

# Progresses in the MXAN Fitting Procedure

Kuniko Hayakawa\*, Keisuke Hatada\*, Stefano Della Longa<sup>†</sup>, Paola D'Angelo\*\* and Maurizio Benfatto\*

*\*Laboratori Nazionali di Frascati, INFN, CP13,00044 Frascati, Italy*

*<sup>†</sup>Dipartimento di Medicina Sperimentale, Universita "L'Aquila", Via Vetoio 67100 L'Aquila, Italy*

*\*\*Dipartimento di Chimica, Universita "la Sapienza", Piazzale A. Moro, Moro 5, 00185 Roma, Italy*

**Abstract.** Recently, a new method (MXAN) of extracting the local structural information available in the XANES spectra has been developed in the framework of the multiple scattering theory and successfully applied to the analysis of several system, both in solid and liquid state. In this paper we show the progress we have done in the MXAN procedure, in particular for what concerns the phenomenological broadening and the electronic charge fitting. We have also implemented parallelization on MXAN code by MPI library for both energy points and annealing for no-structure parameters. This approach reduce the computer time of a factor  $\approx 10$  ( our cluster contains 14 nodes but the computer times scales with the number of nodes ) and at the same time increase the accuracy of the method. The new version of the program will be discussed on the basis of several examples.

**Keywords:** X-ray absorption spectra; XANES; MXAN

**PACS:** 61.10.Ht, 78.70.Dm

## INTRODUCTION

X-ray absorption spectroscopy ( XAS ) is one of the most powerful methods to obtain electronic and structural information on the site around the absorbing atom of different type of matter. The X-ray absorption near-edge structure ( XANES ) part, which is from the rising edge up to a few hundreds of eV, is very sensitive to the structural details of the absorbing site and, in principle, an almost complete recovery of the three-dimensional structure can be achieved from this energy region. However, the quantitative analysis of the XANES spectra presents some difficulties mainly linked to the theoretical approximation in the treatment of the potential and the need for heavy time-consuming algorithms to calculate the absorbing cross section in the framework of full multiple scattering approach.

The possibility to perform quantitative XANES analysis to obtain a structural determination of an unknown compound can be relevant in many scientific fields, like extra-dilute system, trace-element analysis, local investigation of materials under extreme conditions and much more in biological systems where the low S/N ratio and the weak scattering power of the light elements limits the  $k$ -range of the available experimental data.

The MXAN program performs a quantitative analysis of the XANES energy range, *i.e.* from the edge up to 200 eV. This is based on a comparison between experimental data and many theoretical spectra that are calculated by varying selected structural parameters of an initial putative structure, *i.e.* a well defined initial geometrical configurations around the absorber. Hundreds of

different geometrical configurations are needed to obtain the best fit of the experimental data. The best fit condition is reached in a reasonable time, typically few hours for a molecular systems. The optimization in the parameter space is achieved by the minimization of the square residual function (  $R_{sq}$  ) in the parameter space. The calculations are performed in the energy space without involving any Fourier-transform algorithm; polarized spectra can be easily analysed because the calculations are performed within the full MS approach.

The aim of this work is to show several improvements of the MXAN fitting procedure for what concerns both computing time and the increase of the accuracy of the method.

## PARALLELIZATION OF MXAN PROGRAM

The scattering path operator is calculated exactly without the series expansion for all the hundreds of different geometrical configurations needed to obtain the best fit of the experimental data. Typically the computing time to reach the best fit conditions in a serial computer is of the order of several hours depending to the cluster size used in the calculation. To speed up the calculation, we modified the program to perform parallel calculations by using our in-home-made PC-cluster. The parallel version of MXAN uses MPI ( Message Passing Interface ) library<sup>1</sup> to exchange data between each nodes. Parallelization was done by splitting the total energy points and the trials for the Monte Carlo search of the non-

structural parameters within the nodes of our cluster. In this way we got an almost linear speed up with the number of nodes. Our cluster is formed by 15 racks each formed by 2 x Intel Pentium Xeon at 2.8 GHz with 2 GB of memory. For clustering software we installed SCore system<sup>2</sup> with Linux operating system. SCore uses PMvII high performance communication library to increase the communication speed in comparison to normal TCP/IP mode. In our system we have reduced by a factor of 10 the computing time for one full fit.

## THEORY

The detail of basic theory of MXAN method is written in ref. [3]. In this section we describe the changes done in the new version of MXAN procedure. The MXAN method is based on the muffin-tin approximation for the shape of the potential and the use of the concept of complex optical potential, based on the local density approximation of the self-energy of the excited photoelectron. The real part is calculated by the Hedin-Lundqvist potential using the whole charge density. During the calculation, the numerical values are derived at each step of computation (i.e. for each geometrical configuration) on the basis of a Monte Carlo fit.

The inelastic processes are taken into account by a convolution with a broadening Lorentzian function having an energy dependent width of the form  $\Gamma(E) = \Gamma_c + \Gamma_{mfp}(E)$ . The  $\Gamma_{mfp}(E)$  function is zero below an onset energy  $E_s$  (which in extended systems corresponds to the plasmon excitation energy) and begins to increase from a value  $A_s$  following the universal functional form of the mean free path in solids. Both the onset energy  $E_s$  and the jump  $A_s$  are introduced in the  $\Gamma_{mfp}(E)$  function via an arctangent functional form to avoid discontinuities and to simulate the electron-hole pair excitations. The constant part  $\Gamma_c$  includes the core hole lifetime and the experimental resolution, while the energy dependent term represents all the intrinsic and extrinsic inelastic processes.

We have modified this procedure by introducing a further convolution by a Gaussian function ( $\Gamma_{exp}$ ) to mimic the experimental resolution. The contribution coming from the Lorentzian function contains now only the core-hole part. In this way we can obtain a much more accurate description of the inelastic losses suffered by the photoelectron.

We have also introduced the possibility of fitting the charge over all the atomic species in the cluster used in the calculation. Mainly we changed the potential part from the Dirac-Hartree-Fock-Slater equation to the non-local Dirac-Hartree-Fock equation. In this way we can deduce the total net charge over the atomic species and at the same time we can check the influence of the charge details over the structural fit.

## RESULTS AND DISCUSSION

As test we show here the results regarding transition metals in water, in particular the  $\text{Me}(\text{H}_2\text{O})_6$  systems where Me is Co and Ni in the octahedral geometry. The experimental error is kept fixed to 1.8% of the main jump in all calculations.

$$\Gamma_{core} \text{ vs } (\Gamma_{core} + \Gamma_{exp})$$

Table 1 summarizes the results obtained with the new convolution procedure. The residual error function  $R_{sq}$  strongly decreases compared with the values obtained with the old procedure. At the same time the structural determination remain the same within the statistical errors.

### Fit over the charges

The new fitting procedure allows us an optimization over the charges of the atomic species of the used cluster. Hydrogen atoms are kept neutral during the fit. In figure 1, we report the comparison between the calculations at the best fit conditions with the experimental data measured at the k-edge of the metal. The agreement is quite good in the whole energy range. Structural finding are shown in table 2, where we also report for comparison the results obtained for the neutral case.

These fits are performed in 3 steps : first we have optimized the structure by using neutral atoms. In the next step we have fitted the charges of the atomic species keeping fixed the structure at the neutral finding. Last optimization has been made over the structural parameters using the charges found in the second step of the whole procedure.

## CONCLUSION

In this paper we have presented the last improvements of the MXAN fitting procedure. In particular we have shown as the introduction of the experimental convolution strongly improves the agreement between experimental data and the best fits<sup>4</sup>. At the same time the structural determination remains quite stable conforming the fact that this spectroscopy is dominated by the structural arrangements around the absorber.

The fit procedure over the charge clearly indicates the presence of a well defined minimum that corresponds to a decrease of the  $R_{sq}$  of about 20% compared with the neutral fits. Again the structural results are quite stable. To conclude we have described the last improvements of the MXAN procedure and some of the new potentialities of the method.

**TABLE 1.** Comparison of broadening function. : Lorentzian ( $\Gamma_{core}$ ) vs Lorentzian ( $\Gamma_{core}$ ) + Gaussian ( $\Gamma_{exp}$ )

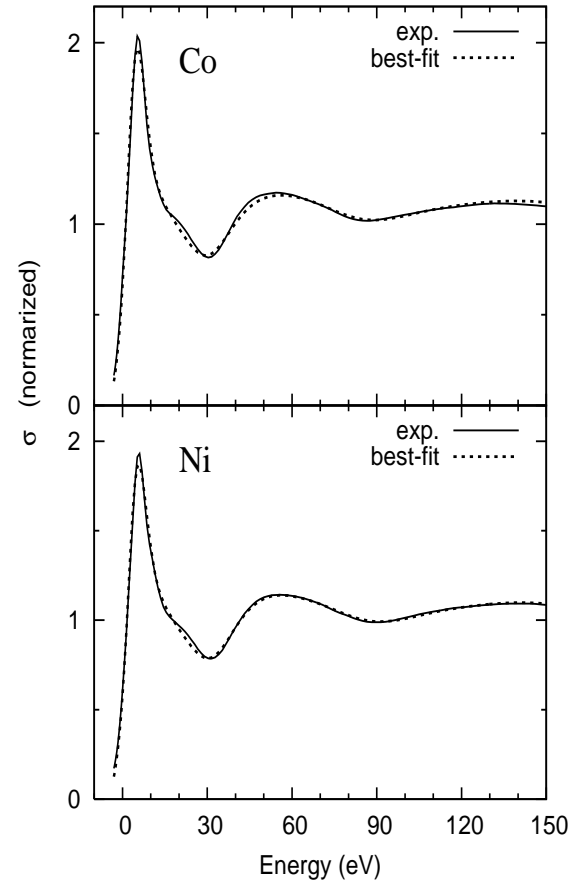
		$R_{sq}$	Broadening		Distance of Me-O
			$\Gamma_{core}$	$\Gamma_{exp}$	
Co(H <sub>2</sub> O) <sub>6</sub>	$\Gamma_{core}$	2.1107	1.92	/	2.06429
	$\Gamma_{core} + \Gamma_{exp}$	1.5436	0.78	1.60	2.06601
Ni(H <sub>2</sub> O) <sub>6</sub>	$\Gamma_{core}$	1.1509	2.41	/	2.03577
	$\Gamma_{core} + \Gamma_{exp}$	0.84283	1.63	1.46	2.03801

**TABLE 2.** Results of the charge fit

	Ionic Charge				Neutral	
	$R_{sq}$	Me	O	R (Me-O)	$R_{sq}$	R (Me-O)
Co(H <sub>2</sub> O) <sub>6</sub>	1.2497	0.49845	-0.00010	2.06875	1.5436	2.06516
Ni(H <sub>2</sub> O) <sub>6</sub>	0.68196	0.37942	-0.00532	2.04323	0.84283	2.03967

## REFERENCES

1. The Message Passing Interface (MPI) standard, <http://www-unix.mcs.anl.gov/mmpi/>
2. PC Cluster Consortium, <http://www.pccluster.org/>
3. M. Benfatto, and S. Della Longa, *J. Synchrotron Rad.* **8** 1087–1094 (2001).
4. P. D’Angelo, M. Benfatto, S. Della Longa, and N. V. Pavel, *Phys. Rev. B* **66** 064209 (2002).



**FIGURE 1.** Comparison between the experimental Me K-edge data of Me(H<sub>2</sub>O)<sub>6</sub> (dotted line) and the best-fit calculation performed by the MXAN procedure (solid line).