A new method for extracting x-ray absorption fine structure and the atomic background from an x-ray absorption spectrum

A new method for extracting x-ray absorption fine structure and the atomic background from an x-ray absorption spectrum

T D Hu, Y N Xie, Y L Jin and T Liu

Synchrotron Radiation Laboratory, Institute of High Energy Physics, Academia Sinica, Beijing 100039, People's Republic of China

Abstract. A new technique for separating x-ray absorption fine structure (XAFS) and the atomic background in an x-ray absorption spectrum is presented. XAFS oscillations are reliably extracted from the Fourier transform of the nth derivative of the experiment data, without making the usual smooth-background approximation. The atomic background is obtained by the subtraction of the XAFS from the experimental data. Multielectron excitations and atomic XAFS (AXAFS) have been observed in the atomic background. This provides a useful tool for the investigation of multielectron excitations and AXAFS in condensed matter.

XAFS is now established as the basis of one of the most important methods of structure analysis. The method consists of analysing the oscillatory modulation of the x-ray absorption coefficient above an x-ray absorption edge, to extract information about bond lengths and coordination numbers. One of the important tasks in the data analysis is that of extracting the XAFS function from the raw data.

The XAFS function, χ, is defined as the oscillatory part of the absorption, beginning just above the absorption edge. It can be written as

$$\chi = \frac{\mu - \mu_0}{\mu_0} \tag{1}$$

where μ is the measured absorption. The atomic background μ_0 is the absorption of an 'isolated' atom. This is the absorption from an atom embedded in the electronic environment of a condensed system, without backscattering from the near neighbours.

In order to obtain the XAFS function, it is necessary to remove the atomic background from the experiment data. The usual procedure consists of two steps [1, 2].

(1) Pre-edge region subtraction, in which most of the energy dependence of the absorption other than that from the absorption edge of interest is eliminated. The pre-edge region can be fitted with a polynomial function or the Victoreen formula, and then extrapolated, and subtracted from the complete data set.

(2) The post-edge background removal, in which the smoothly varying part of the absorption is subtracted from μ to get the XAFS.

The first step is usually straightforward, and no trouble. Removing the post-edge background is the most critical step, as it will affect the final conclusions on the structure information. Atomic background is not in general measurable independently, nor can it

be calculated accurately. In nearly all data-reduction programs, the atomic background is assumed to be a smooth function that can be simply modelled using a polynomial or spline function. Some kind of parametrized smoothing technique, such as fitting the data with polynomials of various degrees and smoothing with cubic splines as an approximation of the atomic background, were used to obtain the background [1, 2].

Due to the strong electron–electron interaction within the photoabsorber atom, the atomic background is generally a structure function showing the presence of discrete resonance and slope changes associated with multielectron-excitation-channel, white-line resonance [3–16]. The XAFS signal often hides the atomic multielectron contribution, and for this reason noble gases have been among the first atoms for which multielectron features have been identified [11–14]. The multielectron process is a fundamental atomic many-body effect. Recently, this process has received special attention, and extensive studies on solids, gases, and vapours have been performed [3–10]. In addition, AXAFS, which arises from scattering within an embedded atom, will produce low-frequency structure in the x-ray absorption spectrum, and a spurious peak in the low-r components in the XAFS Fourier transform [15–18]. Recently Rehr *et al* gave theory, calculations, and measurements that confirmed the existence of AXAFS, and showed that it can dominate contributions such as multielectron excitations [16].

It is well known that simple and smooth μ_0-approximations are not sufficient for obtaining accurate XAFS data, particularly in the case of high-disorder materials, in which XAFS oscillations are weak. Some improved background-removal methods have been developed recently [19–23]. Li *et al* presented an iterative approach to removal of the background [19, 20], and Newville and co-workers extracted the background by optimizing the low-r components in the Fourier transform spectrum [21, 22]. However, the smooth μ_0-approximation was used at the outset.

In the XAFS context, the structures in the atomic background are unwanted features that interfere with the structural analysis. The smooth μ_0-approximation will induce some errors in the XAFS. It is expected that a better way could be found to extract XAFS signals, in order to allow comparison with theory and the obtaining of more accurate structure parameters. On the other hand, the multielectron excitations and AXAFS in the absorption spectra are interesting subjects, from both the fundamental science and applications points of view. Obtaining the real atomic background is very important for the investigation of multielectron excitations and AXAFS in condensed matter.

The measured absorption μ consists of the periodic sine oscillatory part, χ, and the relatively smooth part, μ_0. The latter has some non-periodic structure. In general, μ_0 is associated with unphysical peaks in the low-r region of the Fourier transform [4, 7, 10, 16]. If a Fourier transformation of the measured absorption μ were performed directly without a background removal, it would be impossible to obtain a good result, because the absorption spike and low-frequency part of the background in the experimental data would produce very large low-r components in r-space, which would mix μ_0 and χ. Now we consider use of the nth derivative of μ to decrease the low-frequency components. The contributions from μ_0 in the Fourier transform spectra are mainly confined within the low-r region, which is below the position of the XAFS peak. Therefore, the contributions from μ_0 and χ can be separated by Fourier transformation in principle. If the Fourier transform of $f(k)$ is $F(r)$, then the Fourier transform of the nth derivative of $f(k)$ is obtained by multiplying $F(r)$ by $(ir)^n$:

$$f^n(k) = (ir)^n F(r). \tag{2}$$

Taking the derivative will enhance the higher frequencies, attenuate the lower

frequencies, and suppress any zero-frequency component. Therefore the contributions from the low-frequency components in the experimental data can be substantially suppressed by taking the nth derivative. However, the periodic part, χ, will not be affected. The Fourier transform of the XAFS can be obtained conveniently by dividing the nth derivative of the Fourier transform spectra by $(ir)^n$ according to equation (2). This process should provide more reliable XAFS oscillations than before, because no smooth μ_0-approximation is used in this process.
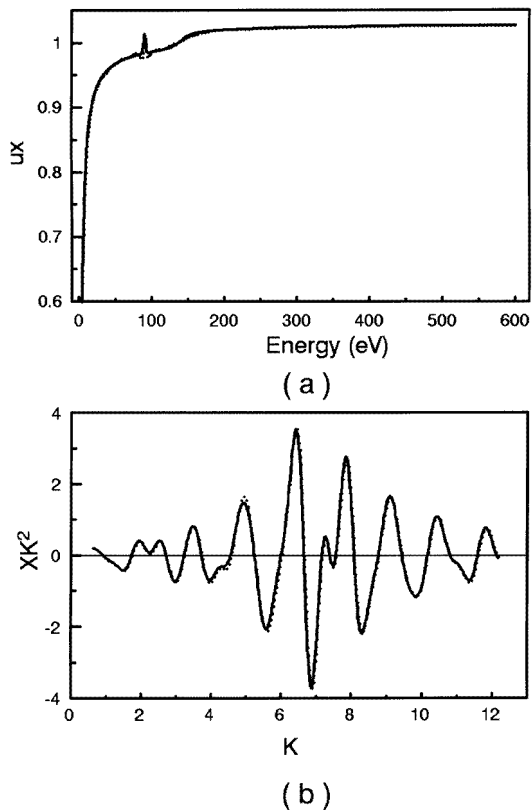

Figure 1. (a) The constructed background (solid line) and the extracted background (dotted line); (b) the extracted EXAFS signal (dotted line) and the theoretical data for four shells of Cu (solid line).

The atomic background can be obtained by subtraction of the XAFS oscillations from μ. The low-frequency part of the atomic background can be obtained, because the extraction of the XAFS oscillations is direct, and no approximations are used. Therefore the smooth atomic background, and the AXAFS, which are located in the low-r region of the Fourier transform [16], can be obtained. The low-frequency part of the multielectron excitation—for example, the steplike atomic background produced by multielectron excitation channels—can be extracted also. In fact, it was recognized early on that the onsets of multielectron excitation channels were able to produce a steplike atomic background, which could not be accounted for by smooth-background models. Now it can be anticipated that the multielectron excitations and AXAFS can be observed in the atomic background.

The frequency components of the atomic background that are located in the extended
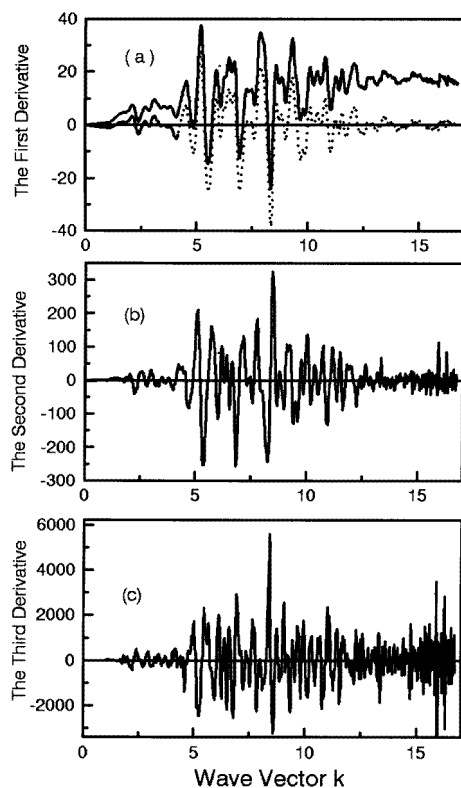
Figure 2. The derivative spectra of the x-ray absorption spectrum of α-Fe foil. A k^2-weighting was adopted. (a) The first-derivative spectrum; (b) the second-derivative spectrum; and (c) the third-derivative spectrum. The solid line is the derivative spectrum obtained directly from the experimental data, and the dotted line is the one obtained from the XAFS by usual background-removal method.

x-ray absorption fine structure (EXAFS) region could interfere with the XAFS signal, and cannot be extracted from the spectrum. In order to test their effect on the XAFS, a test signal of four shells of Cu was constructed by using theoretical data obtained using EXCURV92. The smooth background was simulated by an arctangent function, and the multielectron excitations were added at 90 eV and 140 eV where the 1s3p and 1s3s multielectron excitation channels, respectively, of Cu are positioned, according to the $Z + 1$ approximation. The Gaussian function and arctangent function, with an absorption edge height of 3%, were used to simulate multielectron excitations at 90 eV and 140 eV respectively. The constructed background is shown in figure 1(a) by the solid line. The new method was applied to the test signal in order to separate the XAFS and the background. The extracted background is displayed in figure 1(a) by the dotted line. It can be found that the shape of the Gaussian signal has been distorted, the amplitude decreases by about 30%, and the rising edge of the arctangent signal at 140 eV has to some extent been smoothed because some frequency components have been lost. However, the whole background can be basically restored. The extracted EXAFS signal (dotted line), and the theoretical data (solid line) are shown in figure 1(b). It was found that the error in the distances is less than ± 0.005 Å, and the error in the coordination numbers is less than 5%, i.e., they are exact within the accuracy of the XAFS experiment. Therefore, the interference is negligible as regards EXAFS analysis.

The x-ray absorption experiments were carried out at Beijing Synchrotron Radiation Facility (BSRF) with a electron energy of 2.2 GeV and a storage ring current of 40–60 mA. Data were collected by a two-crystal Si(111) monochromator. Harmonics were rejected by detuning. All of the measurements were done at room temperature, and in the transmission mode.

In order to illustrate the analysis procedure, the new method is applied to the K-edge x-ray absorption spectrum of α-Fe foil.

The pre-edge background was removed by polynomial fitting. The energy position of the inflection point of the absorption edge was taken as the origin of the energy, E_0. The raw data were normalized according to the step height of the absorption edge, and a k^2-weighting was adopted. Then the evaluation of the derivative of the data with respect to k was performed. The first-, second-, and third-derivative spectra of α-Fe are displayed in figure 2. The corresponding derivative spectra of the XAFS, which were obtained by the usual background removal, are shown in figure 2 also. This indicates that they are basically similar from the second derivative.
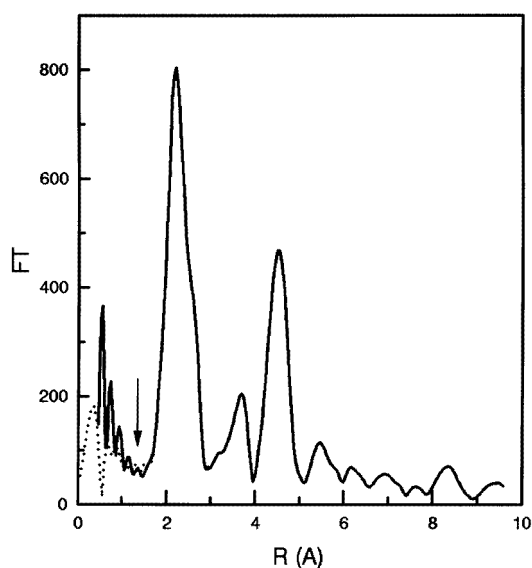

Figure 3. The Fourier transform of α-Fe foil. The solid line is the result obtained by the method of taking derivatives of the Fourier transform, and the dotted line is the one obtained by the usual background-removal method.

Fourier transforms from the derivative spectra to r-space were made using a Hanning function window, with $k_{min} = 0.1$ Å^{-1}, $k_{max} = 16.5$ Å^{-1}, for the high and low ends of the range, respectively, and $\delta k = 0.1$ Å^{-1}. It is natural to construct the Fourier transform with k and $2r$ as the reciprocal variables. Therefore, the Fourier transform spectra of the XAFS can be obtained by dividing the derivative spectra of the Fourier transforms by $(i\,2r)^n$. The Fourier transform of α-Fe, which was obtained by taking the second derivative, is displayed in figure 3. For comparison, the Fourier transform spectrum of α-Fe that was obtained by the usual background-removal procedure is shown in figure 3 also. As shown in figure 3, they have the same structures in the XAFS region. The height of the first coordination peak obtained by the derivative method is larger by 0.5% than the one obtained by the usual

method. This shows that accurate XAFS data can be obtained by this method.

In comparison with the other background-subtraction methods, the new method has some advantages, as follows.

(1) It is very simple and direct. The procedure is easy to automate and standardize without introducing artificial factors, such as the selection of knots of cubic splines, as is necessary in the usual methods.

(2) The absorption background can be obtained more reliably, although some frequency components will be lost. The multielectron excitations can be identified in the background. In the usual methods, structures such as the multielectron excitations will be smeared.

(3) In cases where the structural signal is weak, and the signal resulting from the multielectron excitation is strong—for example, for molten and high-disorder materials, it is very important to remove the multielectron excitation. Usually it is very difficult to obtain satisfactory results by using the other methods to remove the strong multielectron excitation, which is mixed with the weak XAFS signal. The new method is obviously superior to the other background-subtraction methods in view of this. We successfully applied this method to molten materials, where other methods failed.

(4) More information for low k in the data can be used. In the usual background-removal technique, the XAFS data were terminated in the region of 2–3 $\text{\AA}^{-1}$, because the technique becomes unreliable near the absorption edge where the background varies rapidly. In the new method it is possible to terminate data near to E_0. This is important in the case where the range of available data is small—for example, for low-Z elements, some L_3 absorptions, and high-disorder materials.

However, it should be noted that each evaluation of a derivative will amplify the noise. Therefore it is only appropriate to take the second or third derivative.
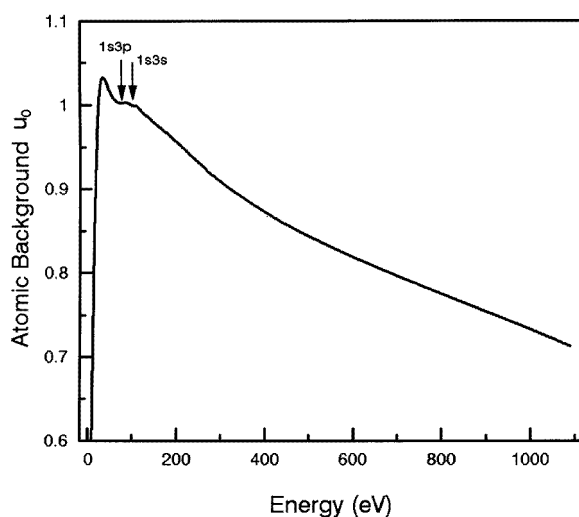

Figure 4. The atomic background of α-Fe foil.

The atomic background μ_0 can be obtained by subtraction of the XAFS from the experimental data. The high-r components, indicated in figure 3 by an arrow, were separated and transformed to k-space to get the XAFS spectrum by Fourier transformation. This spectrum was subtracted from μ to obtain the atomic background. The atomic background

μ_0 of α-Fe is shown in figure 4. Some structures appear in the atomic background. The energy positions indicated by the arrows in figure 4 are 69.5 and 98.2 eV, corresponding to the 1s3p and 1s3s double-electron excitations respectively. According to the $Z + 1$ approximation, the energy positions of the 1s3p and 1s3s double-electron excitations are 58.9 and 101 eV, in agreement with our results. The multielectron excitations can be identified clearly, although the XAFS oscillations are very strong in the absorption spectrum. Therefore it is seen that this method is reliable and effective for obtaining the atomic background.

It is clear that the occurrence of multielectron excitation features in absorption spectra is rather general. For the α-Fe foil, the intensity of the multielectron excitation is much weaker than that of the XAFS oscillation. Therefore the XAFS obtained by the usual methods is the same as that obtained by this method. However, an accurate atomic background is particularly important in the case where the structural signal is weak, and the multielectron excitation is strong.
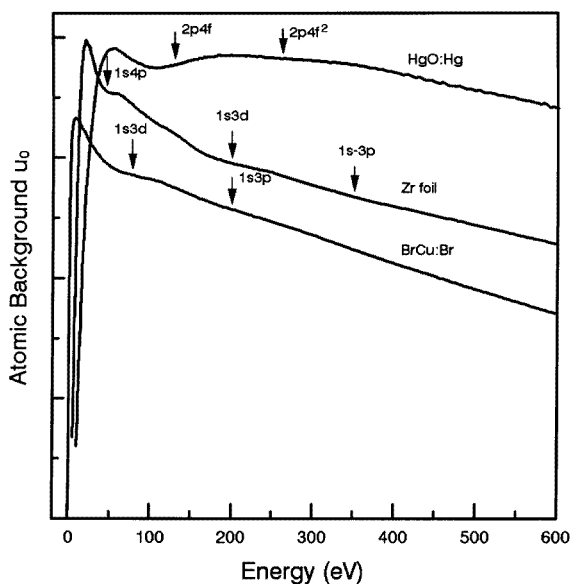

Figure 5. The atomic background of the K edge of Zr and Br, and the L_3 edge of Hg in Zr foil, CuBr, and HgO, respectively.

In order to verify the capability for extracting the atomic background, the absorption spectra of the K edge of Br and Zr, and the L_3 edge of Hg in CuBr, Zr foil, and HgO samples, which are fourth-, fifth-, and sixth-period elements, respectively, have been measured. Their atomic backgrounds obtained by taking derivatives of the Fourier transform are shown in figure 5. The thresholds for the double-electron 1s3d and 1s3p excitation channels are clearly indicated in the atomic background of Br; they are 80.1 and 201 eV respectively. They are in accord with the results for Br_2 and HBr [4, 8].

For Zr foil, the multielectron transitions corresponding to 1s4p, 1s3d, and 1s3p were detected. Their energy positions are 46, 204, and 351 eV respectively. They are in agreement with the results calculated from the Dirac–Fock total energy, where the differences between the 1s4p, 1s3d, and 1s3p positions and the K-edge threshold are 41.6–43.5, 204.8–207.6, and 358.5–373.6 eV, respectively [10]. Filipponi and Di Cicco have

reported a systematic detection of the atomic background features for MoC_x, Rh, Pd, Ag, In, and Sn. In order to decrease the XAFS signals, the samples were measured at high temperature, mostly in liquid. The 1s3d, 1s3p, and 1s3d4p multielectron transitions were detected [10]. But no trace of the 1s4p channel was observed, because XAFS oscillations hide the observation, although the measurements were made at high temperature. The 1s4p channel can be identified by using our method, although the XAFS oscillations of the Zr foil are strong at room temperature in our experiment.

In figure 5 the multielectron excitations of HgO have been assigned to the opening of double-electron excitation channels involving 2p and 4f electrons. 2p4f (133 eV) double-electron and $2p4f^2$ (285 eV) triple-electron excitations are indicated in figure 5. The results agree very well with those for Hg vapour [3]. It should be noted that the shape of the signal at threshold can be strongly affected by the boundary effects of the Fourier transformation, Unphysical features may arise. On the other hand, for a system with a short interatomic distance, more of the high-frequency components will be lost, because the XAFS signal will occur in the lower region of r-space.

In all of the atomic backgrounds displayed in this paper, there is an obvious spike that occurs near the absorption edge. We have investigated a number of materials. The spike always exists in the atomic background, and its energy position depends on the absorption atom. This spike can be reproduced in theoretical calculations of the AXAFS [15, 16]. So we infer that the spike may originate from AXAFS. It merits attention that the energy positions of the multielectron excitations may coincide with those of the AXAFS, according to the work of Rehr *et al*. However, further theoretical and experimental investigations are necessary to identify the contributions from multielectron excitations and AXAFS.

In conclusion, a new method for extracting the XAFS and atomic background by taking derivatives of the Fourier transform, without making the usual smooth-background approximation, has been presented. This method is capable of obtaining a reliable XAFS, and the low-frequency part of the real atomic background. In particular, it can be usefully applied to high-disorder materials, for example, molten and liquid ones. More information for low k in the data can be used. The analysis procedure is very simple, and easy to automate and standardize. The multielectron excitations and AXAFS can be identified in the atomic background obtained by this method, even in crystal samples for which the XAFS signal is very strong. It provides a useful tool for studying multielectron excitations and AXAFS in condensed matter. The present investigation will stimulate further theoretical and experimental work to research the effect of the local chemical environment on the atomic background.

References

  [1] Sayers D E and Bunker B A 1988 *Chem. Anal.* **92** 211
       Koningsberger D C and Prins R (ed) 1988 *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES* (New York: Wiley)
  [2] Cook J W Jr and Sayers D E 1981 *J. Appl. Phys.* **52** 5024
  [3] Filipponi A, Ottaviano L and Tyson T A 1993 *Phys. Rev.* A **48** 2098
  [4] Angelo P D, Di Cicco A, Filipponi A and Pavel N V 1993 *Phys. Rev.* A **47** 2055
  [5] Di Cicco A and Filipponi A 1994 *Phys. Rev.* B **49** 12 564
  [6] Filipponi A, Tyson T A, Hodgson K O and Mobilio S 1993 *Phys. Rev.* A **48** 1328
  [7] Filipponi A, Bernieri E and Mobilio S 1988 *Phys. Rev.* B **38** 3298
  [8] Filipponi A 1995 *Physica* B **208+209** 29
  [9] Chaboy J, Marcelli A and Tyson T A 1994 *Phys. Rev.* B **49** 11 652
 [10] Filipponi A and Di Cicco A 1995 *Phys. Rev.* A **52** 1072
 [11] Beutsch M and Kizler P 1992 *Phys. Rev.* A **45** 2112

[12] Zhang K, Stern E A, Rehr J J and Ellis F 1991 *Phys. Rev.* B **44** 2030
[13] Ito Y, Nakamatsu H, Mukoyama T, Omote K, Yoshikado S, Takahashi M and Emura S 1992 *Phys. Rev.* A **46** 6083
[14] Schaphorst S J, Kodre A F, Ruscheinski J, Crasemann B, Åberg T, Tulkki J, Chen Mau Hsiung, Azuma Y and Brown G S 1993 *Phys. Rev.* A **47** 1953
[15] Holland B W, Pendry J B, Pettifer R F and Bordas J 1978 *J. Phys. C: Solid State Phys.* **11** 633
[16] Rehr J J, Booth C H, Bridges F and Zabinsky S I 1994 *Phys. Rev.* B **49** 1237
[17] Filipponi A and Di Cicco A 1996 *Phys. Rev.* B **53** 9466
[18] Rehr J J, Booth C H, Bridges F and Zabinsky S I 1996 *Phys. Rev.* B **53** 9468
[19] Li G, Bridges F and Brown G S 1992 *Phys. Rev. Lett.* **68** 1609
[20] Bridges F, Booth C H and Li G G 1995 *Physica* B **208+209** 121
[21] Newville M, Livins P, Yacoby Y, Rehr J J and Stern E A 1993 *Phys. Rev.* B **47** 14 126
[22] Newville M, Livins P, Yacoby Y, Rehr J J and Stern E A 1993 *Japan. J. Appl. Phys. Suppl.* **32** 125
[23] Stern E A, Livins P and Zhang Z 1991 *Phys. Rev.* B **43** 8850