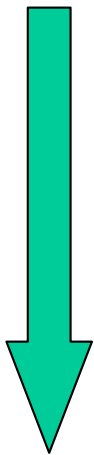iii) We can use polarization dependent spectra

To perform structural fits

- Initial geometrical configurations
- Exp. data
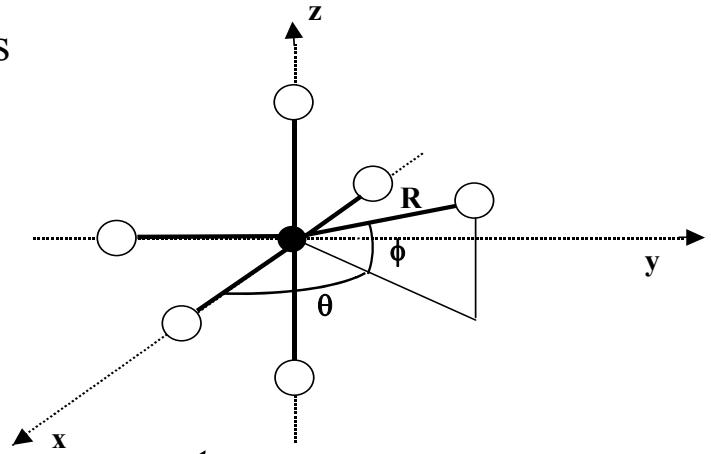
We generate hundred of theor.
spectra by moving atomic coordinates

The potential is calculated at each step – Norman criterion

Minimization of error function

$$R_{sq}{}^2 = \sum_{i=1}^{N} \{ [y_i^{th.}(..r_n, \theta_n,..) - y_i^{exp.}]^2 / \varepsilon_i^2 \} w_i / \sum_{i=1}^{N} w_i$$

By comparison with exp. data we can fit relevant structural parameters

M. Benfatto and S. Della Longa (2001) J. Synch. Rad. 8, 1087
S. Della Longa et al. (2001) PRL 87, 155501
M. Benfatto et al. (2003) J. Synch. Rad. 10, 51

71

To avoid the problems coming from the use of the full HL potential, the Exchange and Correlation part of the potential is calculated on the basis of a phenomenological approach $\longrightarrow$ real HL potential + convolution via a Lorentzian function with $\Gamma_{tot}(E)=\Gamma_c+\Gamma(E)$
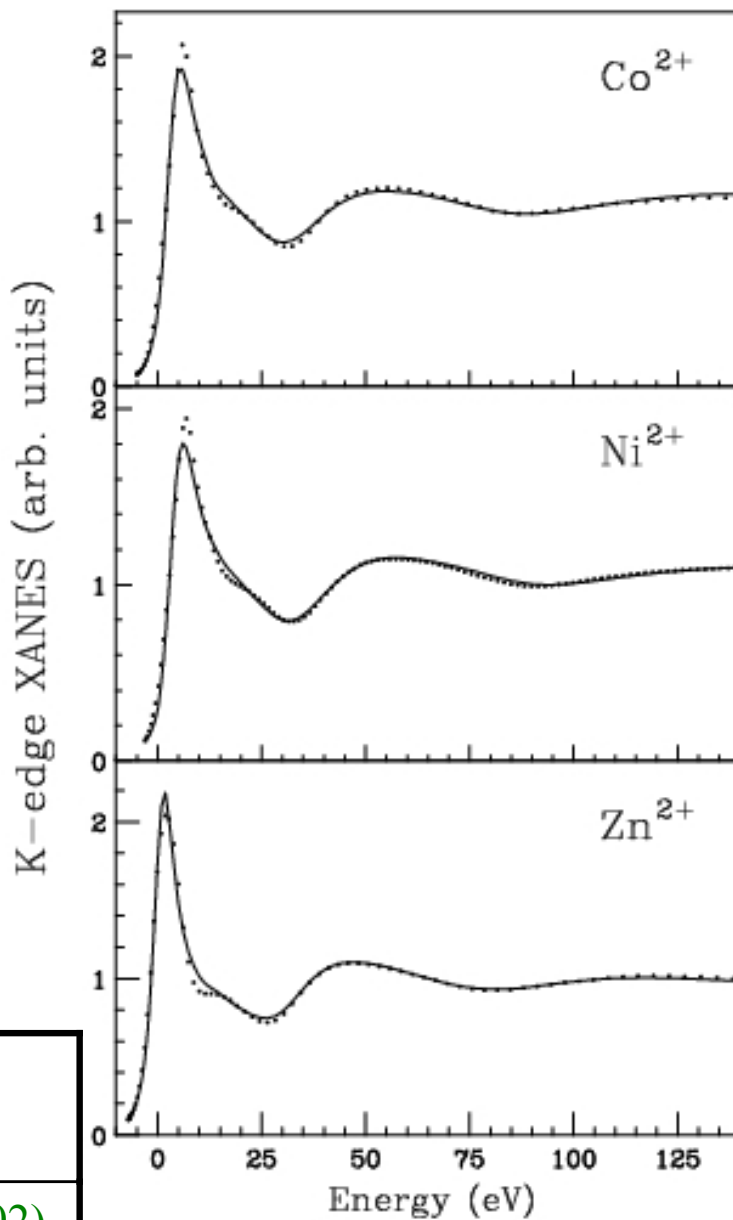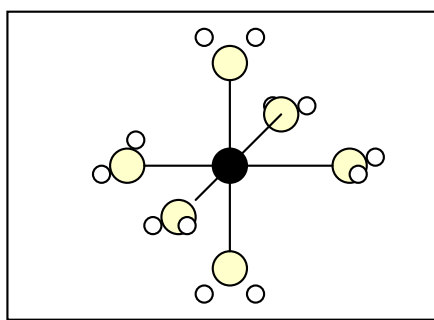
$\Gamma(E)$ Behaves like the universal form and starts from energy E_s with a jump A_s. Both E_s, Γ_c and A_s are derived at each step of computation on the basis of Monte Carlo fit.

A_s

This jump is made via an arctang function

Γ_c

E_s
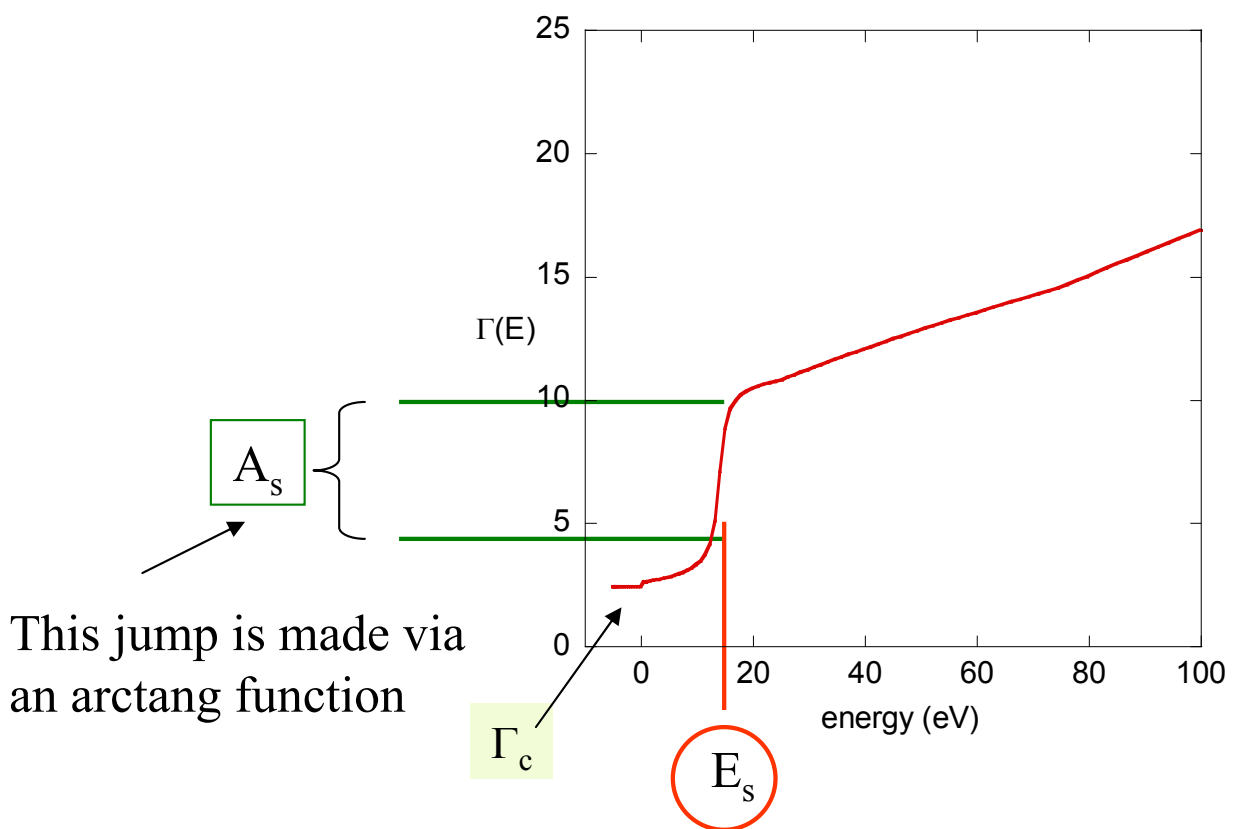
$\Gamma(E)$ contains all the intrinsic and extrinsic inelastic processes

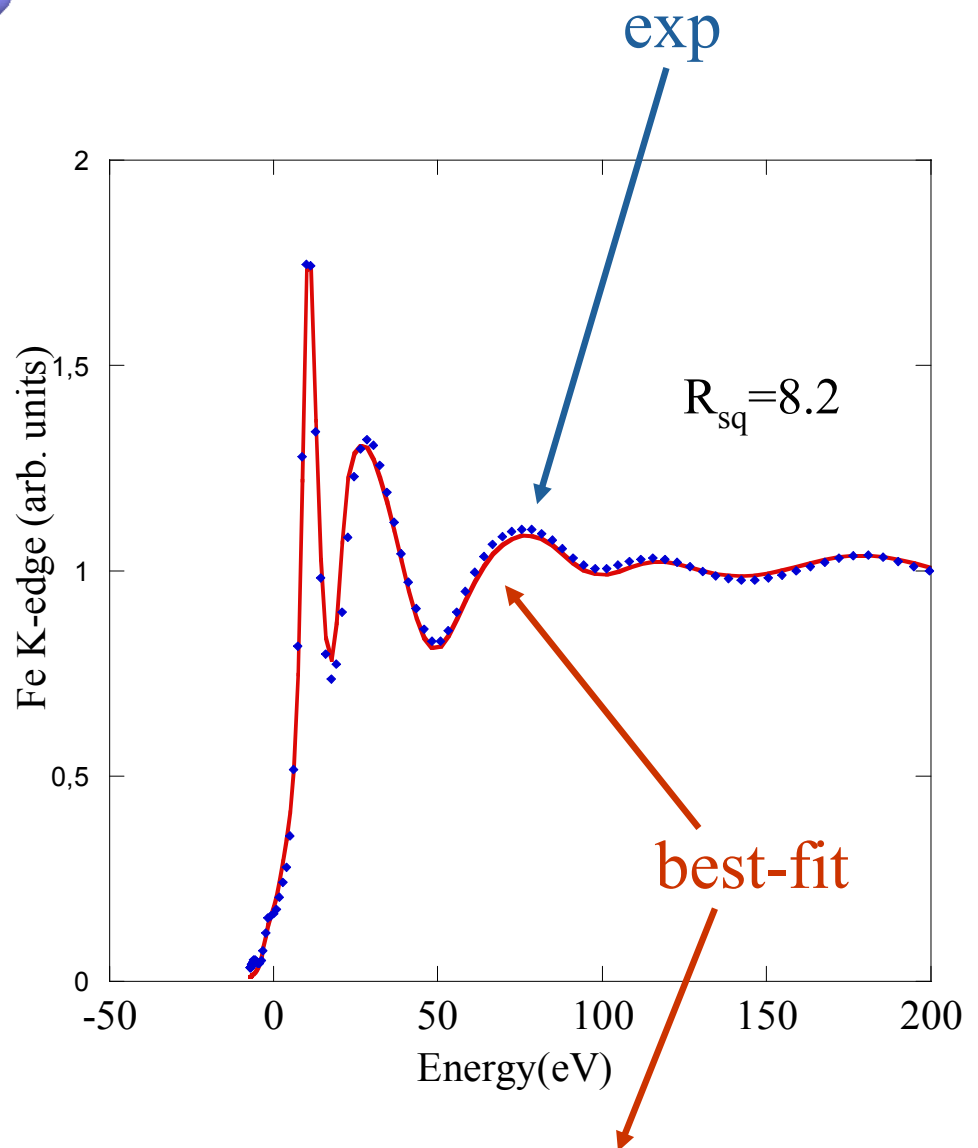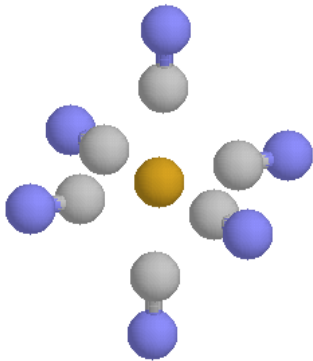# Transition metals in water solution

fits include Hydrogen atoms

MXAN

GNXAS

|	R(Å)	R(Å)
Co²⁺	2.06(0.03)	2.092(0.002)
Ni²⁺	2.04(0.03)	2.072(0.002)
Zn²⁺	2.06(0.02)	2.078(0.002)

73

P. D'Angelo et al. (2002) Phys. Rev B 66, 064209

Fe (CN)$_6$ in water

The best-fit condition corresponds to an octahedral symmetry with Fe-C distance of 1.92(0.01) Å and C-N distance of 1.21(0.01) Å

Previous GNXAS analysis (Westre et al. JACS 117 (1995)) reports Fe-C and Fe-N distances of 1.92 Å and 1.18 Å respectively

Fit with NO molecules
Fe-N =1.91Å and N-O =1.16Å

R_{sq}=50.94

R_{sq}=28.78

Energy(eV)
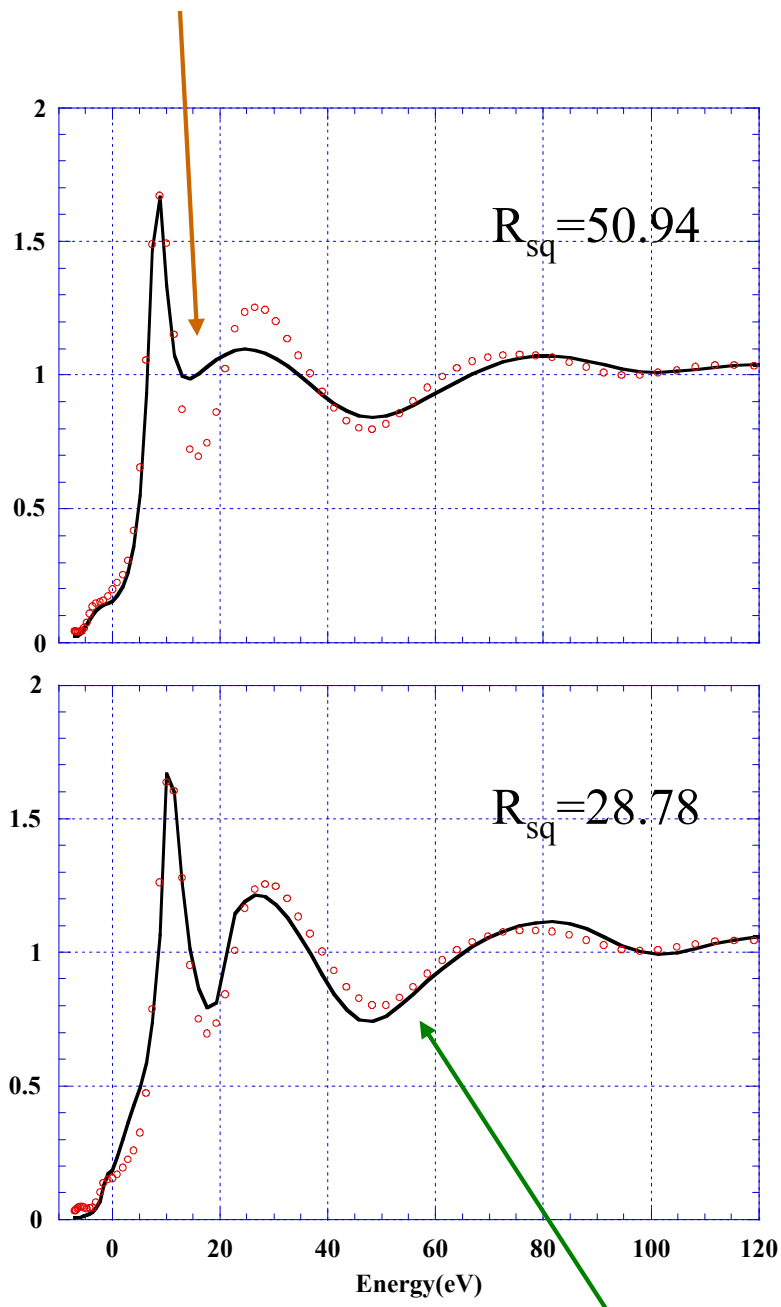
Fit with CO molecules
Fe-C =1.94Å and C-O =1.11Å

Chemical sensitivity

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Test cases indicate a good structural reconstruction at the atomic resolution

high sensitivity to the structural changes

the fit results are weakly affected by the errors in the potential determination

just an increase of the error bar in the structural numbers

Three key points:

The use of a phenomenological damping

The potential is calculated at each step of the atomic movement keeping the same Norman criterion
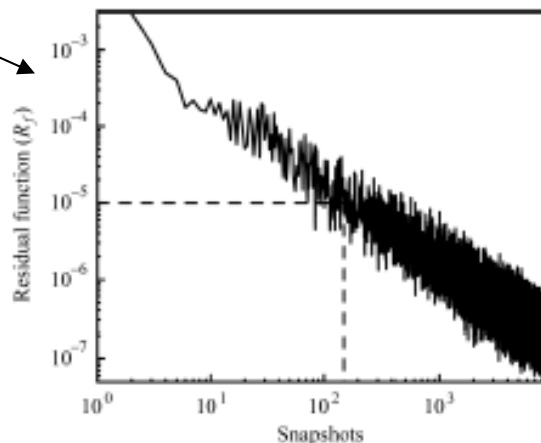
The used energy range is wide enough to minimize errors in the potential determination

thermal and structural disorder

We use MD to generate thousands of geometrical configurations – each snapshot with a time step of 50 fs is used to generated one XANES spectrum – average using $\sim 10^4$ geometrical configuration
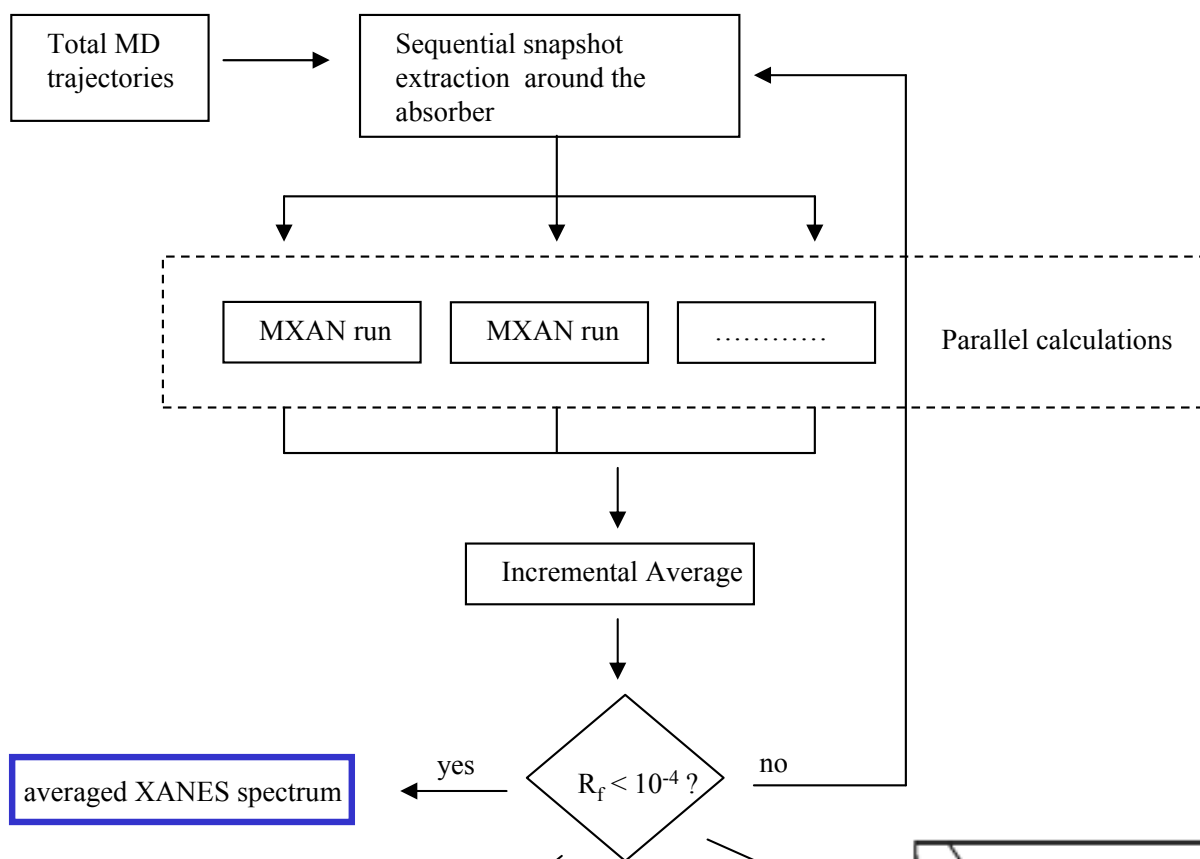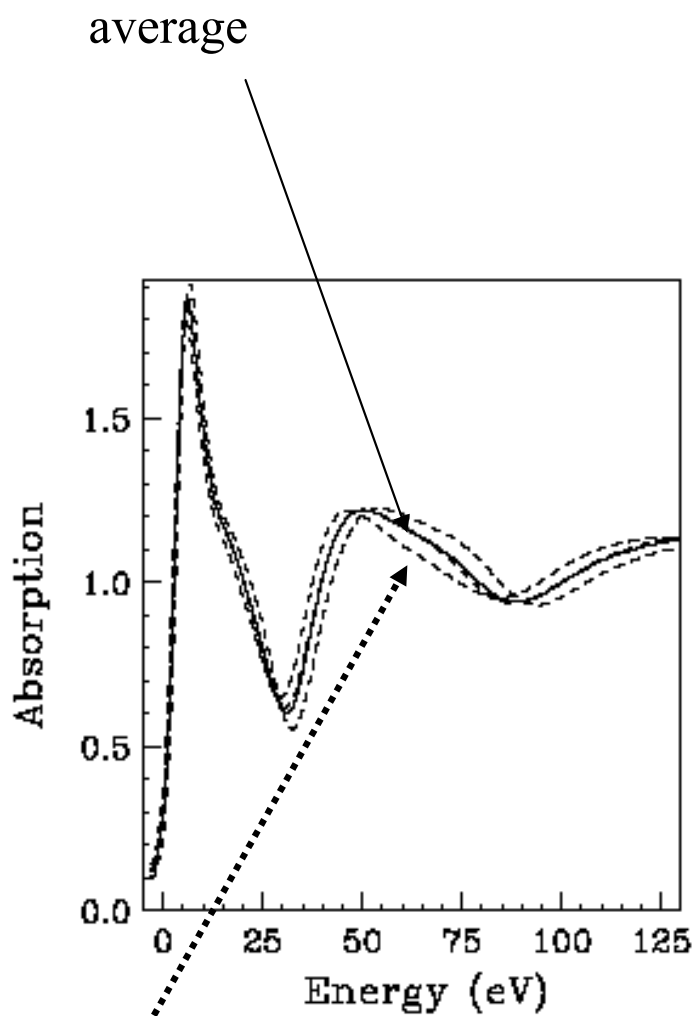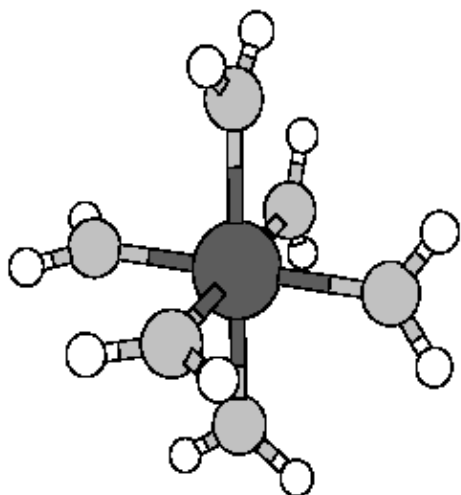

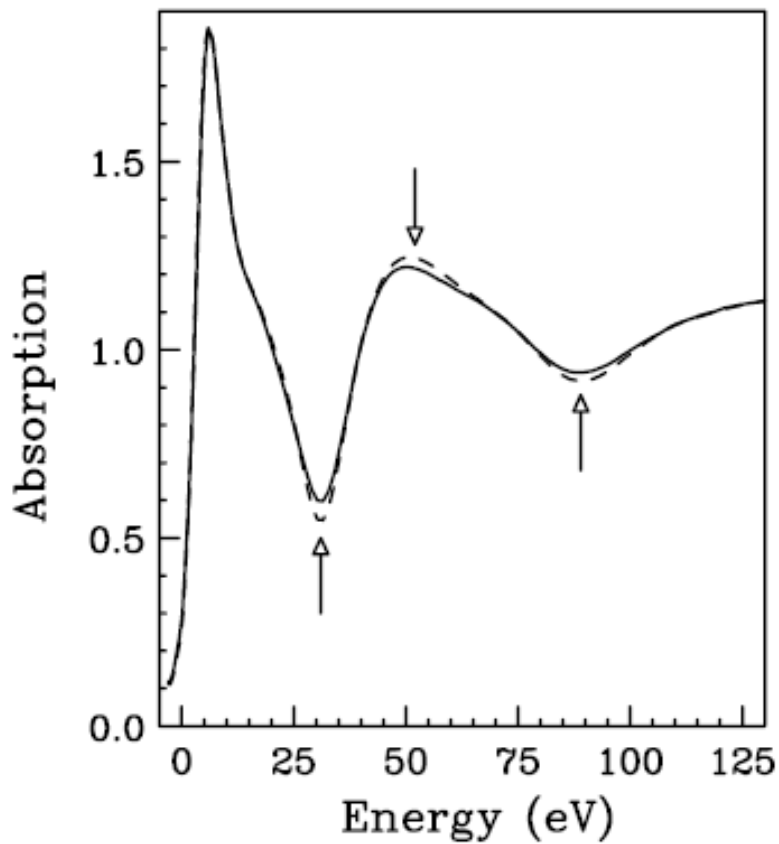$$R_f(N) = \left[\sum_i [\sigma^N(E_i) - \sigma^{N-1}(E_i)]^2 \right]^{1/2}$$

Merkling et al. JACS 124 (2002)
Campbell et al. Jour.Synch.Rad. 6 (1999)

Ni^{2+} in water – Ni Kedge

average

Calculations for some particular snapshots

Comparison between the averaged theoretical spectrum and a single theoretical spectrum at the symmetrical first shell configuration

Arrows indicate the damping - very weak effect - it can be included in the phenomenological treatment of the inelastic losses in MXAN
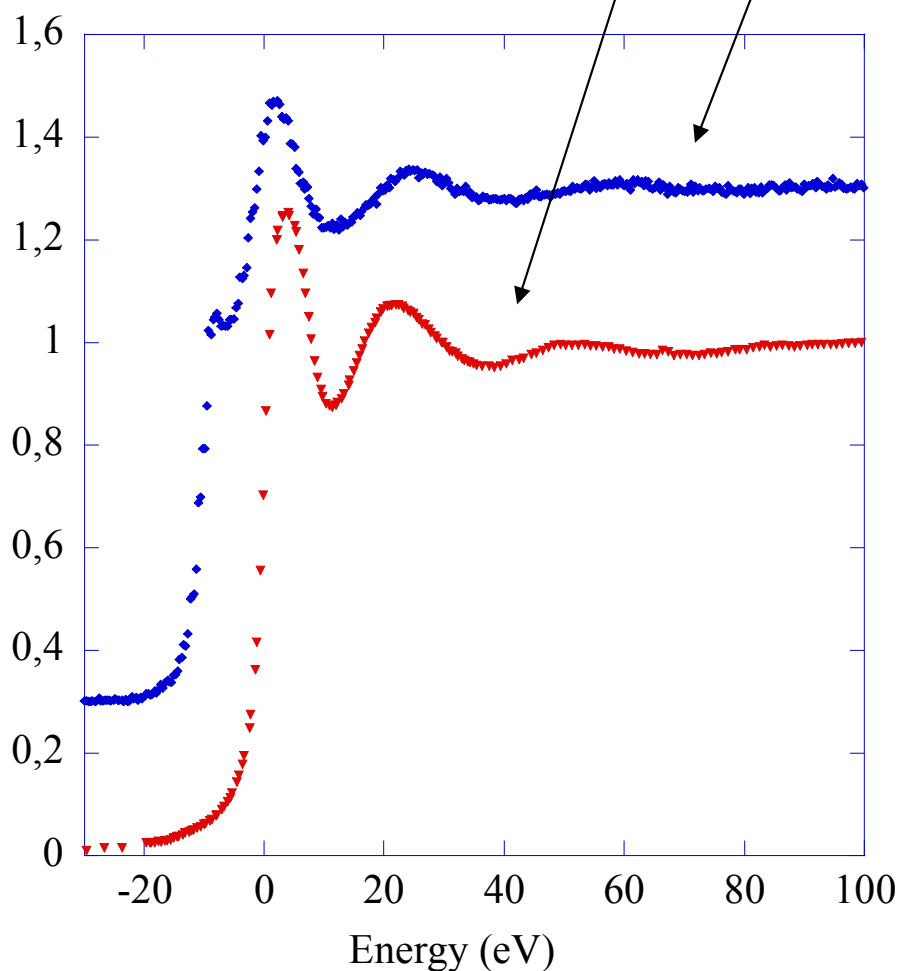
including the second shell

average

first shell average

first + second shells average

114

one shell fit

two shells fit
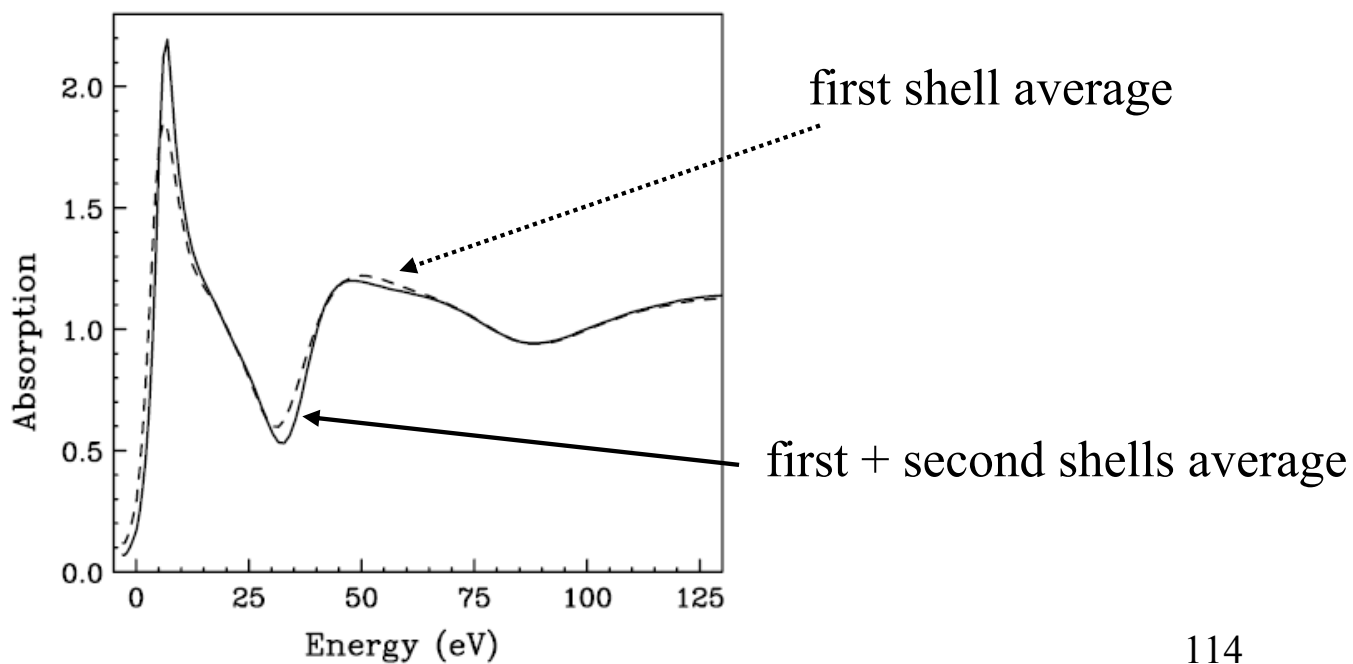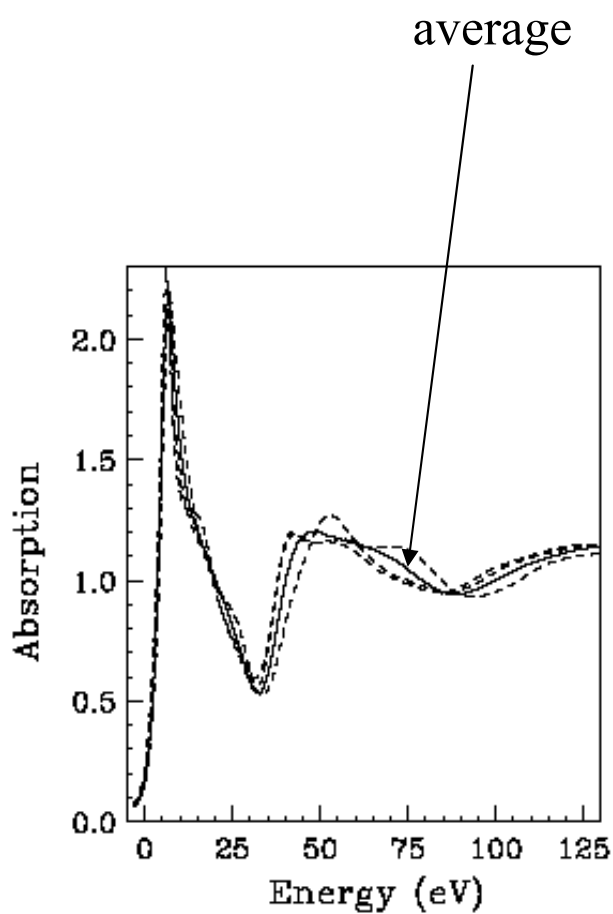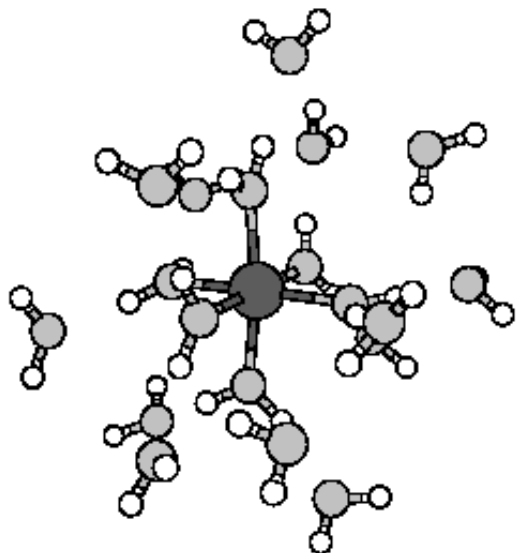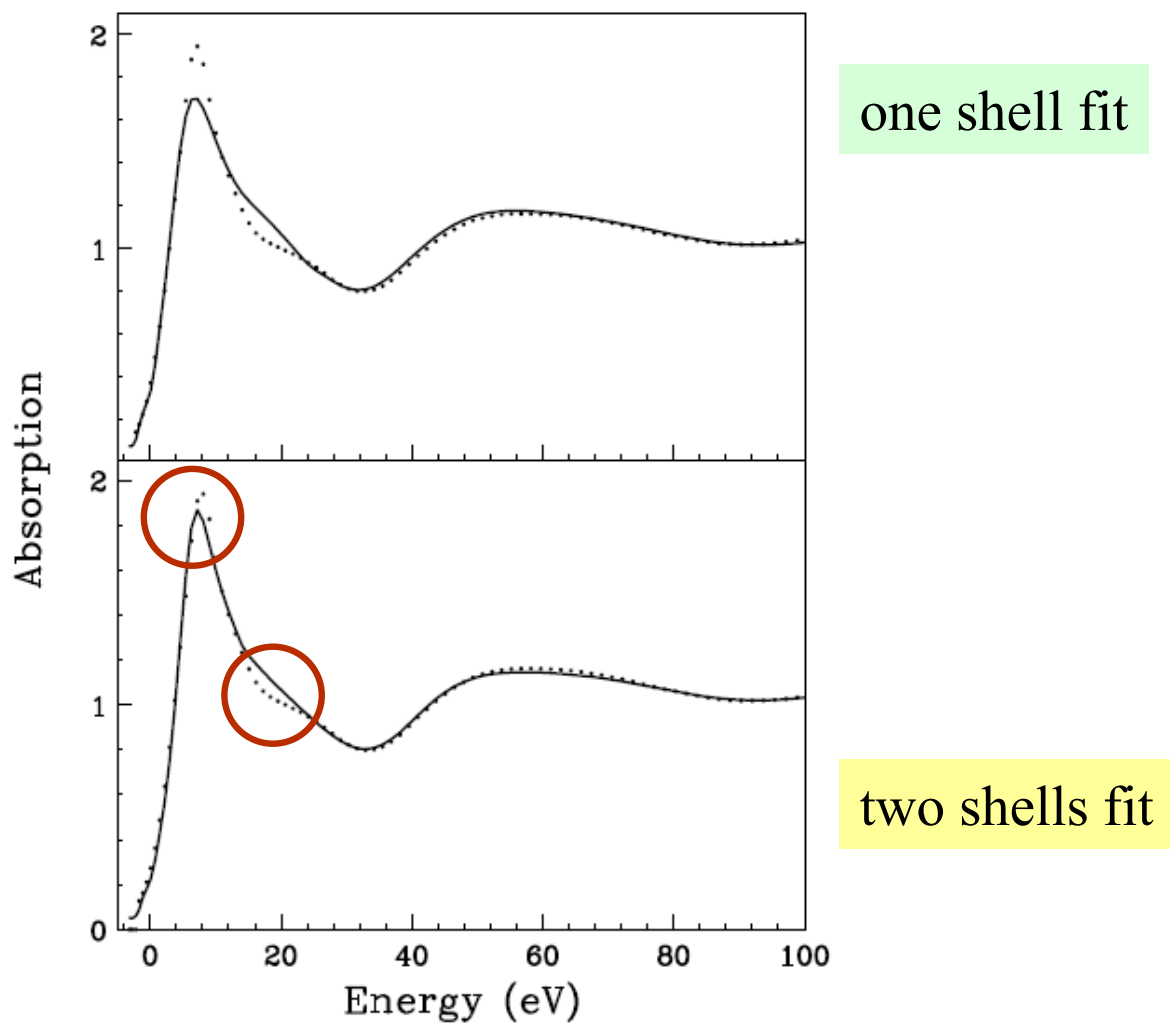
sizeable effects in the energy range 0 - 30 eV

P. D'Angelo et al. JACS 128 (2006)
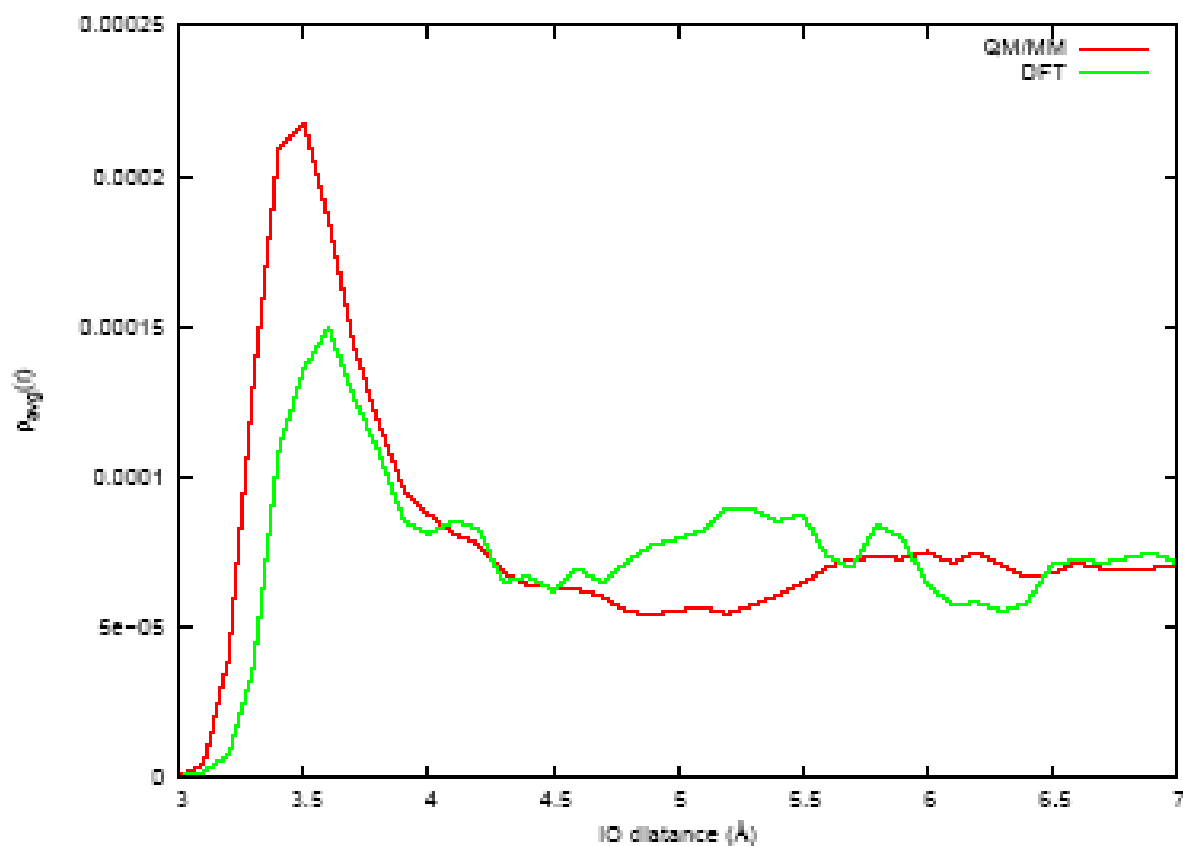
The water solvation of I⁻

L1 - L3 XAS data

as in the previous case we analyze those data by MD snapshots generate by QM/MM and DFT methods

in collaboration with Chergui's group
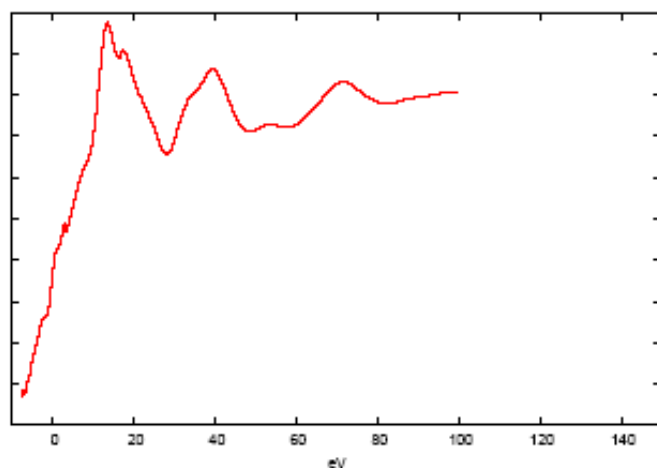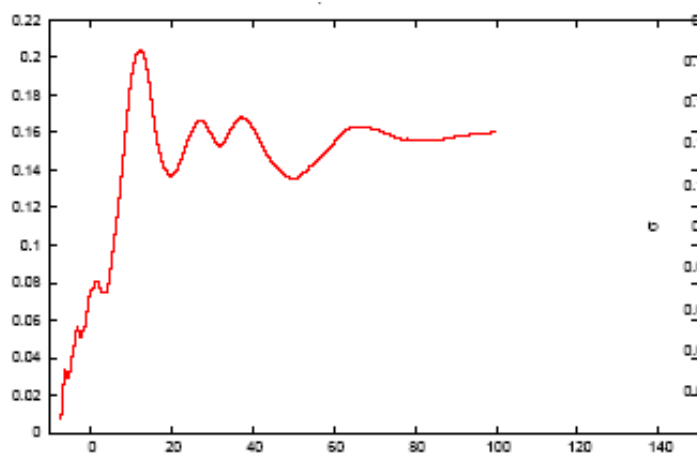
I-O pair distribution function from MD

the calculated coordination number varies from 7 to 9.7 - difficulty to define a solvation shell

We have used more than 1000 frames - three of them at L3 edge

The calculation includes atoms (H and O) up to 7 Å
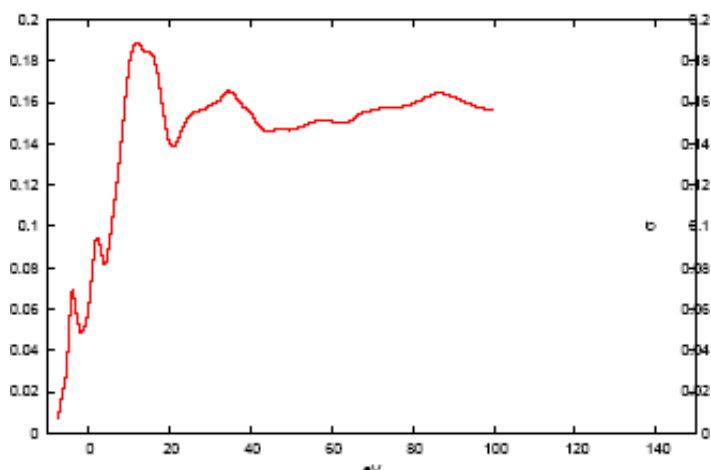
Very disordered system!
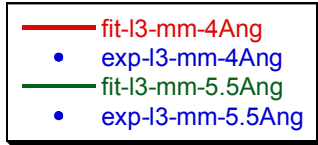
L1 Fits

L1-QM/MM simulation

QM/MM

energy (eV)

L1-DFT-simulation

DFT

120
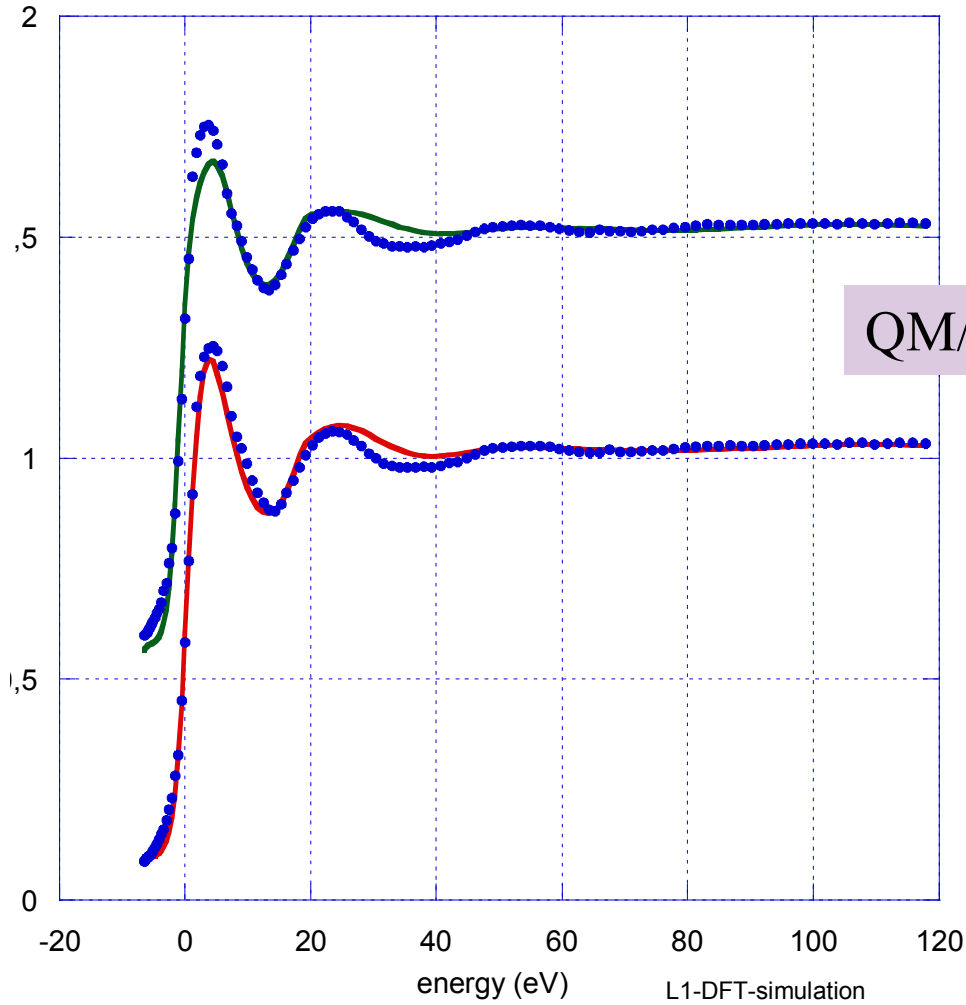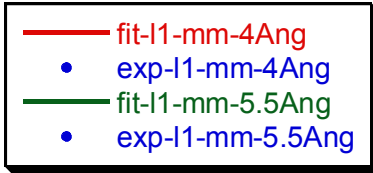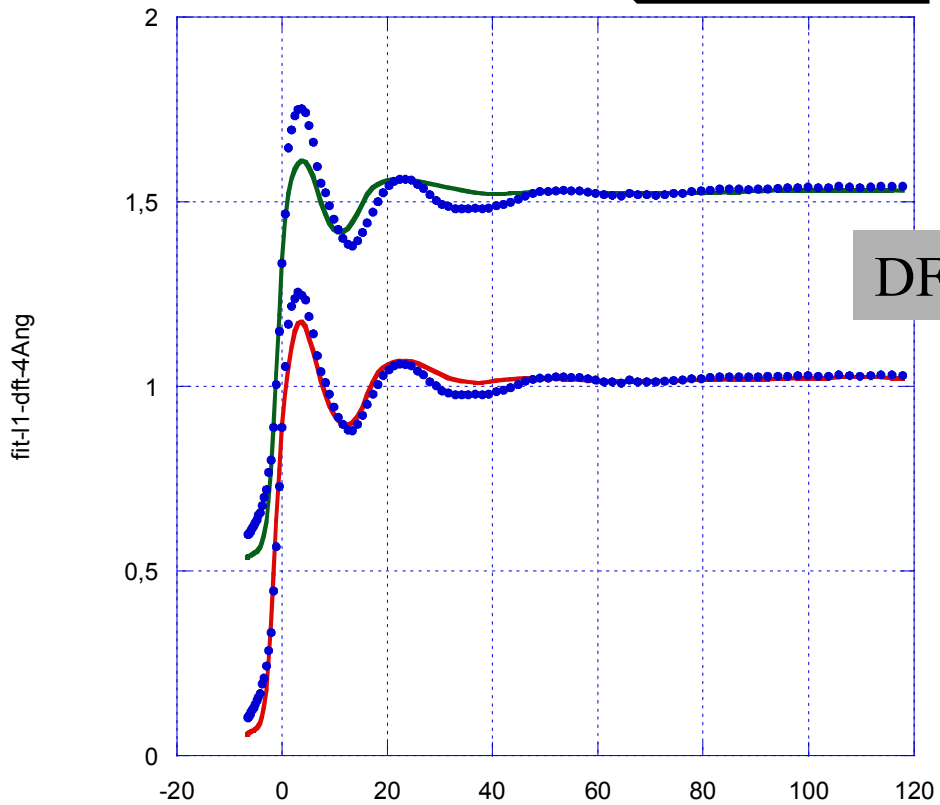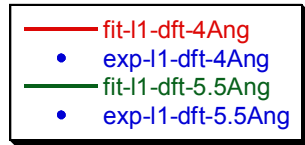
The QM/MM calculations reproduces better than DFT the experimental data for both L1 and L3 edges - Increasing the cluster size DFT becomes worse than QM/MM

It seems that DFT introduces a partial order that is not verify in the reality
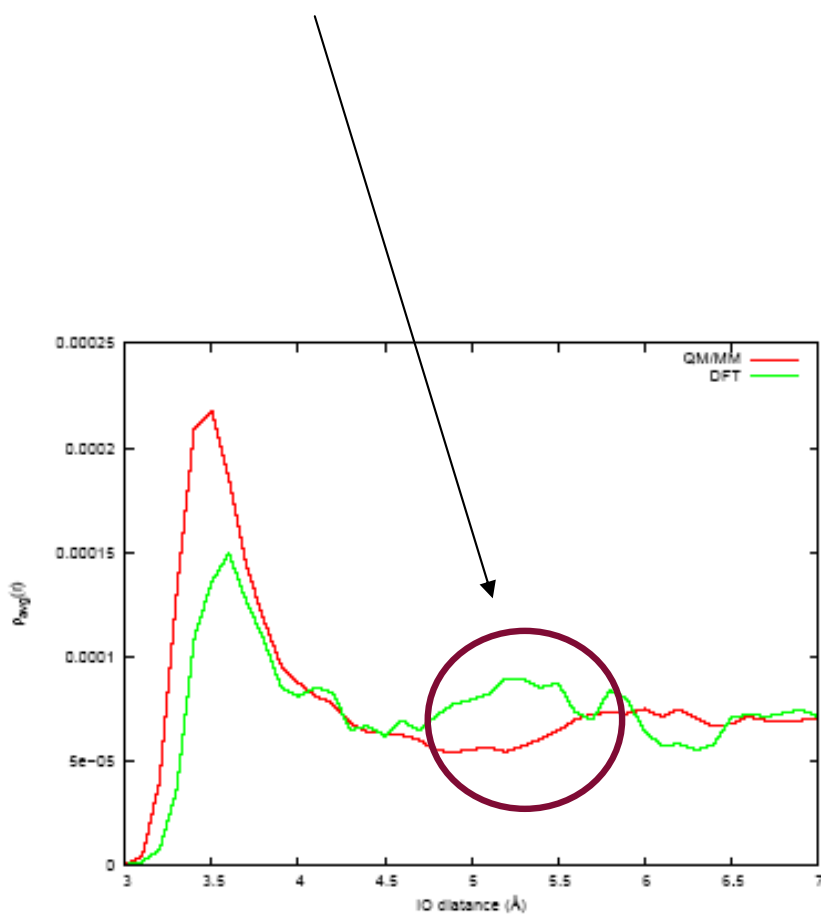
some conclusions
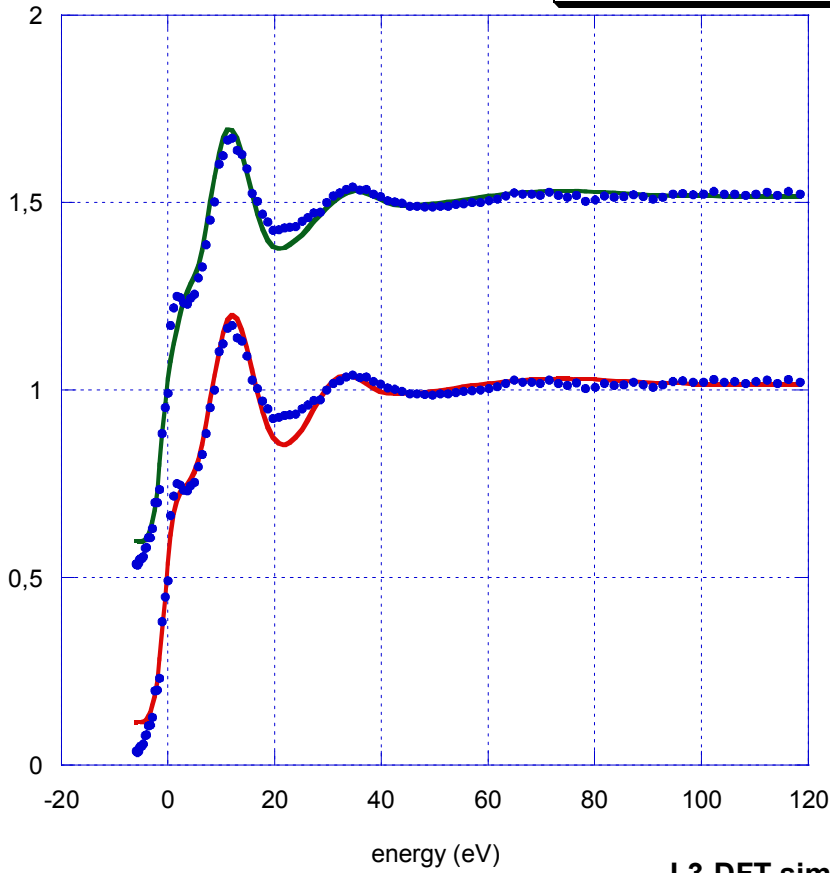
It is possible to fit the XANES energy range starting from the edge to obtain quantitative structural information

We can treat, although numerically, very disorder systems – possible application on nano-materials

Future: new MXAN using the non-MT theory - improvements for the exchange-correlation potential

MT approximation (MXAN)
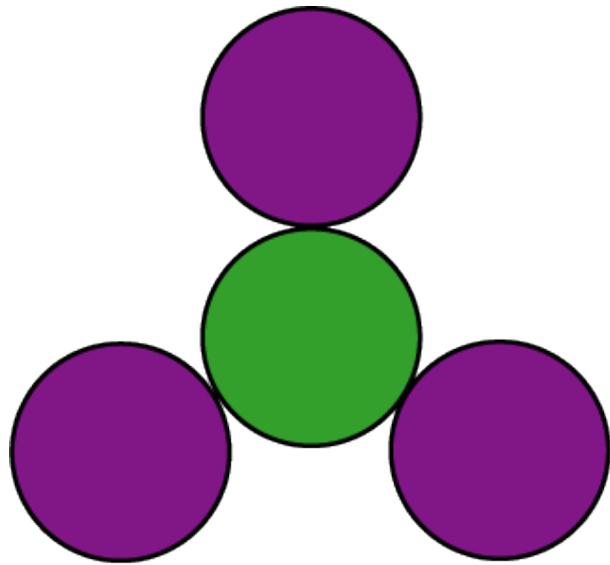
Non-MT (FPMS)

Use spherical shaped and averaged potential

outside the cells potential is flat
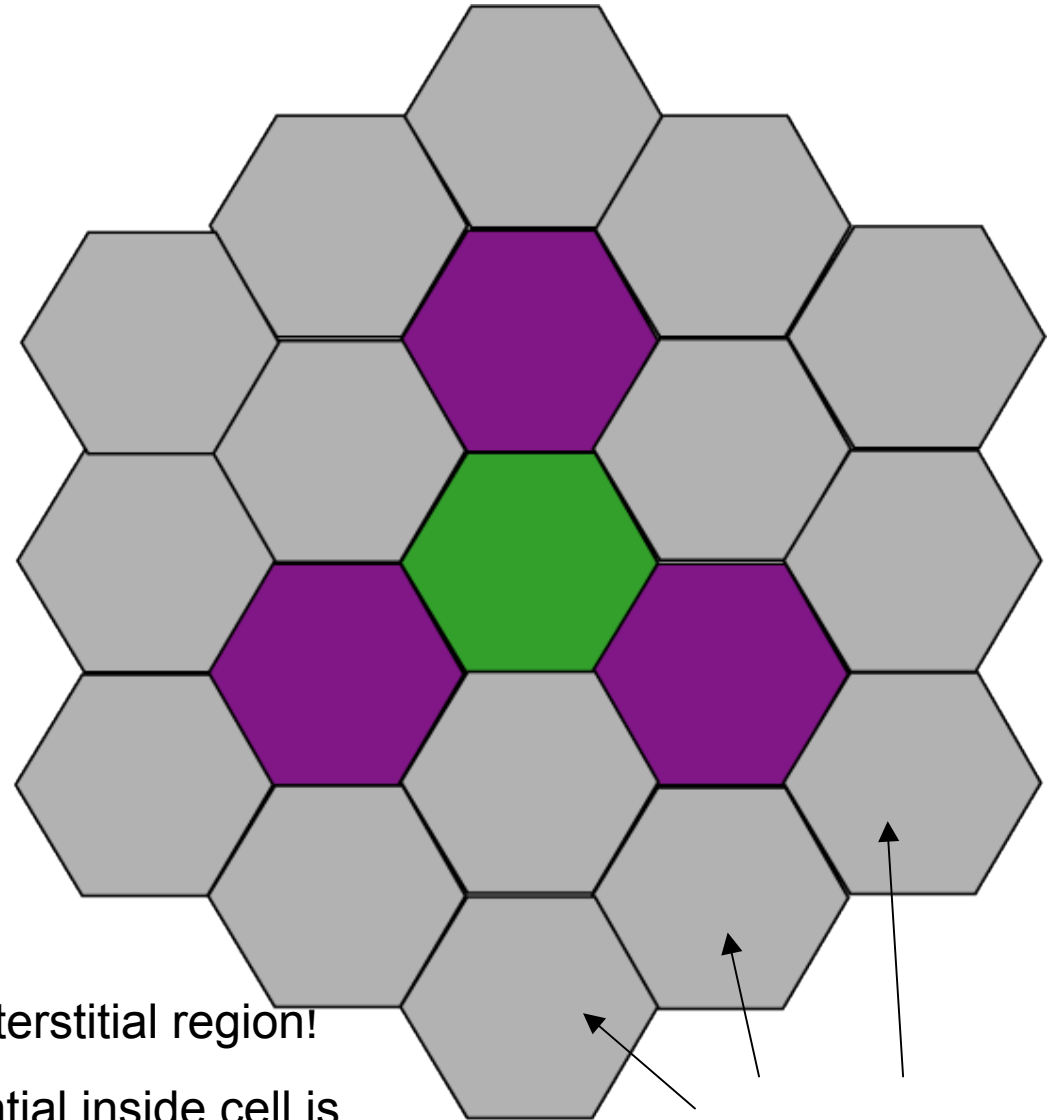
No interstitial region!

Potential inside cell is anisotropic

Empty Cells (EC)

FPMS
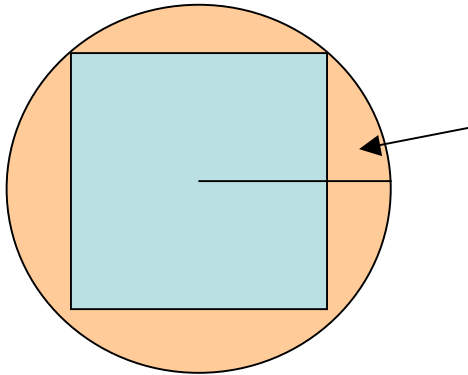
So called moon region.
In this region
expansion by
spherical harmonics
never converges.

There are two types of l_{max} in MS
1. potential power
2. anisotropy

$$V(\mathbf{r}) = \sum_L V_L(r) Y_L(\hat{\mathbf{r}}) \quad (L=(l,m))$$
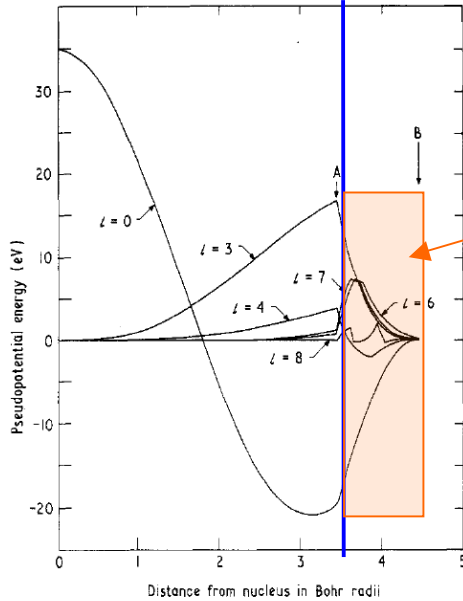
For discontinued function
spherical harmonics
expansion
never converges in
practice.
(Gibbs phenomenon)

Radial component oscillate!

Figure 8. Spherical harmonic components of the pseudopotential of Cohen and Bergstresser.
A, muffin tin radius; B, radius of circumscribed sphere.

=> We expand the wave function.

$$\Phi(\mathbf{r}) = \sum_L R_L(r) Y_L(\hat{\mathbf{r}})$$

$(L=(l,m))$

Since the wave function and its first derivative are continuous,
the series converges uniformly even with truncated potential.

Kellog, *potential theory* (1967)

$$L^2 \Phi(\mathbf{r}) = \sum_L l(l+1) R_L(r) Y_L(\hat{\mathbf{r}})$$

We treat it as inhomogeneus term in Schrödinger equation.

To solve the equation efficiently, we developed modified
Numerov method.

K. Hatada et al, PRB (2007)

Multiple scattering : Green's function picture
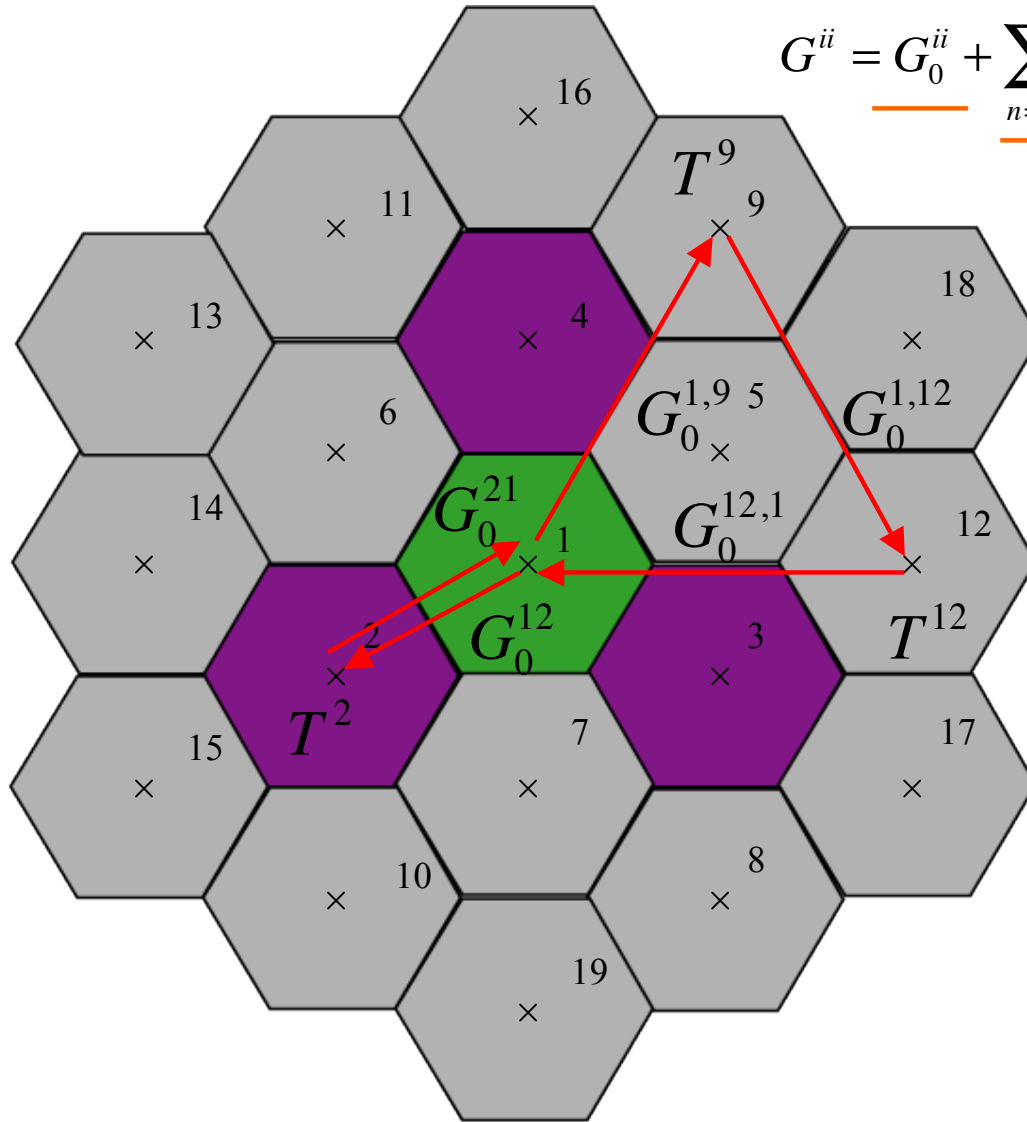
$$G^{ii} = G_0^{ii} + \sum_{n \neq i} G_0^{in} T^n G_0^{ni} + \sum_{n \neq m \neq i} G_0^{in} T^n G_0^{nm} T^m G_0^{mi} + \cdots$$

All cites have centers.

G^{ii}
:Green's function on cite i

G_0^{ii} :isolated

$\sum_n G_0^{in} T^n G_0^{ni}$

:single scattering

$\sum_{nm} G_0^{in} T^n G_0^{nm} T^m G_0^{mi}$

:double scattering

First-principles calculation of x-ray absorption-edge structure in molecular clusters

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F. W. Kutzler

Department of Chemistry, Stanford University, Stanford, California 94305

(Received 30 July 1979)

We report initial results of a systematic study of the calculation of near-edge features in the x-ray absorption spectra of an atom in a molecular cluster as a function of different chemical environments and of varying prescriptions for the effective molecular potential of the excited electron. For a test-case comparison of the K edges of $GeCl_4$ and GeH_4, we find that the chemically induced changes in the molecular potential lead to large changes in the occurrence and strengths of bound-state and shape-resonance spectral features, in semiquantitative agreement with observation.

EXPERIMENTAL (▲) vs CALCULATED GeCl$_4$

Missing!
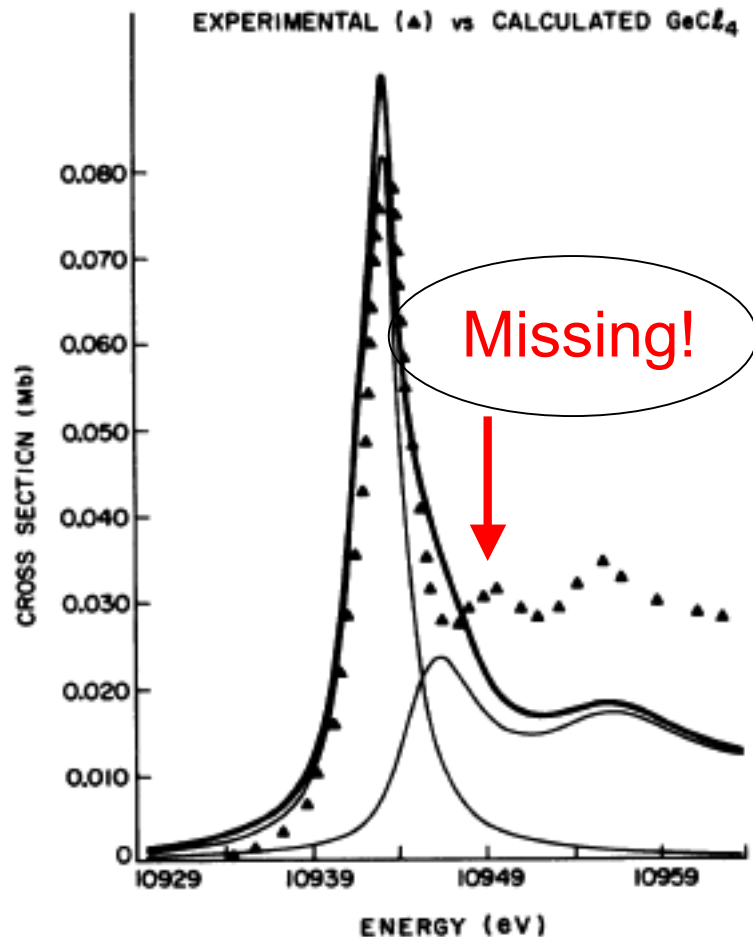
FIG. 1. Computed K-absorption spectra for Ge in GeH$_4$ (upper panel) and GeCl$_4$ (lower panel) after convolution with a Lorentzian to represent lifetime and experimental resolution effects. The light curves represent the bound-state and continuum contributions separately, while the heavy curves give the sum of the two. The energy placement of the experimental points has been adjusted for a reasonable fit (see text). Note that inelastic effects will generally be expected to increase the total cross section over the results given by the present calculation.

As far as energy dependence goes, the overall vertical scale of the experimental points shown in Fig. 1 for GeCl$_4$ has been adjusted by eye to give an overall "best fit." It may be noted that although the number and magnitude of the calculated spectral features are in qualitative agreement with experiment, the separation of the first and second continuum resonances is of order 10.0 eV compared to 6 eV seen experimentally. We ascribe this discrepancy to the inaccurate treatment of the interstitial potential by the use of the muffin-tin approximation.

Check Natoli's prediction of 30 years ago.

Ge K-edge of GeCl$_4$
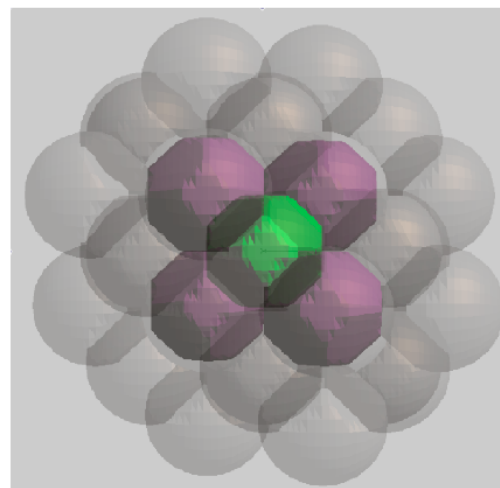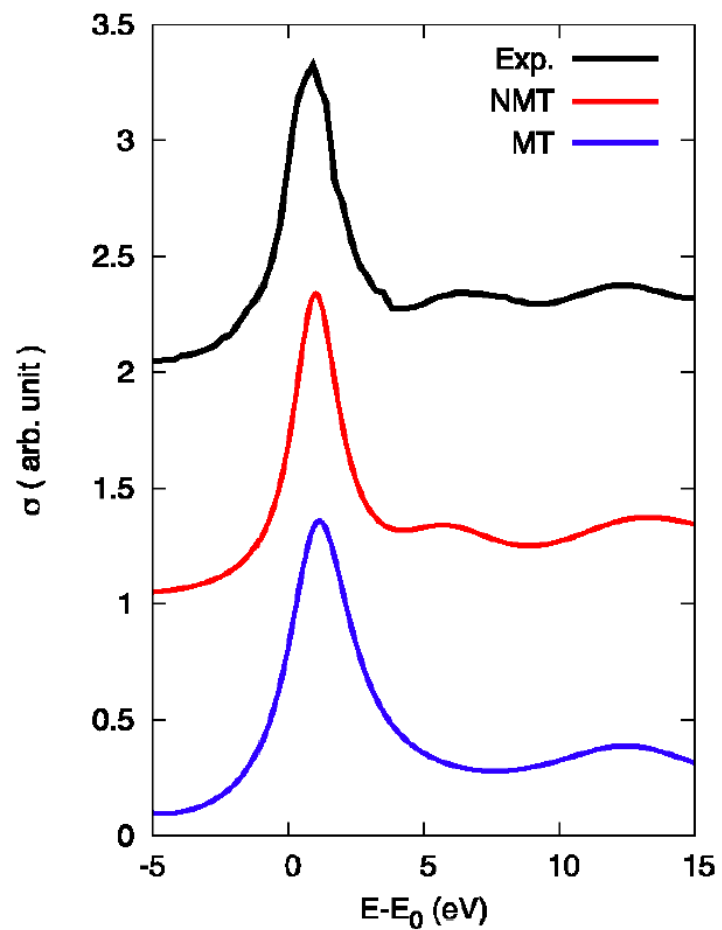
1 Ge + 4 Cl + 38 EC
(Empty cells)

Other spectroscopies

- Energy-Loss Near-Edge Structure (ELNES)

- Resonant X-ray Scattering (RXS)

- X-ray Photoelectron Diffraction (XPD)

ELNES (NMT vs MT)

SiO$_2$ (α–quartz) of Si–L$_{2,3}$–edge with (5 A cluster)

NMT
MT
Experiment

K. Hatada et. al, J. Phys. Cond. (2008)
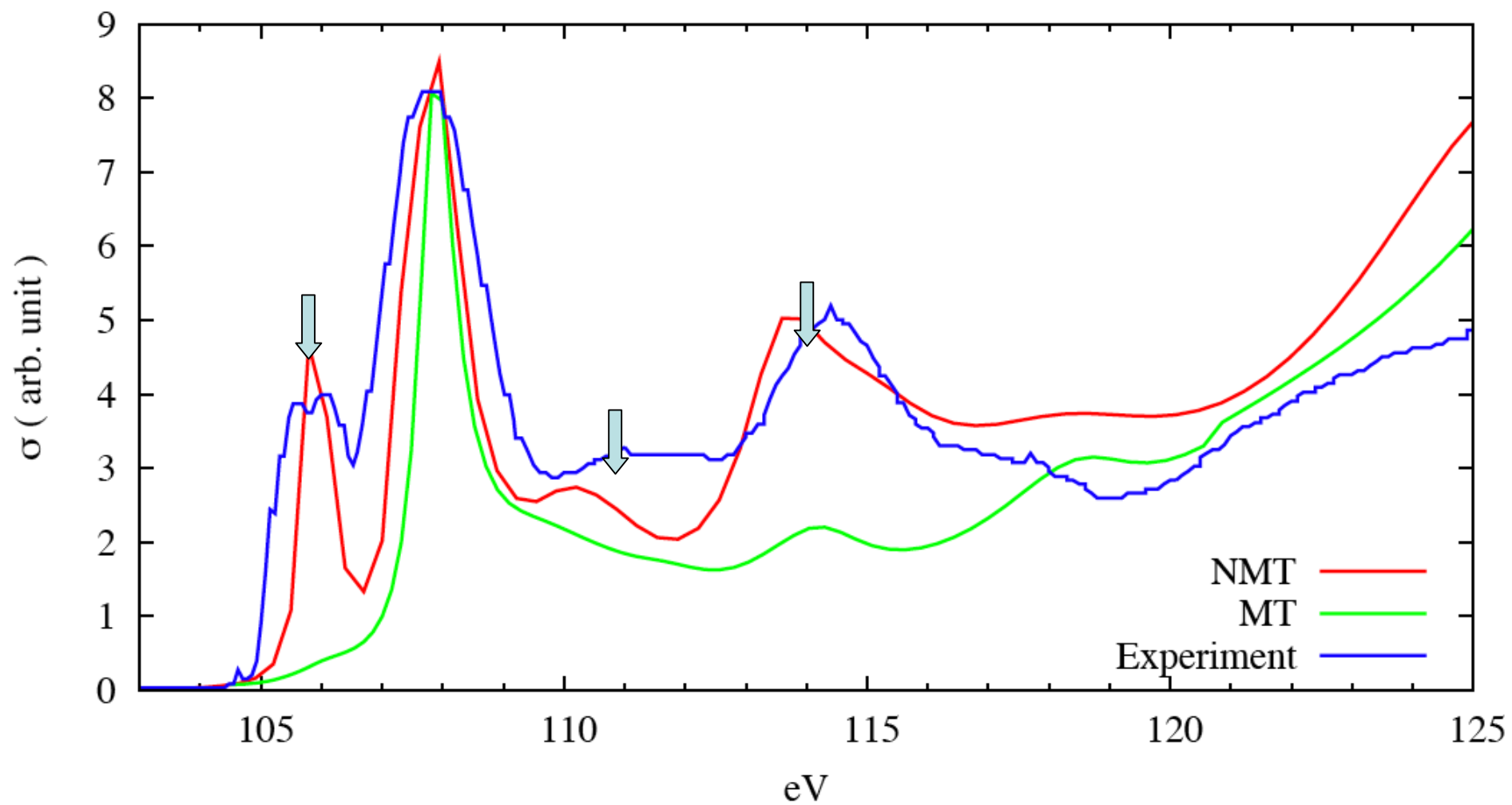
PHD of Ge 1s of GeCl4
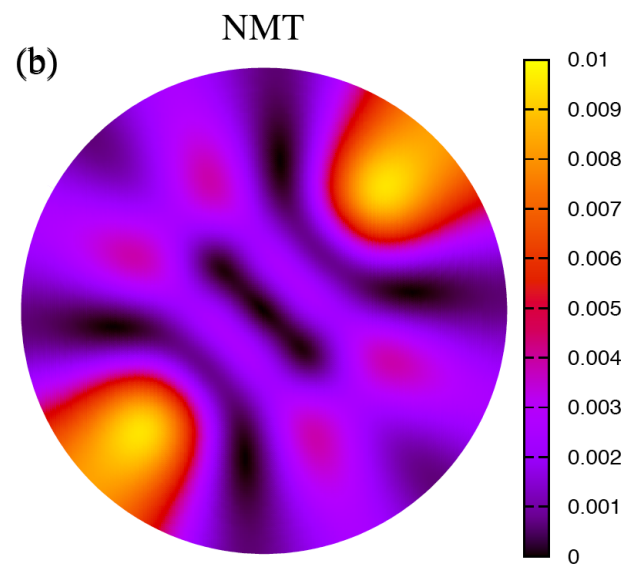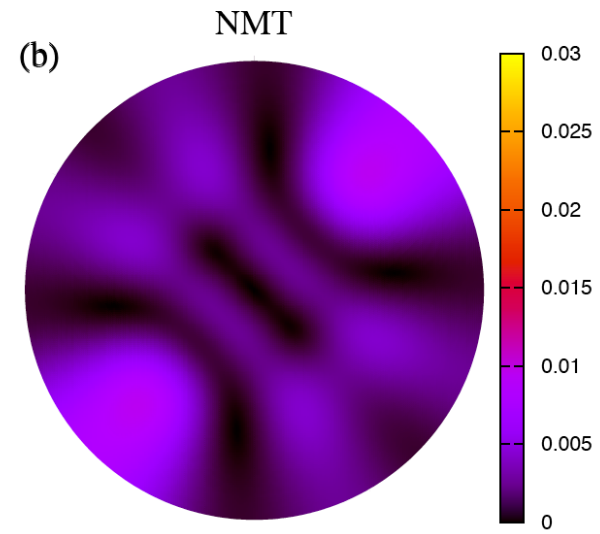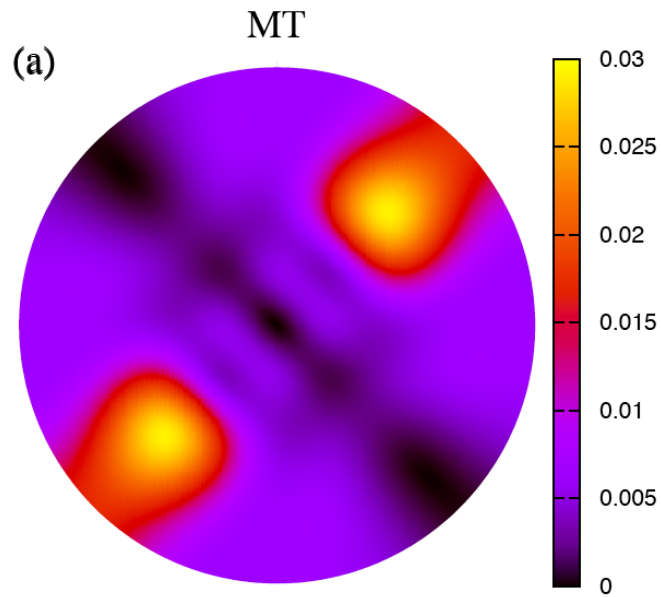
- You can find MXAN and FPMS programs at,

  http://www.lnf.infn.it/theory/CondensedMatter/index.html

  Programs are free, but registration is obligated.

THE MXAN PROCEDURE

How to run

Flow diagram of MXAN

Exp. file   Coordinate file   Commands file

MXAN

MINUIT

Recalculate potential

Select structure

Potential
fixed

VGEN

CONTINUUM

χ^2 test

Best fit files
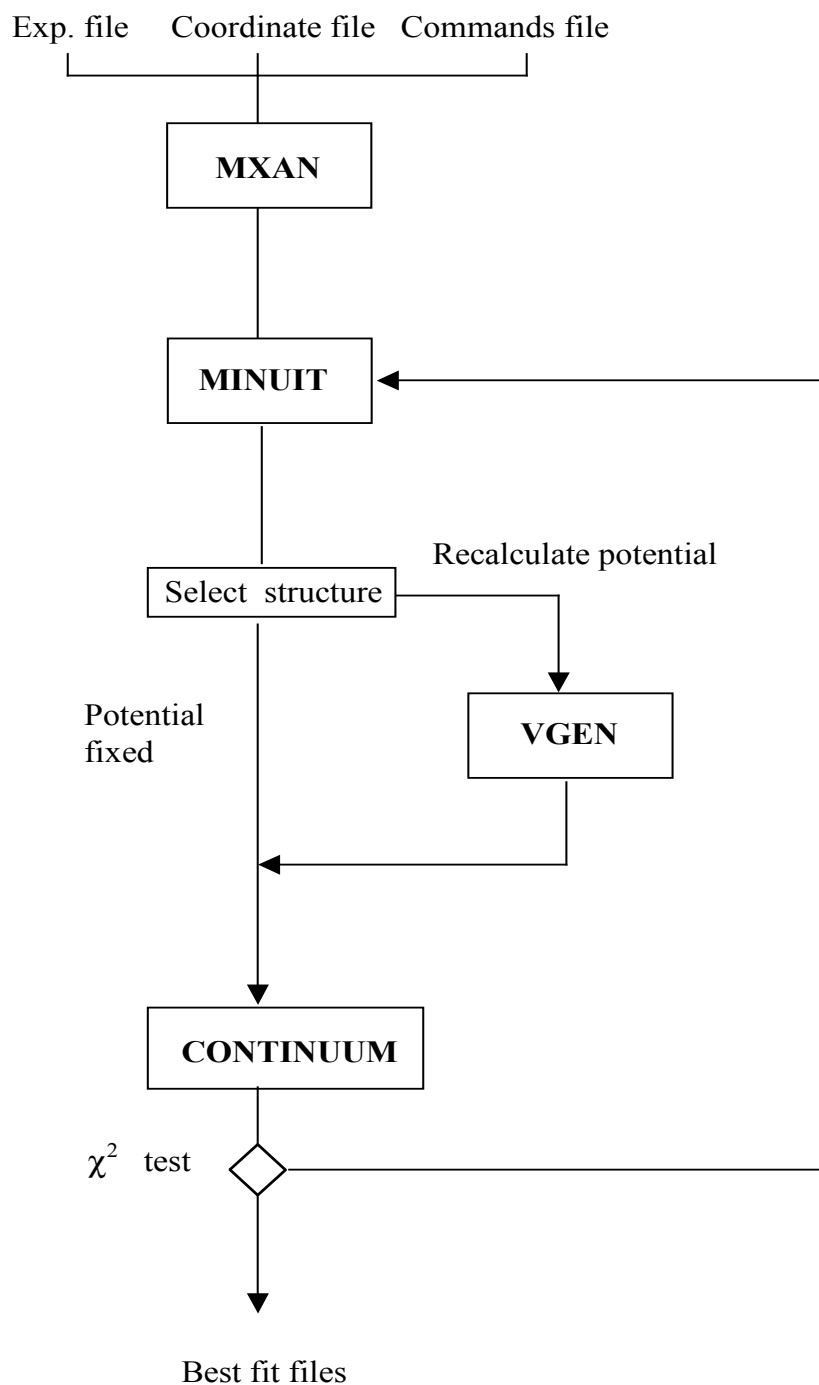
We need three inputs

Experimental data: two columns file with the normalized experimental data

energy(eV) abs
-10.00	0.034048
-9.000	0.037412
-8.000	0.043628
-7.000	0.052225
-6.000	0.068452
-5.000	0.098043
-4.000	0.14981
-3.000	0.23317
-2.000	0.35128
-1.000	0.53214
0.0000	0.74763
1.0000	1.0009
2.0000	1.2878
3.0000	1.5565
……..	………

We can use any energy step

Starting geometry file – The prototype is generated by MXAN – Users must change it for own use

```
&JOB
fname  ='NiH2'
nsca   =  19
lmax   =  3
absorber=  1
outersph=.false.
edge   ='k '
emin   =  -3.000
emax   = 150.000
delta  =   0.200
xscale =   1.400
gamma  =    .000
typot  ='hlrel'
charelx ='ex'
norman  ='extrad'
ovlpfac =    .120
coor   ='angs'
potcalc ='Y'
symcalc ='Y'
parcalc ='Y'
v0imp  =    .000
rhoimp =    .000
&END

tit1
tit2
tit3
tit4 iz   x      y      z  rad  ilig ------- comm ----------

  28  .00000  .00000  .00000 1.26000  0  .00000  Ni_____000
   8  .00000 -1.90711  .00000  .90000  1 2.02119  O_____eq1
...............................................................................
```

```
-----------------------------------------------------------
---- CuN square piramid with O ax with H and more N  --
-----------------------------------------------------------
 CuNH  --parameter- in.deviat. - init.err. --- phys.limits ---
 1     r001     0.0000   0.0200  -0.1000   0.1000
 2     f001     0.0000   3.0000 -20.0000  20.0000
 3     t001     0.0000   0.0000 -10.0000  10.0000
 4     r002     0.0000   0.0200  -0.1000   0.1000
……
……
……
34     r012     0.0000   0.0000  -0.1500   0.1500
35     f012     0.0000   0.0000 -10.0000  10.0000
36     t012     0.0000   0.0000 -10.0000  10.0000


--------- Control options ---------
   36               ! n of parameters (fixed + variable)
NORM   1SHE    ! Mode(NORM,EXTE,RECO),Search(1SHE,CXYZ,OPTN)
U           ! U (Unpol)  XY (PolarXY)  Z (Pol.z)  P (Pol.)
1           ! not active...
 --------- INPUT files -------------
CuNH3.exp            ! EXP. FILE  to fit
 0.01000            ! EXP. ERROR
DATA.CuN8OH         ! Coords and options for potential
N  1               ! Other th. calc. sites? How many?
 0.5 CuN2H-22.BEST 0.0    ! Fract,Input calc.othersite, Shift?
 -------- INTERMEDIATE files -------------
CuNH.PARM            ! params for MS
CuNH.SYMM             ! File with symmetry info and lmax
CuNH.XALP            ! X-alpha potential
CuNH.COUL            ! Coulomb potential
CuNH.RHOD            ! Charge densities
 --------- OUTPUT PREFIX ------------
CuN8OH-1             ! Output files prefix (MAX 8 CHAR)
 -------- PARAMETERS align, norm, broad --------------
 0.025  0.004 1.500 3.000       !norm,+/-,Exp.shift,+/-
 Y   45000                ! Broad?  Tot trials
 -3.500  2.000               ! E.Fermi -- +/-
 1.600  0.400               ! Broad   -- +/-
 0.800  0.600               ! Broad_Exp  -- +/-
 Y                 ! mf ?
  1                   ! # plasmons
 14.000 10.000 10.000  8.000      ! En. +/- , Ampl. +/-
 N     0.02  70.0  0.02   !Extra Exc? ampl,energy,width
-------- OTHER OPTIONS --------------
 Y  6               ! Correlation links? How many?
  1  7
  4 10
  2  8
  5 11
 16 22
 19 25                  ! between which params ?
 Y N                 !Slope?,Concerted motions?
 N     30.000  10.000     !weight?(N,A,T,G) xcentr, width


SET PRINT   3
 SEEK     90
! SCAN   13      10     -.2    .2
! FIX     2.
 SIMPLEX   100    0.03
 CALL FCN  -2
```

Control file – general information – methods for fitting – It is always called COMMAND.MIN

We get several outputs, the most important is the BEST file where you find all information about the fit

FPMS

- Input file must be named as "data.ms".

- In principle the way to use parameters are the same as "data.ms" of program POTGEN or "DATA.****" of MXAN.

- For non-MT calculation, you should add,

  NMT   = "NM"
  truncate = .true. (voronoi)
or
  truncate = .false. (ASA)