

## A New Fast Spherical Approximation (FSA) for Calculation of Multiple-Scattering Contributions in XAFS

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A new Fast Spherical Approximation (FSA) for the calculation of the multiple-scattering contributions in the X-ray-absorption fine structure is suggested. The analysis of the XAFS-spectra of the Re  $L_3$ -edge in  $\text{ReO}_3$ , the W  $L_3$ -edge in  $\text{NaWO}_3$ , the Ir  $L_3$ -edge in  $\text{IrO}_2$  and the Mo  $K$ -edge in  $\text{MoO}_3$  is considered. It is shown that the theoretical spectra, calculated using the FSA, are in good agreement with the experimental data both in the low and high energy ranges.

**KEYWORDS:** multiple-scattering, X-ray-absorption spectra

### §1. Introduction

The modern theory of the X-ray-absorption fine structure (XAFS) based on the multiple-scattering (MS) formalism<sup>1,2)</sup> is very time consuming computationally and cannot be widely used in the routine structural analysis of unknown systems. Due to that several attempts have been made in previous years to find adequate approximations which are simpler and faster than the exact curved-wave approach.<sup>3-6)</sup> However, up to now there is not sufficiently large number of works, in which these approximations have been applied and tested for various compounds. Moreover, it is known that the simplest approach, based on the Plane-Wave Approximation (PWA),<sup>6)</sup> leads to large errors as in the phase as in the amplitude of the XAFS signal especially at low energies.

In this work we present a new Fast Spherical Approximation (FSA) for the MS terms calculation. We demonstrate its use on example of several crystalline compounds ( $\text{ReO}_3$ ,  $\text{NaWO}_3$ ,  $\text{IrO}_2$  and  $\text{MoO}_3$ ) with well known structure and high contribution of the MS processes. Note that the new approach works as fast as the PWA, but gives good agreement with experimental data both in the low and high energy ranges.

### §2. Experimental and Data Analysis

The experimental X-ray-absorption spectra of the Re, Ir, W  $L_3$ -edge and the Mo  $K$ -edge have been measured in transmission mode at room temperature at the ADONE storage ring (INFN LNF, Frascati) using the EXAFS station on the "PWA" BX-1 wiggler beam line. The storage ring ADONE has operated at 20-50 mA and 1.5 GeV with a wiggler current of 4000 A. The synchrotron radiation

has been monochromatized using the channel-cut crystal monochromator (Si(111) or Si(220)), and its intensity has been measured by two ionization chambers filled with a krypton gas. The energy resolution has been estimated equal to  $\sim 1$  eV.

The X-ray-absorption coefficient  $\mu(E)$  was calculated from the intensities of synchrotron radiation before  $I_0$  and after  $I$  passing through the sample. Then, the background contribution  $\mu_b(E)$  was approximated by the Victoreen rule ( $\mu_b = A/E^3 + B/E^4$ ) and subtracted from the experimental spectrum  $\mu(E)$ . The atomiclike term  $\mu_0(E)$  was found by a cubic-spline approximation, and the EXAFS signal  $\chi(E)$  was determined as  $\chi(E) = (\mu - \mu_b - \mu_0) / \mu_0$ . The energy origin  $E_0$  was chosen past the white line on about 15 eV above the inflection point of the absorption edge.

The experimental data and the results of the analysis of the first coordination shell have been published by us earlier.<sup>7)</sup>

### §3. Fast Spherical Approximation

In the multiple-scattering theory the oscillatory structure  $\chi^l$  of the X-ray-absorption spectrum can be expanded into the scattering series<sup>1)</sup>

$$\chi^l = \sum_{n=2}^{\infty} \chi_n^l, \quad (1)$$

where the quantities  $\chi^l$  can be expressed in the general functional form<sup>8)</sup>

$$\chi_n^l = \sum_i A_i(k, R_i) \sin(2kR_i + \Phi_i^l(k, R_i) + 2\delta_c^l). \quad (2)$$

In the PWA without taking into account thermal vibrations the contribution to the total oscillatory struc-

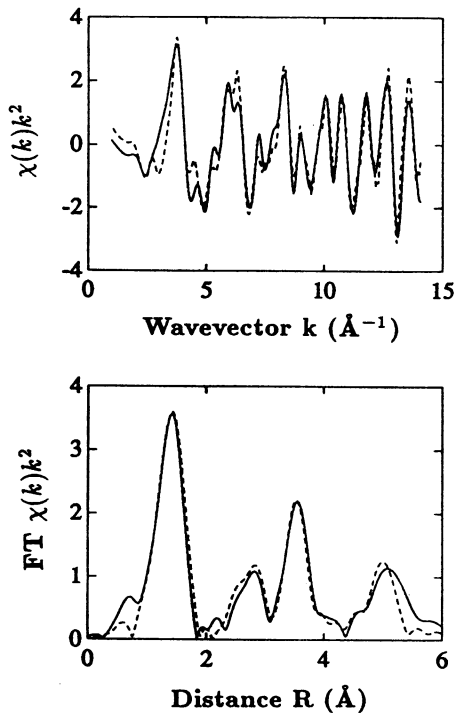


Fig. 1. The experimental (dashed line) and calculated (solid line) XAFS-signals  $\chi(k)k^2$  (upper figure) and their Fourier transforms (lower figure) for the Re  $L_3$ -edge in  $\text{ReO}_3$ .

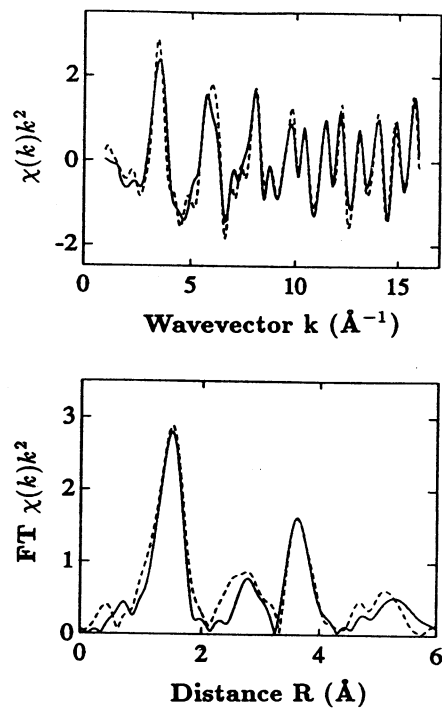


Fig. 2. The experimental (dashed line) and calculated (solid line) XAFS-signals  $\chi(k)k^2$  (upper figure) and their Fourier transforms (lower figure) for the W  $L_3$ -edge in  $\text{NaWO}_3$ .

ture from the process, in which the excited photoelectron experiences ( $n-1$ ) scatterings, is given by<sup>2)</sup>

$$\chi_n^l(k) = (-1)^l \frac{N}{k \prod_{i=1}^n R_i} P_l(\cos \theta_c) \times \text{Im} \left[ e^{2i\delta_c^l} e^{2ik \sum_{i=1}^n R_i} \prod_{j=1}^{n-1} f(\theta_j, k) \right], \quad (3)$$

where  $l$  is the angular momentum of the photoelectron,  $N$  is the degeneracy of the path,  $P_l(\cos \theta_c)$  is the Legendre polynomial,  $\delta_c^l$  is the absorbing atom's phase shift and  $f(\theta, k)$  is the complex scattering amplitude.

In the FSA, taking into consideration the curvature of the photoelectron wave, we propose to calculate the scattering amplitude  $f$ , which will be distance-dependent in this case, according to the expression

$$f(\theta, k, R) = \frac{1}{k} \sum_i (2\bar{l} + 1) t_i P_i(\cos \theta) \times \sum_{\bar{l}} (2\bar{l} + 1) \left\{ \begin{pmatrix} l & \bar{l} & \bar{l} \\ 0 & 0 & 0 \end{pmatrix} C_{\bar{l}}(kR) \right\}^2 \quad (4)$$

where  $t_i$  is the T-matrix element,  $C_{\bar{l}}(\rho)$  is the polynomial factor defined by Rehr et al<sup>9)</sup> and  $R$  is the length of the path from the absorber to the scattering atom. One can see that in the single-scattering case ( $n=2$ ) Eq. (4) becomes exact, but for double ( $n=3$ ) and triple ( $n=4$ )

scatterings it has different from the PWA form, which is essentially simplified in comparison with exact expression.<sup>1)</sup>

The comparative time for the MS terms calculation by the FSA is about  $10^3$  less than in the case of the exact curved-wave approach.

#### §4. Results and Discussion

The calculations have been done for the clusters with  $\sim 7.0$ - $8.5$  Å radii and included all single-scattering contributions and the main multiple-scattering signals inside the first and the second coordination shells.<sup>10)</sup> The T-matrix elements  $t_i$  have been calculated using the MSCALC program, written by Natoli et al.<sup>11)</sup> The use of the complex Hedin-Lundqvist exchange and correlation potential has allowed automatically to take into account the inelastic losses of the photoelectron in extrinsic channels through plasmon excitations. The amplitude damping due to the core hole finite lifetime has been included through the empirically determined core level widths.<sup>12)</sup>

The experimental and calculated XAFS-signals  $\chi(k)k^2$  and their Fourier transforms (FT) are shown in Figs. 1-4. One can see that the agreement between calculated and experimental signals is very good in all energy range. The high amplitude of the FT-signals in the range from 2 to 4 Å in the case of  $\text{ReO}_3$ ,  $\text{NaWO}_3$  and  $\text{MoO}_3$  compounds

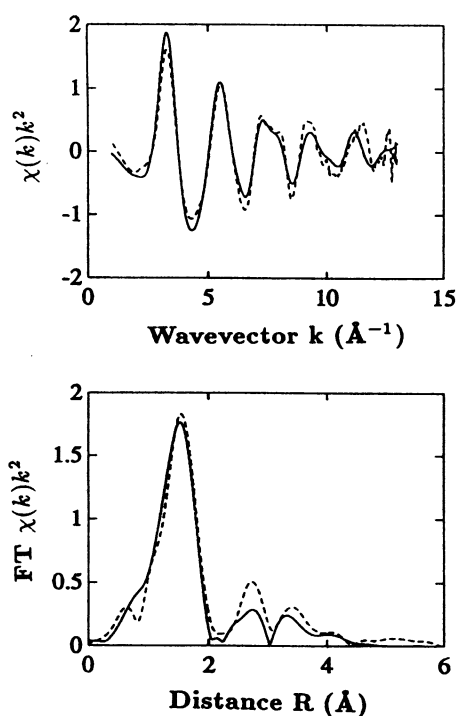


Fig. 3. The experimental (dashed line) and calculated (solid line) XAFS-signals  $\chi(k)k^2$  (upper figure) and their Fourier transforms (lower figure) for the Ir  $L_3$ -edge in  $\text{IrO}_2$ .

(see, Figs. 1, 2 and 3 is due to the focussing effects in the O-Me-O and Me-O-Me (Me = Re, W, Mo) linear, as in  $\text{ReO}_3$  and  $\text{NaWO}_3$ , or nearly linear, as in  $\text{MoO}_3$ , chains in the first and the second coordination shells. In the case of  $\text{IrO}_2$ , where linear chains are absent, only the contribution from the MS processes in the first coordination shell (the peak at 2.5 Å) and the single-scattering signals from the second and outer shells (the peak at 3.5 Å) remain high.

### §5. Summary and Conclusions

The analysis of the X-ray-absorption fine structure (XAFS) of the rhenium  $L_3$ -edge in  $\text{ReO}_3$ , the tungsten  $L_3$ -edge in  $\text{NaWO}_3$ , the iridium  $L_3$ -edge in  $\text{IrO}_2$  and the molybdenum  $K$ -edge in  $\text{MoO}_3$  has been done in the framework of the multiple-scattering theory using the new *fast spherical approximation* approach. We found that the FSA is very fast in comparison with the exact approach (about factor  $10^3$ ) and gives good agreement with experimental data considered in this work both in the low and high energy ranges.

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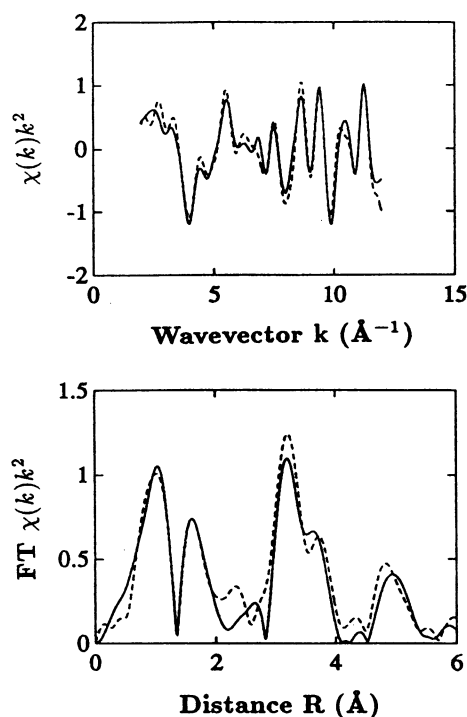


Fig. 4. The experimental (dashed line) and calculated (solid line) XAFS-signals  $\chi(k)k^2$  (upper figure) and their Fourier transforms (lower figure) for the Mo  $K$ -edge in  $\text{MoO}_3$ .

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