

## On the Experimental Calibration of Scattering Factors in EXAFS

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### Abstract

A simple method is described for calibrating EXAFS scattering factors in the region near the absorption edge, employing a modified plane-wave equation with experimental data for model compounds containing  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  ions. Curve-fitting, with refinement of calibration parameters, gives a good fit with experiment to within  $\sim 0.75$  hartree ( $\sim 20$  eV) of the edge. The calibration curves should enable the chemist to extract, without computational difficulties, more reliable structural information from the XANES region.

### Introduction

In X-ray absorption spectroscopy, the problems of calculating reliable absorber phases and back-scattering amplitudes and phases have led to the development of two distinct approaches to the analysis of different regions of the spectra [1]. The calculated scattering factors prove fairly reliable for energies greater than about 2.5 hartree beyond the absorption edge, which has enabled the rapid development of EXAFS spectroscopy (extended X-ray absorption fine structure). Below about 2.5 hartree, the spectra become increasingly difficult to interpret largely due to the scattering factor problems and the analysis of this inner region has been termed XANES (X-ray absorption near edge structure).

To the chemist it is disappointing that the XANES region is rather intractable to reliable analysis, because the region is rich in features sensitive to chemical structure and the electronic state of the absorber. For the chemist who is more interested in deriving this information than in gaining a theoretical understanding of the physics of the XANES region, using model compounds to parameterize simple curve fitting equations offers an attractive short cut to one's objectives.

This paper presents a simple method for extending the scope of the EXAFS approach further towards the absorption edge.

### Theory

A useful form of the standard plane-wave equation used in EXAFS is (for K edges) [2]

$$\chi(k) = - \sum_j \frac{S_i N_j}{k r_{ij}^2} |F_j(k, \pi)| \sin[2k(r_{ij} - \Delta r_{ij}) + 2\phi_i(k) + \phi_j(k)] \times \exp(-2k^2 \sigma_{ij}^2 - 2r_{ij}\eta/k - \theta) \quad (1)$$

where  $i$  is the absorber,  $j$  a back-scatterer,  $S_i$  an attenuation parameter,  $N_j$  the back-scatterer multiplicity,  $k$  the photoelectron wave vector,  $F_j$ ,  $\phi_i$ ,  $\phi_j$  are theoretically calculated back-scattering amplitudes and corresponding phase angles for absorber and back-scatterers,  $r_{ij}$  an interatomic distance,  $\Delta r_{ij}$  the corresponding EXAFS shift,  $\sigma_{ij}$  the corresponding Debye–Waller factor,  $\eta$  the mean free path parameter and  $\theta$  represents more free path terms.

The equation may be rewritten as

$$\chi(k) = - \sum_j \frac{N_j}{k r_{ij}^2} F_{ij}(k) \sin[2k(r_{ij} - \Delta r_{ij}) + \phi_{ij}(k)] \times \exp(-2k^2 \sigma_{ij}^2 - 2r_{ij}\eta_o/k) \quad (2)$$

In eqn. (2), the pair functions  $F_{ij}$  and  $\phi_{ij}$  are (see eqn. (1))

$$F_{ij}(k) = S_i |F_j(k, \pi)| [1 + \alpha_F(k_{lim} - k)] \times \exp[-2r_{ij}(\eta - \eta_o)/k - \theta] \quad (3)$$

$$\phi_{ij}(k) = 2\phi_i + \phi_j + \alpha_\phi(k_{lim} - k) \quad (4)$$

In eqns. (3) and (4),  $\alpha_F(k_{lim} - k)$  and  $\alpha_\phi(k_{lim} - k)$  are linear terms to represent the errors in the calculated values of  $F_j$  and  $2\phi_i + \phi_j$  in the XANES region, and incorporate deviations from the plane wave approximation. The parameter  $k_{lim}$  represents the inner limit of the EXAFS region where the scattering factors cease to be reliable. The constants  $\alpha_F$  and  $\alpha_\phi$ , along with  $k_{lim}$ , can be refined during least-squares curve fitting calculations employing the UMIST

software [3]. In these calculations, the linear terms are set to zero for  $k > k_{\text{lim}}$ , maintaining identity with eqn. (1) where the original scattering factors fit the experimental data. The pair function  $F_{ij}$  also incorporates the attenuation parameter  $S_i$ , the extra free-path parameter  $\theta$  and any deviation of the main free-path parameter  $\eta$  from a standard value  $\eta_0$ , normally  $1.5 \text{ \AA}^{-1}$ . The extension of the pair functions  $F_{ij}$  and  $\phi_{ij}$  into the XANES region can be achieved using experimental data for model compounds. The revised functions can then be employed in routine determinations of the structures of related materials.

## Experimental

We have used our method to calibrate scattering factors for  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  systems at their K-edges, using respectively, as model compounds, [4–6] the Tutton salt  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , the alum  $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$  and the Tutton salt  $\text{MnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , each of which contains hexaquo ions,  $[\text{M}(\text{H}_2\text{O})_6]^{n+}$ . EXAFS measurements at room temperature were made at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory. Transmission experiments were performed at the appropriate K-edges (Fe:  $1.74 \text{ \AA}$ ,  $7.11 \text{ keV}$ ; Mn:  $1.90 \text{ \AA}$ ,  $6.54 \text{ keV}$ ) using for the Fe compounds the Si(220) monochromator with harmonic rejection [7] and for the Mn compound the Si(111) monochromator with double focussing mirror. Data were reduced to background subtracted  $\chi$ -curves using EXAFS programs from the SRS program library [1]. The least-squares curve fitting used the UMIST software [3] employing the modified plane wave eqn. (2) above. The advantage of the UMIST software is in its flexibility. The user has full control of the calculation. One can use any curve fitting function one wishes to devise, one can define one's own variables and refine them in any combination, and also apply constraints wherever necessary. The present work illustrates the scope of the software.

A two-stage regime was employed during the curve fitting to obtain the calibration parameters defined in eqns. (3) and (4). Stage 1 employed only the EXAFS data (photoelectron energy above threshold,  $E > 2.5$  hartree; 1 hartree =  $27.2 \text{ eV}$ ) to obtain the main structural parameters  $\Delta r_{\text{MO}}$  and  $u_{\text{MO}}$  ( $\text{M} = \text{Fe, Mn}$ ; O = oxygen) for the first shell in  $[\text{M}(\text{H}_2\text{O})_6]^{n+}$  with  $r_{\text{MO}}$  and  $N_{\text{O}}$  fixed at literature values [4–6]; also obtained were outer shell parameters including multiple-scattering corrections, as appropriate. It was assumed that for  $E > 2.5$  hartree, the calculated scattering factors  $F_j$ ,  $\phi_i$ ,  $\phi_j$  could be relied upon (*i.e.*  $\alpha_{\text{F}} = \alpha_{\phi} = 0$ , see above). Stage 2 employed data with  $E > 0.9$  hartree, including the data used in stage 1. All the refined parameters from stage 1 were held fixed while  $k_{\text{lim}}$ ,  $\alpha_{\text{F}}$  and  $\alpha_{\phi}$  were refined. This procedure ensured that the fit in the EXAFS region

TABLE I. First Shell and Calibration Parameters (Estimated Standard Deviations in Parentheses)

Atom pair, M–O	$\text{Fe}^{\text{II}}\text{–O}$	$\text{Fe}^{\text{III}}\text{–O}$	$\text{Mn}^{\text{II}}\text{–O}$
Stage 1			
$N_{\text{O}}$ (cryst.)	6	6	6
$r_{\text{MO}}$ (cryst.) (Å)	2.126	1.985	2.180
$\Delta r_{\text{MO}}$ (Å)	0.367(1)	0.381(1)	0.326(1)
$\sigma_{\text{MO}}$ (Å)	0.090(1)	0.103(1)	0.111(1)
Stage 2			
$k_{\text{lim}}$ ( $\text{Å}^{-1}$ )	3.86(2)	4.20(8)	3.83(8)
$E_{\text{lim}}$ (hartree)	2.10(2)	2.46(9)	2.05(9)
$\alpha_{\text{F}}$ (Å)	1.10(3)	0.46(4)	2.36(4)
$\alpha_{\phi}$ (Å)	0.31(3)	0.00(3)	1.11(4)

was retained while the calibration parameters adjusted to ensure a simultaneous fit in the inner region.

## Results and Discussion

Table I gives the results of the refinements for the three samples. For  $\text{Fe}^{2+}$ , the calibration parameters  $\alpha_{\text{F}}$  and  $\alpha_{\phi}$  are quite large although the original calculated scattering factors  $F_j$ ,  $\phi_i$ ,  $\phi_j$  fit the data as far inwards as  $E_{\text{lim}} = 2.10$  hartree ( $k_{\text{lim}} = 3.86 \text{ \AA}^{-1}$ ). The necessary corrections to our calculated scattering factors for  $\text{Fe}^{3+}$  are quite small ( $\alpha_{\text{F}} = 0.46 \text{ \AA}$ ,  $\alpha_{\phi} = 0.00 \text{ \AA}$ ). The corrections necessary for  $\text{Mn}^{2+}$  are by far the biggest, and we are at present investigating the reasons for this.

Figure 1 illustrates the two stages of curve fitting for the  $\text{Fe}^{2+}$  Tutton salt. Stage 1 provides a good fit for  $E > 2.5$  hartree, but (as shown) if the uncorrected parameters from stage 1 are used in the inner region the resulting calculated curve deviates considerably from experiment. When, however, the calibration parameters are refined (stage 2) a good fit is achieved. It is possible to extend the treatment below  $0.9$  hartree and the shoulder in the experimental curve at  $\sim 0.6$  hartree can be reproduced. Curves similar to Fig. 1 were obtained for the  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  samples.

Figures 2 and 3 show the extent of the corrections to the scattering amplitudes and phases which are needed in the inner-data region, for each of the samples. The calibration curves for the amplitudes  $F_{\text{MO}}$  increase markedly, below  $E_{\text{lim}}$  (Fig. 2); the curve for  $\text{Mn}^{2+}$  requires correction by about a factor of five at  $E \sim 0.5$  hartree. The calibration curves for phases (Fig. 3) show smaller changes, although they are correcting the composite phase  $2\phi_1 + \phi_j$ ; for  $\text{Fe}^{3+}$  no correction is needed. Some effects of multiple scattering are absorbed in the calibration curves, although, in addition, our conventional stage 1 plane-

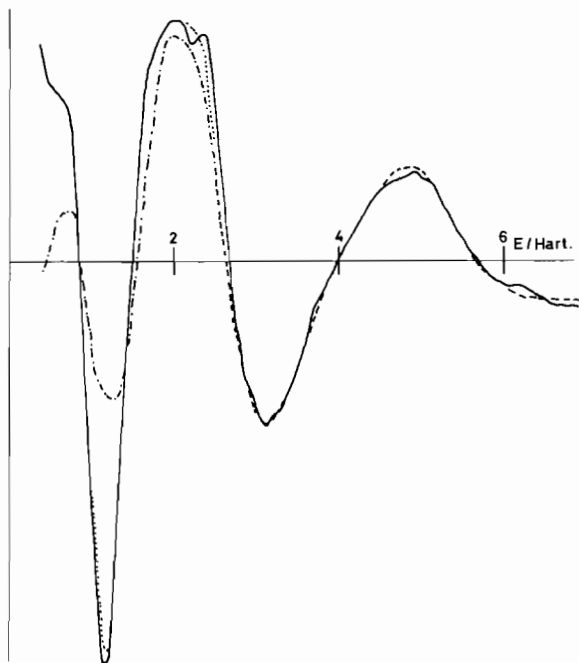


Fig. 1. Curve fitting for the  $\text{Fe}^{2+}$  Tutton salt. Expt. —; calc. stage 1 ----, stage 1 parameters used for the inner region ----, stage 2 .....

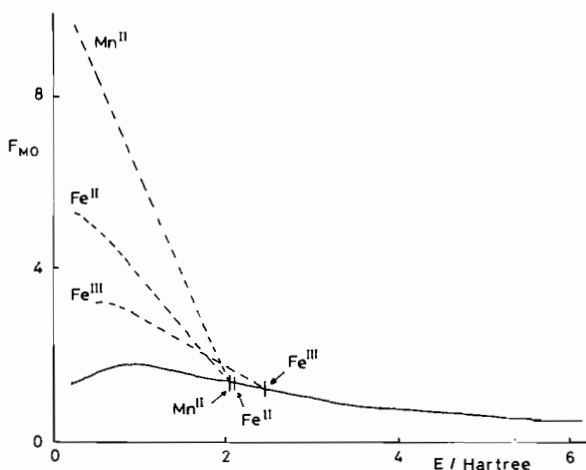


Fig. 2. Calibration curves for scattering amplitudes  $F_{\text{MO}}$ . Without calibration —; calibration required ----. The  $E_{\text{lim}}$  positions are indicated.

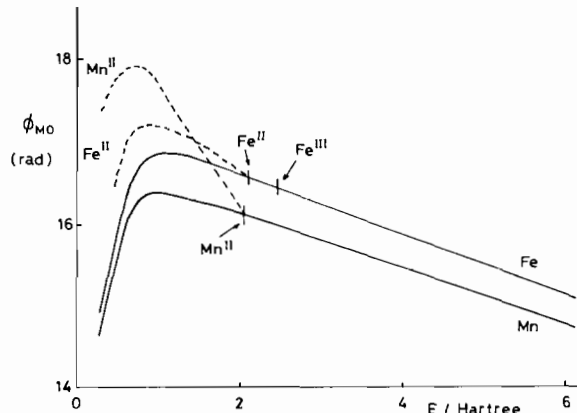


Fig. 3. Calibration curves for scattering phases  $\phi_{\text{MO}}$ . Details as for Fig. 2.

wave fits incorporate appropriate multiple scattering corrections for outer shell parameters.

In our current programme of structure determinations by EXAFS, we are beginning to incorporate the scattering factor calibration curves we report here. The UMIST software facilitates this approach without further software development.

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