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On the neglecting of higher-order cumulants in EXAFS data analysis

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The cumulant expansion is one of the most powerful and useful methods for EXAFS data analysis, in which the higher-order cumulants allow to consider deviations from a simple Gaussian distribution. In this work, analytical expressions have been derived to show the effects of neglecting higher-order cumulants in EXAFS analysis by the ratio method. The errors in the best-fitting procedure owing to the omission of the higher-order cumulants, as well as of the coordination number, can be determined.

Keywords: EXAFS; cumulant analysis of EXAFS.

1. Introduction

The cumulant method is a model-independent technique based on the expansion of extended X-ray absorption fine-structure (EXAFS) amplitudes and phases as a series of cumulants of the interatomic distance distribution (Teo, 1986). In the EXAFS analysis, the contributions of the different coordination shells are singled out by Fourier filtering and separately analyzed. The Fourier filtering process allows the phase $\Phi(k)$ and amplitude $A(k)$ of the single shell to be separated. The difference between the EXAFS phases and the logarithm of the amplitude ratio can be written through the ratio method as (Bunker, 1983; Fornasini *et al.*, 2001)

$$\Phi_s(k) - \Phi_r(k) = 2k\Delta C_1 - \frac{4}{3}k^3\Delta C_3 + \frac{4}{15}k^5\Delta C_5 + \ldots, \quad (1)$$

$$\ln\frac{A_s(k)}{A_r(k)} = \ln N - 2k^2\Delta C_2 + \frac{2}{3}k^4\Delta C_4 - \frac{4}{45}k^6\Delta C_6 + \ldots, \quad (2)$$

where k is the photoelectron wavevector, $N = N_s/N_r$ is the coordination number ratio, ΔC_n indicates the cumulant difference $C_n^s - C_n^r$, and the subscripts s and r refer to the sample and reference, respectively. The cumulant method allows the characterization of the first coordination shell in terms of parameters which describe the distance distributions: the first cumulant C_1 is the mean value, C_2 is the variance, C_3 measures the distribution asymmetry and C_4 measures its flatness. For a Gaussian distribution the cumulants C_n are zero for $n > 2$.

Anharmonicity effects on EXAFS were detected quite early (Eisenberger & Brown, 1979). After the first pioneering studies on AgI (Boyce *et al.*, 1981) and CuBr (Tranquada & Ingalls, 1983), it has been shown that anharmonicity cannot be neglected even in systems like germanium (Dalba *et al.*, 1995) or copper (a Beccara *et al.*, 2003), where the third cumulant has been taken into account in the analysis to obtain accurate values of the first cumulant; even more so in the case of systems affected by structural disorder, such as liquids, glasses, molten salts and alloys, where the higher-order cumulants must be taken into account when fitting the EXAFS data (Wei *et al.*, 2000; Sanson *et al.*, 2008; Swilem *et al.*, 2005). In strongly disordered systems, where the convergence of the cumulant series is in principle questionable (Filipponi, 2001), the cumulants can sometimes be considered to parameterize only the short-range component of the whole distance distribution, as tested in α-AgI (Boyce *et al.*, 1977, 1981) and more recently in silver molybdate glasses (Sanson, Rocca, Dalba *et al.*, 2007).

The importance of including higher-order cumulants in EXAFS analysis has been recognized in many works (Yokoyama *et al.*, 1997; Soldo *et al.*, 1998; Bus *et al.*, 2006; Vaccari *et al.*, 2007; Ahmed *et al.*, 2009). Other groups recognized the asymmetry in the distance distribution, but did not use the cumulants beyond the second order (Diaz-Moreno *et al.*, 1997; Berlier *et al.*, 2002; Katsikini *et al.*, 2008; Chu *et al.*, 2009), with the consequence that the resulting errors in the fit parameters may have drastic effects on the EXAFS structural parameters. In some specific cases, the errors owing to the use of a Gaussian pair distribution have been estimated (Mobilio & Incoccia, 1984; Wei *et al.*, 2000), with the result that it produces a significant error for the distance and coordination number. At present, a general treatment of this problem is still lacking.

In this work, for the first time, analytical expressions have been derived to determine the errors in the best-fitting procedure owing to the neglect of the higher-order cumulants (up to the sixth order). The paper is organized as follows: the procedure to derive these expressions is briefly described in §2; the results are reported in §3 and discussed in §4; §5 is dedicated to conclusions.

2. Procedure

Let us consider the best fit of the phases difference, assuming that it is sufficient to truncate equation (1) at the third order (ΔC_3) to have a good fit. In order to evaluate the resulting error on the relative first cumulant (*i.e.* on the bond distance variation) owing to the neglect of the third cumulant, we can solve the following equation with respect to $\Delta C_1'$,

$$\frac{\partial}{\partial \Delta C_1'} \int_{k_m}^{k_M} \left[\left(2k\Delta C_1 - \frac{4}{3}k^3\Delta C_3 \right) - 2k\Delta C_1' \right]^2 \mathrm{d}k = 0, \qquad (3)$$

which corresponds to minimize the fitting difference between $2k\Delta C_1 - (4/3)k^3\Delta C_3$ and $2k\Delta C_1'$; $k_{\rm m}$ and $k_{\rm M}$ are the minimum and maximum values of the fitting interval, respectively. Expanding (3) we obtain

$$\left[\frac{8}{3}k^3 \left(\Delta C_1' - \Delta C_1 \right) + \frac{16}{15}k^5 \Delta C_3 \right]_{k_m}^{k_M} = 0, \qquad (4)$$

and so

$$\Delta C_1' = \Delta C_1 - \left(\frac{2}{5} \frac{k_M^5 - k_m^5}{k_M^3 - k_m^3} \right) \Delta C_3. \qquad (5)$$

As a result, from (5) it can be observed that for $\Delta C_3 > 0$ the neglect of the third cumulant gives an underestimation of the relative first cumulant. On the contrary, for $\Delta C_3 < 0$ the relative first cumulant is overestimated. More important, equation (5) allows the error on ΔC_1 to be quantitatively estimated. For example, by (5), the neglect of a third cumulant $\Delta C_3 \simeq 0.0005$ Å^3 in the fitting interval k = 2–10 Å^{-1} (*i.e.* $k_{\rm m}$ = 2 and $k_{\rm M}$ = 10 Å^{-1}) gives an underestimation of ΔC_1 of about 0.020 Å.

As a second example, let us consider the best fit of the amplitudes ratio, assuming that it is sufficient to truncate (2) at the fourth order (ΔC_4) to have a good fit. To evaluate the resulting error on the coordination number and on the second cumulant owing to the neglecting of the fourth cumulant, we can solve the following system of equations with respect to N' and $\Delta C_2'$,

$$\frac{\partial}{\partial \ln N'} \int_{k_m}^{k_M} \left[\left(\ln N - 2k^2\Delta C_2 + \frac{2}{3}k^4\Delta C_4 \right) - \left(\ln N' - 2k^2\Delta C_2' \right) \right]^2 \mathrm{d}k = 0, \qquad (6)$$

$$\frac{\partial}{\partial \Delta C_2'} \int_{k_m}^{k_M} \left[\left(\ln N - 2k^2\Delta C_2 + \frac{2}{3}k^4\Delta C_4 \right) - \left(\ln N' - 2k^2\Delta C_2' \right) \right]^2 \mathrm{d}k = 0, \qquad (7)$$

whose solutions are

$$\ln N' = \ln N - \left(\frac{2}{35} \frac{4k_M^6 + 16k_M^5k_m + 40k_M^4k_m^2 + 55k_M^3k_m^3 + 40k_M^2k_m^4 + 16k_Mk_m^5 + 4k_m^6}{4k_M^2 + 7k_Mk_m + 4k_m^2} \right) \Delta C_4 \qquad (8)$$

and

$$\Delta C_2' = \Delta C_2 - \left(\frac{1}{7} \frac{8k_M^4 + 17k_M^3k_m + 20k_M^2k_m^2 + 17k_Mk_m^3 + 8k_m^4}{4k_M^2 + 7k_Mk_m + 4k_m^2} \right) \Delta C_4. \qquad (9)$$

As a result, from (8)–(9) it can be seen that the neglect of the fourth cumulant gives an underestimation/overestimation of the relative second cumulant and of the coordination number ratio, according to the sign of ΔC_4. These errors, which depend on the fitting interval ($k_{\rm m}$–$k_{\rm M}$), can be quantitatively estimated by (8) and (9). For example, the neglect of the fourth cumulant $\Delta C_4 \simeq 0.0001$ Å^4 in the fitting interval 2–10 Å^{-1} gives an underestimation of ΔC_2 of about 0.0032 Å^2 and on the logarithm of N of about 0.096.

3. Results

Following the procedure described in the previous section, the errors on the cumulants analysis have been derived for different cases. The results are listed below.

3.1. Phases difference

3.1.1. Neglect of the third and fifth cumulant. Neglecting both the third and fifth cumulant, the relative first cumulant results as follows,

$$\Delta C_1' = \Delta C_1 - \left(\frac{2}{5} \frac{k_M^5 - k_m^5}{k_M^3 - k_m^3} \right) \Delta C_3 + \left(\frac{2}{35} \frac{k_M^7 - k_m^7}{k_M^3 - k_m^3} \right) \Delta C_5. \qquad (10)$$

When the fifth cumulant is negligible ($\Delta C_5 = 0$), (10) reduces to (5).

3.1.2. Neglect of the fifth cumulant. With the neglect of the fifth cumulant, the first and third cumulant become

$$\Delta C_1' = \Delta C_1 - \left(\frac{2}{63} \frac{4k_M^{10} + 16k_M^9k_m + 40k_M^8k_m^2 + 80k_M^7k_m^3 + 140k_M^6k_m^4 + 175k_M^5k_m^5 + 140k_M^4k_m^6 + 80k_M^3k_m^7 + 40k_M^2k_m^8 + 16k_Mk_m^9 + 4k_m^{10}}{4k_M^6 + 16k_M^5k_m + 40k_M^4k_m^2 + 55k_M^3k_m^3 + 40k_M^2k_m^4 + 16k_Mk_m^5 + 4k_m^6} \right) \Delta C_5 \qquad (11)$$

and

$$\Delta C_3' = \Delta C_3 - \left(\frac{1}{9} \frac{8k_M^8 + 32k_M^7k_m + 80k_M^6k_m^2 + 125k_M^5k_m^3 + 140k_M^4k_m^4 + 125k_M^3k_m^5 + 80k_M^2k_m^6 + 32k_Mk_m^7 + 8k_m^8}{4k_M^6 + 16k_M^5k_m + 40k_M^4k_m^2 + 55k_M^3k_m^3 + 40k_M^2k_m^4 + 16k_Mk_m^5 + 4k_m^6} \right) \Delta C_5, \qquad (12)$$

respectively. As a result, both the relative first and third cumulant are underestimated when $\Delta C_5 > 0$ and overestimated when $\Delta C_5 < 0$.

3.2. Amplitudes ratio

3.2.1. Neglect of the coordination number, fourth and sixth cumulant. In the case that the coordination number, fourth and sixth cumulant are neglected, the second cumulant becomes

$$\Delta C_2' = \Delta C_2 - \left(\frac{5}{6}\frac{k_M^3 - k_m^3}{k_M^5 - k_m^5}\right)\ln N - \left(\frac{5}{21}\frac{k_M^7 - k_m^7}{k_M^5 - k_m^5}\right)\Delta C_4 + \left(\frac{2}{81}\frac{k_M^9 - k_m^9}{k_M^5 - k_m^5}\right)\Delta C_6. \quad (13)$$

3.2.2. Neglect of the fourth and sixth cumulant. Neglecting both the fourth and sixth cumulant, the coordination number and the second cumulant become

$$\ln N' = \ln N - \left(\frac{2}{35}\frac{4k_M^6 + 16k_M^5k_m + 40k_M^4k_m^2 + 55k_M^3k_m^3 + 40k_M^2k_m^4 + 16k_Mk_m^5 + 4k_m^6}{4k_M^2 + 7k_Mk_m + 4k_m^2}\right)\Delta C_4 - \left(\frac{4}{945}\frac{8k_M^8 + 32k_M^7k_m + 80k_M^6k_m^2 + 125k_M^5k_m^3 + 140k_M^4k_m^4 + 125k_M^3k_m^5 + 80k_M^2k_m^6 + 32k_Mk_m^7 + 8k_m^8}{4k_M^2 + 7k_Mk_m + 4k_m^2}\right)\Delta C_6, \quad (14)$$

$$\Delta C_2' = \Delta C_2 - \left(\frac{1}{7}\frac{8k_M^4 + 17k_M^3k_m + 20k_M^2k_m^2 + 17k_Mk_m^3 + 8k_m^4}{4k_M^2 + 7k_Mk_m + 4k_m^2}\right)\Delta C_4 + \left(\frac{2}{63}\frac{4k_M^6 + 9k_M^5k_m + 12k_M^4k_m^2 + 13k_M^3k_m^3 + 12k_M^2k_m^4 + 9k_Mk_m^5 + 4k_m^6}{4k_M^2 + 7k_Mk_m + 4k_m^2}\right)\Delta C_6. \quad (15)$$

When the sixth cumulant is negligible ($\Delta C_6 = 0$), equations (14) and (15) reduce to (8) and (9), respectively.

3.2.3. Neglect of the sixth cumulant. When the sixth cumulant is neglected, the coordination number, the second and the fourth cumulant change as

$$\ln N' = \ln N - \left(\frac{4}{2079}\frac{64k_M^{12} + 576k_M^{11}k_m + 2880k_M^{10}k_m^2 + 9335k_M^9k_m^3 + 20655k_M^8k_m^4 + 32535k_M^7k_m^5 + 37695k_M^6k_m^6 + 32535k_M^5k_m^7 + 20655k_M^4k_m^8 + 9335k_M^3k_m^9 + 2880k_M^2k_m^{10} + 576k_Mk_m^{11} + 64k_m^{12}}{64k_M^6 + 351k_M^5k_m + 855k_M^4k_m^2 + 1135k_M^3k_m^3 + 855k_M^2k_m^4 + 351k_Mk_m^5 + 64k_m^6}\right)\Delta C_6, \quad (16)$$

$$\Delta C_2' = \Delta C_2 - \left(\frac{2}{99}\frac{64k_M^{10} + 401k_M^9k_m + 1305k_M^8k_m^2 + 2895k_M^7k_m^3 + 4695k_M^6k_m^4 + 5535k_M^5k_m^5 + 4695k_M^4k_m^6 + 2895k_M^3k_m^7 + 1305k_M^2k_m^8 + 401k_Mk_m^9 + 64k_m^{12}}{64k_M^6 + 351k_M^5k_m + 855k_M^4k_m^2 + 1135k_M^3k_m^3 + 855k_M^2k_m^4 + 351k_Mk_m^5 + 64k_m^6}\right)\Delta C_6, \quad (17)$$

$$\Delta C_4' = \Delta C_4 - \left(\frac{2}{11}\frac{64k_M^8 + 366k_M^7k_m + 990k_M^6k_m^2 + 1655k_M^5k_m^3 + 1935k_M^4k_m^4 + 1655k_M^3k_m^5 + 990k_M^2k_m^6 + 366k_Mk_m^7 + 64k_m^8}{64k_M^6 + 351k_M^5k_m + 855k_M^4k_m^2 + 1135k_M^3k_m^3 + 855k_M^2k_m^4 + 351k_Mk_m^5 + 64k_m^6}\right)\Delta C_6. \quad (18)$$

Accordingly, they are underestimated when $\Delta C_6 > 0$ and overestimated when $\Delta C_6 < 0$.

3.2.4. Neglect of the coordination number. Let us consider the case that (2) truncated at the fourth order (ΔC_4) gives a good fit. If the variation of the coordination number is neglected, the second and the fourth cumulant result as follows,

$$\Delta C_2' = \Delta C_2 - \left(\frac{7}{6}\frac{8k_M^8 + 32k_M^7k_m + 80k_M^6k_m^2 + 125k_M^5k_m^3 + 140k_M^4k_m^4 + 125k_M^3k_m^5 + 80k_M^2k_m^6 + 32k_Mk_m^7 + 8k_m^8}{4k_M^{10} + 16k_M^9k_m + 40k_M^8k_m^2 + 80k_M^7k_m^3 + 140k_M^6k_m^4 + 175k_M^5k_m^5 + 140k_M^4k_m^6 + 80k_M^3k_m^7 + 40k_M^2k_m^8 + 16k_Mk_m^9 + 4k_m^{10}}\right)\ln N, \quad (19)$$

$$\Delta C_4' = \Delta C_4 - \left(\frac{63}{10}\frac{4k_M^6 + 16k_M^5k_m + 40k_M^4k_m^2 + 55k_M^3k_m^3 + 40k_M^2k_m^4 + 16k_Mk_m^5 + 4k_m^6}{4k_M^{10} + 16k_M^9k_m + 40k_M^8k_m^2 + 80k_M^7k_m^3 + 140k_M^6k_m^4 + 175k_M^5k_m^5 + 140k_M^4k_m^6 + 80k_M^3k_m^7 + 40k_M^2k_m^8 + 16k_Mk_m^9 + 4k_m^{10}}\right)\ln N. \quad (20)$$

Equation (19) shows the correlation between coordination number and EXAFS Debye–Waller factor. As expected, a decrease (or increase) of the coordination number, if neglected, leads to an increase (or decrease) of the second cumulant, according to the amplitude of the EXAFS signal. This is particularly important in EXAFS studies of glasses or disordered systems, where coordination number and Debye–Waller factor play a key role (Kuzmin *et al.*, 2006; Sanson,

Table 1
Fit of the phases difference.

First part: relative cumulants obtained from the fits. Second part: relative cumulants predicted from the equations calculated in §2 and §3.

	ΔC_1 (Å)	ΔC_3 (Å^3)	ΔC_5 (Å^5)
Resulting cumulants by fit			
(*a*) ΔC_1	−0.0397	–	–
(*b*) $\Delta C_1 + \Delta C_3$	−0.0201	3.37×10^{-4}	–
(*c*) $\Delta C_1 + \Delta C_3 + \Delta C_5$	−0.0179	4.42×10^{-4}	3.24×10^{-6}
Estimated cumulants of fit			
(*a*) by (5) with values of fit (*b*)	−0.0397	–	–
(*a*) by (10) with values of fit (*c*)	−0.0397	–	–
(*b*) by (11)–(12) with values of fit (*c*)	−0.0201	3.37×10^{-4}	–

Rocca, Dalba *et al.*, 2007; Sanson, Rocca, Fornasini *et al.*, 2007).

4. Discussion

Let us test the equations calculated in the previous sections through an experimental example. To this aim, let us consider the phases difference and the logarithm of the amplitudes ratio of the EXAFS signals measured in silver molybdate glasses at room temperature against the same glass at 25 K used as reference (Sanson, Rocca, Dalba *et al.*, 2007).

Fig. 1 shows the difference of the phases and the corresponding best fits in the range k = 2.5–12 Å^{-1}. The fits were performed (*a*) using only the first cumulant (ΔC_1), (*b*) including the third cumulant ($\Delta C_1 + \Delta C_3$) and (*c*) including the fifth cumulant ($\Delta C_1 + \Delta C_3 + \Delta C_5$). The corresponding fitting results are reported in the first part of Table 1. It can be observed that the third cumulant is essential to obtain accurate relative values of the first cumulant. In this example, the discrepancy on ΔC_1 between fit (*a*) and fit (*b*) [or fit (*c*)] is about 0.02 Å. The discrepancy on ΔC_3 between fit (*b*) and fit (*c*) (although less important) is about 10^{-4} Å^3. These discrepancies can be directly estimated by (5), (10) and (11)–(12) (depending on the fit case) with k_m = 2.5 and k_M = 12 Å^{-1}. The results are listed in the second part of Table 1. It can be seen that the agreement between predicted values (*i.e.* second part of Table 1) and best-fit values (*i.e.* first part of Table 1) is excellent.

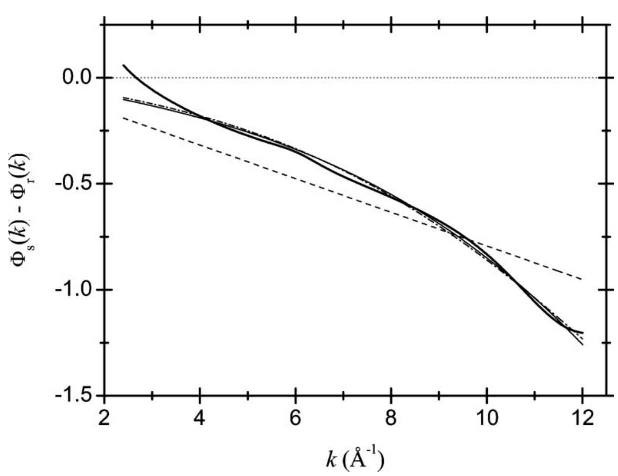

Figure 1
Example of phases difference (black solid line) fitted with ΔC_1 (dashed line), $\Delta C_1 + \Delta C_3$ (solid line) and $\Delta C_1 + \Delta C_3 + \Delta C_5$ (dash-dotted line). The results are listed in the first part of Table 1 and compared with the values predicted from equations of §2 and §3.

Table 2
Fit of the logarithm of amplitude ratio.

First part: relative cumulants obtained from the fits. Second part: relative cumulants predicted from the equations calculated in §2 and §3.

	N	ΔC_2(Å^2)	ΔC_4 (Å^4)
Resulting cumulants by fit			
(*a*) ΔC_2	–	4.98×10^{-3}	–
(*b*) $\Delta C_2 + \Delta C_4$	–	7.20×10^{-3}	6.48×10^{-5}
(*c*) ln $N + \Delta C_2$	0.795	3.66×10^{-3}	–
(*d*) ln $N + \Delta C_2 + \Delta C_4$	0.787	3.45×10^{-3}	-4.76×10^{-6}
Estimated cumulants of fit			
(*a*) by (13) with values of fit (*b*)	–	4.98×10^{-3}	–
(*a*) by (13) with values of fit (*c*)	–	4.98×10^{-3}	–
(*a*) by (13) with values of fit (*d*)	–	4.99×10^{-3}	–
(*b*) by (19)–(20) with values of fit (*d*)	–	7.20×10^{-3}	6.45×10^{-5}
(*b*) by (19)–(20) with values of fit (*c*)	–	7.25×10^{-3}	6.63×10^{-5}
(*c*) by (8)–(9) with values of fit (*d*)	0.795	3.67×10^{-3}	–

Analogously, Fig. 2 shows the logarithm of the amplitude ratios and the corresponding best fits in the same interval k = 2.5–12 Å^{-1}. The fits were performed (*a*) using only the second cumulant (ΔC_2), (*b*) including the fourth cumulant ($\Delta C_2 + \Delta C_4$), (*c*) only including the coordination number and the second cumulant ($N + \Delta C_2$) and (*d*) including coordination number, second and fourth cumulants ($N + \Delta C_2 + \Delta C_4$). For simplicity, the best fits that include the sixth cumulant are not reported, but the reliability of the corresponding equations (14)–(18) is assured anyway.

The best-fitting results are listed in the first part of Table 2. It can be seen, for example, that the changes of the coordination number, when neglected, drastically affect the values of the second cumulant, as well as of the fourth cumulant. The

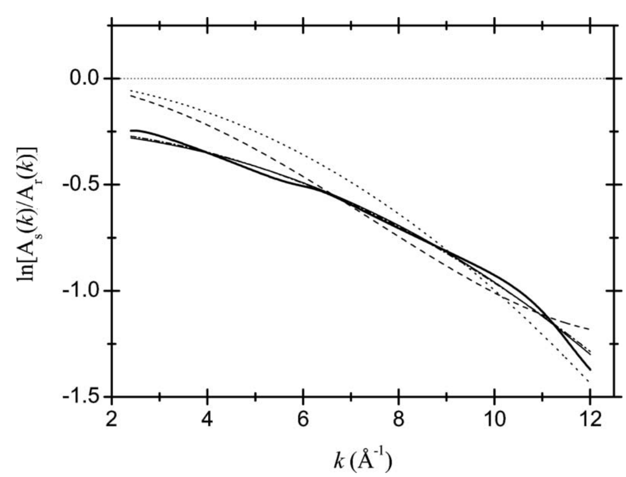

Figure 2
Example of logarithm of amplitudes ratio (black solid line) fitted with ΔC_2 (dotted line), $\Delta C_2 + \Delta C_4$ (dashed line), $N + \Delta C_2$ (dash-dotted line) and $N + \Delta C_2 + \Delta C_4$ (solid line). The results are listed in the first part of Table 2 and compared with the values predicted from equations of §2 and §3.

discrepancy on ΔC_2 between fit (*b*) and fit (*d*) is almost 0.004 $Å^2$, and about 7×10^{-5} $Å^4$ on ΔC_4. The cumulant differences among the fits can be directly estimated from the equations of §2 and §3. The results are listed in the second part of Table 2. The agreement with the best-fit values (*i.e.* with the first part of Table 2) confirms the goodness of the analytical expressions derived in this paper.

Before the conclusions, let us make a final observation. The experimental data cannot be fitted using an unrestricted number of fitting parameters, otherwise the fit becomes better but the essential parameters (*i.e.* distance, Debye–Waller factor, coordination number) can give worse results. However, on the other side, the main higher-order cumulants cannot be neglected in many cases, but it is necessary to find a good balance.

5. Conclusions

In this work, analytical expressions have been derived to determine the errors in the EXAFS analysis, by the ratio method, owing to the neglect of the higher-order cumulants. The reliability of the present results has been tested on experimental data. The importance of the higher-order cumulants to obtain accurate values of the lower-order cumulants, *i.e.* bond distance, coordination number and Debye–Waller factor, is demonstrated.

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